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Bioremediation of Petroleum Hydrocarbon-contaminated Soils

Comprehensive Report

December, 1999

Prepared for
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Executive Summary

Executive Summary

Introduction

The US Department of Energy and the Institute for Ecology of Industrial Areas (IETU), Katowice, Poland have been cooperating in the development and implementation of innovative environmental remediation technologies since 1995. A major focus of this program has been the demonstration of bioremediation techniques to cleanup the soil and sediment associated with a waste lagoon at the Czechowice Oil Refinery (CZOR) in southern Poland. After an expedited site characterization (ESC), treatability study, and risk assessment study, a remediation system was designed that took advantage of local materials to minimize cost and maximize treatment efficiency. U.S. experts worked in tandem with counterparts from the IETU and CZOR throughout this project to characterize, assess and subsequently, design, implement and monitor a bioremediation system.

The CZOR, our industrial partner for this project, was chosen because of their foresight and commitment to the use of new approaches for environmental restoration. This program sets a precedent for Poland in which a portion of the funds necessary to complete the project were provided by the company responsible for the problem. The CZOR was named by PIOS (State Environmental Protection Inspectorate of Poland) as one of the top 80 biggest polluters in Poland. The history of the CZOR dates back more than 100 years to its establishment by the Vacuum Oil Company (a U.S. company and forerunner of Standard Oil). More than a century of continuous use of a sulfuric acid-based oil refining method by the CZOR has produced an estimated 120,000 tons of acidic, highly weathered, petroleum sludge. This waste has been deposited into three open, unlined process waste lagoons, 3 meters deep, now covering 3.8 hectares. Initial analysis indicated that the sludge was composed mainly of high molecular weight paraffinic and polynuclear aromatic hydrocarbons (PAHs). The overall objective of this full-scale demonstration project was to characterize, assess and remediate one of these lagoons. The remediation tested and evaluated a combination of U.S. and Polish-developed biological remediation technologies. Specifically, the goal of the demonstration was to reduce the environmental risk from PAH compounds in soil and to provide a green zone (grassy area) adjacent to the site boundary. The site was characterized using the DOE-developed Expedited Site Characterization (ESC) methodology. Based on the results of the ESC, a risk assessment was conducted using established U.S. procedures. Based on the results of the ESC and risk assessment, a 0.3-hectare site, the smallest of the waste lagoons, was selected for a modified aerobic biopile demonstration. This Executive Summary and the supporting report and appendices document the activities and results of this cooperative venture.

Site Characterization

Site Characterization was conducted in the summer of 1996 using DOE-developed Expedited Site Characterization (ESC). ESC makes use of direct push technologies (e.g., cone penetrometer), on-site chemical analysis and real-time data display and interpretation to conduct rapid and efficient site characterization. This approach brings experts and data together in the field to interpret a set of results and, based on those results, direct the placement of the next set. Data were developed in the ESC to support subsequent risk assessment and remedial design

stages. IETU specialists working in conjunction with U.S. counterparts conducted all phases of the ESC. This collaboration ensured an active exchange of ideas, philosophies and approaches to site characterization. The ESC utilized and compared several different technologies for the rapid qualitative and quantitative evaluation of hydrocarbon contamination in the lagoon area.

This ESC was conducted in two phases. Phase 1 utilized immunoassay (IMA) sampling kits, active and passive soil vapor sampling as well as geophysical and soil conductivity surveys to describe site stratigraphy and to qualitatively determine the nature and extent of site contamination. The concurrent use of IMA kits from several different manufacturers provided an opportunity to compare and contrast these screening tools while delineating the extent of soil contamination. Phase 1 also involved the use of active and passive soil gas collection and analysis. These sampling procedures provide general information on the presence of volatile compounds in the vadose zone and help to estimate the risks posed to humans by exposure to contaminated soil. Phase 2 involved the collection of detailed hydrogeologic and definitive chemical data.

The Physical Conceptual Site Model was developed as follows. Groundwater was located at approximately 11 meters below grade and may have been partially confined during the ESC. It was confirmed that the site was underlain by low permeability clay, however evidence was produced suggesting a degree of heterogeneity in this layer. This heterogeneity could provide relatively permeable pathways allowing surface contaminants to migrate to groundwater. As was anticipated, ground penetrating radar was not able to penetrate the dense soils or sludges at the refinery. The EM61 electromagnetic detector was able to confirm the location of known subsurface features (e.g., pipes) and also identified other features that were subsequently avoided in the subsurface investigation. A cone penetrometer (CPT) vehicle was deployed to collect both stratigraphic (piezocone) and laser fluorescence data. However, soft soil conditions at the site resulting from heavy rains restricted the application of heavy CPT to improved roadways in the vicinity of the lagoons.

The Chemical Conceptual Site Model involved a variety of sample collection and analysis techniques and provided the following description of site contamination. Surface soils were highly variable in contaminant level as a result of the nature of disposal practices at the refinery. As a result, there are a number of “hot spots” around the lagoon area. These surficial locations are contaminated with the non-volatile PAHs, while VOCs and BTEX are generally at low levels. IMA kits proved to be useful tools in screening site soils for PAH and BTEX contamination. PAHs and BTEX (mainly benzene) heavily impacted groundwater. This may be due to impacts from the lagoons, from refinery material loss and subsequent transport through areas of high soil permeability or from an outside source. The patterns of contamination were unexpected, with elevated contaminant concentrations both north and south of the lagoons. The dense industrial activity surrounding the refinery and the possibility for containment of the aquifer reduced our ability to define sources and plume directions.

The ESC proved to be an excellent instrument with which to initiate this cooperative relationship between DOE and IETU. During this activity, a working relationship between DOE, the IETU and a number of U.S. partners was established. The cooperation required to plan, conduct and evaluate this site characterization provided the basis for subsequent activities in a number of areas. From a technical aspect, the ESC provided information that was necessary to support the risk assessment and bioremediation. It documented the relative performance of different IMA

kits as useful screening tools for this type of activity and provided valuable data for comparing different direct push fluorescence light sources.

Risk Assessment

Based on the ESC, a risk assessment was conducted to quantify the risks posed by contaminated soils and groundwater to present and future site workers at the CZOR. The risk assessment was sponsored by the U.S. Department of Energy (DOE) and was conducted by Florida State University (FSU) working with staff from the Institute for Ecology of Industrial Areas (IETU) in Katowice, Poland. The goal of the risk assessment was to introduce the U.S. approach to risk-based environmental evaluations while determining the sources and magnitudes of risk posed by the site and developing target clean-up goals. A working collaboration between U.S. experts and their counterparts from the IETU ensured that both the philosophy and application of risk assessment was transferred and discussed. The final risk assessment utilized the general U.S. approach, but was modified to include aspects of occupational exposure that were considered to be unique to Poland.

The risk assessment process is an integral part of any remedial investigation/feasibility study, conducted at contaminated sites in the U.S. Risk assessment is designed to evaluate the potential for adverse effects on humans and the environment from existing conditions, and to establish health-based remediation goals for appropriate environmental media (e.g., soils, groundwater). The procedure, based on U.S. EPA methodology and upon which this risk assessment was based, encompasses the following areas:

- site characterization;
- selection of indicator chemicals;
- toxicity assessment for carcinogenic and non-carcinogenic substances;
- human exposure assessment under site-specific exposure scenarios;
- risk characterization; and
- development of remedial goals.

Site Characterization was performed by the Ames Laboratory and their IETU counterparts and is summarized above.

Selection of Indicator Analytes identifies those compounds that are representatives of the toxicity and environmental behaviors of contaminants at the site. Indicator analytes are selected as an initial step in a site-specific risk assessment in order to focus the assessment activities on those compounds that are judged to pose the most significant potential risks based on their inherent toxicity. For the CZOR site benzene, ethylbenzene, toluene, xylenes (BETX), six polycyclic aromatic hydrocarbons (PAHs) and nine heavy metals were selected to represent site contamination. For these chemicals information on environmental occurrence, physical/chemical properties, fate and transport in the environment (e.g., biodegradation, evaporation, and hydrolysis) was gathered.

Toxicity Assessment summarizes and evaluates the toxicity and potential adverse effects of the chemicals of concern. Toxicity assessment is based on available scientific data on adverse effects in humans and nonhuman species (e.g., mammalian and human health effects, toxicity to aquatic species). Toxicological characteristics of each chemical of concern are summarized, including

the identification of important measures of toxicity, i.e., reference doses to evaluate non-carcinogenic effects and slope factors for carcinogens.

Exposure Assessment includes determination of exposure scenarios, estimation of factors associated with each scenario (e.g., exposure frequency, exposure duration, life expectancy, inhalation rate, etc.), and collection of data to support each factor. Exposure scenarios were based on standard U.S. exposure considerations but were modified to reflect conditions unique to the CZOR site. For the purposes of this risk assessment surface soils and groundwater in the sludge lagoon at the CZOR were evaluated with regard to the potential risks that they may pose to humans. Ingestion, inhalation and dermal exposure routes were considered. The CZOR site is currently classified as industrial and land use at the site is not expected to change in the future. Based on this land use category and for purposes of estimating contaminant intakes at the site, the following three exposure scenarios were developed for the CZOR lagoon site:

- **Scenario I** (Adult, On-site Future Construction/Remediation): occupational exposures to adults who may be exposed to surface soils and groundwater at the sludge lagoon at the CZOR site during potential construction or remediation activities. Exposure to soil was assumed to occur for 250 days/year for 0.33 years of a 70 year lifetime;
- **Scenario II** (Adult, Industrial): occupational exposure to adults who may be exposed to surface soils during their work-related activities at the sludge lagoon site (50 days/year for 25 years of a 70 year lifetime); and,
- **Scenario III** (Adult, On-site Groundwater, Future Irrigation): exposure to adults who may be exposed to site groundwater on a daily basis (25 days/year; 1 hr/day) for a period of 25 years of 70-year lifetime.

Risk Characterization combines toxicity assessment with exposure assessment in order to quantify risks posed by a contaminated site under a given set of conditions. Risk characterization is considered separately for carcinogenic and non-carcinogenic effects and includes the accompanying uncertainties. Potential noncarcinogenic risks for exposures at the CZOR site were evaluated by comparing the estimated contaminant intakes with the U.S. EPA Reference Dose (RfD). The estimated carcinogenic risks were compared with the risk of 1E-06, used as conservative point-of-departure for carcinogenic risk. Surface soils in the sludge lagoon at the CZOR site pose a limited potential carcinogenic risk under Scenario II (3.7E-06 predicted excess cancer deaths resulting from exposure as described). The main portion of this risk is contributed by potential oral exposure to benzo(a)pyrene in surface soils. Groundwater at the CZOR site is judged to represent a limited potential carcinogenic risk under the Scenario III (7.4E-06 predicted excess cancer deaths resulting from exposure as described). The main portion of this risk is contributed by potential dermal and inhalation exposure to benzene in groundwater. It should be mentioned that, while these scenarios are reasonable for present and short-term future conditions at the CZOR, they would probably not be protective of exposure to this site under less restrictive conditions (e.g., residential). In addition, the risk assessment considered only exposure by soils or groundwater. Exposure to site air also may contribute significantly to overall risk. However, it was decided that it would not be possible to isolate the role of the lagoons in contributing to air quality problems.

Media-specific risk based concerns (RBCs) were calculated for each indicator chemical in soil and groundwater at the sludge lagoon at the CZOR for the purposes of guiding remediation activities. RBCs were calculated for combined oral, dermal and inhalation exposure to

chemicals. The calculated RBCs were compared with the concentrations of indicator contaminants that were detected in surface soils and groundwater at the sludge lagoon of the CZOR site. The mean detected concentration of benzo(a)pyrene exceeds the calculated RBCs for surface soils under Industrial Scenario. The mean detected concentration of benzene exceeds the calculated RBCs for groundwater under Irrigation Scenario. The risk assessment documented the risks posed by site contamination to present and future refinery workers. A significant aspect of that risk is posed by the presence of PAHs in surface soils near the lagoons. The remedial technology selected for demonstration at the CZOR was bioremediation, which is well suited to the cleanup of petroleum-contaminated soils. The remedial goals developed in the risk assessment were used to guide the design and operation of the biopile (bioremediation technology).

Bioremediation

The Polish petroleum refinery biopile field demonstration had a number of significant findings. These are tied back to the criteria for success that were stated at the beginning of this section and in the original Test Plan for the demonstration (Altman et al., 1997).

First criteria for the success of this demonstration

The first criteria for success was to demonstrate the application of bioventing/biosparging as a viable cost-effective process to remediate contaminated sites to reduce risk to man and environment and resulting in a green zone. The ability of the remediation process to degrade large molecular weight compounds (PAHs) will be evidenced by utilizing state-of-the-art monitoring equipment, analytical techniques and treatability studies to determine the rate and volume reduction in the starting concentrations of the contaminants.

Over the entire field demonstration more than 120 metric tons or 81% of the total petroleum hydrocarbons were present (Table ES.1). By the end of the 20 month biopile demonstration, concentrations of TPH and all PAHs were below the Polish and US risk guidelines for even shallow soils (0.3-15 m) for sites with multi-uses (including residential). All the metal concentrations in the soil, which were initially only acceptable for industrial use sites, fell below the MCL guidelines for shallow multi-use sites because of the injection of nutrients and the recirculation of leachates. This full scale demonstration simultaneously remediated the contaminants present in the soil to acceptable risk levels and created a permanent green zone with a park like atmosphere in less than 20 months. The comparison of passive with active aeration demonstrated that the Baroballs, a DOE patented technology, could be used effectively to provide aeration of biopile for petroleum remediation via barometric pumping. This comparison showed that passive air injection required 3-5 months longer to reach the same end point as blower injection of air. Passive injection could thus provide significant cost savings whenever there is no urgency for remediation due to immediate risk to human health or the environment. The details of the cost comparison to baseline technologies are covered in chapter 5 on cost analysis.

New field instruments that were used to monitor physical and chemical parameters in the field had variable success. The landfill gas analyzer proved extremely robust for measuring changes in carbon dioxide, oxygen, and methane in the soil gas. These measurements helped verify the respiration rates, the degree of injected air penetration into the biopile and a measure of aerobic conditions in the biopile. The installed temperature and moisture blocks were not sensitive

enough to indicate significant changes in either parameter, thus were of minimal value. However, the moisture blocks did provide evidence that the biopile was drying out in the later part of operating campaign 5. The photoacoustic infrared spectrophotometer proved difficult to operate and did not provide reliable data on soil gas concentrations in the later part of the demonstration. This was primarily due to humidity interference from water vapor becoming entrained in the instrument. These measurements had to be eliminated from the final analytical data set due to these problems. The HydroLab surveyor worked well but was not of significant use due to the small quantity of leachate that was measurable from the biopile system.

The five operating campaigns showed that initially air injection alone (OC1 & OC2) stimulated dramatic reductions of contaminants (>50%) in the biopile in less than 7 months (Table ES.1). Subsequent operating campaigns using the addition of fertilizer with the air (OC3) and leachate recirculation (OC4) removed only an additional 1% of the contaminant inventory in a similar period of time. However, the final operating campaign (OC5), which added surfactants, decreased the contaminant inventory an additional 30% and caused a significant reduction of all of the metals in the soil. These findings are verified by the biodegradation rates observed during the different operating campaigns (Table ES.2). The first two operating campaigns had high rates of biodegradation in the active injection areas and these fell off during OC3 and OC4, but were increased to their highest levels in any area during OC5. This suggests that surfactants make more of the strongly sorbed contaminants bioavailable. The passive section of the biopile responded in a similar manner but with about a 3-5 month lag and did not achieve the rates seen in the active aeration sections. The rates observed are similar for bioremediation of other petroleum contaminated soils, and quite good for similar biopile studies, {e.g., prepared beds (52-641 mg/kg soil/day), biopiles (20-60 mg TPH/kg soil/day), bioventing (2.5-10 mg TPH/kg soil/day)} (Bartha, 1986; Lombard and Hazen, 1994; Kastner et al., 1997). This demonstration suggests the combination of active aeration, fertilizer, and surfactants with leachate recirculation will provide the fastest site remediation and substituting passive aeration will reduce the cost but increase the time to reach endpoint.

Second criteria for success of this demonstration.

The second criteria for success was to demonstrate evidence of biological destruction (biodegradation) of petroleum (PAH, TPH and BTEX) from the contaminated material. Since a major advantage of bioremediation is destruction, it is important and significant to demonstrate that biodegradation is occurring. The evidence is expected to come primarily from comparison of the biopile material and soils analysis taken before, during and after the material is subjected to the treatment process (nutrient addition, aeration, pH adjustment and moisture control) to stimulate biodegradation.

Multiple lines of evidence show that biodegradation of PAH and TPH occurred during the demonstration. BTEX compounds were undetectable in the soil after the first samples. The field photo-acoustic infrared spectrophotometer gave unreliable results of soil gas concentrations especially later in the demonstration when the humidity in the detection column became high. First, the contaminant inventory changes showed that large concentrations of petroleum contaminants were being removed at rates that could only have been attributed to rapid biodegradation (Table ES.1). Second, respiration studies showed that the oxygen demand in the active area corresponded to the rates of contaminant reduction observed. Third, over the entire demonstration there was a highly significant inverse correlation between bacterial density and contaminant concentration. Fourth, limiting nutrients like phosphate concentrations were

directly correlated to bacterial density, as were enzymatic activity measurements of soil (TTC). This suggests that bacteria were being biostimulated by the nutrient amendments being applied during the operating campaigns. The treatability and column simulation studies also verified in a like manner that biodegradation was responsible for reduction of contaminants and that the nutrient and surfactant amendments being applied in the field caused similar responses in the laboratory. Fifth, the aeration of the biopile soil created an aerobic environment conducive to aerobic biodegradation of petroleum contaminants. Sixth, all PAHs measured were also being degraded. Seventh, very active, low pH tolerant petroleum and PAH degraders could be isolated from the biopile that used petroleum and PAHs as their sole carbon and energy source. And eighth, the modeling studies of the field data showed that the biodegradation of the contaminants observed during the demonstration could be simulated by a kinetic model of contaminant biodegradation. The effects of each operating campaign were discussed in the previous section.

Third criteria for success of this demonstration.

The third criteria of success was to demonstrate a relatively simple and trouble-free operation. A critical assumption for the successful demonstration of the technology is that the system, as designed, will function with little or no down time and provide operating conditions that minimize fugitive air emissions and maximize biodegradation rates. The proposed project has no precedence in Poland and as such represents new technology for the country. However, since several other nations have demonstrated similar technologies, it represents a relatively low risk and should have high public acceptance. The simplistic design contributes direct benefits associated with the ease of management and operation. A minimal staff will be required to operate the equipment, again adding to the low risk factor by limiting exposure to operations personnel.

The equipment and operation went through a number of delays during the initial 3 months of operation, due to differences in voltage, planning, weather and manpower delays from a variety of sectors in this multi-institutional and multi-national demonstration. However once the initial problems were solved, operation was relatively simple and maintenance free. See the cost analysis in chapter 5 for a complete description of costs and comparison to international differences. The simplistic design served the project well and helped make the project the success it was. The large number of tours, symposia, presentations and publications (see the Appendices for complete list) are also a direct index of the overall success of this project and its public outreach and acceptability.

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Table ES.1 TPH Inventory by Operating Campaign

	Baseline	OC1	OC2	OC3	OC4	OC5
Metric Tons	148	100	68.6	68.6	66.8	28.1
% Remaining	100	68	46	46	45	19

Table ES.2 Biodegradation Rate by Operating Campaign and Treatment

Campaign	Average	Passive	Active
OC-1	80	44	119
OC-2	88	82	94
OC-3	<33	33	0
OC-4	<37	0	37
OC-5	91	60	121

All values in mg/kg soil/day

Chapter 1

Introduction

Introduction

Since 1995, the U.S. Department of Energy (DOE EM-50) has been working together with the Institute for Ecology of Industrial Areas (IETU), Poland and Florida State University (FSU), to identify, evaluate and deploy mutually beneficial, cost effective environmental remediation technologies. These collaborative activities between DOE and the IETU are conducted within the context of the Joint Coordinating Committee for Environmental Science (JCCES) agreement.

The initial project conducted under this agreement involved the field testing of innovative approaches to the bioremediation of petroleum hydrocarbon contaminated soils. The overall objective of the project was to evaluate innovative and cost-effective bioremediation technology for these waste materials. The Czechowice Oil Refinery located in southern Poland was chosen as a suitable demonstration site and an industrial partner for this project.

The project was divided into three stages, including: site characterization – directed by Ames Laboratory; environmental and health risk assessment – directed by Florida State University; and remediation technology selection and implementation – directed by the Savannah River Technology Center (SRTC). Overall field management was provided by Florida State University. The project began with IETU scientists collaborating with U.S. counterparts to characterize key environmental aspects of the site (e.g., geological, hydrological, chemical and microbiological) and to evaluate the potential risks to refinery workers and local inhabitants. The purpose of these activities was to document the nature and extent of environmental problems associated with the site and to formulate possible remediation strategies for the site. During the course of site characterization, the project focused on the clean-up of sludge contaminated soils.

Characterization and treatability study results indicated that the site would be a good location to test bioremediation technologies. Biopiling was selected as a technology compatible with both the site conditions as well as the scientific expertise of the IETU. Bioremediation activities began at the site in 1997.

Historical Background

For more than one hundred years the Czechowice Oil Refinery, formerly the Vacuum Oil Company, owned by the Standard Oil Company of New York, a United States based company, has been producing petroleum products for industrial and commercial applications. Many of the refinery's products are specialty items such as semi-synthetic motor oils, hydraulic oils, high temperature lubricants and waxes. The history of the refinery dates back to 1896 where the refinery processed approximately 35,000 metric tons of paraffinic crude oil a year in the production of vacuum oil. Over the next several decades the refinery's capacity steadily increased with production exceeding 500,000 metric tons per year. During the early 1930s, the addition of several new product lines and processes transformed the refinery into the largest petroleum processing facility in Poland. With the onset of World War II, the refinery became a military target of the Allied Forces. Due to its high production and strategic location, the Allies bombed the facility in August of 1943. While under German occupation during the war, the Germans rebuilt only part of the refinery; the Poles completed the major restoration shortly after the end of World War II. Full scale production resumed in February 1946 (Czechowice Oil Refinery, 1995).

Today, with the end of the cold war and more than 1,300 employees and production exceeding million tons per year, in a variety of product lines, the Czechowice Oil Refinery faces many new challenges. The move to a market driven economy and privatization of many State (government) owned industries brings with it new responsibilities, not only in fiscal and business management but also environmental stewardship and ownership. Many years of a production-oriented philosophy have created environmental conditions that now present a potential risk to human health and the environment. The disposal practices for process wastes generated by the refining of crude oil have created conditions that are unacceptable under today's environmental standards. An estimated 120,000 tons of acidic petroleum sludge have been deposited in three unlined process waste lagoons covering 3.8 hectares within the refinery. The use of unlined lagoons for process waste disposal was the industry norm for many years, not only in Poland but the United States as well. As late as the 1980s, some process waste lagoons were still in use in the United States. In Poland, the practice still exists.

The Czechowice Oil Refinery, while still following traditional disposal practices, has undertaken new and bold initiatives to begin the environmental restoration of the refinery. In collaboration with the Institute for Ecology of Industrial Areas (IETU), located in Katowice, Poland and the United States Department of Energy (DOE), a program for the demonstration of U.S. based technologies has been initiated with the Czechowice Oil Refinery as the industrial partner. This partnership not only includes the use of the refinery as the demonstration site, but also shared responsibilities in fiscal, construction and engineering management of the project(s).

The primary objectives for the program are to advance Research and Development of EM technologies for use at DOE facilities in the United States and to transfer proven technologies and expertise to Poland. Performing advanced remediation activities on Upper Silesien test sites that have similar contamination problems as those at U.S. sites should accelerate U.S. and foreign cleanup efforts. The program will serve to address mutual objectives of both Poland and the U.S. related to environmental management. Included among these objectives are the demonstration and international transfer of U.S. environmental technologies, as well as topics related to these issues i.e., risk based management, technology transfer, communications and other forms of information dissemination (FSU, 1995).

Technical Need

In 1991, 750 million tons of industrial wastes were deposited in the Upper Silesian Region of Poland, mostly in the Katowice Province. Annually, the industry of Katowice Province generates 60-70 million tons of waste. Even though solid waste generation has decreased significantly in recent years, this region still generates 50% of all the solid wastes in Poland. The Upper Silesian Region while rich in natural resources and densely populated is considered to have very poor quality surface waters (the major source of potable water). Most rivers and streams in the region have very low flow rates on the order of only a few m^3/s. As much as 70% of the volume of these rivers is made up of municipal sewage and industrial wastewater. Some 62.6% of the 1,400 km of rivers in the region are out-of-class {i.e., class 4 (wastewater) or lower} (IETU, 1994). Despite some improvements in surface water quality, the problem is far from solved. Contaminated, highly polluted sites are a real threat to groundwater and surface water reservoirs used as potable water sources. As sources of clean surface water steadily decline in Poland and throughout the world, our reliance on groundwater will undoubtedly increase far into the next century. Therefore, with increasing urgency, ways have been sought to

clean up, (i.e., remediate, petroleum and PAH contaminated soil and groundwater) (Hazen, 1991). The Czechowice Oil Refinery demonstration will provide DOE-EM and the IETU with the opportunity to demonstrate and evaluate innovative, environmentally sound, and cost effective remediation techniques that can be used throughout the industrialized world to address clean-up of petroleum contaminated sites.

The basic concepts of this technology are expected to be applicable to other sites in the DOE complex having similar problems, especially low pH; however, the particular process designs will be site specific. The experience gained at the Polish demonstration will provide the basis for designs for other sites in Poland (i.e., other refineries and former Soviet military bases). There are also many other waste sites in Poland where adaptations of this technology (approach) could be implemented, (e.g., coke production industry, landfills, etc).

Technology Description

Bioremediation is a process that mineralizes or transforms hydrocarbons (both xenobiotic and naturally occurring) introduced into the environment to less toxic or innocuous forms (Hazen, 1997). This technique can be applied either in situ or ex situ. There are a variety of bioremediation approaches, including biopiling, bioventing, biosparging and landfarming that can be applied in a large variety of ways. In as much as there are many approaches, there are problems that accompany the application to a full-scale remedial effort. Such issues include biodegradation enhancement, nutrient and electron acceptor delivery and the integration of combinations of treatment technologies.

The microbial metabolism and fate of BTEX, TPH, PAHs and straight-chain and branched alkanes in the natural environment are areas of intense concern since many of these compounds and their break-down products display toxic and carcinogenic properties (Hazen, 1991). Many microorganisms including bacteria, fungi, yeasts and algae have the enzymatic capacity to completely mineralize petroleum hydrocarbons and utilize the carbon component to generate new biomass. For example, bacteria under aerobic conditions oxidize PAHs to form dihydrodiols that are utilized in cell production (Atlas, 1984). An example of this bacterial oxidation pathway is the biotransformation of naphthalene to catechol (Fig. 1.1). Naphthalene and other arenes are among the most water soluble and potentially toxic compounds of petroleum and associated products. Indigenous microorganisms in the soil and groundwater can degrade large quantities of petroleum hydrocarbons if they are provided sufficient amounts of water, oxygen, and other limiting nutrients, usually nitrogen and phosphorus (Bartha and Bossert, 1984). Knowing these facts, it is easy to understand why the use of bioremediation as a remedial action is the best method for the treatment of PAHs at the Czechowice Oil Refinery site. Currently, Leaking Underground Storage Tank (LUST) Programs, in many states in the U.S., have selected bioremediation as the clean-up technology of choice. Use of this technology has shown that the 16 PAHs targeted by the USEPA in soil and sludge, in concentrations higher than 5,000 ppm, can be reduced by 95% in twenty weeks or less depending on the ambient conditions (Huis in't Veld et al., 1995).

Benefits

Bioremediation technologies are based on biological destruction of the contaminants at the site. Therefore, risks normally associated with handling, transporting, and treating or storing contaminated residuals are lessened, if not avoided. In this sense there is a very significant

reduction of risk (Hazen, 1997). Costs for in situ bioremediation of semi-volatile petroleum contamination {i.e., polycyclic aromatic hydrocarbons (PAHs)} are not well documented since this is an emerging technology. However, current in situ bioremediation technologies for other organics (such as gasoline) are nearly always less expensive than alternative technologies that provide physical destruction of the contaminants. In addition, bioremediation typically takes only a fraction of the time that are required by other remediation technologies, this is clearly an advantage when the site poses an urgent human health or environmental threat.

Bioremediation using techniques like landfarming, biopiling, bioventing, biosparging and nutrient injection will lead to a significant reduction in the time required to complete the remediation because bioremediation provides a pathway for removal (destruction) of the PAHs. Furthermore, the stimulated indigenous microorganisms will gain access to the organic compounds in the soil and water matrices that may be very difficult or impossible to remove by soil vapor extraction or diffusion alone. The enzymes induced in the microorganisms oxidize a host of organic compounds, including toluene, benzene, and PAHs. Many previous laboratory studies have demonstrated the proof of this principle, thus a "cleaner" end point is reached in less time (Hazen, 1991; Hazen, 1997).

Additionally, IETU will benefit by participating in cooperative projects that advance the R&D of Polish environmental technologies, demonstrate risk assessment methods and techniques related to soil contamination, which seriously effect the region, and engage in technology transfer, thus laying the foundation for future growth of the remediation and risk assessment fields, including education and skill transfer through cooperation.

Alternatives

A variety of alternative technologies to land disposal or storage in lagoons and basins of untreated petroleum contaminated wastes exist today. They include in situ/ex situ bioremediation, soil stabilization and solidification, soil vapor extraction, bioventing, excavation and subsequent soil washing and/or chemical treatment and incineration. In order to assure complete remediation, the technology chosen must be able to effectively treat the entire site and produce definable measures of remediation. Additionally, time to remediate, energy costs, required sampling (number of samples and required monitoring period after remediation), etc. must be considered. Several of these technologies have disadvantages that far outweigh the advantage of being used in lieu of ex situ bioremediation (biopiling).

For example, soil stabilization and solidification, although relatively low cost, generate a volume increase in material that requires additional handling and disposal. Because these processes only immobilize the contaminants and do not destroy them, possible limitations on future site use may also exist. Soil vapor extraction and bioventing are viable methods but they can require extensive site characterization and have very site specific applications. These methods also do not provide the level of control or the increased rates of biodegradation that a biopile would. Soil washing (flushing) and chemical treatment can be used as a permanent treatment method but additional waste streams with potentially toxic by-products are generated thus requiring further treatment, disposal and expense. High and low temperature incineration is an effective method to destroy the contaminants of concern (COCs) from this project. However, maintaining the high destruction temperature required to support the removal efficiency of 99.9% can be costly, requiring the use of large amounts of supplemental fuel to support even the lowest operating parameters. Low temperature (catalytic) incineration is more applicable to petroleum

contaminated material remediation but with both high and low temperature applications, permit conditions, contaminant concentrations, material volume, incinerator efficiency, catalyst cost, heating values of the waste, etc. all impact the final cost.

Due to the relatively high carbon content of the refinery waste (≈ 60%), based on information provided by the refinery engineering staff, the refinery has, through cooperation with the IETU, elected to remove the bulk of the lagoon's material and sell it as an energy source for fuel in a cement kiln. At the kiln, a test burn of the acidic refinery waste blended with basic waste from a local chemical plant, was very successful (B. Jagosz, personal communication, 1996). This is an excellent disposal method for the bulk removal of the COCs, which will provide the refinery with an additional source of revenue from what was once considered a waste. This will also provide the cement kiln with a relatively low cost, high BTU fuel supply for their production facility. Additionally, the refinery has also developed an extraction process. By steam heating the highly viscous material found in the lagoon, the usable product is recovered for burning in their own steam plant. These forms of energy conservation and usage are highly commendable and should be recognized as innovative in Poland's new market driven economy.

In addition to the lagoon material, the refinery has identified areas of surface contamination (i.e., truck and tank draining locations) which will be utilized as the bed material for the biopile.

Biopiling collects of all the contaminated soil, amends it to provide needed nutrients and favorable physical properties, and provides complete containment of the contaminants through the use of a liner and cover material. Biopiling provides optimal conditions for microbial activity through leachate recirculation and aeration, requires relatively low energy usage, and permits the reuse of the soil once remediation has been completed. In addition, the physicochemical characteristics of the newly identified material such as pH (7.5 ± 0.2), moisture content ($24.5\% \pm 10$), and petroleum content ($14.2\% \pm 2$) is superior to the originally selected lagoon material thus making it nearly ideal for a biopiling operation. Therefore biopiling is the only technology that completely degrades the contaminants, without creating a secondary waste stream, and permits the reuse of the previously contaminated material without restriction.

Site Description and Area Maps

The Czechowice Oil Refinery is located in the eastern portion of the city of Czechowice-Dziedzice which is located in the Katowice Voivodship in southern Poland (Fig. 1.2; 1.3). The history of the town dates back to the year 1337. Some of the old hamlets like Grabowice, Zbijow or Swierkowice still exist. The Czechowice Oil Refinery, the main industry in the town is the third largest refinery in Poland (Przedsiebiorstwo Geodezyjno-Kartograficzne 1996). A small city, with a population of approximately 35,000, Czechowice-Dziedzice is located approximately 45 kilometers south of Katowice and 8 kilometers north of Bielsko-Biala (Fig. 1.4). This region is one of the leading industrial areas of Poland.

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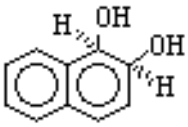
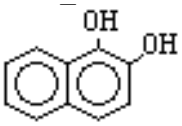
Figure 1.1 Bacterial Oxidation Pathway of Naphthalene to Catechol (Atlas, 1984)

Naphthalene

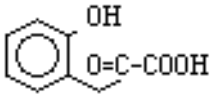
in the presence of:
Bacteria + O_2 + Dioxygenase



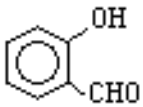
(+)-cis-1,2-Dihydroxy-1,2-dihydronaphthalene



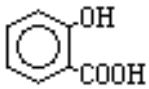
1,2-Dihydroxynaphthalene



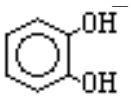
cis-o-Hydroxy benzal pyruvic acid



Salicylaldehyde



Salicylic acid



Catechol

Meta Pathway Ortho Pathway

Figure 1.2 Poland and Katowice/Bielsko-Biala Regional Map

Figure 1.3 Refinery Location Map

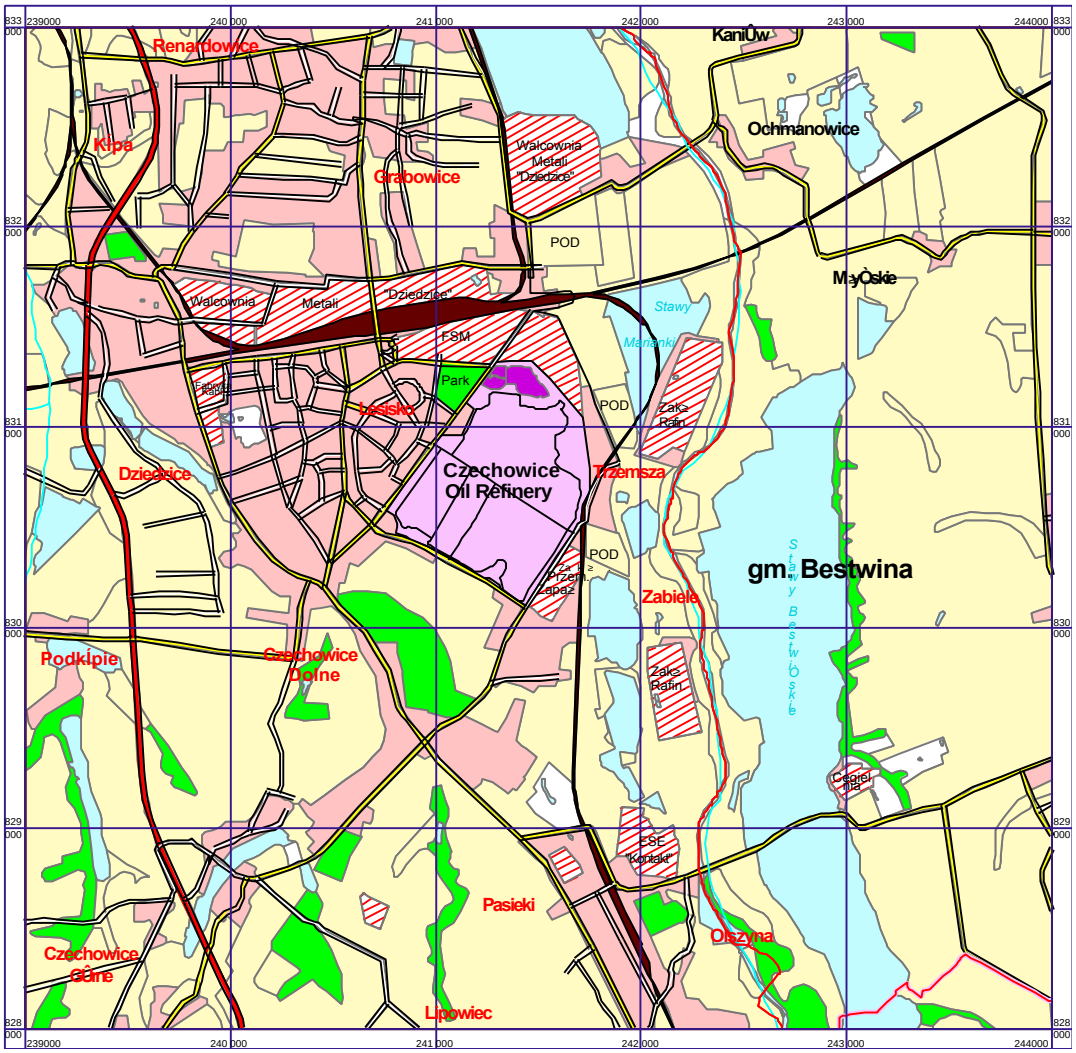


Figure 1.4 Katowice/Czechowice-Dziedzice Regional Map

Chapter 2

Site Characterization

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Expedited Site Characterization

Introduction

The following is taken from preliminary reports written by Ames Laboratory in 1996.

This document describes the technical aspects of an environmental site characterization demonstration project that was conducted at the Czechowice Oil Refinery (CZOR) in Czechowice-Dziedzice, Poland. This activity was coordinated and conducted by a joint team from the Institute for Ecology of Industrial Areas (IETU) in Katowice, Poland; the U.S. Department of Energy (DOE), Office of Science and Technology (EM-50); Ames Laboratory (Ames), Florida State University (FSU), and Savannah River Technology Center (SRTC).

This chapter addresses site characterization activities, which were conducted using the Expedited Site Characterization (ESC) methodology, as developed by the U.S. Department of Energy (DOE) (Burton, 1994). Characterization activities addressed groundwater and soil affected by refinery activity in the vicinity of petroleum sludge lagoons. Risk assessment and the development of remedial goals using established U.S. procedures were based on this characterization effort. Subsequently, treatability studies as well as construction, and implementation of the bioremediation process were accomplished, also based on this characterization.

The characterization consisted of two Phases: Phase 1 (field screening) from April 1 through April 5, 1996 and Phase 2 (quantitative evaluation) from May 8 to May 31, 1996. During that time, a variety of characterization technologies were fielded in the context of ESC at the Czechowice Refinery site. This report summarizes the characterization activities and results.

Experimental Plan

<u>Protocol/Hypothesis</u>

The Expedited Site Characterization (ESC) demonstration was conducted to illustrate the innovative application of *in situ* samplers, direct push technologies, directional drilling and rapid turnaround chemical analysis to the characterization of a contaminated site. The ESC methodology was developed for the U.S. DOE to decrease the time and cost associated with site characterization (Burton, 1994). Typical waste characterization involves a long iterative process of sampling, waiting for results, interpretation, resampling, waiting for results, etc. By mobilizing analytical instruments on site and using more direct measurement technologies with the scientists and engineers that can interpret the results we can immediately redirect further sampling. This allows a single sampling campaign that provides all the necessary characterization. This expedited site characterization formed the basis for a subsequent risk assessment and the deployment of an innovative application of bioremediation at the site. The specific goals of the ESC were to identify the sources and nature of contamination and to determine the depth and width of the contamination plume.

Based on prior information and analytical capabilities at IETU, the following types of contaminants were investigated:

Organic	Inorganic
Benzene	Lead (Pb)
Toluene	Copper (Cu)
Ethylbenzene	Arsenic (As)
Xylenes	Mercury (Hg)
1,3,5-TMB	Nickel (Ni)
1,2,4-TMB	Zinc (Zn)
Naphthalene	Chromium (Cr)
Fluoranthene	Cadmium (Cd)
Benzo-(b) fluoranthene	Cobalt (Co)
Benzo-(k) fluoranthene	
Benzo-(a) pyrene = B(a)P	
Benzo-(g,h,i) perylene	
Ideno (1,2,3-c,d) pyrene	
Total Petroleum Hydrocarbons = TPH	

It is noted that not all of these contaminants have regulatory limits imposed by Polish or American law. Some water quality parameters such as pH, conductivity, and alkalinity were measured in real time. Many of the chemical quantitative measurements were performed at the IETU laboratory.

Materials & Methods

Site Characterization Scope of Work

The site characterization technical activities were divided into two general phases. Phase 1 developed information to support the initiation of the detailed quantitative investigation conducted in Phase 2. Phase 1 involved: collection of hydrogeologic and stratigraphic information about the subsurface (i.e., surface geophysics, CPT, drill core), collection of screening-level, qualitative data on surface or near surface contaminant levels, collection of vadose zone (aquifer sediment) contaminant concentrations and collection of site-specific hydrologic data.

Phase 2 of the site characterization included the collection of soil and groundwater samples for quantitative analysis to determine the degree and extent of subsurface contamination by petroleum hydrocarbons. Due to the diverse capabilities of the deployed direct-push technologies, and a need to minimize time on-site, there was some overlap in the performance of these two phases.

All samples were preserved by cooling to approximately 4ºC (on ice) following collection and during transport to the IETU laboratories. Water samples intended for metals analysis were also

preserved by acidification. Decontamination and health and safety procedures were conducted in accordance with accepted industry practice and/or Polish State Environmental Protection Inspectorate guidance. Chain of custody forms were used throughout the characterization effort.

Geophysical survey

Parsons Engineering carried out two geophysical surveys designed to detect potentially obstructive or dangerous subsurface debris. These surveys were conducted using ground penetrating radar (GPR) and EM61, an electromagnetic device designed to detect metallic objects (Parsons Engineering Science, Fairfax, VA). Originally the GPR was also to have been used to determine the depth of sludge in the two small lagoons. Attempts to use GPR were unsuccessful because the penetration depth was less than one meter through the heavy soils and sludge. The EM61 survey was more successful and covered the areas adjacent to, but not over the three lagoons. The EM61 consisted of a non-magnetic cart carrying a magnetic detection array connected to a backpack mounted electronics package and data logger. The cart was pulled across the area to be surveyed along predetermined grid lines. The data were then downloaded and reduced into a graphic form that displayed the magnitude of magnetic fields detected by the array.

Piezometer installation

Three piezometers (P-1 through P-3) were installed in the late winter of 1995/96 in accordance with standard local practices and regulations (locations are shown in Figure 2.1). The piezometers were located adjacent to the subject lagoons based on accessibility and known subsurface obstructions. The piezometers were spaced to provide an accurate determination of hydraulic head variations and groundwater flow direction.

Each borehole was drilled by hollow-stem auger methods, cored, and descriptive logs recorded. The depth of each borehole was established at the point where the Tertiary aquitard was breached, but no deeper than 3 meters into the aquitard. The piezometers were constructed of PVC, with a screened section approximately 4 meters in length. The screen was positioned such that the water table was located approximately in the middle of the screen at the time of installation. The original piezometer logs are provided in the Expedited Site Characterization Final Report.

Water Level/Free Phase Hydrocarbon Monitoring

Following installation, piezometers were allowed to equilibrate prior to any measurements. Water levels were monitored, initially, with an electronic water-level indicator and subsequently with electronic data loggers (In-Situ Troll, Laramie, WY). The piezometers were inspected periodically to monitor for the presence of LNAPLs on the water surface and to download the data loggers.

The water/hydrocarbon interface was monitored using a translucent, bottom-filling bailer. The presence and thickness of free liquid hydrocarbon noticed on the water surface was recorded (In-Situ Troll, Laramie, WY).

<u>Unit Specific Hydrostratigraphic Investigation</u>

Hydrostratigraphic data, pertinent to an understanding of groundwater flow characteristics as it relates to geologic strata, was collected during both phases by several methods. Lithologic data

of the strata from the ground surface to, and including, the first aquitard was obtained from borehole descriptions and sample analysis and from direct-push technologies (DPT). Depth, dip, and permeability characteristics of the Quaternary near-surface and aquifer strata and the Tertiary aquitard were determined.

Borehole Logging

Baseline stratigraphic information was obtained from boreholes associated with the installation of the three water table aquifer piezometers. During the drilling operation, the supervising geologist inspected and described characteristics of the soil, including approximate depth range, grain size, sorting, soil strength, color, moisture content, and other distinguishing features. A minimum of three physical samples were collected from each borehole. Samples of aquifer sediments were subjected to geotechnical analysis, including grain size distribution.

Cone Penetrometer Technology

Cone Penetrometer Technology (CPT) services were provided by UWG (Bernau, Germany). An important aspect of the CPT deployment was the availability of two different types of *in situ* fluorescence probes. This application represented the first time that both laser and Hg lamp based systems were applied to the same site (Bevolo, 1996). The two types of probes were set to a single wavelength detection window, which was selected to optimize detection sensitivity for petroleum products, and, therefore, they both integrated over more than one compound. The detection wavelengths were such that the Hg lamp should have had higher response to lighter aromatics than the laser system.

Eleven CPT pushes were attempted and all but one were successful at reaching but not penetrating the water table aquifer. The ten locations where piezocone measurements (sleeve friction, tip pressure and pore pressure) and laser measurements were obtained were shown in Figure 2.3. At five of these locations (CPT-2, 3, 5, 9 and 10) Hg lamp profiles also were obtained. Hg lamp measurements were terminated by the loss of the probe at CPT-11. Unfortunately because of heavy rains, the lagoon berms could not support the 20-ton weight of the CPT truck, except along the eastern edge of the two smaller lagoons where a concrete pathway was constructed. This limitation constrained the extent of CPT sampling.

Detailed stratigraphic data was collected from various locations in the vicinity of the lagoons using CPT piezocone methods. The first three CPT pushes were located adjacent to the piezometers as a means of interpreting CPT logs and interpreting neighboring CPT pushes. All piezocone data was collected in accordance with ASTM D3441-86. The piezocone probe was pushed to the first confining unit, the Tertiary clay sediments beneath the Quaternary aquifer. Tip stress, sleeve friction, friction ratio, and pore pressure data were used to develop a consistent method for identification of significant strata. Upon completion of each push, each hole was plugged on removal of the rod.

Horizontal drilling

Horizontal drilling technology was provided by Ditch Witch, Inc. and was used to acquire soil samples from beneath the two small lagoons (Perry, OK).

Soil Electrical Conductivity Measurements

A soil electrical conductivity percussion probing system was utilized to gather direct stratigraphic and potential NAPL plume data from the strata above the Tertiary unit. A system manufactured by Geoprobe® was mobilized in conjunction with the groundwater and soil sampling effort (Geoprobe® Systems, Salina, KS).

The first three probe pushes were located adjacent to the piezometers, thus providing three log types (physical core, CPT, and electrical conductivity) within a few meters of each other. This approach was intended to provide a means of interpreting further conductivity logs and to help determine the reliability of the two direct push methods.

Data from the conductivity logging system was downloaded in electronic form and hardcopy immediately upon completion of each push. The data was transferred to ESC on-site personnel for quality evaluation and interpretation.

Field Permeability Testing

Field hydraulic permeability tests (slug tests) were performed on the three piezometers. These tests were performed to estimate the hydraulic conductivity (K) and transmissivity of the water table aquifer within the vicinity of the refinery. This data became an important component of the groundwater conceptual model that was developed for the site. Multiple tests were performed on each well and the data were analyzed using the Bouwer and Rice method.

Screening-level Contaminant Analysis

This aspect of Phase 1 was designed to define the approximate extent of targeted contaminants and to determine the location of "hot spots" or contaminated soil which might serve as an on-going source of contamination to groundwater. The media under investigation during this activity were near surface soils and vadose zone aquifer sediments.

Immunoassay Analysis of Surficial Soil

The purpose this activity was to qualitatively determine the concentration of petroleum hydrocarbons in near-surface soils. These tests helped to provide an understanding of the location of some subsurface contamination and a general understanding of the relative level of hydrocarbons in soil. Immunoassay analyses were performed on near-surface soil samples. Immunoassay (IMA) kits designed for the detection of petroleum hydrocarbons (from three vendors: Ensys, Ohmicron and DTECH) were utilized at appropriate opportunities during the execution of both the Phase 1 and Phase 2 of site characterization work. (Ohmicron, Newton, PA)

Soil samples for IMA analysis were collected from a depth of 1 to 2 m at forty-seven locations around the perimeter of the subject lagoons, the western fence, by the tanks and in the park to the west. Locations for these samples are shown in Figure 2.4. During installation of passive soil vapor collectors (described below), soil samples were collected at the depth at which the collector was installed. These samples were analyzed using the selected IMA system(s) to determine total petroleum hydrocarbon (TPH) or PAH levels. Additional sample locations and depths were chosen, as IMA analysis supplies permitted, to supplement this data set. Analyses were conducted in accordance with manufacturer's specifications.

Passive Soil Vapor Survey

A passive soil vapor survey using EMFLUX sorbers (Beacon Environmental Services, Forest Hill, MD) was conducted in shallow soils on the Refinery property near the subject lagoons during Phase 1. The NERI and GORE sorbers did not arrive in time for Phase 1 but were installed at locations inside and along the boundary of the Refinery property during Phase 2. These surveys were conducted by first installing passive vapor collectors into the ground at predetermined locations and depths. After an appropriate amount of time (approximately one week) the collectors were retrieved, containerized, transported to the IETU laboratories, and analyzed to determine the concentrations of targeted volatile organic compounds. The sorbers collect volatile organic compounds as they diffuse through the soil. The purpose of the passive soil vapor survey is to obtain information about the approximate extent of contamination in the top few meters of soil and to estimate potential exposure to humans.

Approximately forty passive collectors from each vendor were installed to the recommended depths (Gore = 1.5 m, EMFLUX = 15 cm, NERI = 30 cm). Two styles of collector were used: carbon-coated wire inside a glass housing (NERI Petrex system) and adsorbent material inside a gas-permeable fabric (Gore and EMFLUX) (Gore Technologies, Elkton, MD, and Beacon Environmental Services, Forest Hill, MD). The locations were determined, in part, by results obtained from IMA analysis of near-surface soils (described above). In general, collectors were installed in locations where IMA samples were taken, around the perimeter of the lagoons, in upgradient positions, and along the property boundary in the vicinity of the target lagoons. Redundant collectors were installed at ten locations for the purpose of comparing results of the two Phase 2 collector vendors i.e., Gore and NERI. Locations for EMFLUX are given in Figure 2.5A, for Gore in Figure 2.5B, and for NERI in Figure 2.5C.

The collectors were installed by first opening a hole in the ground to a depth of 1 to 2 meters using a manual auguring device. The collector was then inserted to the bottom of the hole in accordance with the manufacturer's specifications. The hole was plugged with loose soil to prevent ambient air from influencing the adsorption rate of organic compounds onto the collector. The location of the hole was marked using yellow ribbon to facilitate recovery following the desired exposure time.

Active Soil Vapor Survey

An active soil vapor survey was conducted as part of Phase 1 to determine the nature and extent of volatile organic compounds in the unsaturated zone of the Quaternary aquifer sediments (sand and gravel). This information was used to assist in determining the necessary scope of Phase 2 sampling for delineation of the groundwater plume.

A Geoprobe® percussion-probing device was used to push a perforated vapor-sampling rod to two depths, approximately 6 and 2 meters above the water table. These depths were a modification of the original work plan when it was discovered that these two depths seemed to give vastly different results. Soil vapors were extracted by vacuum and injected directly into a portable gas chromatograph (GC) located onboard the probe vehicle. The concentration of the aromatic hydrocarbons benzene, toluene, ethylbenzene, and xylenes (BTEX) were determined and reported to the ESC team immediately upon completion of the analysis.

The location and number of active soil gas analyses were determined by the extent of measurable hydrocarbon concentrations, the physical limits of the investigation area, and the costs associated

with performance of the tests. Given the physical restrictions on equipment mobility at the site and the direction of groundwater flow, 16 locations were selected based on the results of the passive soil gas survey, immunoassay analysis, or other data sources.

Induced-fluorescence Hydrocarbon Detectors

Two technologies based on induced-fluorescence of aromatic and PAH compounds were employed during the characterization activity. One is known commercially as the Rapid Optical Screening Tool (ROST), is deployed with a cone penetrometer or Geoprobe®, and makes measurements *in situ* during the pushing process (Fugro Geosciences, Houston, TX). The second is a hand-held instrument designed for use on individual samples. This second instrument is an innovative Fuel Fluorescence Detector and was operated by a team from the Technical University of Budapest. It has a fixed excitation and detection wavelength and integrates over a large number of fluorescent compounds, especially PAHs. The *ex situ* instrument was housed in the refinery office.

Both of these systems use an ultra-violet light source directed at the sample media. Hydrocarbon materials adsorbed in the soil matrix or free hydrocarbon liquid absorb UV light of a specific wavelength range and, in response, emit light of a longer wavelength. The emitted light wavelength and intensity indicate hydrocarbon type and concentration.

Both instruments provided screening-level data for hydrocarbons that was used by the ESC field team to identify areas of high hydrocarbon concentrations in the vadose zone soils or non-aqueous phase liquids in the vadose zone or aquifer.

Groundwater Sampling Procedures

Groundwater sampling targeted those areas that exhibited the highest concentrations of mobile contaminants e.g., the tanks and areas between the three lagoons. Sampling proceeded outward from these locations to either the outermost edges of the plume or to the limit of the accessible investigation area. Samples were collected from multiple depths at each sampling location, corresponding to the upper, middle and lower portions of the aquifer. The spacing, locations and number of sampling depth intervals were determined by the size of the area of investigation, the complexity of stratigraphic layering detected in Phase 1, and allowable sampling and analysis rate as determined by the sampling services contractor and the IETU laboratory.

Groundwater samples from the Geoprobe® were collected using a shielded screen attached to the push rod, which was exposed at the desired depth. This allowed groundwater to be pumped to the surface and captured in containers appropriate for each type of compound class (BTEX, PAH, metals). Groundwater samples from the saturated zone piezometers were collected using a sampling pump or bailer. Water was filtered in the field with 45-micron mesh filters. Field water parameters including dissolved oxygen, oxidation-reduction potential (ORP), pH, specific conductivity, and temperature, were monitored using a Hydrolab Surveyor (Hydrolab Inc, Houston, TX). The Hydrolab Surveyor probes used for estimation of dissolved oxygen and pH were calibrated prior to each use. All other probes on the Hydrolab were calibrated monthly.

Measurements of CH_4, CO_2 and O_2 concentrations in soil gas were performed using a Landtec GEM-500 Gas Extraction Monitor. This instrument is a highly reliable gas-monitoring unit originally designed for the detection of landfill gases. It was used for these purposes in the ESC and subsequently as a monitoring device during the remediation activity (Landtec, Colton, CA).

All analyses were performed by the IETU using EPA approved methods. Samples were acidified (where appropriate) and stored at 4°C prior to analysis. Chemical Oxygen Demand (COD) analyses were conducted using the 410.1 method. Soluble reactive phosphate concentrations were measured by the ascorbic acid colorimetric determination method (EPA 365.2). Total Phosphorus was determined by the persulfate digestion and ascorbic acid colorimetric determination (EPA 365.2). Total Kjeldahl Nitrogen (TKN), which includes free-ammonia plus organic nitrogen was determined colorimetrically following digestion, distillation and Nesslerization (EPA 351.3). Ammonia as distilled ammonia nitrogen was determined colorimetrically following distillation and Nesslerization (EPA 350.2). Nitrate, nitrite, and sulfate were determined using the potassium chloride method (ISO 14256). Alkalinity was evaluated using the pH 4.5 titrametric method (EPA 625/410).

Soil Sampling Procedures

Soils were collected during the ESC for analysis of BTEX, microbial counts, physical parameters, and miscellaneous parameters. Soils for BTEX analysis were collected using a modified syringe tube and plunger and were placed in a headspace vial. Six milliliters of distilled water was added to the vial. The vials were sealed with crimped aluminum rings over Teflon-lined septa.

Core specimens for microbial analysis were obtained directly from the soil sampler. Cores were sectioned with sterile spatulas and the outermost layer scraped off using a sterile scoopula. The sample was then placed in a sterile Whirl-Pak bag and transported on ice to the laboratory for immediate analysis. Personnel at the IETU laboratory performed microbial analyses.

Soil Gas Sampling Procedures

A magnehelic gauge was attached to a quick-connect fitting for measurement of pressure. A high volume pump was attached to the quick-connect and well gas was evacuated until oxygen readings stabilized indicating the presence of soil gas rather than well gas. A Landtec landfill gas analyzer (Landtec, Colton, CA) was attached and measurements of oxygen, carbon dioxide, and methane were collected. A B&K photoacoustic infrared spectrophotometer was used for analysis of VOCs.

Results and Discussion

The results of the site characterization effort are presented by first describing those data that support a physical conceptual site model (PCSM), addressing issues such as hydrogeology and stratigraphy. Next the chemical conceptual site model (CCSM) will be developed to address the current location and concentrations of the targeted analytes. Together the PCSM and the CCSM constitute the overall conceptual site model. The division of the site model into chemical and physical aspects emphasizes the nearly equal importance of each to a thorough understanding of the site.

Physical Conceptual Site Model (PCSM)

Historical Review

Regional information on the Czechowice Refinery was reviewed to develop a more complete environmental setting of the refinery. This information was obtained from existing documents that describe the geologic and hydrogeologic properties of the Czechowice area. The site-

specific environmental setting is presented in the following sections. Additional details are contained in the Risk Assessment (Chapter 3).

Brown and pedosolic soils are present on the surface. Soils are developed from loamy sands and glacial loam. In the river valley, soils developed from alluvial deposits are present. Subsurface soils consist of glacial loam, clays, sands and silts. The glacial deposits are 1 to 15 m thick. Glacial features occur below alluvial deposits. Gravels with sand and clay are up to 10 to 30 m thick. These quaternary deposits cover Tertiary age clays. The clays are up to 100 m thick and cover a Carboniferous mudstone series with hard coal beds.

The surface clays and silts have a very low permeability. The estimated hydraulic conductivity of the sand and gravel deposits beneath the refinery is 0.005 m/sec, based on published information. Hydrogeologic information was collected from wells, which are used for pumping industrial water into the refinery. In 1995, the water table was measured monthly in nine wells. During the measurement period, the water table was about 12m below ground surface (bgs), corresponding to a few meters below the top of the granular aquifer unit.

The thickness of the Quaternary sand and gravel aquifer varies between 8 to 30 m. The groundwater flow direction is from SW to NE, based on information from the refinery wells. Surface topographic data suggests a somewhat more easterly direction of flow.

ESC Phase 1

Table 2.1 shows various unit elevations with depth referenced to sea level. The original piezometer logs are provided in the Expedited Site Characterization Final Report. From Table 2.1 it is clear that the depth above sea level to the top and bottom of aquifer unit (GW) is nearly the same across the lagoon area, indicating a relatively flat subsurface strata. The aquifer unit is approximately 11 m below the original ground surface (approximately 13 m below the top of the lagoon berms), and the aquifer is approximately 6.5 m thick in the vicinity of the lagoons.

Table 2.2 shows results of IETU definitive analyses for metals, polynuclear aromatic hydrocarbons (PAHs) and total petroleum hydrocarbons (TPH) from five core samples at various depths for the three piezometers installed during this time. The pattern of metal distribution with depth was similar among the three piezometers, i.e. concentrations are high at the near surface, decline with depth and increase at the bottom of soil cores. The PAH results for P2 show the same trend as for the metals but for P1 and P3 there is a monotonic decrease in concentration with depth.

ESC Phase 2

Measurements of water levels in the piezometers made during Phase 2 indicated that the groundwater had risen to the level of the upper clay unit (CL unit in Table 2.1). As a result, the aquifer was partially confined during the characterization activity.

The water table elevations measured during Phase 2 indicated a southerly groundwater flow direction, opposite to historical regional patterns and away from the nearby river. This anomaly may be a result of the partially confining conditions and associated heavy rainfalls.

Given the piezometer log indications of a relatively flat aquifer topography, one of the first tasks for stratigraphic characterization was to confirm, with the Geoprobe® electrical conductivity system, how flat it was on a finer scale than that provided by the piezometer logs. The locations of the 18 Geoprobe® conductivity logs are shown in Figure 2.1 along with all other Geoprobe®

sampling locations. The Geoprobe® could not penetrate the aquifer/Tertiary clay (GW/CH units in Table 2.1) interface in most locations.

The depths to the CL/GW boundary, derived from both the conductivity logs and the CPT piezocone logs, are shown in Table 2.3. There is a general uniformity of the subsurface strata, with the exception of an area to the southwest of the lagoons. In this area, in the vicinity of GP-12 and GP-27, the ground conductivity is significantly lower and stratigraphic interfaces are not as easily identified. The conductivity logs and piezocone logs are available in the ESC Final Report.

The average elevation of the top of the aquifer was determined to be 250.2 m above sea level (asl), with a maximum variation of plus 2.1 m and minus 1.8 m. Generally, the depth to the top of aquifer was about 1 to 3 m shallower over the NW lagoon compared to over the eastern boundary road or the other lagoons. Figure 2.2 is an E-W cross section through the lagoon area showing conductivity logs and generalized stratigraphic interpretations. A zone of high conductivity is visible on the eastern half of the section, which may be the result of fluids leaching from the large lagoon on the east.

Geoprobe conductivity data and sleeve/tip data from the CPT (sampling locations are shown in Figure 2.3) were analyzed in order to identify potential high permeability zones in the vadose zone (CL unit). These zones are important for both the risk assessment, because it addresses pathways from sources to receptors, and the remediation, because these features can be used to monitor the remediation progress. Evidence for contaminant migration also is an indirect measure of permeability, and the CPT fluorescence logs were analyzed for that purpose. CPT sleeve/tip and pore pressure logs are provided in the ESC Final Report.

Ideally, a homogeneous CL unit would be characterized by a high uniform electrical conductivity in the Geoprobe® logs and uniform clay-like values for the soil classification values in the sleeve/tip (S/T) logs, denoted by high values of the sleeve/tip ratio. Only rarely was this observed, indicating that the CL unit is heterogeneous, with interbedded silty and sandy zones. Generally, the conductivity logs with characteristic lengths of several feet, vary less rapidly with depth than the CPT sleeve/tip logs, which vary sharply within a few tenths of a meter. Focusing on the conductivity logs around the targeted NW lagoon (GP-04, -27, -07, - 30, -05 and -06), there are two consistent zones of lower conductivity in the CL unit, possibly indicating zones of high silt content and higher permeability. One zone ranges from 0 to about 7 m bgs, and the other from 9 to 11 m bgs. The indications are not dramatic but together a consistent result seems to be evident. The CPT-05, -06 and - 07 sleeve/tip logs from the eastern edge of the NW lagoon show results that do not contradict those from the conductivity logs. The softer soil layers, potentially resulting from higher silt content, indicated in these logs by high values of S/T are fewer and thinner than those of the conductivity logs. Since electrical conductivity logs are susceptible to nonstratigraphic effects (e.g., pore water conductivity), CPT fluorescence logs can be used for further understanding by tracking the vadose zone PAH type contamination. These logs confirm shallow hits from 1 to 8.6 m, but there is little evidence of PAH type contamination at the 10 m depth.

Therefore, it is concluded that the best monitoring depths for the BR are located in the shallow 0 to 8.6 meter range. Given that their locations will be adjacent to the NW lagoon it is suggested that these locations be close to those already probed with the conductivity and CPT instruments so that detailed depths can be picked with better confidence that they will yield reliable data.

Locations near CPT-06, -07, and -08 are prime candidates. Locations of GP-30, -38, -40 -03 and -07 also are recommended, especially GP-07 and GP-39 where soil cores SL-3 and SL-6 respectively are available from 4.8 to 12.0 m. A description of these and the other soil cores SL-1, SL-2 and SL-5 are given in Table 2.4, noting that no SL-4 was taken.

The EM61 (electromagnetic) survey identified a number of potential geophysical anomalies. In the area of the target (NW) lagoon, identified anomalies appear to be associated with surface features or were in the vicinity of buried piping known to be present from discussions with Refinery personnel. Features identified were marked for reference in subsequent site operations. A color map of the EM61 data can be found in the ESC Final Report.

Chemical Conceptual Site Model

Historical

The maximum allowable concentrations of the targeted chemicals, for soils and groundwater of industrial areas, are listed in Table 2.5 based on "Guidance for Soil and Groundwater Contamination of Hydrocarbons and other Chemical Compounds in Remediation Processes" published by the Polish State Environmental Protection Inspectorate.

There was only limited information on soil and water monitoring in the vicinity of the refinery. In September, 1995, IETU took 4 soil samples from the vicinity of the lagoons. In 1992 "Ekokonrem" company performed investigations in the vicinity of the lagoons. They took a few samples of soil and provided chemical analysis. The results include concentrations of hydrocarbons from 50 to 2,990 mg/kg of soil. The samples were taken from depths of 0.5 m to 10.0 m.

A limited site field screening was conducted by IETU in September, October and November 1995. The IETU laboratory conducted the analysis of heavy metals and hydrocarbons. The results of this screening activity are described below.

Strategy

The primary purpose of groundwater and soil sampling is to define the nature and extent of hazardous substances released to the environment within and surrounding the subject lagoons. This information is necessary to support the assessment of risk to human health and the environment and to obtain technical information necessary to assess the feasibility of various remedial options. The site characterization sampling plan was designed to meet the following objectives:

- Determine site-specific hydrologic and lithologic characteristics through the use of piezometers, geophysical methods, direct push technology, and direct sample collection, to a maximum depth corresponding with the top of the Tertiary sediments below the unconfined Quaternary aquifer.
- Determine if waste material in the lagoons is mobile and migrating through the soil matrix to the water table.
- Determine the lateral and vertical extent of petroleum hydrocarbon contaminants in groundwater exceeding applicable action levels and background concentrations through the collection and analysis of groundwater samples from various depths within the water table aquifer beneath, adjacent to, and downgradient of the lagoons.

Screening Results

Immunoassay

The IMA results from surface soil samples suggest that the main source of onsite surface contamination are the storage tanks while either the tanks or the lagoons or both have impacted the first few meters of soil along the western boundary.

Results from Ohmicron BTEX for core SL-2 at six depths, suggests low levels of contamination (all results < 1 ppm) except for a slightly higher result at 8.4 m. This sample location (see Figure 2.3) was along the western roadway (NW property boundary). Active soil gas results from this location (GP-04) at 5 and 10 m depths showed large but unknown GC peaks at 10 m and 471 ppm benzene at 5 m. These concentrations for the Ohmicron samples are for BTEX adsorbed on the soil particles.

The Ensys kits were used to analyze samples at passive soil gas locations near the lagoon berms during Phase 1. Ohmicron and DTECH IMA kits were used to analyze samples during Phase 2 primarily at locations away from the berms (e.g., near tanks), along western road in the park and north of the Refinery. Some of the Ohmicron and DTECH kits collected samples near the berms to make technical comparisons of IMA vendors not to learn any more about site conditions. In addition, Ohmicron PAH and carcinogenic PAH (CPAH) kits were used to investigate SL-3 and SL-2 as well as the soil samples retrieved from beneath the lagoons by the Ditch Witch horizontal drill rig. All of the IMA results are shown in Table 2.6.

The TPH ENSYS results from SRF 3 to 14 all show high contamination. This was not unexpected because during installation of the EMFLUX sorbers at these same locations, the soil removed often either smelled of petroleum or appeared to be saturated with it. The low PAH results from SRF14 to 40 (not inclusive) were a bit surprising. SRF 34 to 39 were just north of the tanks and showed 1 – 10 ppm PAH higher than the other four samples away from the tanks. Samples SRF15, 17, 39 and 40 were taken from lagoon berms but did not detect PAH.

The surface BTEX results (SRF-45 to -70) from both Ohmicron and DTECH suggest significant BTEX contamination only near the north and east areas of the tanks (SRF-47 to -52).

The DTECH and Ohmicron surface PAH data sets are poorly correlated as evidenced by the wide scatter in the Ohmicron data (from SRF-61 at 4.65 ppm to SRF-45 at 43.08 ppm) as compared to the same five samples analyzed with DTECH (all were 0.3 ppm). Better correlation between Ohmicron-PAH and Ohmicron-CPAH results are found and they both indicate that SRF-58 and SRF-56 have among the highest PAH levels even though they lie outside the western fence, while the other high PAH detections (SRF-45, -51, -52) are near to the tanks.

The BTEX and PAH IMA results from both Phase 2 vendors for the three samples taken from the park (SRF-61, -62, -63), had the lowest values relative to those from Refinery locations (SRF-53 to -60). This suggests little offsite surface impact from the Refinery.

Passive Soil Vapor Survey

The relative concentration of organic compounds detected in a passive soil vapor survey will not necessarily correlate with the relative concentrations in the associated soil. Factors such as soil permeability, temperature and volatility of individual compounds will influence the efficiency and soil volume from which the collector gathers contaminants and thus the results. Therefore, this technique is considered to be a screening-level tool, although the modified on-site laboratory

procedure involving liquid phase extraction is considered to be quantitative. Passive sampling of soil vapors provides the benefit of higher sensitivity and lower susceptibility to variations in ambient conditions when compared to active vapor sampling.

Complete EMFLUX results are shown in Table 2.7. A field blank (never exposed to air at the Refinery) and samples A, B and C (exposed for ten seconds to Refinery air but never placed into the soil) showed very low or non detect values indicating little influence of sorber transportation procedures or Refinery air contamination. Figures 2.6, 2.7, 2.8 and 2.9 show contour plots of benzene, ethylbenzene, toluene and total xylenes, respectively. All but benzene have similar spatial distributions indicating high values to the east of the large lagoon, although toluene shows an area of elevated concentration just NW of the tank area. Benzene also shows a high concentration in the same area as the other three but it has a significant lobe from the western side of the two lagoons back to the tank area. It is doubtful that benzene could come from the lagoon sludge so this result suggested for the first time that the tanks may have impacted the area of these two western lagoons. There appeared to be a curious drop in benzene near the island that separates these two lagoons. Both of these features required further study at deeper depths. The first such study was an active soil vapor survey.

Active Soil Vapor Survey

With very few exceptions, only benzene was detected in the active soil gas samples.

At 5 m, the highest concentrations were found around the west side of the tank area at GP-13 (33,520 ppb) and at GP-15 (15,330 ppb) followed by GP-12 (1,201 ppb) and GP-14 (948 ppb). These were much higher than detections at the intervening locations (toward the tanks); GP-02 (107 ppb), GP-01 (146 ppb) and GP-11 (323 ppb). The trend toward lower benzene values toward the north and the two western lagoons (away from the tanks), GP-07 (235 ppb), GP-06 (86 ppb) and GP-03 (24 ppb) was dramatically reversed at GP-04 (471 ppb) and GP-05 (449 ppb).

At 10 m, the highest benzene concentrations were found well away from the tanks along the fence SW of the lagoon at GP-12 (15,170 ppb). The rest of the deep benzene detects followed the pattern of the shallow hits with high values near the tanks, low values by the two west lagoons and an increase towards the north edges of the two lagoons. The deep trends are not as clear as those seen in the shallow benzene evaluations. The remaining question is the concentration of petroleum in the upper clay unit and if there has been any impact to the groundwater itself.

Ex Situ Induced-fluorescence Detector

Fluorescence depth profiles were generated from *ex situ* induced-fluorescence analysis of soil cores SL-01, -02 and -03. Significant activity is evident at depths just above the water table at about 11 m for these cores, in addition to a major concentration at a depth of six meters for SL-03. Given moderate intensity in all of the 12 m samples, which were at or below the water table, these results suggest significant vertical and horizontal migration of semivolatiles below and away from the Refinery. Indeed it is noted that SL-01 and SL-2 are both along and outside the western fence of the Refinery.

Ohmicron CPAH and PAH results for SL-2 are low in contrast to the *ex situ* fluorescence analysis of SL-2. A large fluorescence reading occurs at 9.6 m and some contamination is found

at all six depths. Visual and odor observations made when these SL-2 core samples were acquired would tend to support the *ex situ* fluorescence results rather than the IMA results.

For SL-3 differences between OHM-BTEX and OHM-PAH occur especially at depths below 7.2 m, with higher PAH levels than SL-2. Unfortunately, the OHM-PAH depth specific results for SL-3 are not in agreement with the *ex situ* fluorescence detector, indeed the results are almost perfectly anti-correlated. For example, soil sample SL-03-060 (taken at SL-03 from a 6.0 m depth) gave the lowest OHM-PAH value and yet gave the lowest fluorescence value. These differences may be due to sampling slightly different portions of the SL-02 core or relative sensitivity of the two methods to the various PAH constituents that each method measures. This is a well-known effect in this area of qualitative screening methods. Still the trend in the observations indicates serious disagreement between the IMA and *ex situ* Fluorescence Detector for SL-3 soil cores.

It is interesting to compare the *ex situ* Fluorescence Detector results for SL-01 with those from the definitive analysis taken from soil samples at the same depths shown in Table 2.8 (a complete listing of the definitive soil analyses). The SL-01 *ex situ* profile shows a large hit at 10.8 m. Only benzene and naphthalene (see Table 2.8) have their highest hits at 10.8 m. Since the *ex situ* detector is unlikely to be very sensitive to benzene this leaves naphthalene as the most likely contaminant at this depth. Unfortunately it is also true that the *ex situ* detector should be more sensitive to the higher benzene ring count compounds, (e.g., B(k)F) and yet these compounds have their lowest hits at 10.8 m. These results for SL-01 are not understood unless benzene overwhelms the PAHs at the 10.8 m depth.

Before proceeding to the *in situ* fluorescence probes the other results in Table 2.8 deserve consideration. First no analyte appears above the Polish limits for soils. Second, VOCs have penetrated directly below the two small lagoons to depths of 8.5 m based on sample results in Table 2.8 and to the same depth at the SL-05 location on the SW berm along the NW lagoon.

In-situ Induced-fluorescence Probes

Two contaminated zones are evident at all locations based on the laser and Hg lamp CPT fluorescence logs; a shallow zone from the surface to, at most, 8.4 m and a deeper zone from 11 to 16 m that corresponds to the depths of the water table.

Generally, the upper plume has the same depth range whether the laser or Hg lamp probe was used, except for CPT-3 where the laser portion from 4.2 to 6.0 m is not confirmed by the Hg probe. The intensity of the laser signals are nearly the same range from 0 to about 150 but the Hg maximum intensities vary from 7 at CPT-9 to 32 at CPT-10. The depth resolution of both probes is very good at about 0.1 m or better. Also the intensity distribution with depth is roughly the same for either probe. Table 2.9 shows the depth range of the upper plume, the elevation corrected depth to the maximum depth of the upper plume, the upper plume width and the relative integrated laser intensity of the upper plume.

Several properties of the upper plume are evident from Table 2.9. First, the deeper plumes appear to be wider with the possible exception of CPT-11 which has the third deepest plume but a relatively narrow plume width. This is to be expected if the sources are at the surface. Although not as evident, there does seem to be a general trend that the thicker plumes also have the most intense laser signals. Exceptions are CPT-9 with very high intensity but relatively narrow width and CPT-6 with very low laser intensity but a rather large plume width.

When analyzed geographically (see Figure 2.3 for CPT locations) some trends in the upper plume are clear. The most intense portion of the upper plumes (CPT-3, -9, -10 and -11) occurs near to the tanks south of the lagoons. These locations also have the highest laser intensities for the lower plume at or near the water table. These trends suggest that the tank areas are major contributors to both plumes. However, evidence for direct lagoon involvement is most clearly seen from the CPT-8 logs that show moderate upper plume intensity and plume width, even though CPT-8 is well away from the tanks. Indeed CPT-5 and -7 which are closer to the tanks than CPT-8 do not indicate as much contamination as CPT-8. CPT-2 and -5, which are just north of the tanks and south of the lagoons have some of the weakest laser intensities, shallowest upper plume depths and narrowest upper plume widths. These characteristics of CPT-2 and -5 tend to confirm the notion that both the tanks and the lagoons are contributing to the upper plume. It should be noted that at CPT-10 and to a lesser extent at CPT-11, visual and olfactory evidence of gasoline-like free product at the water table were found.

The evidence for subsurface vadose zone contamination from the surface to as deep as 8 m and for water table contamination are very strong from the CPT *in situ* fluorescence results. To determine which contaminants are involved in the water table aquifer an extensive groundwater sampling program was performed.

Groundwater Contaminant Plume Investigation

Twenty-four locations were selected for groundwater analysis and their locations are shown in Figure 2.10. Four of these had groundwater samples taken from the three depths indicated: GP-07, GP-39 and GP-38 on the NW lagoon berms and GP-32 near P2 between the tanks and the SW lagoon. Five locations had groundwater samples from two depths: GP-04 upper and middle of aquifer, GP-41 middle and lower portion of aquifer, GP-15 middle and lower, GP-43 upper and lower, and GP-33 from upper and lower portions of the aquifer. All others had only one groundwater sample, all from the upper aquifer region, except for GP20 taken from the aquifer middle. Each groundwater sample was numbered consecutively from GW01 to 39 with the 40th labeled 01D (a duplicate sample). Every sampling day a field blank was obtained and analyzed for BTEX and naphthalene as though it were a groundwater sample. Except for about 5 ppb toluene no significant interferences were obtained from the field blank results. The GP location and depth for each of the 40 groundwater samples are given in Table 2.10.

The compete set of groundwater data is shown in Table 2.11 for BTEX, Table 2.12 for PAHs and Table 2.13 for metals, alkalinity, conductivity and pH. In addition, the U.S. EPA MCL and Polish limits are given for each analyte where available. The number of hits above each of these limits also is given in these tables.

Data for samples GW01FD and GW04 are of special interest since both were taken from the same location (GP12) and at the same depth of 12.5 m on successive days with complete removal of the sampling probe between the two sampling events. Except for Cr (both NDs), Pb (both NDs), B(b)F, Hg, pH, alkalinity and conductivity, there are large differences in the other reported values. In most cases, except for fluoranthene, the values for GW01FD are much lower than those for GW04 for B(k)F, B(a)P, IP, Ni, Zn, Cu, Co, and As. Because these two samples are duplicates rather than splits, the variance can be due to either sampling variances and/or laboratory variances. Past experience indicates that these large variances are likely due to sampling and not laboratory variances.

Benzene, with a hit above both national limits for every groundwater sample taken, is by far the most likely major contributor to any groundwater risk scenario. B(a)P, B(ghi)P, fluoranthene and naphthalene all have significant hit ratios and these PAHs must be a major consideration in the groundwater risk assessment. Toluene, ethylbenzene and total xylenes also have some samples above the action levels. Of the metals only Cd and Hg show any hits and only for one sample each. In the case of Cd that one sample is below the Polish limit but above the US limit. These data indicate clearly that the groundwater has been contaminated with VOCs and PAHs at all aquifer depths within the Refinery and near to the Refinery property along the western fence line.

Contour maps of the groundwater results from the upper half of the aquifer are shown for selected analytes in Figures 2.11-2.21.

For the BTEX group, each analyte shows similar distribution across the site and with depth. There are two areas of high concentration, one south of the tanks and the other around the northern portion of the NW lagoon. In both areas analyte concentrations increase with depth into the aquifer. It is unlikely that the lagoons are contributing to the BTEX concentrations given their volatility and the self sealing properties of the sludge at the bottom of the lagoon disposal area . These lagoons extend several meters below the ground surface, yet benzene hits above 1 ppm are found at the bottom of the aquifer along the northern berm of the NW lagoon.

These two BTEX plumes are either due to two sources or to the tanks alone. The latter hypothesis requires an explanation of the reduced BTEX in the intermediate zone around the SW lagoon while the former suggests a non-Refinery source. Enhanced biological activity in the immediate lagoon areas could explain the reduced BTEX between the two plumes. It was observed during the feasibility sampling in1995 by the bioremediation group that such activity has been found in the surface soils at the edges of the lagoons. To date there have been no samples taken at depths involved in these results (i.e., to 20 m below the ground surface), to confirm sufficient natural biologic activity to account for this reduced BTEX concentration zone in the groundwater.

The lateral and depth distribution of both alkalinity and groundwater conductivity show the same pattern as the BTEX components. Elevated alkalinity and conductivity values are correlated with high BTEX concentrations.

For metals, trends are difficult to determine because of their low concentrations. Hg, As, Ni and to a lesser extent Cr all seem to be found near and around the small SW lagoon.

For the PAH group, B(a)P and naphthalene which have the highest hits of all of the PAHs. B(a)P shows evidence of two plumes similar to those found for the BTEX group. More involvement toward the NW and NE directions from the tanks exists, but both PAHs still have somewhat isolated high hits to the NW of the NW lagoon. No trends with depth for either PAH are discernable although the two locations south of the tanks indicate higher concentrations at deeper depths. The opposite trend is found more often around the NW lagoon.

Conclusions and Recommendations

Clays are a dominant sediment type in near-surface soils, potentially mitigating the degree of vertical migration of hydrocarbons. The semi-solid state of the lagoon sludge and their relatively low solubility in water suggest that the lagoons make a relatively minor contribution to subsurface contamination. With some notable exceptions, the qualitative and quantitative analysis methods were in agreement with each other.

Baseline Risk Assessment

Concentrations of the targeted analytes and their spatial distribution on or very near the Refinery property are of sufficient number that reasonable interpolations can be used to assess their risk by pathways such as surface ingestion, inhalation and contact, and groundwater ingestion once land use has determined likely human receptors. Beyond the Refinery boundaries risk assessment will require careful modeling and extrapolation of on-site data and it is likely that wide variance in impact will result. For soils, PAHs are likely to be the main contributor, while for groundwater, PAHs and benzene will dominate the total risk.

Bioremediation

It was clear before ESC was undertaken that the lagoons represented potential targets for the remediation effort. The early encouraging bioassay results from the near surface soil sampling, conducted independently of the results reported here, gave confidence that the NW lagoon could be remediated. The results reported have shown that there are soil contaminants, most likely PAHs and probably VOCs, throughout the site to depths up to 8 m bgs based primarily on the *in situ* (CPT based) and *ex situ* fluorescence measurements. These data simultaneously provide an indication of the extent of the remediation required and a means to monitor the bioremediation progress with soil vapor probes positioned about the targeted NW lagoon. Further, the ESC results on the groundwater have identified VOCs, especially benzene, as well as PAHs, especially B(a)P and naphthalene, at concentrations above allowable limits that will ultimately require action involving renewed consideration beyond the originally planned bioremediation.

References

Bevolo, A, 1996. Draft report on the results of the expedited site characterization demonstration at the Czechowice oil refinery, Poland, Ames Laboratory

Burton, J.C., 1996. "Expedited Site Characterization for Remedial Investigations at Federal Facilities," pp. 1407-1415 in Vol. II, Proceedings of the Federal Environmental Restoration III and Waste Minimization II Conference and Exhibition, New Orleans, Louisiana, April 25-29, 1994.

Figure 2.1 - Locations of piezometers (P) and Geoprobe electrical conductivity survey sampling points (GP)

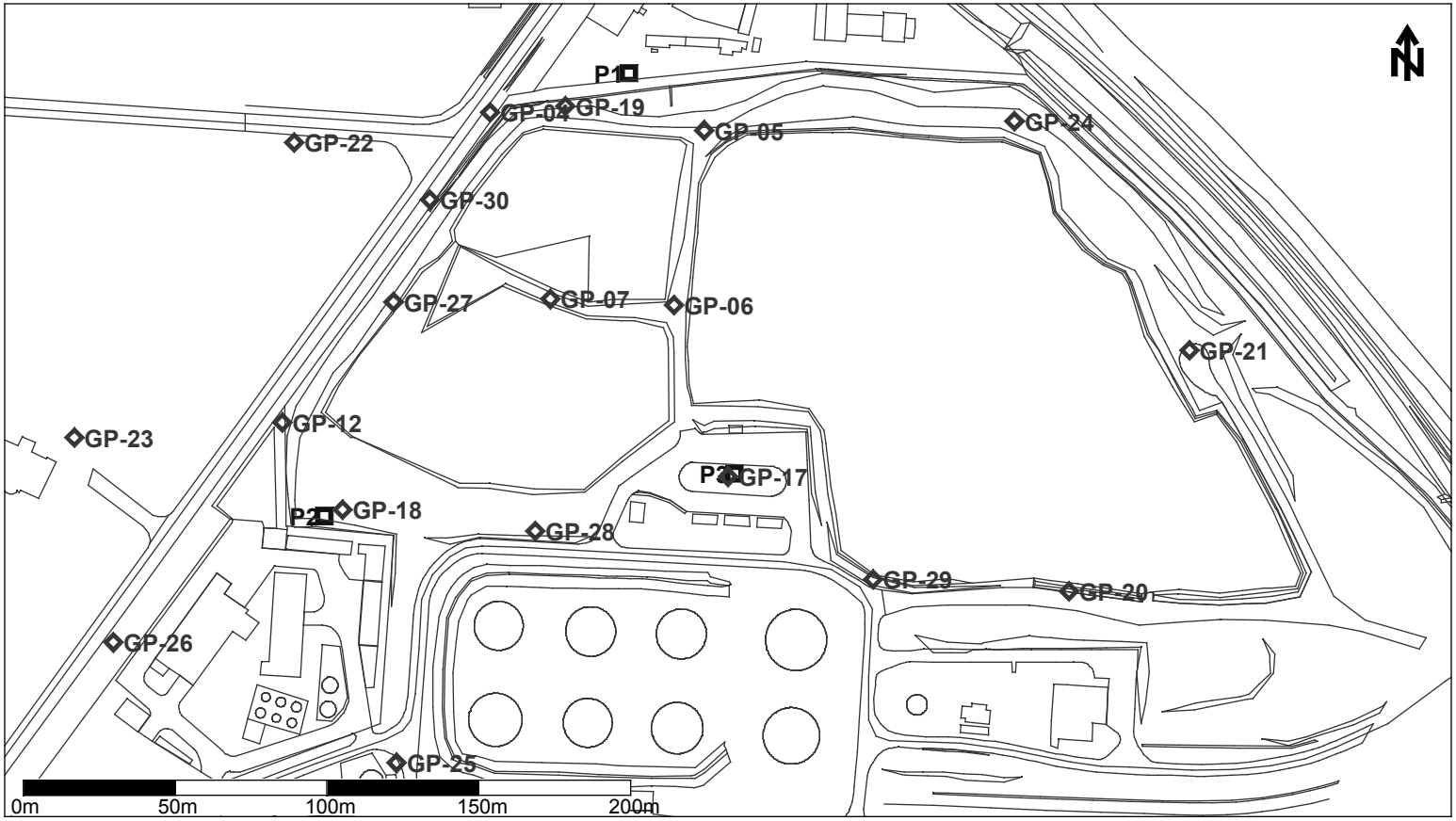

Figure 2.2 E-W cross section through the lagoon area

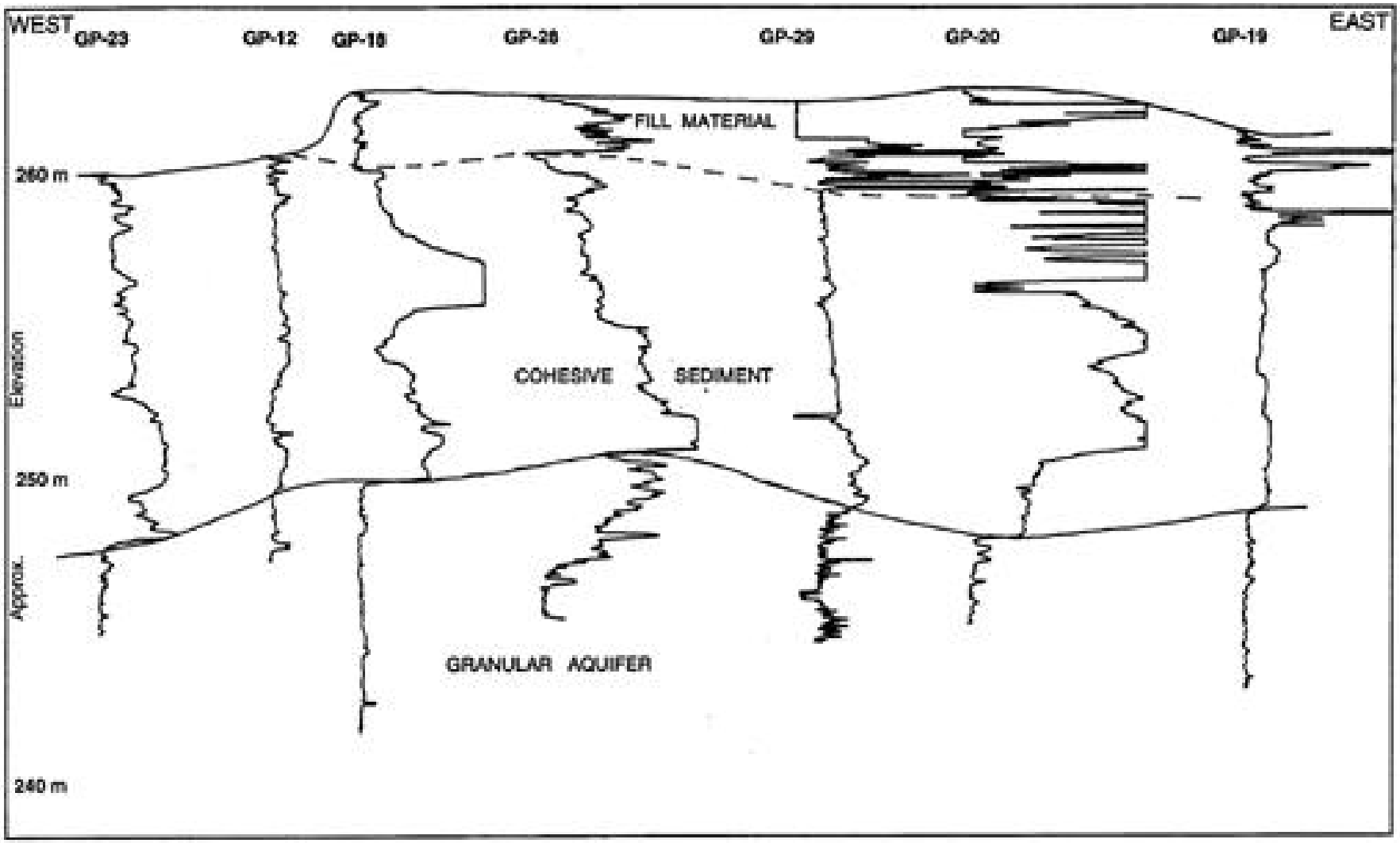

Figure 2.3 - Cone Penetrometer (CPT), Soil Core (SL), and Ditch Witch (DD) Sampling Locations

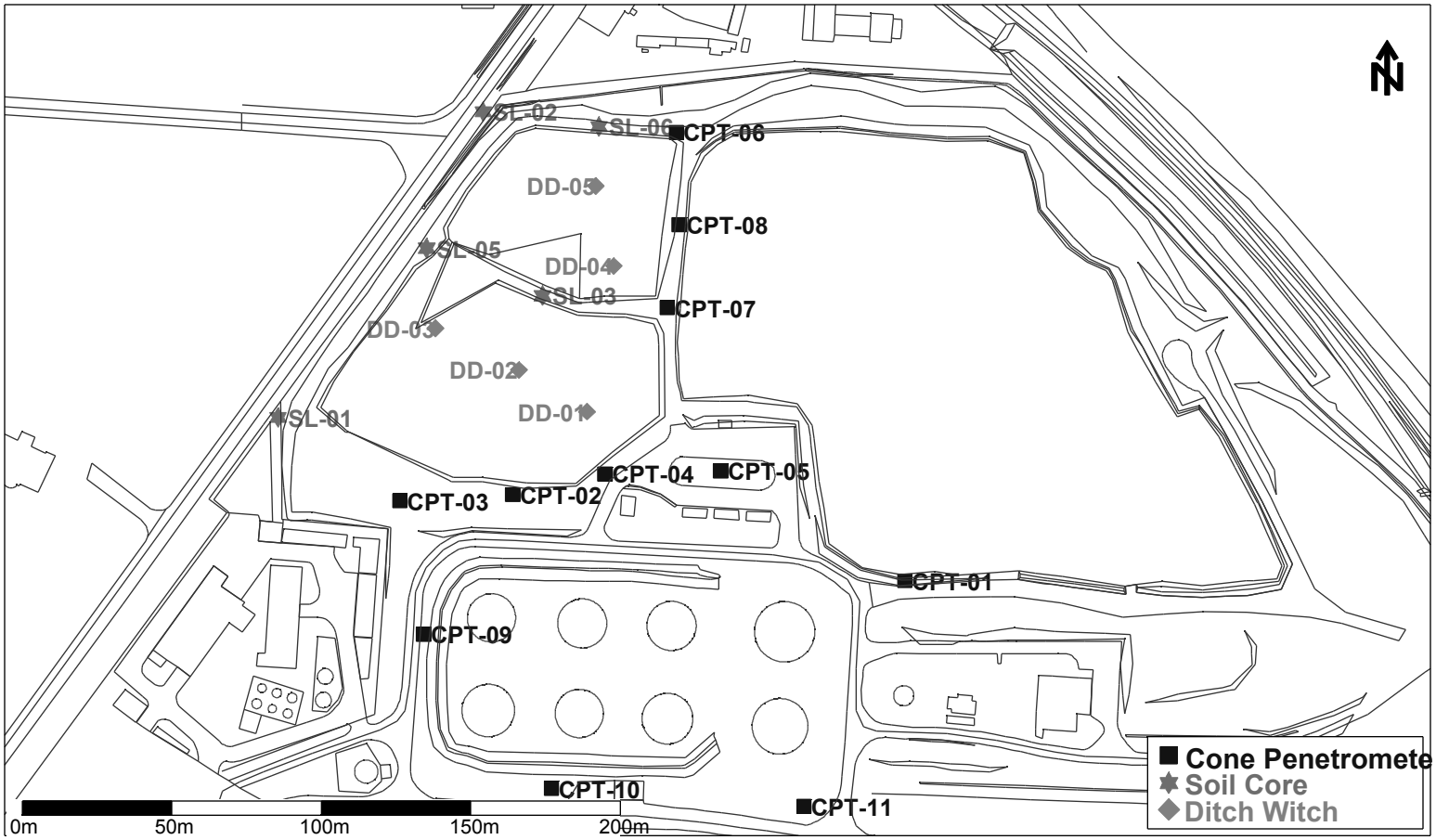

Figure 2.4 - DTECH and Ohmicron IMA Locations- Surface (SRF) Sample Locations

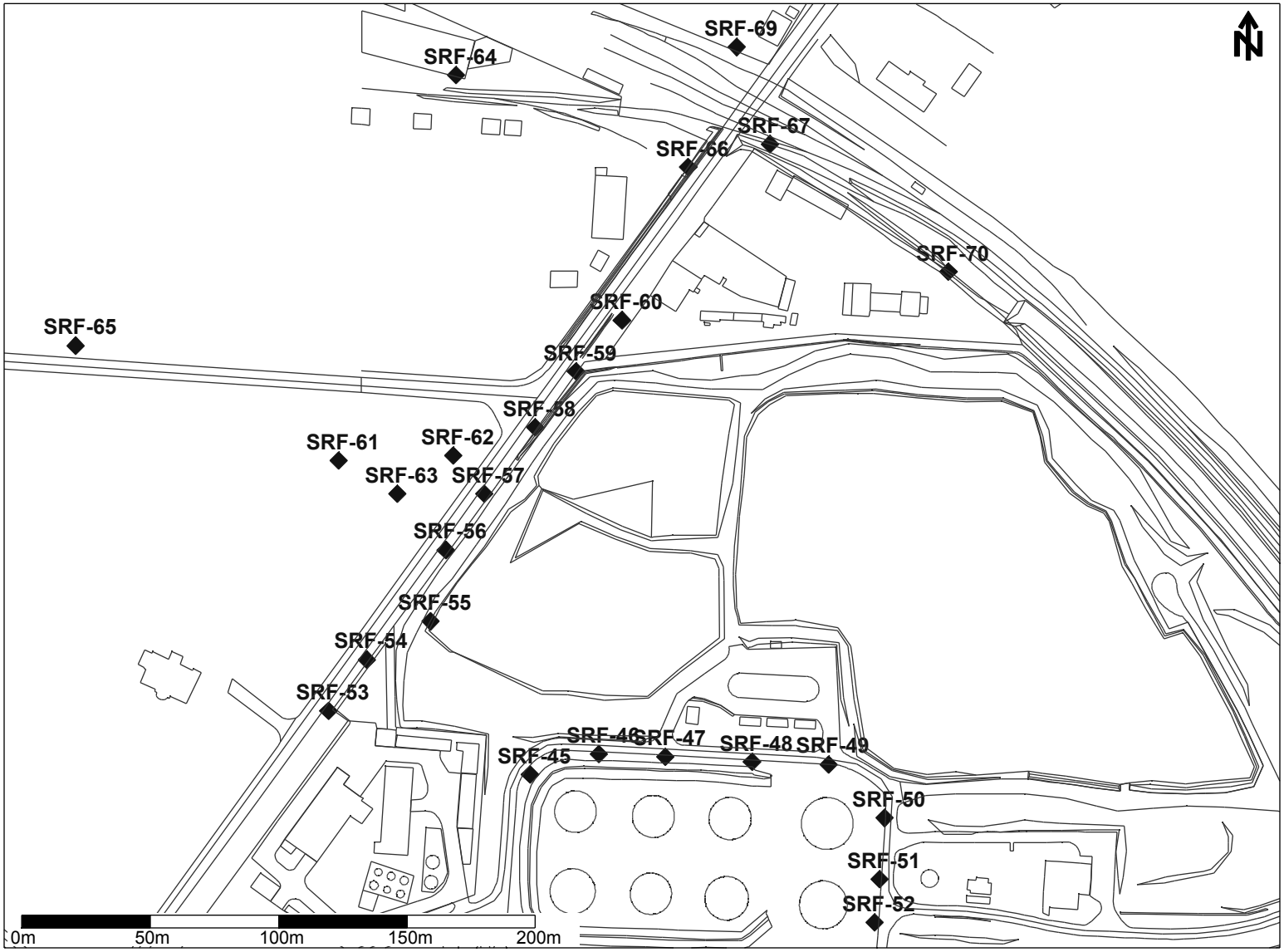

Figure 2.5A - Locations of EMFLUX passive soil vapor samplers

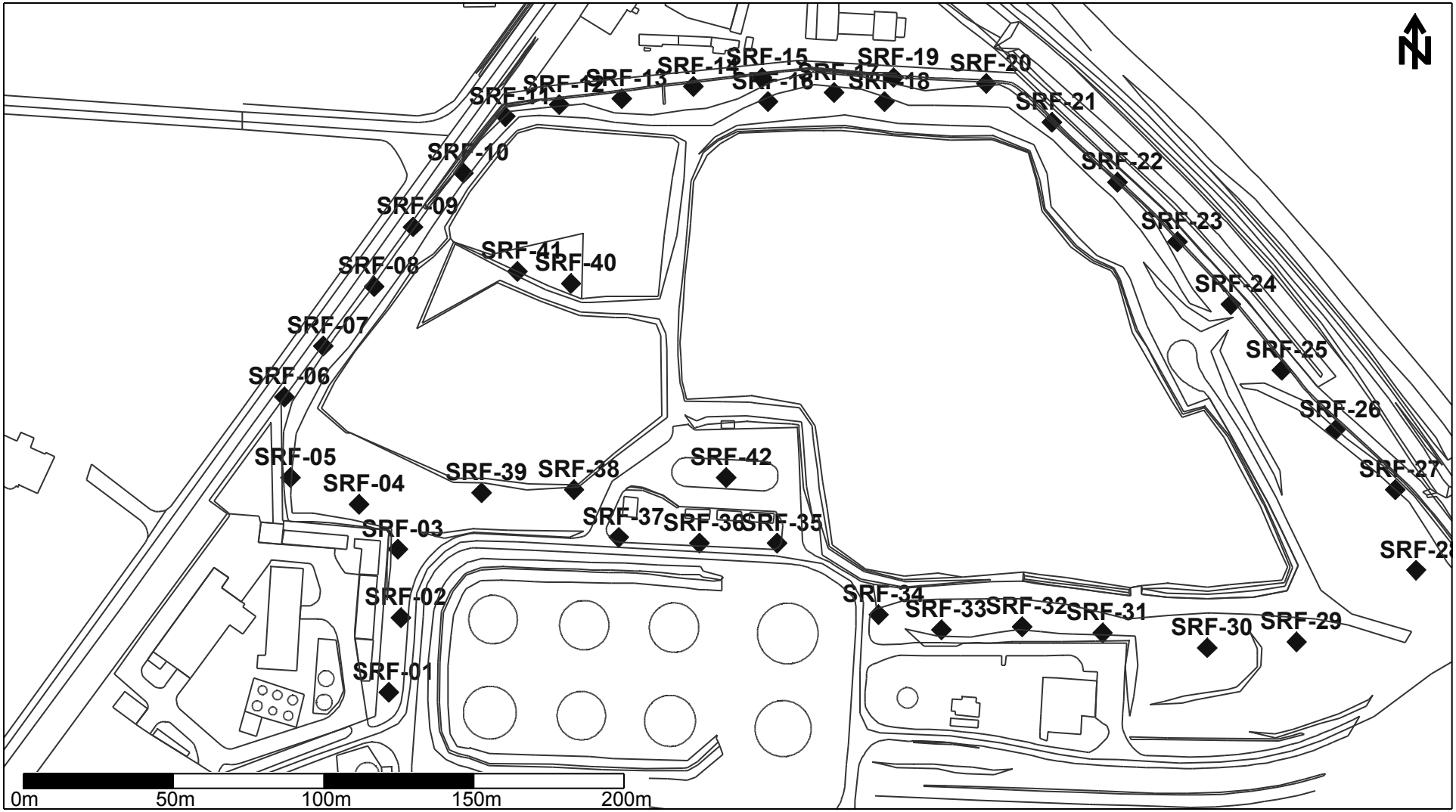

Figure 2.5B - Locations of Gore passive soil vapor samplers

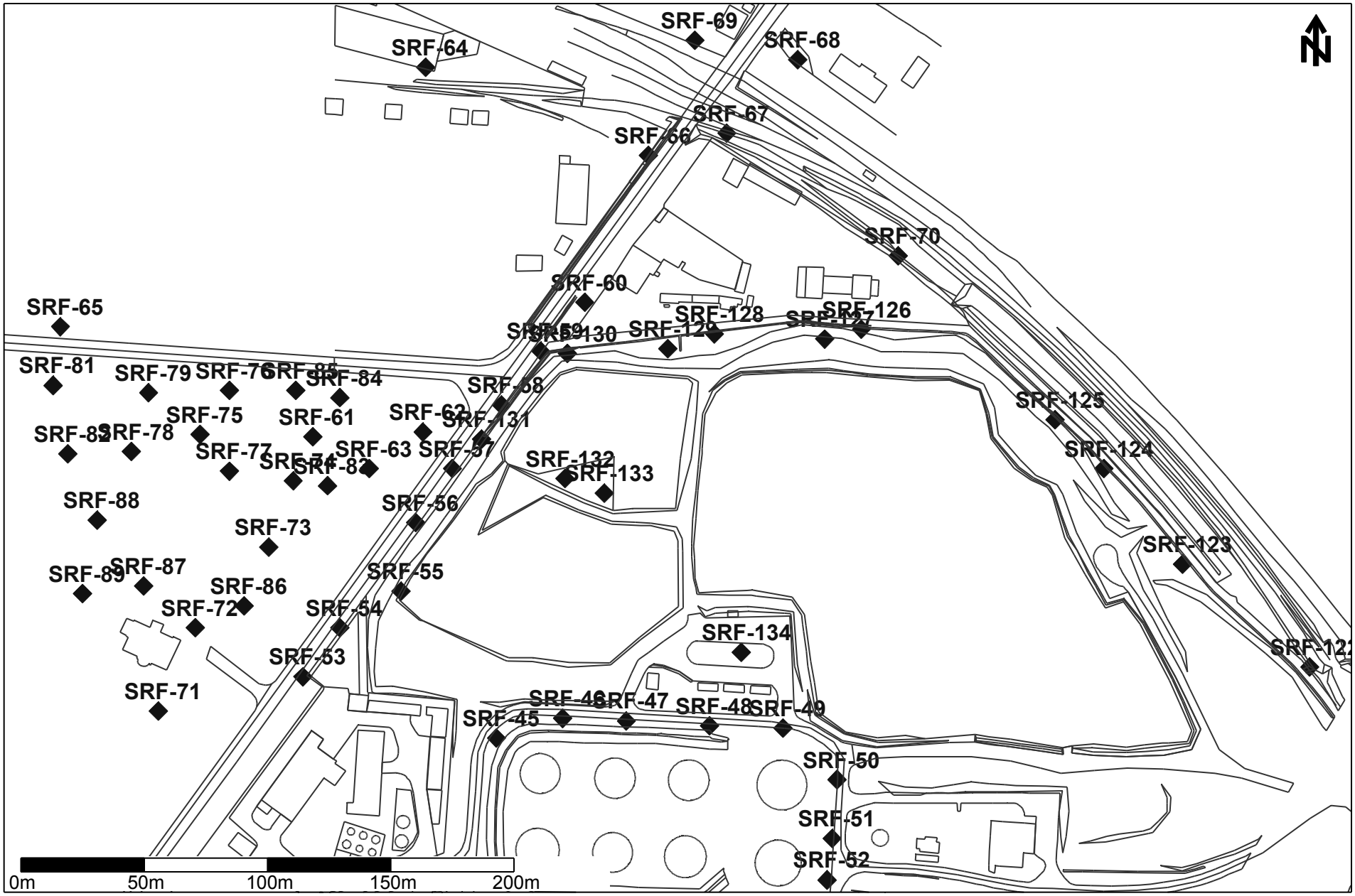

Figure 2.5C - Locations of NERI passive soil vapor samplers

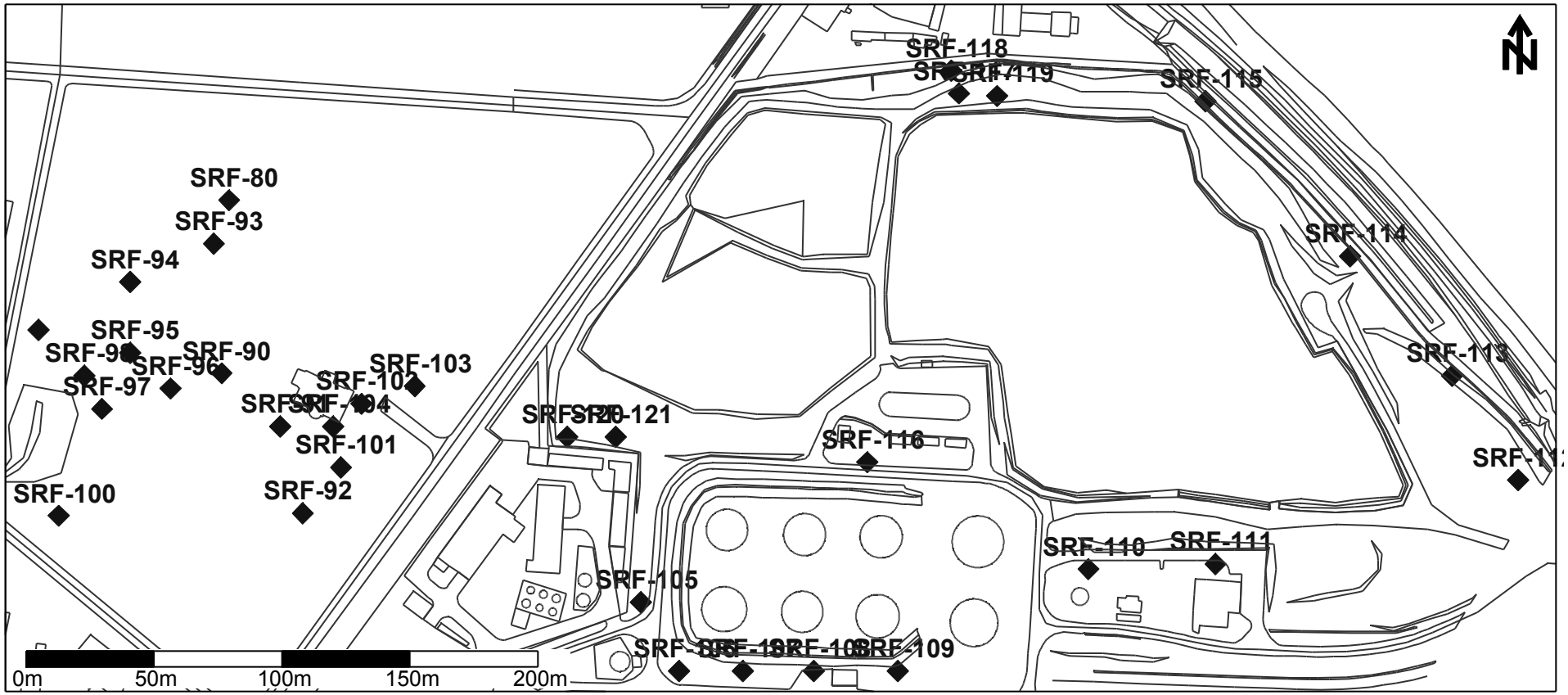

Figure 2.6 - Contour plot of benzene distribution as measured by EMFLUX passive soil vapor sorbers. Concentrations are in log units.

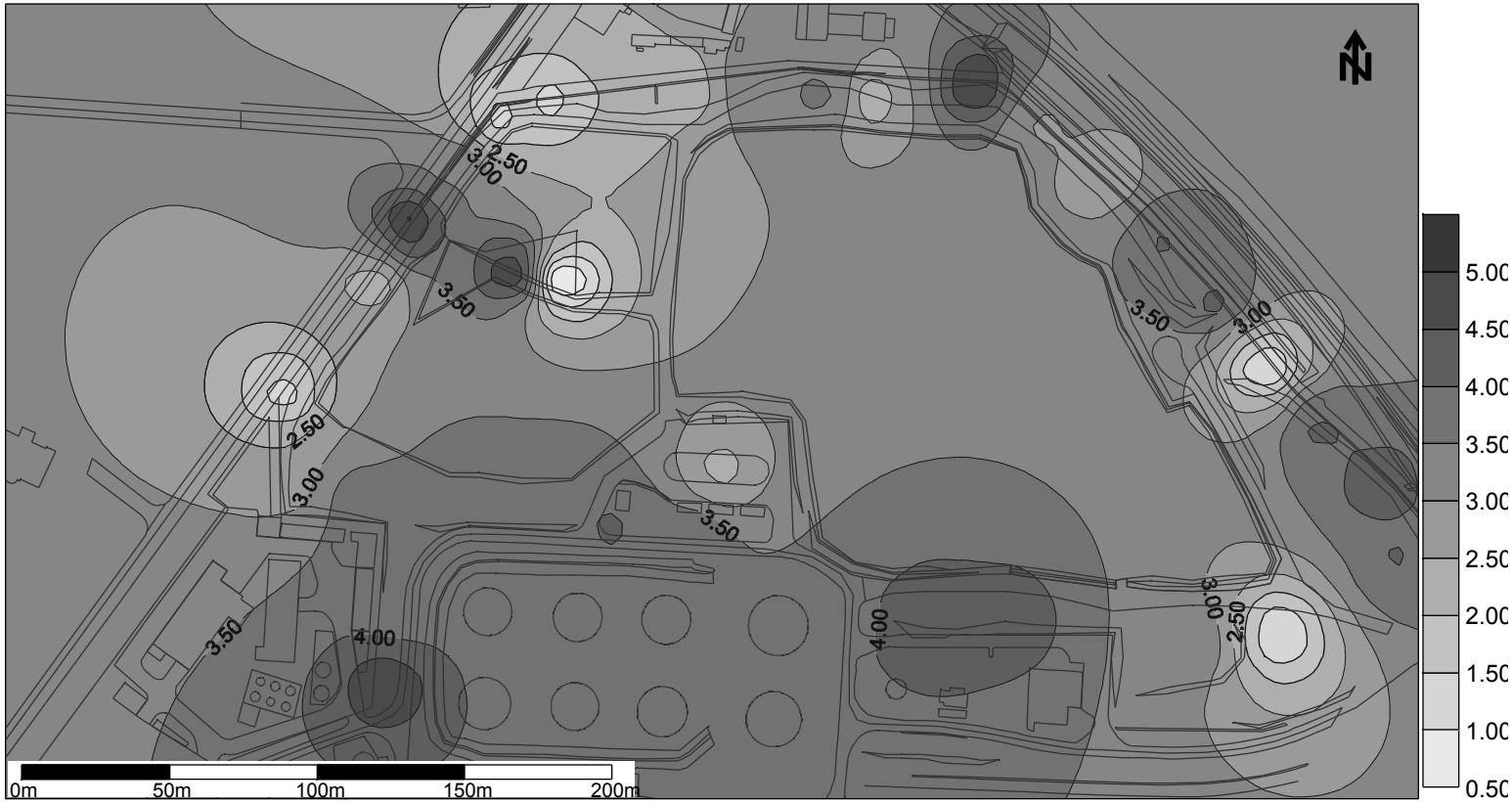

Figure 2.7 - Contour plot of ethylbenzene distribution as measured by EMFLUX passive soil vapor sorbers. Concentrations are in log units.

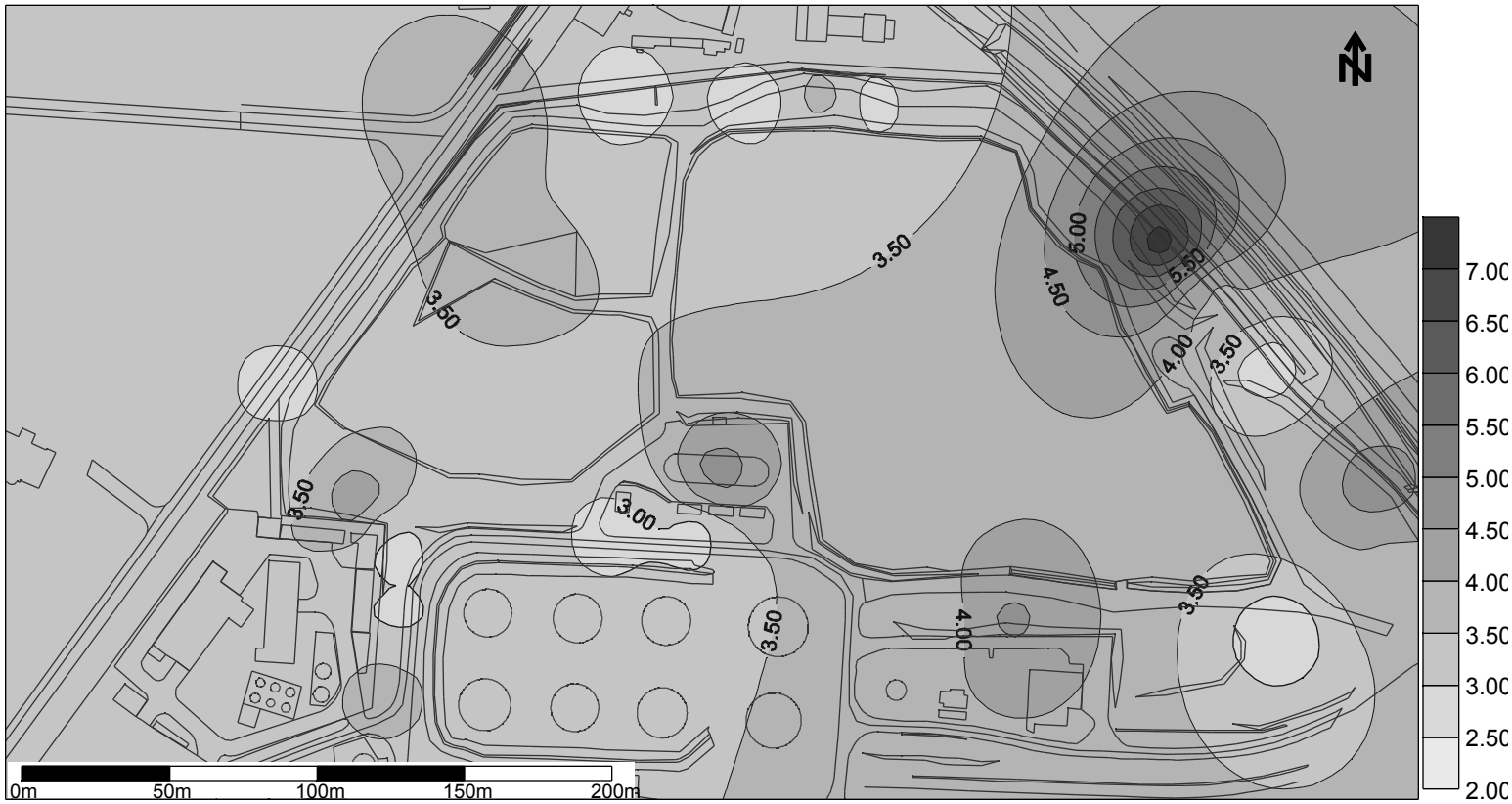

Figure 2.8 - Contour plot of toluene distribution as measured by EMFLUX passive soil vapor sorbers. Concentrations are in log units.

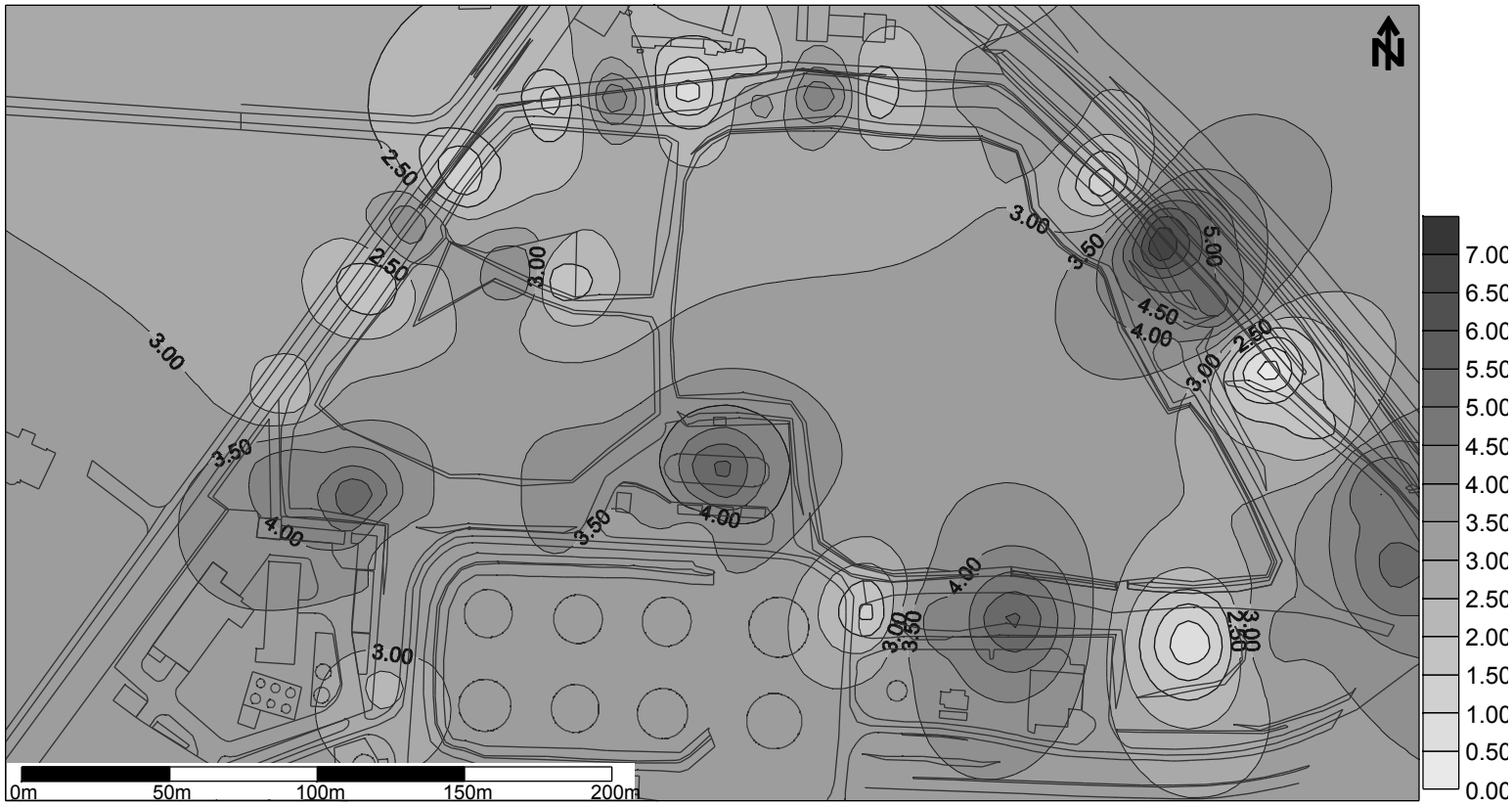

Figure 2.9 - Contour plot of total xylenes distribution as measured by EMFLUX passive soil vapor sorbers. Concentrations are in log units.

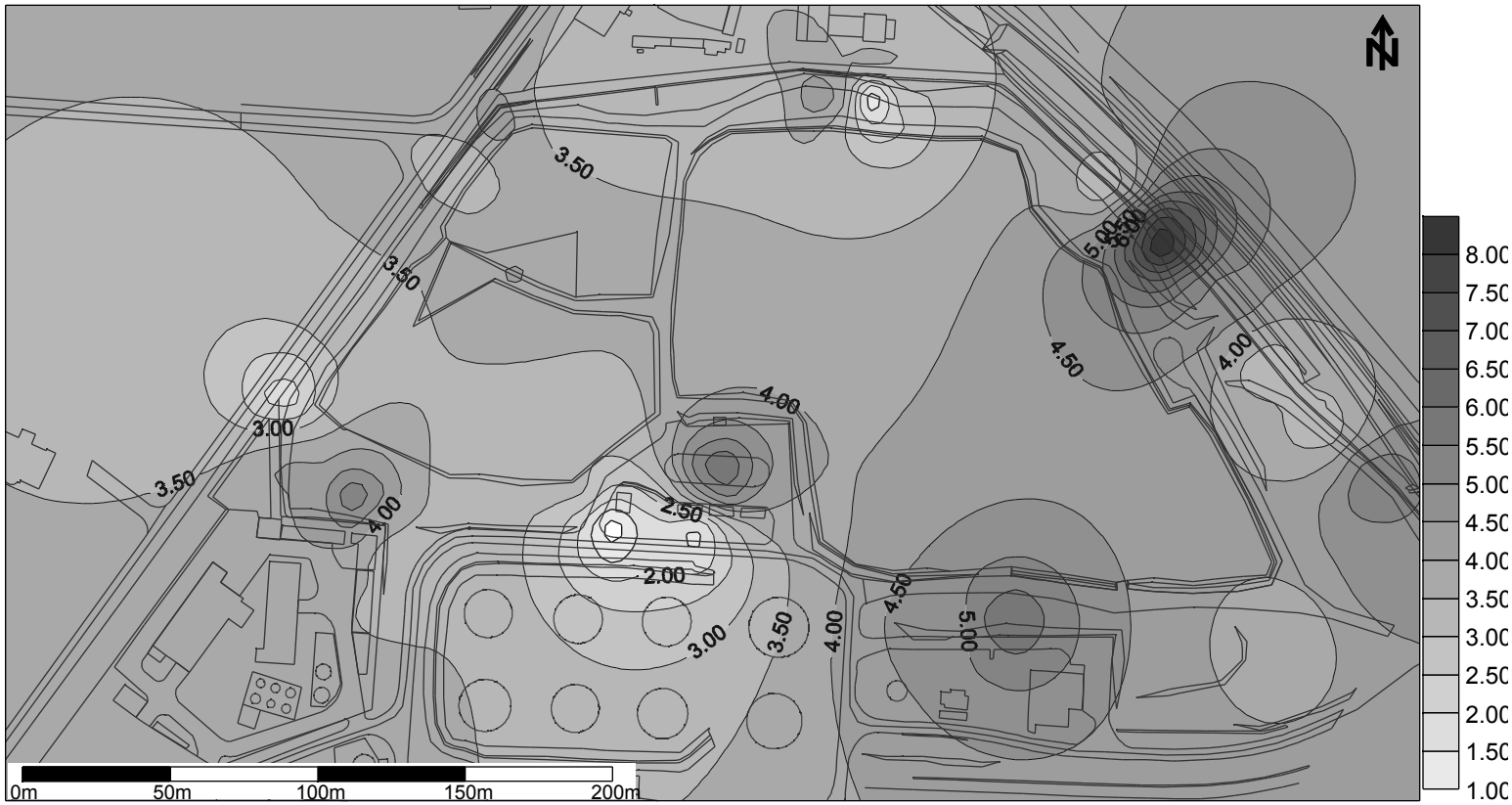

Figure 2.10 - Groundwater (GP) Sampling Locations

Figure 2.11 - Benzene Groundwater Results from Upper Aquifer in Natural Logarithm Scale

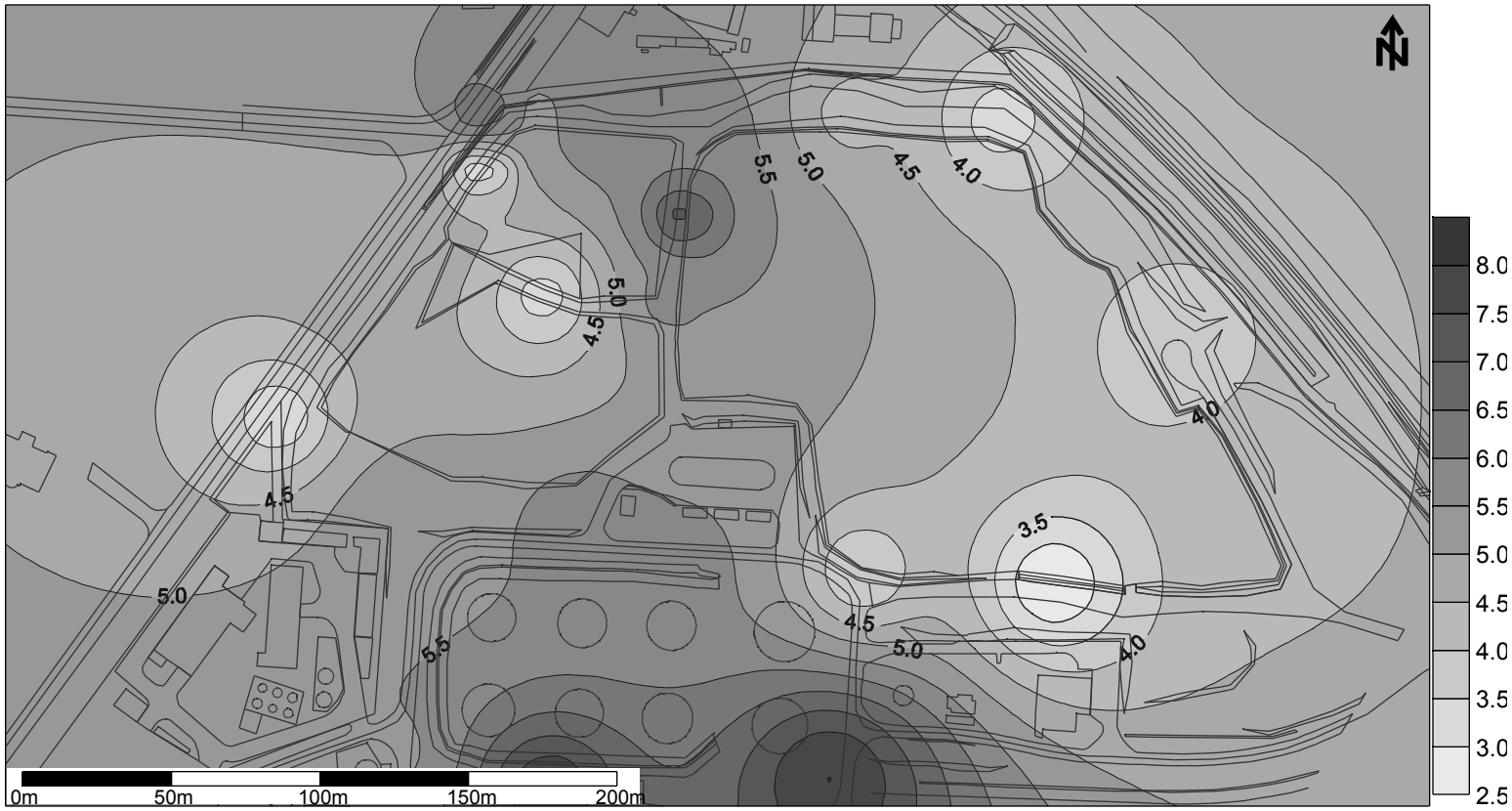

Figure 2.12 - Toluene Groundwater Results from the Upper Aquifer in Natural Logarithm Scale

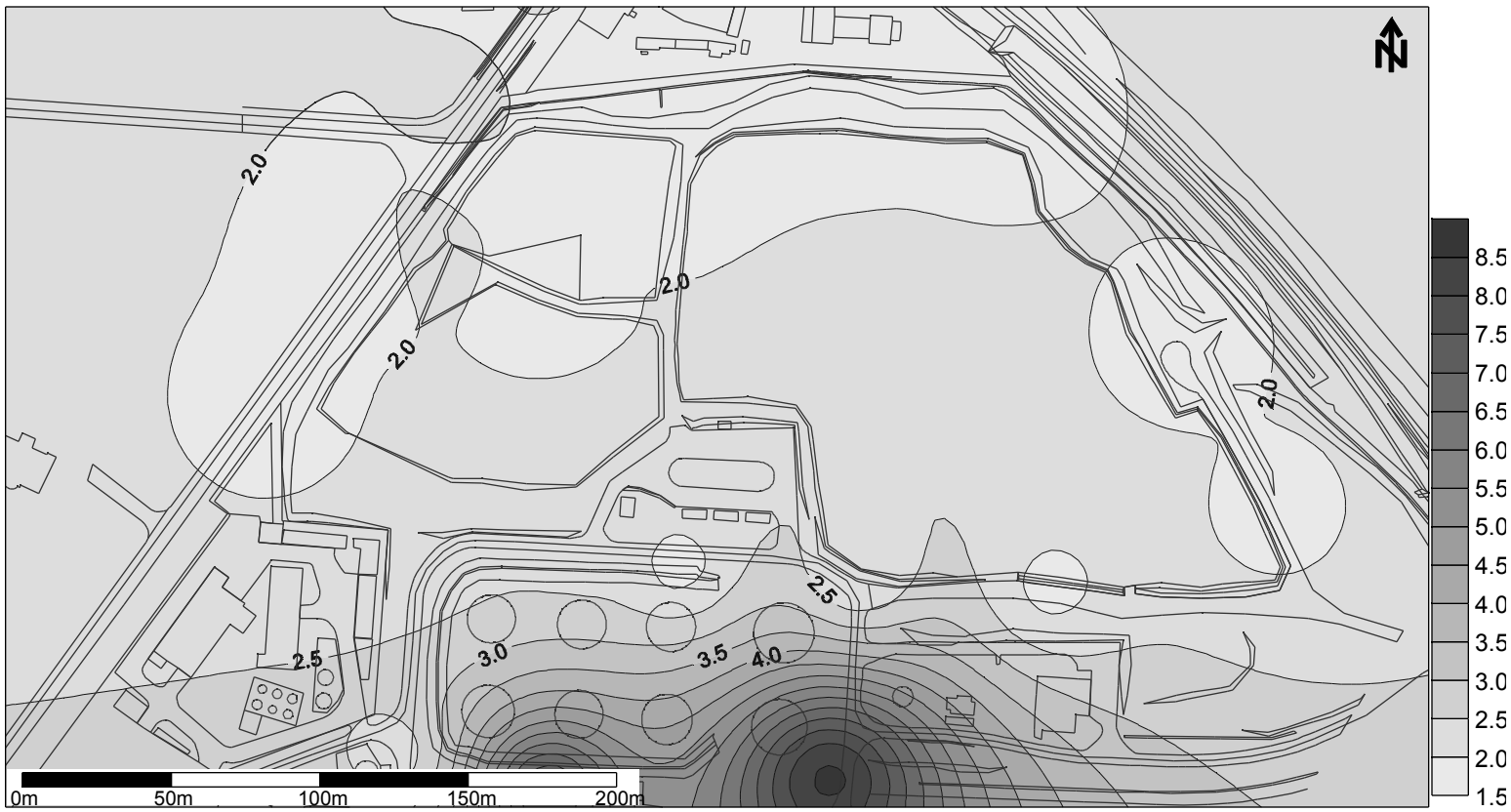

Figure 2.13 - Ethylbenzene Groundwater Results from the Upper Aquifer in Natural Logarithm Scale

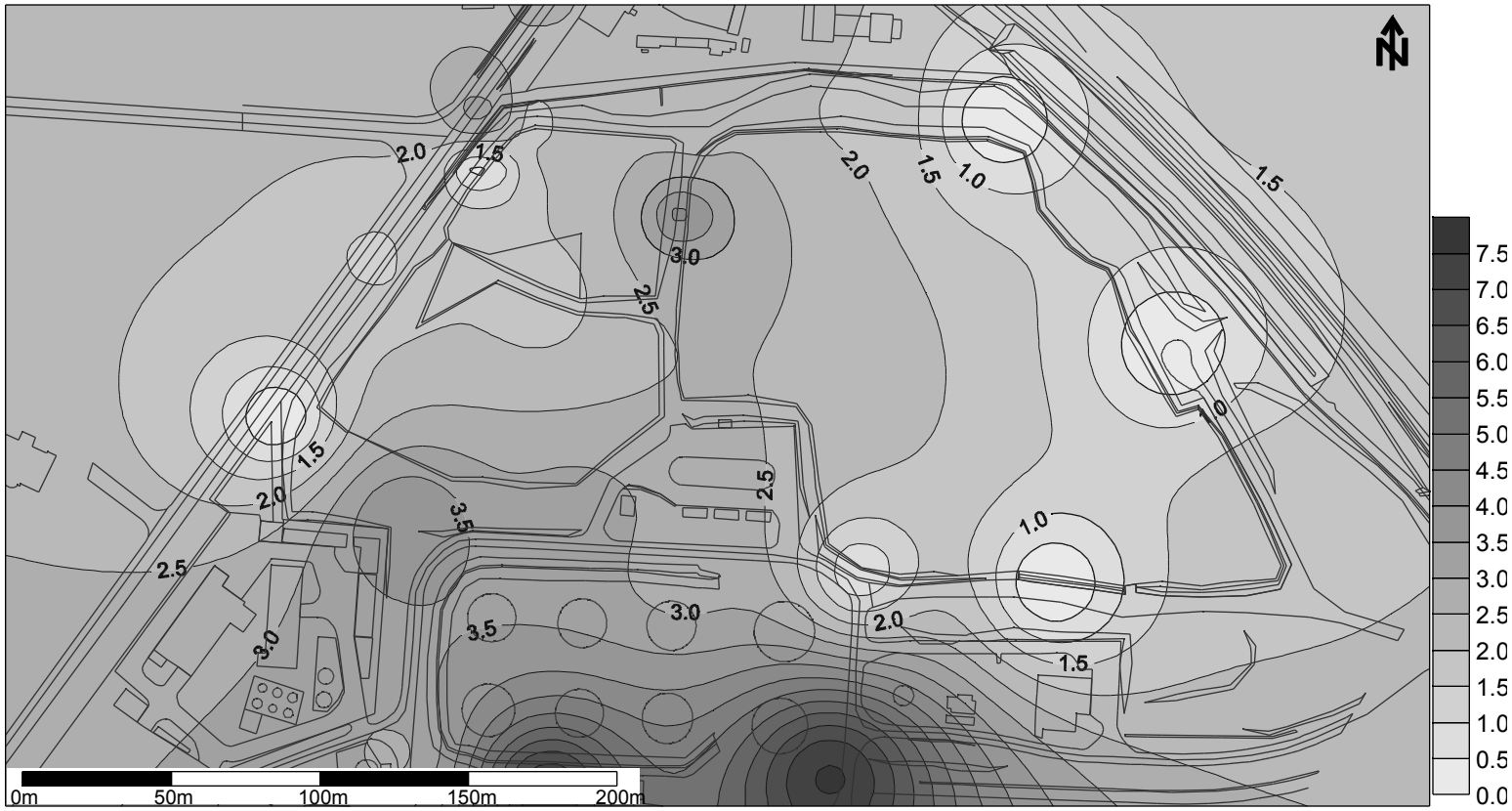

Figure 2.14 - Total Xylene Groundwater Results from the Upper Aquifer in Natural Logarithm Scale

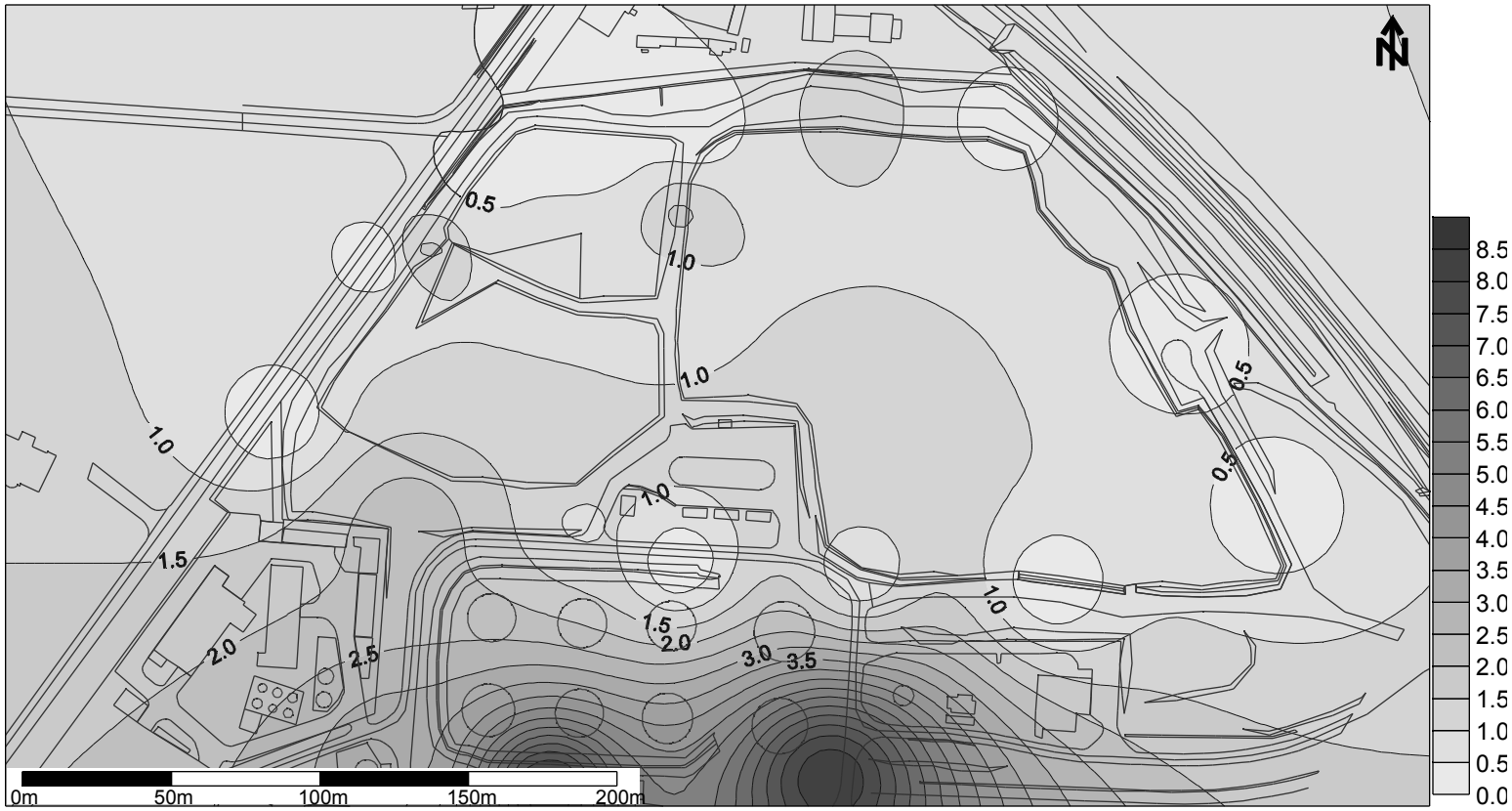

Figure 2.15 - Napthalene Groundwater Results from the Upper Aquifer in Natural Logarithm Scale

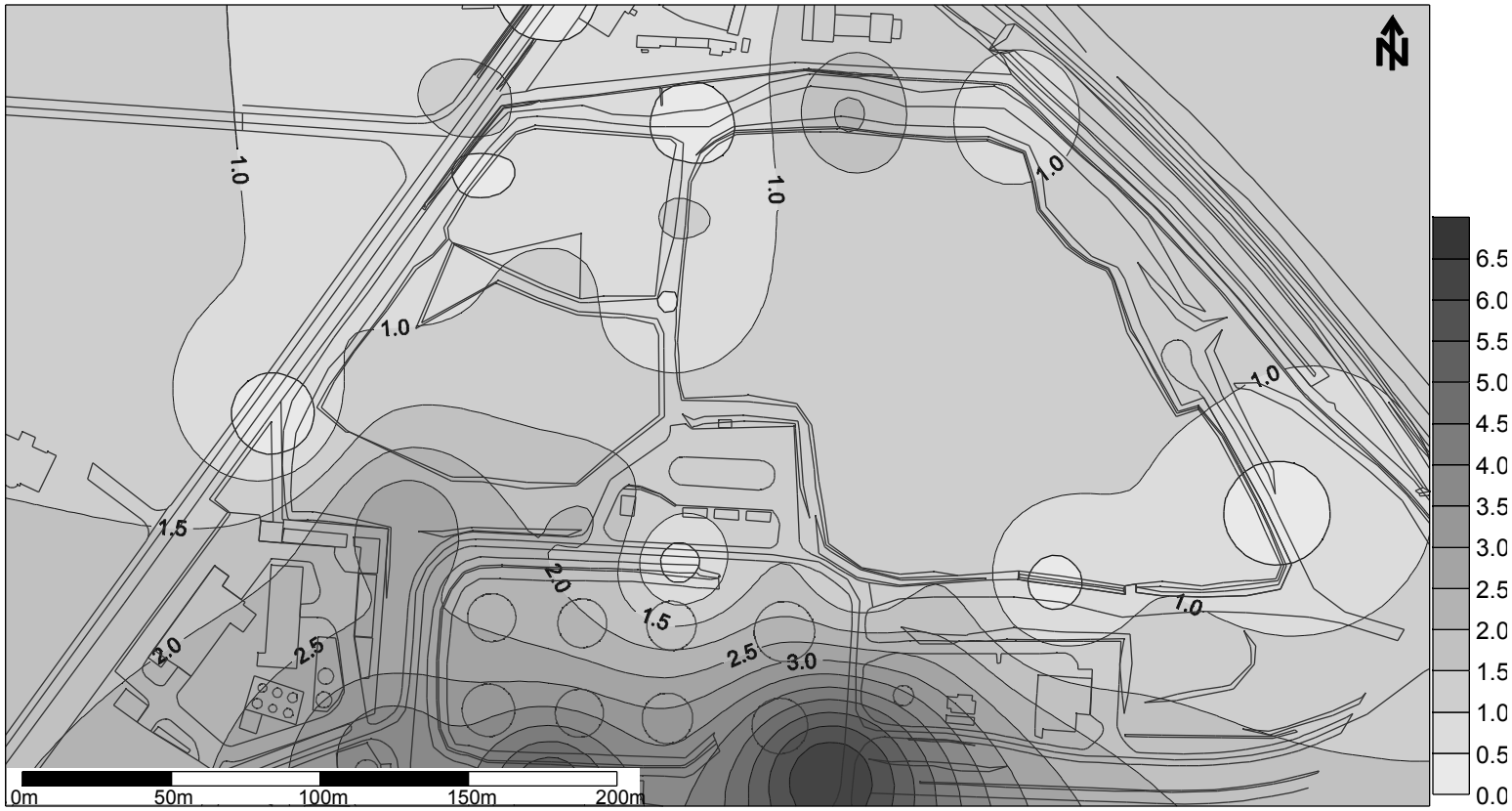

Figure 2.16 - Benzo(a)pyrene Groundwater Results from the Upper Aquifer in Natural Logarithm Scale

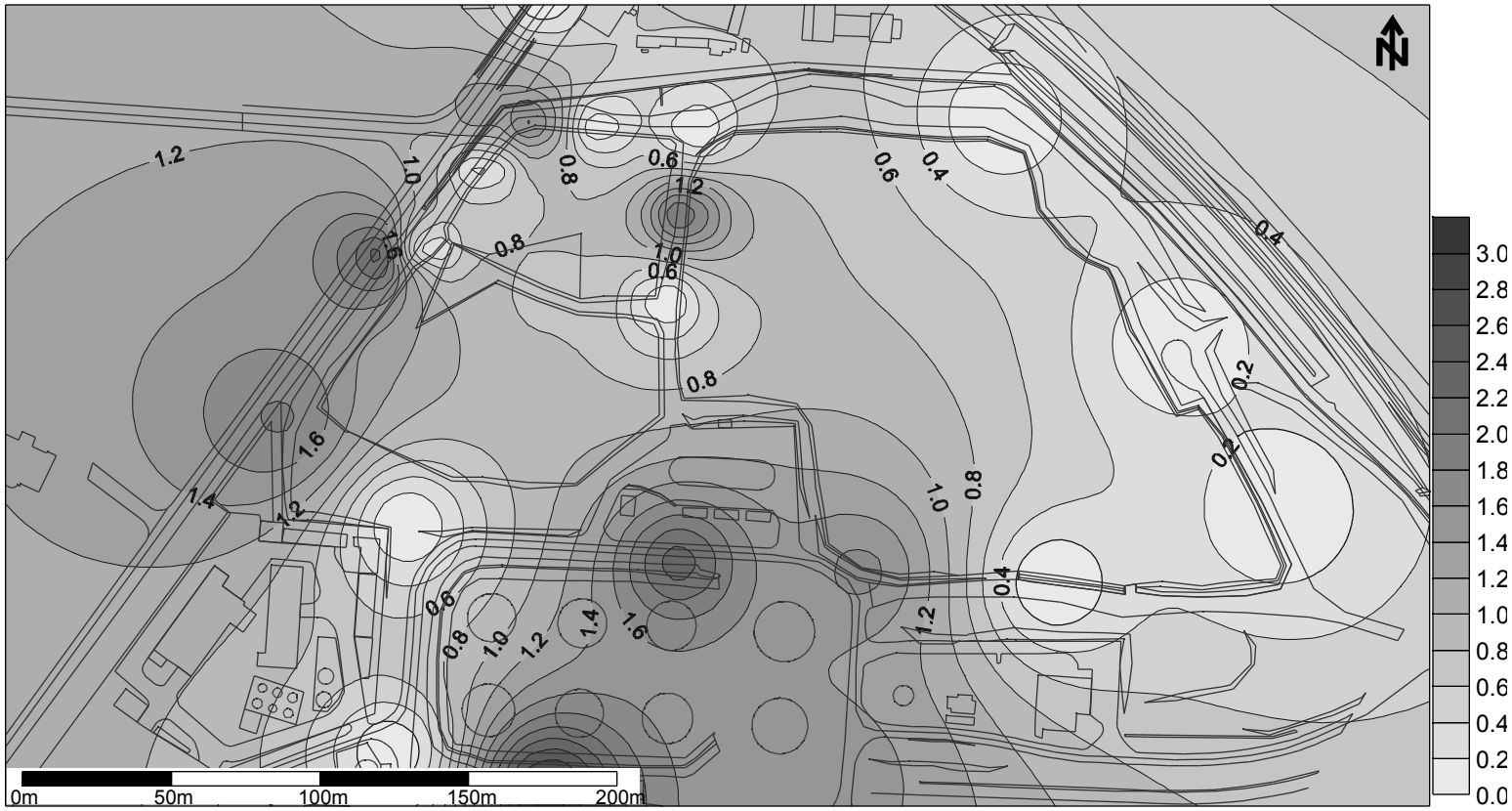

Figure 2.17 - Benzo(ghi)pyrene Groundwater Results from the Upper Aquifer in Log Contour Format

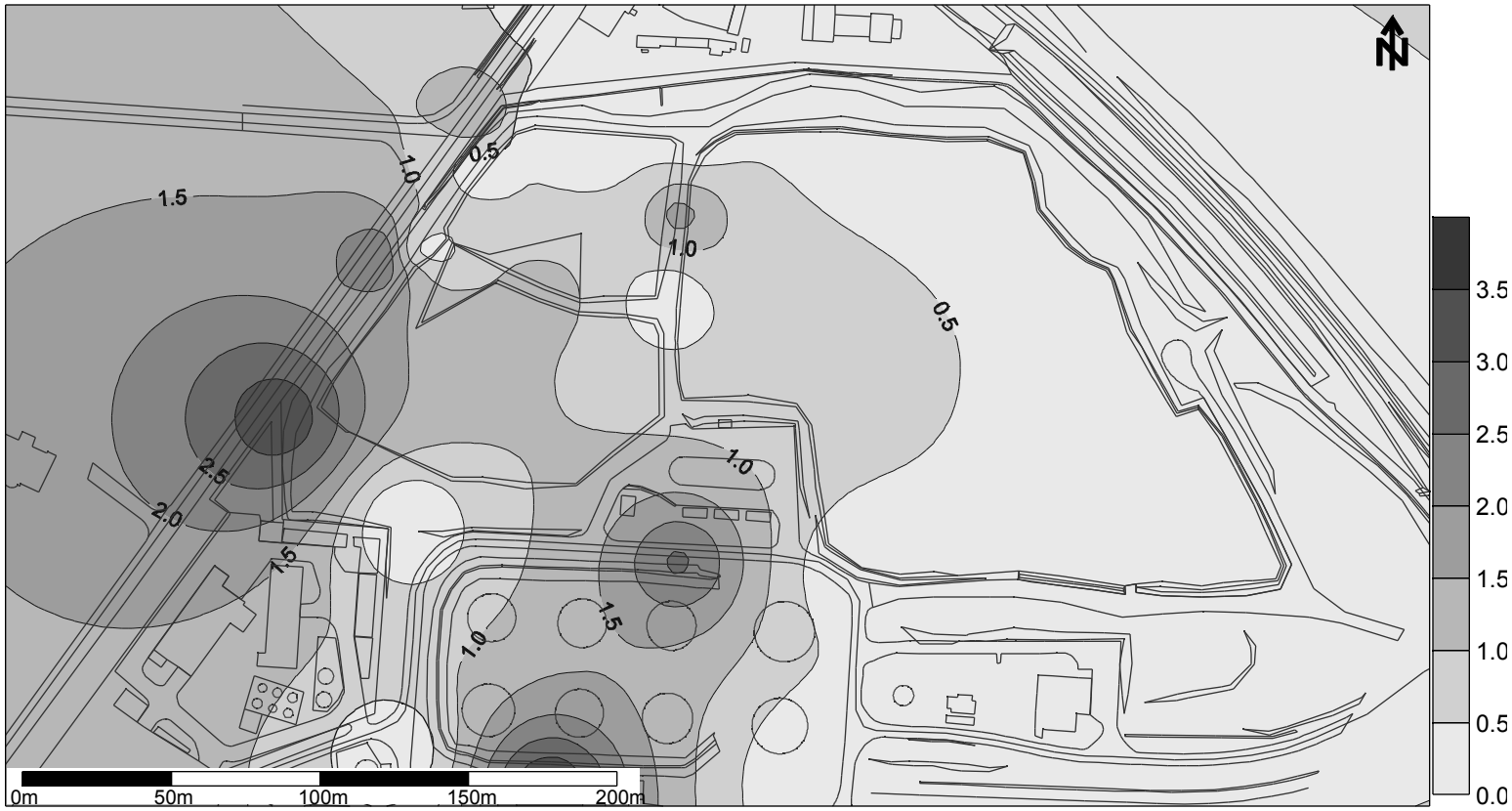

Figure 2.18 - Nickel Groundwater Results from the Upper Aquifer in Linear Scale

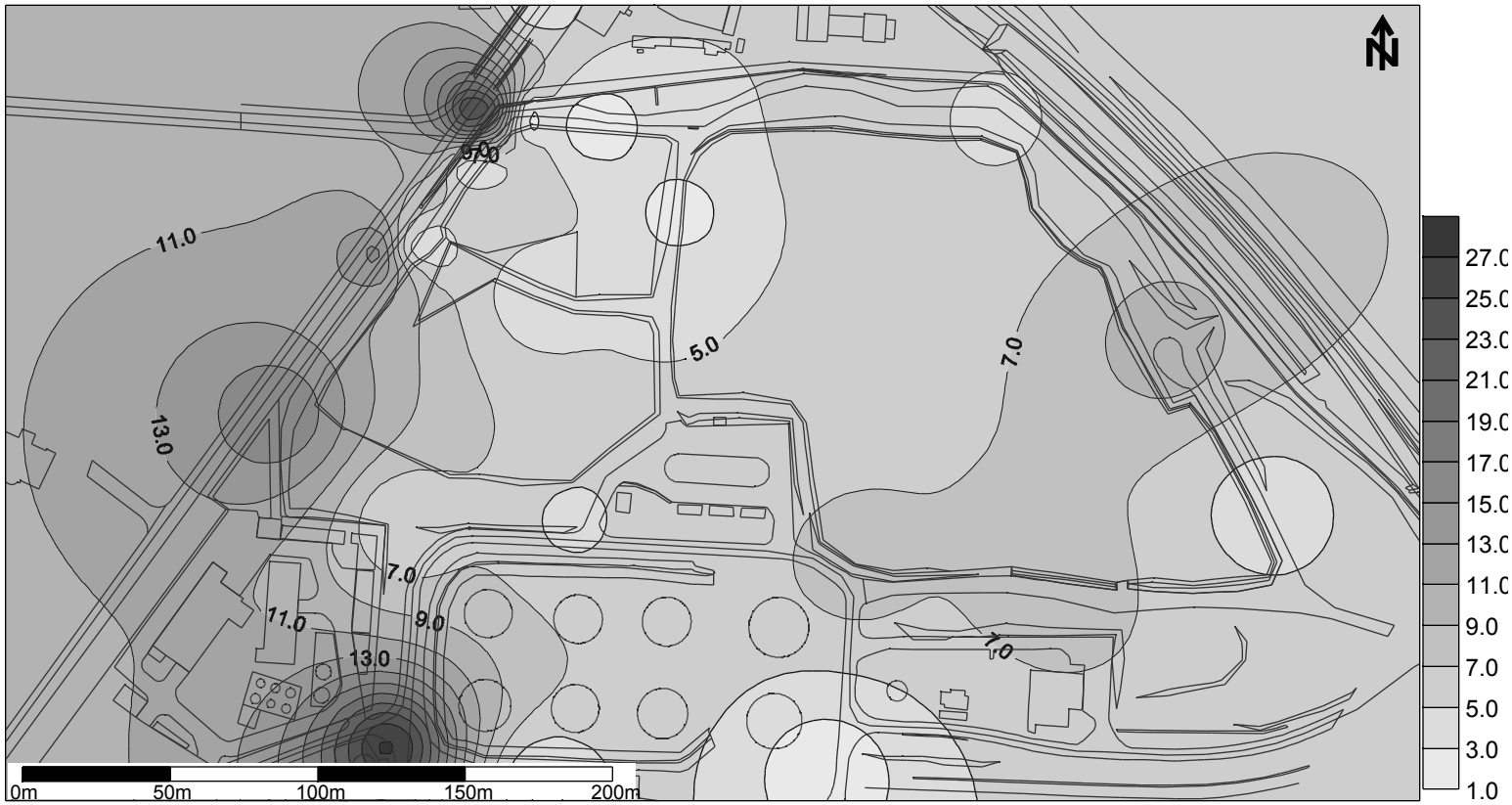

Figure 2.19 - Zinc Groundwater Results from the Upper Aquifer in Linear Scale

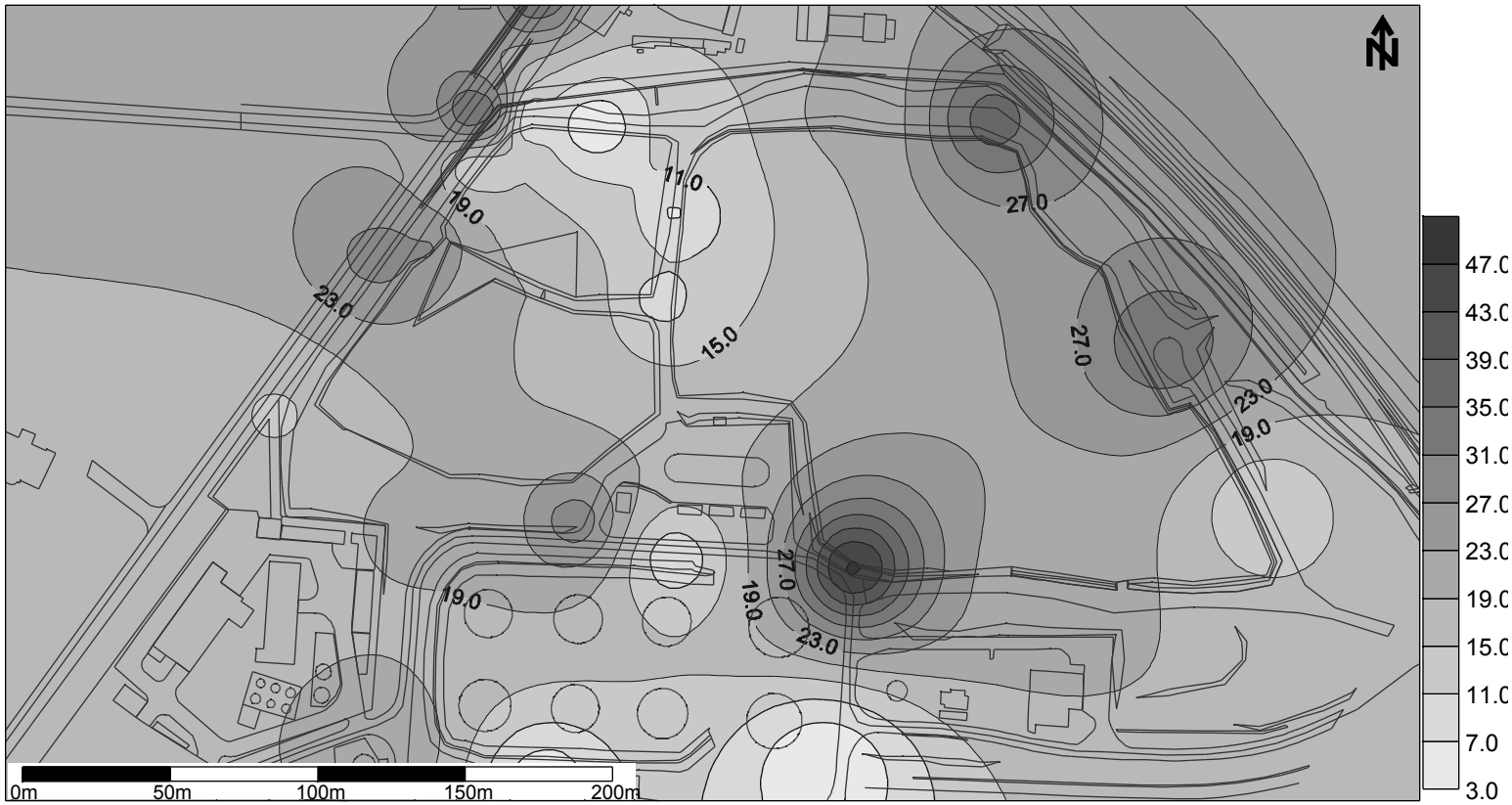

Figure 2.20 - Mercury Groundwater Results from the Upper Aquifer in Linear Scale

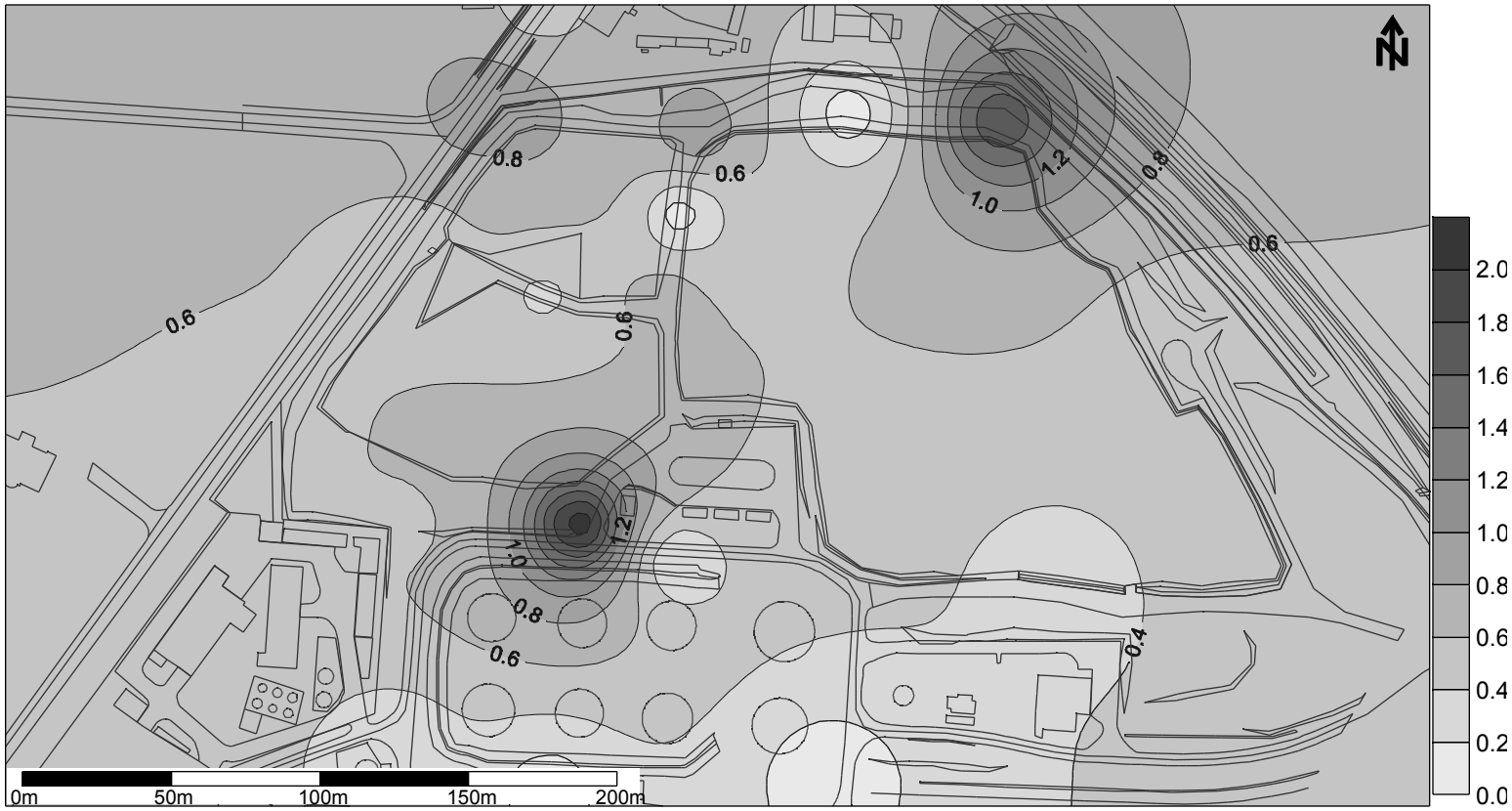

Figure 2.21 - Arsenic Groundwater Results from the Upper Aquifer in Linear Scale

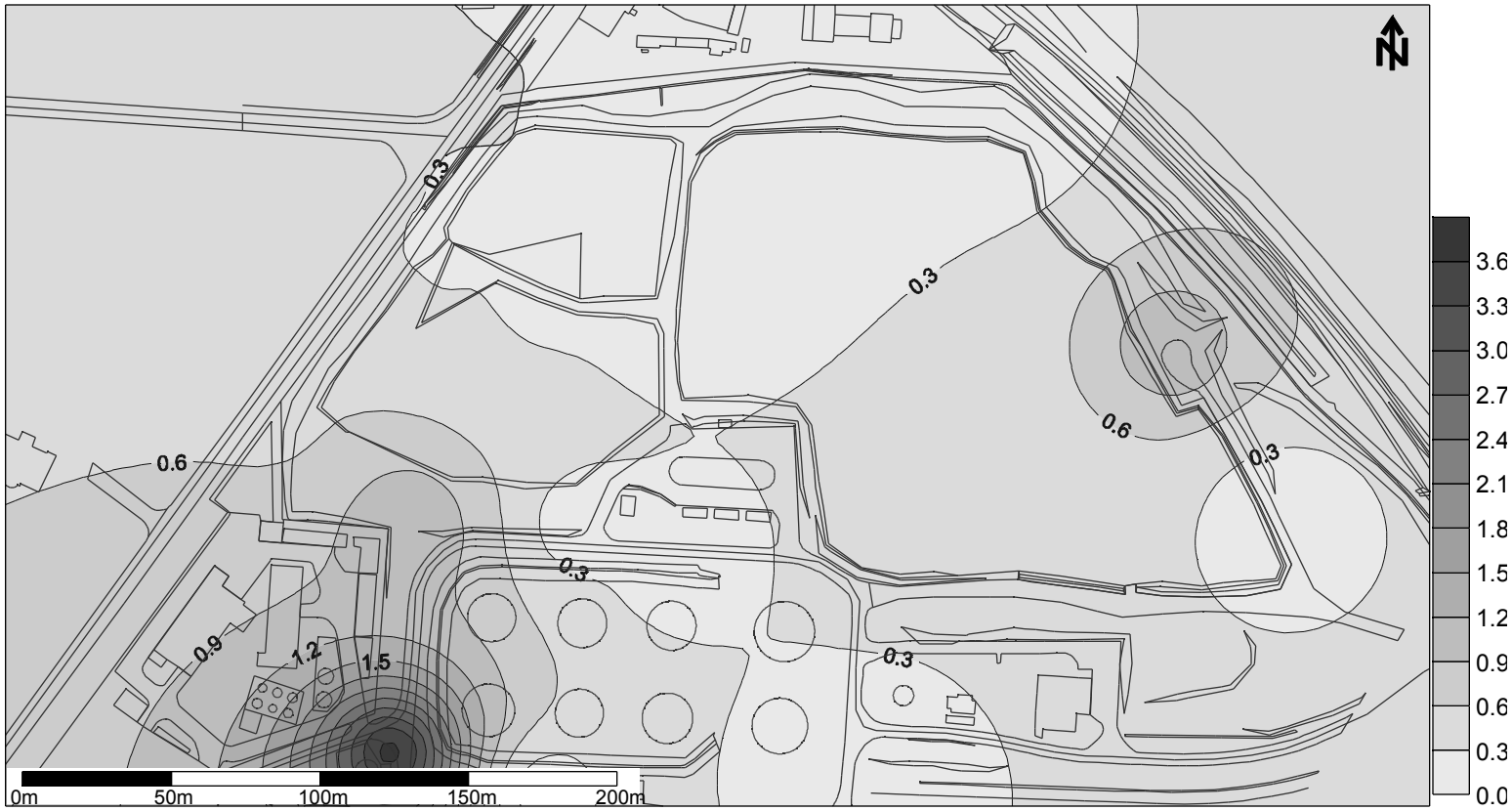

Table 2.1 Stratigraphic Data on Piezometers (all lengths are in meters).

Piezometer	ELEVATION TO THE BOTTOM OF:				
	Surface Elevation	Fill	CL	GW	CH
P-1	261.0	261.0*	250.7	244.3	240.0
P-2	263.2	260.5	250.6	244.1	238.2
P-3	263.5	259.8	250.4	243.7	238.5

** Indicates no Fill*
CL is fine-grained clay of low to medium plasticity
GW is a coarse-grained gravel sand mixture
CH is a fat clay or very fine high plasticity clay.

Table 2.2 Piezometer soil core analyses.
Metals [mg/kg]

Sample	Depth [m]	Ni	Cr	Zn	Cu	Pb	Co	Cd	Hg	As
(34) P1-1	2.5	9.95	26.43	41.76	20.08	9.01	3.62	<0.05	0.041	4.87
(37) P1-2	5.8	12.29	27.58	40.63	12.22	11.11	5.02	<0.05	0.037	4.62
(39) P1-3	8.8	9.22	30.06	54.6	23.51	12.23	2.9	<0.05	0.039	1.4
(40) P1-4	12	11.87	20.22	43.24	14.99	6.81	3.11	<0.05	<0.037	1.7
(42) P1-5	18.8	25.4	30.1	49.8	19	9.1	6.16	<0.05	0.07	11.6
(1) P2-1	0.7	22.3	30	137	32.3	64.9	11.4	0.51	0.19	6.08
(96) P2-2	5.5	10.2	43.8	45.6	23.2	10	5.53	0.06	<0.037	3.18
(12) P2-3	10.3	6.15	13.5	28.5	9.22	4.4	2.5	0.06	<0.037	1.19
(20) P2-4	15	10.6	24.2	49.2	22.6	6.89	5.69	<0.05	<0.037	1.94
(22) P2-5	19	16.4	35.5	63.7	11.4	6.84	7.54	0.12	0.137	1.6
(14) P2-6	24	32.5	62.5	77.8	24.5	11.7	12.4	<0.05	0.043	10.9
(23) P3-1	2.5	50	89	120	35.3	58.5	17.7	0.18	0.107	4.23
(25) P3-2	5	10.7	34.3	39.6	9.88	8.97	5.84	<0.05	<0.037	5.24
(29) P3-3	9.8	13.6	48.8	35	16.2	12.2	9.43	<0.05	0.064	3.13
(30) P3-4	11	5.03	30.6	33.6	16.4	10.3	3.89	<0.05	0.039	0.87
(31) P3-5	12.2	15.3	59.7	72	21.4	14	5.17	<0.05	0.06	1.35
	Soil MDL	1.62	1.96	9.97	3.66	2.69	0.25	0.05	0.037	0.72

Table 2.2 (cont.) Piezometer soil core analyses

Sample	Depth [m]	PAHs (mg/kg)						TPH
		Fluor	B[b]F	B[k]F	B[a]P	B[ghi]P	IP	[mg/kg fresh weight]
(34) P1-1	2.5	<2.9	<2	<2.1	<1.8	<1.7	<2.6	<0.23
(37) P1-2	5.8	<2.9	<2	<2.1	<1.8	<1.7	<2.6	<0.23
(39) P1-3	8.8	<2.9	<2	<2.1	<1.8	<1.7	<2.6	<0.23
(40) P1-4	12	<2.9	<2	<2.1	<1.8	<1.7	<2.6	<0.23
(42) P1-5	18.8	<2.9	<2	<2.1	2.69	7.41	<2.6	<0.23
(1) P2-1	0.7	885	366	204	307	299	202	0.997
(96) P2-2	5.5	47.1	14.2	2.93	2.16	2.19	3.07	0.472
(12) P2-3	10.3	<2.9	3.42	<2.1	<1.8	<1.7	<2.6	<0.23
(20) P2-4	15	3.72	2.78	<2.1	<1.8	<1.7	<2.6	<0.23
(22) P2-5	19	<2.9	<2	<2.1	<1.8	<1.7	<2.6	<0.23
(14) P2-6	24	10.7	5.65	3.02	13	25	7.22	<0.23
(23) P3-1	2.5	3144	445	234	403	355	244	0.855
(25) P3-2	5	11	9.88	21.4	3.44	2.61	nd	<0.23
(29) P3-3	9.8	27.3	8.73	<2.1	5.28	nd	nd	0.354
(30) P3-4	11	<2.9	1.3	<2.1	nd	nd	nd	<0.23
(31) P3-5	12.2	<2.9	1.2	<2.1	nd	nd	nd	<0.23
	Soil MDL	2.9	2	2.1	1.8	1.7	2.6	0.23

Table 2.3 Conductivity and CPT picks of depths to CL/GW interface

Location	Elevation in meters	CL/GW (bgs) depth in meters	CL/GW (asl) depth in meters
GP4	260.4	10.6	249.8
GP5	264.3	12.8	251.5
GP6	264.4	14.3	250.1
GP7	263.0	12.3	250.7
GP12	261.1	11.6	249.5
GP17	263.4	13.6	249.8
GP18	263.2	12.4	250.8
GP19	262.0	12.0	250.0
GP20	264.0	14.3	249.7
GP21	262.5	12.8	249.7
GP22	261.1	10.5	250.6
GP23	260.1	11.7	248.4
GP24	262.5	12.5	250.0
GP25	262.5	NA	NA
GP26	261.8	11.1	250.7
GP27	262.7	10.4	252.3
GP28C	263.4	14.6	248.8
GP29	262.9	13.0	249.9
GP30	260.6	10.7	249.9
CPT1	263.5	13.5	250.0
CPT2	263.5	14.0	249.5
CPT3	263.2	11.3	251.9
CPT5	263.5	13.7	249.8
CPT6	264.3	12.5	251.8
CPT7	264.4	14.0	250.4
CPT8	264.4	13.5	250.9
CPT9	262.6	12.5	250.1
CPT10	262.5	11.0	251.5
CPT11	262.7	11.5	251.2

bgs = below ground surface
asl = above sea level
NA = not possible to interpret log.

Table 2.4. SL-XX Soil Core Descriptions.

SL-01	Soft/silty 4.9 to 6.5 m. Firm at 6.5 to 9.0 m. Softer at 9.0 to 9.2 m. Firm again 9.2 to bottom. Sandy starting at about 11.0 m.
SL-02	Silty from 4.8 to about 9.0 m. Very firm from 9.0 to 10.0 m. Sandy below 10 m.
SL-03	Very silty from 4.8 to about 8.0 m. Sandy beginning at about 9.0 m.
SL-05	Soft between 6 and 8.2 m. Firm at 8.2 to 8.4 m. Missing core between 8.4 and 9.6 m (about 20% full).
SL-06	Somewhat silty 4.8 to 6 m. Silty 6 to 7 m. Dense clayey 7 to 10.8m and black from 9 to 10 m. Dense and clayey 10.8 to 11.5 m. Sandy to clayey from 11.5 to 12.0 m.

Table 2.5. Maximum permissible contamination at Czechowice Refinery according to Polish State Environmental Protection Inspectorate (Warsaw, 1994).

	Soil (mg/kg dry mass)			Water (ug/l)
	A	B	C	
Metals				
Cr	500	100	800	200
Co	200	50	300	200
Ni	300	70	500	200
Cu	300	60	500	200
Zn	1000	200	3000	800
As	60	25	100	100
Cd	15	8	20	20
Hg	30	4	50	2
Pb	600	200	1000	200
Aromatic Hydrocarbons				
Benzene	100	3	150	5
Ethylbenzene	200	10	250	60
Toluene	200	5	230	50
Xylene	100	5	150	60
PAHs				
naphthalene	50	10	40	30
fluoranthene	50	10	40	5
benzo(a)pyrene	50	5	40	1
benzo(ghi)peryle	50	5	100	5

A 1 to 2m
B depths of 2-15m with hydraulic conductivity up to 10^{-7}
C depths of 2-15m with hydraulic conductivity below 10^{-7} respectively.

Table 2.6 IMA Results
Ohmicron and DTECH IMA Results

SAMPLE	Ohmicron BTEX (ppm)	DTECH BTEX (ppm)	DTECH PAH (ppm)	Ohmicron PAH (ppm)	Ohmicron CPAH (ppm)
SRF45	0.79	7.50	0.30	43.08	10.21
SRF46	0.41	1.25	3.00	9.88	7.08
SRF47	2.02	7.50	7.50	0.00	12.22
SRF48	1.25	15.50	0.30	38.26	10.73
SRF49	2.46	15.50	3.00	54.77	12.74
SRF51	4.61	15.50	7.50	46.18	17.38
SRF52	14.78	45.00	7.50	47.46	24.76
SRF53	0.11	1.25	0.30	0.00	23.14
SRF54	0.21	3.75	17.50	0.00	14.26
SRF55	0.39	50.00			
SRF56	0.36	3.75	3.00	29.34	20.06
SRF57	0.16	3.75	3.00		
SRF58	0.31	3.75	50.00	59.22	30.43
SRF59	0.28	3.75	0.80		
SRF60	0.25	1.25	3.00		
SRF61	0.03	3.75	0.30	4.65	1.95
SRF62	0.14	3.75	0.30		
SRF63	0.06	3.75	0.30		
SRF64	0.28	1.25	0.30	9.54	7.32
SRF65	0.25	1.25	0.30	17.29	11.42
SRF66	0.17	1.25			
SRF67	0.37				
SRF69	0.14				
SRF70	0.57				
SL03060	0.02	0.09			
SL03096	0.01	3.52			
SL03072	0.05	4.37			
SL03108	0.02	3.70			
SL03120	0.01	5.94			
SL03084	0.03	9.37			
SL02060	0.32	0.00	0.03		
SL02072	0.20	0.00	0.20		
SL02084	0.98	0.00	0.15		
SL02096	0.00	0.00	0.19		
SL02108	0.00	0.00	0.06		
SL02120	0.20	0.00	0.63		

Table 2.6 (cont.) IMA Results - Ohmicron and DTECH IMA Results

SAMPLE	Ohmicron BTEX (ppm)	DTECH BTEX (ppm)	DTECH PAH (ppm)	Ohmicron PAH (ppm)	Ohmicron CPAH (ppm)
DDO1085	5.27				
DD01048	0.67				
DD02080	4.65				
DD02048	0.64				
DD03086	4.41				
DD04063	3.25				
DD05060	0.70				
DD05072	3.43				
DD05084	1.76				
DD05096	0.00				
DD05108	0.08				
DD05060	1.30				
DD05048	8.46				

Table 2.6 (cont.) IMA Results - Ensys IMA Results

Sample	Location	15 ppm	150 ppm	TPH (ppm)	1 ppm	10 pmm	PAH (ppm)
EMF03	SRF03	-0.62	-0.55	>150			
EMF04	SRF04	-0.59	-0.41	>150			
EMF05	SRF05	-0.58	-0.34	>150			
EMF06	SRF06	-0.6	-0.48	>150			
EMF07	SRF07	-0.6	-0.5	>150			
EMF08	SRF08	-0.69	-0.67	>150			
EMF09	SRF09	-0.25	0.15	15-150			
EMF10	SRF10	-0.7	-0.7	>150			
EMF11	SRF11	-0.55	-0.52	>150			
EMF12	SRF12	-0.48	-0.45	>150			
EMF13	SRF13	-0.58	-0.59	>150			
EMF14	SRF14	-0.56	-0.37	>150	-0.69	-0.7	>10
EMF15	SRF15				0.2	0.68	<1
EMF17	SRF17				0.6	0.69	<1
EMF33	SRF34				-0.45	0.01	1-10
EMF34	SRF35				-0.41	0.04	1-10
EMF35	SRF36				-0.46	0.08	1-10
EMF36	SRF37				-0.41	0.15	1-10
EMF37	SRF38				-0.37	0.37	1-10
EMF38	SRF39				-0.69	0.07	1-10
EMF39	SRF40				0.48	0.59	<1
EMF40	SRF41				0.16	0.95	<1

**Photometer readings of optical density when compared to indicated ppm standard. Lower readings correspond to higher concentrations.*

Table 2.7 EMFLUX passive soil gas results

Name	X (E)	Y (N)	B	T	E	M,p-X	o-X	1,3,5-TMB	1,2,4-TMB	Naphth
EMF 01	241249	831119	146	10.3	38.6	46.7	nd	nd	nd	0.69
EMF 02	241253	831156	40.4	33.1	17.9	22.5	4.8	nd	15	9.6
EMF 03	241252	831167	54.7	25	16.3	22.5	3.3	nd	nd	nd
EMF 04	241239	831182	43.5	259	85.4	128	82.6	nd	116	35.7
EMF 05	241216	831191	13.5	90.2	28.5	33.8	25.4	nd	22.2	18.6
EMF 06	241214	831218	3.53	7.8	15.6	nd	5.6	nd	nd	15.2
EMF 07	241227	831235	----------no data----------							
EMF 08	241244	831255	9.07	4.1	nd	22.8	1.2	nd	5.8	nd
EMF 09	241257	831275	165	52.4	nd	46.3	8.6	nd	nd	nd
EMF 10	241274	831293	33.7	2.27	nd	21.6	nd	nd	nd	nd
EMF 11	241288	831312	3.61	10.3	47.8	32.4	43.2	nd	52.9	42.6
EMF 12	241306	831316	3.68	3.37	nd	21.8	2.6	nd	10.8	nd
EMF 13	241327	831318	7.86	83.1	15.4	24.4	1.4	nd	6.7	3
EMF 14	241351	831322	7.31	1.66	nd	nd	nd	nd	nd	nd
EMF 15	241374	831325	30.1	4.31	nd	nd	nd	nd	nd	nd
EMF 16	241376	831317	26.3	26.9	15.6	23.2	3.8	nd	22	9.6
EMF 17	241398	831320	42.5	116	40.9	55	30.6	nd	33	13.8
EMF 18	241415	831317	7.31	5.23	15.7	nd	2.7	nd	113	21.4
EMF 18A	241418	831325	19	6.18	23.1	37.4	13.2	n.o	85.4	136
EMF 19	241449	831323	179	24.5	nd	nd	nd	nd	nd	27.4
EMF 20	241471	831310	18.8	29.5	nd	nd	nd	nd	0.1	nd
EMF 21	241493	831290	12.6	3.12	nd	22.5	nd	nd	nd	nd
EMF 22	241513	831270	58.1	1191	1359	2064	2777	nd	9888	3611
EMF 23	241531	831249	60.5	191	47.5	75.6	45.9	nd	93	48.1
EMF 24	241548	831227	2.45	1.17	14.6	21.8	1.7	nd	15.2	9.2
EMF 25	241566	831207	62.4	5.89	nd	23.8	nd	nd	nd	nd
EMF 26	241586	831187	74.3	169	122	126	120	nd	303	607
EMF 27	241593	831160	56.6	188	48.3	80.3	47.8	nd	56.6	18.4
EMF 28	241553	831136	2.65	38.3	14.6	28.6	7.8	nd	nd	nd
EMF 29	241523	831134	29.4	1.77	nd	nd	nd	nd	n.o	nd
EMF 30	241488	831139	----------no data----------							
EMF 31	241461	831141	76.6	270	97	147	199	10.7	259	135
EMF 32	241434	831140	90.6	66.5	41.2	38.1	67.8	28.2	191	63.2
EMF 33	241413	831145	52.2	3.85	nd	nd	nd	nd	5.8	nd
EMF 34	241379	831169	----------no data----------							
EMF 35	241353	831169	52.7	27.1	16.3	nd	3.6	nd	nd	nd
EMF 36	241326	831171	58.7	29.1	15.8	nd	2.1	nd	nd	nd
EMF 37	241311	831187	54	53.3	20.9	22.9	1.5	nd	3.3	nd
EMF 38	241311	831186	54.4	24.8	nd	22.1	nd	nd	nd	nd
EMF 39	241310	831256	1.34	4.7	nd	nd	nd	nd	nd	nd
EMF 40	241292	831260	181	69.3	42.3	50.9	7	nd	2.3	nd
EMF 41	241362	831191	9.58	318	121	254	166	nd	231	82.5

All results are in nanograms of analyte in extract.
nd = Not Detected.

Table 2.8 Definitive analysis of various soil samples

BTEX in ug/kg of fresh soil

Soil sample	Depth [m]	Benzene	Toluene	Ethylb	m+p Xyl	o-Xyl	135-TMB	124-TMB
SL-01	6	5.85	5.85	0.48	0.71	0.64	0.17	0.27
SL-01	7.2	6.49	4.14	0.34	0.49	0.39	0.18	0.25
SL-01	8.4	3.8	6.57	0.46	0.79	0.7	0.28	0.94
SL-01	9.6	4.68	5.29	0.4	0.59	0.56	0.29	0.32
SL-01	10.8	7.87	5.25	0.34	0.49	0.42	0.26	0.4
SL-01	12	2.4	2.94	0.15	0.16	0.18	0.16	0.15
DD-01-048		nd	7.39	0.39	0.33	0.58	0.43	0.53
DD-02-048		16	17.8	5.3	4.31	3.98	2.14	8.13
DD-03-086		ND	3.83	nd	0.13	0.24	0.27	0.18
DD-01-085		113	6.12	0.21	0.16	0.32	nd	nd
SL-05-096		nd	2.85	0.13	0.1	nd	nd	nd
SL-05-048		nd	4.07	0.19	0.23	0.29	0.25	0.26
DD-05-060		41.1	6.2	1.81	2.03	1.93	0.29	1.92

PAH's in mg/kg

Soil sample	Depth [m]	Naphth	Fluor	B[b]F	B[k]F	B[a]P	B[ghi]P	IP	TPH mg/kg
SL-01	6	0.27	23	23	6.44	1.2	6.37	15	0.03
SL-01	7.2	0.34	16.9	13.9	4.56	2.73	5.18	6.34	<0.23
SL-01	8.4	0.56	18.4	15.6	9.27	5.15	6.23	7.82	<0.23
SL-01	9.6	0.45	35.1	29	14.5	9.71	10.6	20.8	<0.23
SL-01	10.8	1.24	17	7.55	2.56	0.77	2.82	2.06	<0.23
SL-01	12	0.41	26.3	6.91	1.63	1.5	2.17	2.36	<0.23
DD-01-048		Nd							
DD-02-048		Nd							
DD-03-086		Nd							
DD-01-085		Nd							
SL-05-096		Nd							
SL-05-048		Nd							
DD-05-060		0.05							

Metals in mg/kg

Soil sample	Ni	Cr	Zn	Cu	Pb	Co	Cd	Hg	As
SL-01	15.3	29.8	35.4	11.9	6.01	6.26	0.25	0.39	7.13
SL-01	8.74	19.7	25	9.2	3.51	2.86	0.16	0.2	1.04
SL-01	4.6	8.54	12.6	5.23	<2.69	1.32	<0.05	0.07	0.81
SL-01	9.04	21.2	31.5	10.3	3.81	1.88	0.08	0.17	1.29
SL-01	7.47	15.5	31.2	5.78	<2.69	3.43	0.08	0.09	1.57
SL-01	8.19	14.6	23.5	6.33	<2.69	2.55	0.12	0.12	1.33

TABLE 2.9 Features of Upper Plume as determined from laser induced ex situ CPT logs

Sample location	Plume range (meters asl)	Plume width (m)	Elevation (meters asl) of Plume bottom*	Relative Total Intensity
CPT01a	1 to 6.9m	5.9m	256.0	medium
CPT2	0 to 4.1m	4.1m	259.3	low
CPT3	0 to 6.4m	6.4m	257.1	high
CPT5a	1.4 to 3.6m	1.8m	259.9	low
CPT6	1.0 to 7.1m	6.1m	257.2	v low
CPT7	1.0 to 6.8m	5.8m	257.6	low
CPT8	1.0 to 5.6m	4.6m	258.8	medium
CPT9	0.8 to 3.6m	2.8m	259.3	high
CPT10	0.8 to 8.4m	7.6m	253.8	high
CPT11	1.3 to 5.6m	4.3m	256.8	high

** Derived using elevations of these locations and laser log maximum depth of the upper plume.*

Table 2.10 Groundwater (GW) sample names, locations and depths

Name	GW01	GW01D	GW02	GW03	GW04	GW05	GW06	GW07	GW08	GW09
Location	GP12	GP12	GP31	GP04	GP12	GP31	GP04	GP32	GP32	GP32
Depth (m)	11.0	12.5	12.5	12.5	12.5	12.5	14.5	18.5	15.5	12.5
Name	GW10	GW11	GW12	GW13	GW14	GW15	GW16	GW17	GW18	
Location	GP33	GP33	GP29	GP20	GP35	GP24	GP24	GP21	GP36	
Depth (m)	18.5	12.5	12.5	14.5	13.2	13.2	3.2	13.8	13.2	
Name	GW19	GW20	GW21	GW22	GW23	GW24	GW25	GW26	GW27	
Location	GP03	GP07	GP06	GP38	GP39	GP05	GP40	GP25	GP07	
Depth (m)	13.8	13.8	13.8	13.8	13.8	13.8	13.8	12.5	18.0	
Name	GW28	GW29	GW30	GW31	GW32	GW33	GW34	GW35	GW36	
Location	GP07	GP42	GP38	GP38	GP39	GP39	GP41	GP41	GP15	
Depth (m)	15.0	14.0	18.0	15.6	17.8	15.0	18.0	16.0	17.8	
Name	GW37	GW38	GW3							
Location	GP15	GP43	GP43							
Depth (m)	15.0	16.0	13.2							

Table 2.11. BTEX group groundwater results

	Benzene	Toluene	Ethylb	m+p Xyl	o-Xyl	135-TMB	124-TMB
GW-01F							
GW-01FD							
GW-02							
GW-03	735	14.2	26.5	1.77	1.56	0.84	2.71
GW-04	21.9	4.93	0.55	0.14	0.23	0.46	0.46
GW-05	105	4.52	3.38	0.13	0.29	1.27	0.63
GW-06	529	6.68	25.1	0.58	0.27	5.66	0.78
GW-07	835	11.2	127	43.6	25.6	49.1	147
GW-08	263	9.34	35.9	6.76	0.86	16.7	36.2
GW-09	175	6.43	77.3	11.8	0.98	29.1	79.2
GW-10	262	5.86	30.2	0.56	0.85	2.94	5.02
GW-11	375	8.26	32	1.05	1.48	7.25	3.71
GW-12	32.9	7.26	1.86	0.84	0.96	1	1.26
GW-13	12.3	6.34	0.5	0.51	0.58	0.44	0.56
GW-14	323	6.1	13.9	0.34	0.47	0.85	0.57
GW-15	25.9	5.61	0.89	0.69	0.63	0.63	1.42
GW-16	33.3	5.57	0.59	0.52	0.69	0.69	1.52
GW-17	79.1	6.08	6.14	0.54	0.69	0.78	0.5
GW-18	303	7.56	13.5	0.75	0.77	1.81	0.63
GW-19	110	12.4	7.21	3.07	2.5	3.21	2.09
GW-20	17.7	5.1	7.78	2.61	1.77	2.3	2.47
GW-21	275	7.46	12.3	1.01	1	0.58	1
GW-22	83.9	5.13	1.54	0.21	nd	nd	0.28
GW-23	152	6.03	9.71	0.46	0.51	1.32	0.38
GW-24	367	6.38	10	0.31	nd	0.65	0.35
GW-25	15.7	5.41	0.37	0.19	nd	0.36	0.35
GW-26	223	9.91	18.4	22.6	5.03	15.2	51.6
GW-27	378	7.05	16.4	1.91	1.27	2.08	8.82
GW-28	39.4	7.09	3.82	0.93	0.71	1.19	1.08
GW-29	73.4	6.54	6.88	1.27	2.5	1.79	8.46
GW-30	1223	12.4	48.2	5.52	7.53	14.5	34.4
GW-31	574	5.44	25.3	0.86	0.78	0.32	1.58
GW-32	1090	3.67	38.5	1.37	1.2	nd	2.04
GW-33	975	3.2	13.3	0.62	0.35	nd	0.16
GW-34	817	4.76	17	0.95	0.9	nd	nd
GW-35	1277	7.38	64.9	2.35	2.84	nd	2.67
GW-36	34551	26011	11550	16762	13176	15269	37496
GW-37	3020	2025	1988	2770	2267	1727	3645
GW-38	4904	9180	2944	4146	3266	4141	13156
GW-39	1844	3246	1308	1701	1341	817	1611

Table 2.11 (cont.) BTEX group groundwater results

National limits in ppb (USEPA = MCLs)

	Benzene	Toluene	Ethylb	m+p Xyl	o-Xyl	135-TMB	124-TMB
USEPA	5	1000	700	Total Xyl = 10		NA	NA
Hits	37/37	4/37	4/37	8/37	8/37		
Polish	5	60	60	Total Xyl = 60			
Hits	37/37	4/37	7 of 17	4/37	4/37	NA	NA

Table 2.12 PAH group groundwater results.

	Naphth	Fluor	B[b]F	B[k]F	B[a]P	B[ghi]P	IP
GW-01F	191	44.8	4	2.79	12.7	nd	
GW-01FD	236	10.8	1.88	3.7	9.1	nd	
GW-02	210	43.6	11.3	11.5	6.86	nd	
GW-03	6.85	119	23.4	8.59	14.1	23.7	30.4
GW-04	0.99	nd	8.84	7.28	23	168.6	304.8
GW-05	2.47	nd	nd	5.8	7.27	18.9	nd
GW-06	2.86	nd	nd	nd	nd	nd	nd
GW-07	23.7	nd	nd	10.5	13	nd	nd
GW-08	7.42	nd	nd	nd	nd	nd	nd
GW-09	41.1	nd	nd	nd	nd	nd	nd
GW-10	5.02	nd	nd	nd	4.2	nd	nd
GW-11	7.89	---------- No sample ----------					
GW-12	2.7	nd	nd	9.38	5.27	nd	nd
GW-13	1.41	nd	nd	6.31	nd	nd	nd
GW-14	1.32	nd	17.5	12.5	9.85	13.1	nd
GW-15	2.21	nd	nd	nd	nd	nd	nd
GW-16	2.93	nd	39.1	3.04	nd	nd	nd
GW-17	1.28	nd	nd	nd	nd	nd	nd
GW-18	0.97	nd	nd	nd	nd	nd	nd
GW-19	1.7	nd	nd	nd	nd	nd	nd
GW-20	7.78	nd	nd	nd	nd	9.96	nd
GW-21	1.54	nd	nd	nd	nd	nd	nd
GW-22	1.8	nd	nd	4.73	5.43	nd	nd
GW-23	1.54	nd	nd	3.32	nd	nd	nd
GW-24	0.8	nd	nd	nd	nd	nd	nd
GW-25	0.8	nd	nd	nd	nd	nd	nd
GW-26	52.1	nd	nd	nd	nd	nd	nd
GW-27	3.22	nd	nd	2.74	nd	nd	nd
GW-28	1.4	150	nd	5.53	4.63	nd	nd
GW-29	8.15	nd	nd	nd		nd	nd
GW-30	16	nd	nd	nd	3.53	8.82	nd
GW-31	1.72	nd	nd	nd		nd	nd
GW-32	2.82	nd	nd	nd	8	nd	nd
GW-33	1.9	nd	nd	nd		nd	nd
GW-34	0.39	nd	nd	nd		nd	nd
GW-35	3.04	nd	nd	6.3	7.4	5.5	nd
GW-36	2545	594	nd	22.2	56	65.8	50.6
GW-37	265	295	nd	9.57	18.7	34	nd
GW-38	2862	19.8	nd	nd	5.79	nd	nd
GW-39	156	nd	nd	nd	3.5	nd	nd

Table 2.12 (cont.) PAH group groundwater results.

National Limits in ppb (USEPA = MCLs)

USEPA	NA	NA	NA	NA	0.2	NA	NA
Hits	NA	NA	NA	NA	19/35	NA	NA
Polish	30	5	NA	NA	1	5	NA
Hits	6/37	8/40	NA	NA	19/35	12/39	NA

nd = non detect
NA = not applicable

Table 2.13 Groundwater data for metals, alkalinity, conductivity and pH

	Ni	Cr	Zn	Cu	Pb	Co	Cd	Hg	As	Alkal	Cond	pH
GW-01F	13.4	<1	23.3	8.1	<5.0	2.5	<0.7	0.36	0.38	2.2	51.8	6.84
GW-01FD	<1	<1	1.8	3.9	<5.0	<1.0	<0.7	0.72	0.36	2.4	50.4	6.78
GW-02F	16.7	<1	31	10.5	<5.0	2.2	11.7	0.68	0.37	2.5	97	6.74
GW-03F	31.6	2.2	52.2	7.8	<5.0	7.5	<0.7	1.28	0.62	0.26	143.7	6.65
GW-04	35.5	<1	19	22.4	<5.0	2.2	<0.7	0.67	0.99	2.4	43	6.71
GW-05	13.6	<1	26.3	10.7	<5.0	1.3	<0.7	0.5	0.62	2.8	76.4	6.59
GW-06	21.9	1.5	21.4	5.6	<5.0	3.3	<0.7	0.6	0.53	2.8	100.9	6.56
GW-07	2.3	<1	12.7	5.1	<5.0	<1.0	<0.7	0.66	3.24	5.8	77	6.98
GW-08	8.9	<1	18.9	10.6	<5.0	1.2	<0.7	0.59	1.38	5.4	76.8	6.83
GW-09	1.4	<1	19.8	4.5	<5.0	<1.0	<0.7	0.57	0.95	5.7	72.2	6.85
GW-10	<1	<1	17.1	1.1	<5.0	<1.0	<0.7	1.7	<0.1	5.8	83.6	6.7
GW-11	4.1	<1	29.2	3.7	<5.0	<1.0	<0.7	2.11	<0.1	5.6	80.7	6.76
GW-12	8.1	<1	47.9	3.1	<5.0	<1.0	<0.7	0.4	0.35	3.4	98.2	6.69
GW-13	8.3	<1	20.4	2.9	<5.0	<1.0	<0.7	0.26	0.31	2.8	111.4	6.5
GW-14	6.2	<1	8.2	2.4	<5.0	<1.0	<0.7	0.22	<0.1	6.2	86.3	6.97
GW-15	4.4	<1	36.9	<0.8	<5.0	<1.0	<0.7	1.74	<0.1	3.6	106.6	6.56
GW-16	10.4	2.4	34.8	<0.8	<5.0	<1.0	<0.7	0.48	1.13	0	117.2	4.25
GW-17	4	<1	12	<0.8	<5.0	<1.0	<0.7	0.5	0.14	3	89.4	6.71
GW-18	2.8	1.2	35.4	2.1	<5.0	<1.0	<0.7	0.4	<0.1	4	107.4	6.68
GW-19	1.1	<1	28.1	2.4	<5.0	<1.0	<0.7	0.34	<0.10	2	72.6	6.57
GW-20	5.1	2.3	20.7	3.2	<5.0	2.3	<0.7	0.59	0.4	4.8	117.1	6.58
GW-21	3.7	1.1	9.4	<0.8	<5.0	<1.0	<0.7	0.69	0.18	2.4	114.2	6.63
GW-22	1.4	<1.0	1.8	<0.8	<5.0	<1.0	<0.7	1.7	<0.10	3.8	227	6.29
GW-23	<1.0	<1.0	3.2	<0.8	<5.0	<1.0	<0.7	1.2	<0.10	4	199	6.73
GW-24	2.9	<1.0	13.6	1.2	<5.0	<1.0	<0.7	1.01	<0.10	5	176	6.59
GW-25	<1.0	<1.0	9.3	1.1	<5.0	<1.0	<0.7	0.78	<0.10	5.6	171	6.51
GW-26	27.4	2.3	22.4	6.8	<5.0	<1.0	<0.7	0.21	3.69	5.2	83.4	6.71
GW-27	14.8	<1.0	22.6	2.1	<5.0	<1.0	<0.7	0.19	0.13	4.2	171	6.5
GW-28	<1.0	<1.0	17.4	1.3	<5.0	<1.0	<0.7	0.15	0.12	2	213	6.17
GW-29	6.9	<1.0	20.2	1.5	<5.0	<1.0	<0.7	<0.1	0.17	1.4	215	6.02
GW-30	<1.0	<1.0	2.9	<0.8	<5.0	<1.0	<0.7	<0.1	0.15	5	160	6.86
GW-31	3.9	<1.0	13.2	3.2	<5.0	<1.0	<0.7	<0.1	0.3	5.2	199	6.98
GW-32	1.4	<1.0	6.7	<0.8	<5.0	<1.0	<0.7	0.1	0.16	5.2	175	6.77
GW-33	<1.0	<1.0	3.3	<0.8	<5.0	<1.0	<0.7	0.11	<0.1	4.4	184	6.84
GW-34	2.7	<1.0	2.9	<0.8	<5.0	<1.0	<0.7	<0.1	<0.1	4.8	165	6.87
GW-35	1.4	<1.0	6.3	1.8	<5.0	<1.0	<0.7	<0.1	<0.1	4.9	162	7.06
GW-36	1.4	<1.0	2.5	1.3	<5.0	<1.0	<0.7	0.11	0.39	7.2	182	6.65
GW-37	2.4	<1.0	3.7	1.1	<5.0	<1.0	<0.7	<0.1	0.11	3.5	167	6.43
GW-38	2.3	<1.0	4.2	<0.8	<5.0	<1.0	<0.7	0.1	0.1	2.9	188	6.49
GW-39	1.3	<1.0	1.9	<0.8	<5.0	<1.0	<0.7	<0.1	<0.1	2.6	166	6.29
National Limits in ppb (U.S. EPA = MCLs)												
U.S. EPA	100	100	none	1300	15	none	5	2	50			
Hits	0/40	0/40	NA	0/40	0/40	NA	0/40	1/40	0/40			
Polish	200	200	800	200	200	200	20	2	100			
Hits	0/40	0/40	0/40	0/40	0/40	0/40	1/40	1/40	0/40			

Chapter 3

Risk Assessment

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Risk Assessment

Historical Perspective of the Sludge Lagoon

Introduction

This risk assessment process is one component of the project conducted at the Czechowice Oil Refinery (CZOR) in Czechowice-Dziedzice, Poland. The project is coordinated and conducted by the joint team consisting of representatives of the U.S. Department of Energy (DOE), Ames Laboratory (Ames), Savannah River Technology Center (SRTC), Florida State University (FSU), and the Institute for Ecology of Industrial Areas (IETU) in Katowice, Poland. The project consists of three primary technical tasks: site characterization, risk assessment, and bioremediation of source material in petroleum waste lagoons at the refinery. Site characterization activity was undertaken according to the principles of the Expedited Site Characterization (ESC) process, as developed by the U.S. Department of Energy (U.S. DOE). Risk assessment using established U.S. procedures was conducted based on the results of the site characterization activity. The risk assessment process is designed to evaluate the potential risk of the existing contamination to humans and the environment, and to establish site-specific, health-based remediation goals for appropriate environmental media (e.g., soils, groundwater and surface water).

The goals of the project are to establish ESC expertise, risk-based evaluation expertise, and bioremediation expertise at IETU. Ultimately, this project was an important element in the establishment of the Risk Abatement Center for Eastern Europe (RACE). A complete description of the IETU-DOE partnership is presented in the document entitled Program Plan: U.S. DOE/Polish Partnership, which was prepared by FSU.

Site History

The Czechowice Oil Refinery, (CZOR) started its operation in 1896, when the Schodnica refinery was built. In 1902, in the vicinity of the Schodnica refinery, the construction of a larger and much more competitive modern refinery was started. This second refinery was built by Vacuum Oil Company, which was owned by Socony Vacuum Oil Incorporation, New York, USA. In these early days the refinery was processing 35 thousand tons of a paraffin crude oil per year. In 1931, the first distillation unit of a Foster Wheeler system in Poland was built in Czechowice. The refinery was bombed in August 1943 by the Allies and only partly rebuilt by the Germans during the war. Polish engineers and workers finished the restoration shortly after the end of the World War II. The production resumed in February 1946. The first new parts of the plant in Poland were built in 1954. It was a cresol refining plant. Then the grease plant was revamped and developed up to the capacity of 25,000 tons a year. The capacity of the new part of the refinery was increased in the period between 1959 and 1962. Its capacity was 500,000 tons a year. A big fire damaged a part of the refinery in 1971 but it was very quickly rebuilt. In 1985, thallic and turpentine oils processing plants from a separate company were incorporated into the CZOR. In recent years the refinery has been transforming into an effective free market company. Petroleum is the main raw material in the refinery. The basic products are

as follows: ethyl gasoline, engine oil, fuel oil, paraffin and paraffin products, asphalt, engine and special oil products.

In the refinery, there are three lagoons that cover the area of about 3,8 ha. The lagoons are about 3 m deep. They are filled up with oil-water sludge containing post-refining sulfuric acid, solids and rubble (the acid treatment was stopped in 1984). Sludge of over 121 thousand tons is deposited there [PROXIMA, 1993]. Two of the three lagoons (1,9 ha) are to be remediated.

Geography and Local Land Use

The CZOR is located in the eastern part of Czechowice-Dziedzice town. Czechowice-Dziedzice is situated in the southwest of Poland, in the southern part of the Katowice province - 45 km from Katowice, 8 km from Bielsko-Biala and about 6 km from the Goczalkowice Lake. The Goczalkowice Lake is an artificial water reservoir, which supplies drinking water to the Upper Silesian Industrial Region. The health resort Goczalkowice Zdrój and the recreational area are situated in its vicinity. Czechowice-Dziedzice is situated in the Oswiecim Valleys belonging to the Fore-Carpathian Valleys.

The town of Czechowice-Dziedzice covers an area of 33 km^2 and is inhabited by 35615 people; the population density is 1079 people/km^2 [Rocznik Statystyczny Województwa Katowickiego, 1995]. From the east, it borders on the Biala River which flows into the Wisla River about 3 km to the north. From the west, it borders on the villages and from the south on a country area and the area of Bielsko-Biala. In the northern and northwestern part of the town there are meadows, garden allotments, residential buildings, fish nurseries, ponds, a coal mine, a paper factory and a metal rolling mill. In the western part of the town some small ponds are located. In the central part of the town there are concentrated residential buildings of several stores, offices, a cable factory and a motor car factory. The CZOR, a match factory, garden allotments and fish nurseries (Marianki ponds) are localized in the east of the town. In the east and southeast of the town, there is an electrotechnical equipment factory, a power plant, a bakery, a factory of dressing materials, a meat factory and a coach station [City/County map, Czechowice-Dziedzice, 1994]. The refinery covers an area of 75 ha. Elevation of the refinery area is about 260 - 280 m above the sea level.

Four streets (from the west, the southwest, the east, the northeast) and a railway from the north surround the refinery. Farther to the north there are industrial and residential areas. Garden allotments are situated within about 200 m from the refinery. From the northwest there is a motor car factory and a residential area; from the northeast - an undeveloped area and garden allotments. Thallic and turpentine oils processing plants (Terpen) as well as the Marianki ponds, which are cut by a railway line, adjoin these areas. At a distance of 250-600 m in the northeastern direction there are agricultural areas (arable lands, meadows, pastures). In the southeast of the refinery, the railway station (the railway line to Bielsko-Biala), and garden allotments, are located. About 300 m farther in this direction are located more agricultural areas and the fish nurseries. The Biala River flows from the south to the north about 50-100 m to the northeast and southeast of the refinery. The Bestwiñskie Ponds and agricultural areas are situated along this river. From the south the refinery borders on the street, where scattered housing occurs. From the southwest and west the refinery adjoins the street where multi-family houses, a kindergarten,

a sports field, office buildings, health centers and the park are situated [City/County map, Czechowice-Dziedzice, 1994].

Two of the lagoons, which are to be remediated within this project, are located in the northern part of the CZOR [City/County map, Czechowice-Dziedzice, 1994]. They border on:

- the railway - from the north,
- the street and the park - to the west,
- the third lagoon (biggest) - to the east,
- the area belonging to the refinery - to the south.

Geology and Hydrology

Geology

The area of the refinery is located in the southern part of Upper Silesian Slump. On the terrain of the refinery both Quaternary and Tertiary formations occur. Tertiary formations consist predominantly of gray clay where sandy layers of different granulation occur. The tertiary roof is uneven and is deposited between 20.5 m and 24.0 m under the ground level from the west, and around 16.5 m from the east. Tertiary strata are topped by Quaternary formations originated from glacial processes as sandy and gravel formations. They are covered by clays to the surface level [PROXIMA, 1993a].

Hydrogeology

Within this area two water-bearing layers in Quaternary and Tertiary formations occur. The Quaternary formation consists of sandy and gravel strata which thickness varied between 7.0 and 10.0 m. The water-bearing layer within this formation is characterized by potential water efficiency of $Q > 5\ m^3/h$. The abovementioned water-bearing layer borders on the Main Underground Water Reservoirs from the north and the south. Quaternary ground water level has predominantly free character, only locally it is under slight pressure. From the west of the area the ground water level is 11 - 12 m under the ground level, from the east, where terrain slopes downward to the river, the ground water level is around 3.9 m under the ground level. The ground water level is stabilized around 251.8 - 249.0 m above the sea level and the overall flow direction is SSW – NNE; however, on the local scale other directions should be considered. Water-bearing level capacity is high; obtained efficiency is around 33.0 m^3/h with $s = 3.95$ m. Tertiary strata consist of sand and gravel formations interbeded with clay. A water table under pressure occurs within this formation. The Tertiary ground water level is covered by clays at a depth of 40 to 49.5 m. The clay layer isolates and protects both Quaternary and Tertiary waters against pollutants migration from surface soils [PROXIMA, 1993a].

Environment

The vicinity of the refinery has been transformed to a principally industrial area with limited remaining areas of naturally occurring ecosystems. The Bestwiñskie ponds, located to the east of the Biala River are regarded as valuable ecosystems and in the ponds fish farming is conducted. In the vicinity of the Bestwiñskie ponds agricultural soils of relatively high quality occur. These are

alluvial and podzolic soils originated on loess, classified as III and IV soil quality classes with good water and air properties. They are proper for wheat and potatoes cultivation [Janikowski et al., 1995].

Elsewhere within the Czechowice-Dziedzice region there are also mainly podzolic and brown soils, originated from loamy sands, glacial drift or coarse sandy soils [Dynowska and Maciejewski, 1991]. Brown, gray brown podzolic and alluvial soil, originated from glacial drift and loess, occur in the river valleys [Kondracki, 1981]. Lime-trees, maple-trees, sycamores and hornbeams grow within the Czechowice-Dziedzice region in the vicinity of rivers and ravines. Ash, oaks, and poplars of at least ten years old grow along the Biala River [Janikowski et al., 1995].

There are two forest areas in the Czechowice-Dziedzice region: a large one situated in the north-west and a smaller one in the south. There also is the Rotuz Sanctuary on the western border of the Czechowice-Dziedzice region. This is a peat-bog, overgrown by mosses, where pine trees grow and blind-worms and adders live [Janikowski at al., 1995].

Pattern of Site Contaminant Detection

Site characterization was conducted using the DOE-developed Expedited Site Characterization methodology. The target of the Expedited Site Characterization (ESC) was to characterize the area surrounding the CZOR sludge lagoons in support of this risk assessment and subsequent remediation activities. ESC makes use of direct push technologies (e.g., cone penetrometer), on-site chemical analysis and real-time data display and interpretation to conduct rapid and efficient site characterization. This approach brings experts and data together in the field to conduct dynamic data interpretation and sample collection decisions. A critical aspect of this characterization, as well as of ESC in general, is the use of direct push technologies such as cone penetrometer (CPT) and Geoprobe to conduct subsurface investigations. The advantages to direct push over conventional (i.e., drilling) technologies are the speed of development, the absence of drilling waste, and the ability to collect a variety of data over a short period of time. Each "push" enables the continuous collection one of a variety of data types depending on which of several probes is attached to the rod and advanced through the subsurface. Data were developed in the ESC to support subsequent risk assessment and remedial design stages. All phases of the ESC were conducted by IETU specialists working in conjunction with U.S. counterparts. This collaboration ensured an active exchange of ideas, philosophies and approaches to site characterization. The ESC utilized and compared several different technologies for the rapid qualitative and quantitative evaluation of hydrocarbon contamination in the lagoon area.

This ESC was conducted in two phases. Phase 1 utilized immunoassay (IMA) sampling kits, active and passive soil vapor sampling as well as geophysical and soil conductivity surveys to describe site stratigraphy and to qualitatively determine the nature and extent of site contamination. The concurrent use of IMA kits from several different manufacturers provided an opportunity to compare and contrast these screening tools while delineating the extent of soil contamination. Phase 1 also involved the use of active and passive soil gas collection and analysis. These sampling procedures provide general information on the presence of volatile compounds in the vadose zone and help to estimate the risks posed to humans by exposure to contaminated soil. Phase 2 involved the collection of detailed hydrogeologic and definitive chemical data. This was accomplished using Geoprobe (groundwater), Ditchwitch (directional drilling to collect soil samples from beneath the lagoons) and both *in situ* and laboratory-based chemical analysis.

The ESC represents a first for its application in Poland. The Physical Conceptual Site Model was developed as follows: Groundwater was located at approximately 11 meters below grade and may have been partially confined during the ESC. It was confirmed that the site was underlain by low permeability clay, however evidence was produced suggesting a degree of heterogeneity in this layer. This heterogeneity could provide relatively permeable pathways allowing surface contaminants to migrate to groundwater. As was anticipated, ground-penetrating radar was not able to penetrate the dense soils or sludges at the refinery. The EM61 electromagnetic detector was able to confirm the location of known subsurface features (e.g., pipes) and also identified other features that were subsequently avoided in the subsurface

investigation. The extreme weight (20 tons) of the CPT vehicle and soft soil conditions at the site resulting from heavy rains restricted the application of CPT to improved roadways in the vicinity of the lagoons.

The Chemical Conceptual Site Model involved a variety of sample collection and analysis techniques and provided the following description of site contamination. Surface soils were highly variable in contaminant level as a result of the nature of disposal practices at the refinery. As a result, there are a number of "hot spots" around the lagoon area. These surficial locations are contaminated with the non-volatile PAHs, while VOCs and BTEX are generally at low levels. IMA kits proved to be useful tools in screening site soils for PAH and BTEX contamination. While the absolute accuracy of these tests was not evaluated in this study, comparisons among manufacturers were carried out. It was found that IMA kits correlate well within manufacturers, but not between manufacturers, suggesting that the consistent application of one type of analysis can lead to useful results. Groundwater was found to be heavily impacted by PAHs and BTEX (mainly benzene). This may be due to impacts from the lagoons or from refinery material loss and subsequent transport through areas of high soil permeability. The patterns of contamination were unexpected, with elevated contaminant concentrations both north and south of the lagoons. The dense industrial activity surrounding the refinery and the possibility for containment of the aquifer reduced our ability to define sources and plume directions.

Significance of Findings

The ESC proved to be an excellent instrument to develop a working relationship between DOE, the IETU and a number of U.S. partners. The cooperation required to plan, conduct and evaluate this site characterization provided the basis for subsequent activities in a number of areas. From a technical aspect, the ESC provided information that was necessary to support the risk assessment and bioremediation. It documented the relative performance of different IMA kits as useful screening tools for this type of activity and provided valuable data for comparing different direct push fluorescence light sources.

The ESC that was conducted at the CZOR was designed and implemented under the direction of Ames Laboratory for the United States Department of Energy (DOE), the Institute for Ecology of Industrial Area (IETU), CZOR, and Florida State University (FSU). This collaboration between IETU, DOE and their partners, provides the basis for international technology transfer of new and innovative remediation technologies which can be applied to DOE sites, in Poland and at sites, worldwide.

Risk Assessment Procedures/Exposure Assessment

Introduction

The risk assessment process is an integral part of the remedial investigation/feasibility study process that typically is conducted at contaminated sites in the United States. Risk assessment using established U.S. procedures is designed to evaluate the potential risk of current and future adverse effects on humans and the environment, and to establish health-based remediation goals for appropriate environmental media (e.g., soils, groundwater and surface water). Risk assessment, performed as a part of the CZOR Project, is based on the U.S. experiences in this field, and utilizes U.S. standards and procedures.

The process of risk assessment for environmental contaminants is described in a number of guidance manuals, published by the United States Environmental Protection Agency (U.S. EPA) in recent years.

Examples of these guidance manuals include the following:

- Superfund Public Health Evaluation Manual (U.S. EPA, 1986);
- Superfund Exposure Assessment Manual (U.S. EPA, 1988);
- Alternate Concentration Limit Guidance; Part I: ACL Policy and Information Requirements (U.S. EPA, 1987);
- Risk Assessment Guidance for Superfund (Volume I): Human Health Evaluation Manual (U.S. EPA, 1989a; U.S. EPA 1991);
- Risk Assessment Guidance for Superfund (Volume II): Environmental Evaluation Manual (U.S. EPA, 1989b);
- Exposure Factors Handbook (U.S. EPA, 1989c);
- Supplemental Guidance on Performing Risk Assessments in Remedial Investigation/Feasibility Studies (RI/FSs) Conducting by Potentially Responsible Parties (PRPs) (U.S. EPA, 1990);
- Soil Screening Guidance: Technical Background Document (U.S. EPA, 1996a).

A risk assessment process should be viewed as a flexible process that can be adjusted to specific circumstances and information needs of individual sites. In general, however, the procedures which are used for risk assessments encompass the following areas:

- site characterization, data collection and evaluation for relevant environmental media;
- selection of indicator chemicals;
- human exposure assessment under site-specific exposure scenarios;
- toxicity assessment for the chemicals of concern;
- site-specific risk characterization;
- development of remedial goals.

The general procedures described in these guidance documents were employed for the purposes of the risk assessment at the CZOR site. It is the first application of the risk assessment process as an integral part of remedial/feasibility studies, conducted at a contaminated site in Poland.

The site characterization is based upon data from environmental samples taken by the Ames Laboratory and their IETU counterparts as discussed in Section II of this report. The site characterization was conducted using the U.S. DOE Expedited Site Characterization (ESC) System, which is an innovative approach to site characterization that integrates data from several disciplines to provide more efficient and cost-effective results. During the site characterization historical information and data on geography and local land use, geology, hydrology and ecology were gathered. Characterization mainly focused on groundwater and soil affected by refinery activities in the vicinity of petroleum waste lagoons. The primary purpose of groundwater and soil sampling was to define the nature and extent of hazardous substances released to the environment within and surrounding the subject lagoon in order to obtain technical information necessary to assess the feasibility of various remedial options. Those data are presented in greater detail in Section II.

Data collection and evaluation involved also gathering and analyzing the site data relevant to the human health evaluation and identification of the substances present at the site that are the focus of the risk assessment process. For the purposes of this risk assessment the site data are not sufficient to characterize ecological impacts at the sludge lagoon site, so ecological risk was not considered in this document.

Selection of indicator chemicals

Indicator chemicals are selected as representatives of the toxicity and environmental behavior of the contaminants at the site. They are selected as an initial step in a site-specific risk assessment, in order to characterize the site and to focus the assessment activities on those compounds which are judged to pose the most significant potential risks due to their inherent toxicity and/or the pattern of detection on the site.

Based on experts' experiences and analytical capabilities of IETU, the following 19 organic and inorganic parameters were selected as the indicator chemicals in groundwater and soil for the sludge lagoon at the CZOR site:

BETX:

- Benzene
- Ethylbenzene
- Toluene
- Xylenes

Polycyclic Aromatic Hydrocarbons (PAHs):

- Benzo(a)pyrene
- Benzo(b)fluoranthene
- Benzo(g,h,i)perylene
- Benzo(k)fluoranthene
- Fluoranthene
- Indeno(1,2,3-cd)pyrene

Metals:

- Arsenic (As)
- Cadmium (Cd)
- Chromium (Cr)
- Cobalt (Co)
- Copper (Cu)
- Lead (Pb)
- Mercury (Hg)
- Nickel (Ni)
- Zinc (Zn).

The concentrations of chemicals which were detected at the CZOR site were first compared to the default regulatory guidance for remediation activity in Poland, represented by recommendations published by the Polish State Environmental Protection Inspectorate (PIOS) (Table III-1). Concentrations of metals in soil were additionally compared to the off-site (area of Czechowice-Dziedzice) background data for soil (Table III-2). Selected physical/chemical properties for the indicator chemicals are presented in Table III-3.

Human exposure assessment under site-specific exposure scenarios

Introduction

An exposure assessment is conducted to estimate the magnitude of actual and/or potential human exposure, the frequency and duration of these exposures, and the pathways by which humans are potentially exposed. In the exposure assessment, "Reasonable Maximum Exposure" (U.S. EPA 1989a) parameters are estimated for both current and future land-use assumptions. Current exposure estimates are used to determine whether a potential threat exists based on existing exposure conditions at the site. Future exposure estimates are used to provide decisions-makers with an understanding of potential future exposures and threats and include a qualitative estimate of the likelihood of such exposures occurring. Conducting an exposure assessment involves analyzing contaminant releases, identifying exposed populations, identifying all potential pathways of exposure, estimating exposure point concentrations for specific pathways and estimating contaminant intakes for specific pathways. The results of this assessment are pathway-specific intakes for current and future exposures to individual substances.

Identification of potential exposure routes

For the purposes of this risk assessment, surface soils and groundwater in the vicinity of the sludge lagoon at the CZOR were evaluated with regard to the potential risks that they may pose to humans or to environmental receptors. The ingestion, inhalation and dermal exposure routes were considered. Calculations of daily intakes were conducted using the 95% Upper Confidence Limit (UCL) of the arithmetic mean for the concentrations of contaminants which were detected in surface soils and groundwater in the sludge lagoon. In cases where reported analytical results were below detection limits (BDL), 1/2 of the stated method detection limit was used in calculation of the mean (U.S. EPA, 1989a). The BDL concentrations which exceed the maximum concentration are not included in the calculation of the mean or 95% UCL. The arithmetic mean concentrations were not included in daily intake calculations because they differed from 95% UCL values by less than of 50% in most cases. The use of 95% UCL values for daily intake calculations provides a "Reasonable Maximum Exposure" estimate for the potential risks which may be associated with present or future site contamination under the assumptions regarding site exposure (e.g. residential exposure, construction exposure). This is discussed in greater detail in Section III-C-3 and Section V.

Identification of potential receptors by exposure route

Identification of potential exposed populations by exposure routes regarding current and future land use patterns results in determination of exposure scenarios, determination of factors associated with each scenarios and collection of data to support each factor. The CZOR site is currently classified as industrial and probably land use of the site will not change in the future. For the defined land use category, for the purposes of estimating contaminant intakes at the site, several scenarios were evaluated. The assumptions and the specific calculations of contaminant intakes regarding each scenario are discussed in detail in Section V for potential exposure to soil and groundwater.

· Soil

For the purposes of estimating contaminant intakes for this assessment at the sludge lagoon at the CZOR, two exposure scenarios were assumed and evaluated considering ingestion, dermal and inhalation exposure to contaminated soils. Ingestion or dermal exposure to contaminated soils as a result of incidental contact are common assumptions which are employed in site-specific risk assessment, though frequently it is difficult empirically to verify or to quantify such intakes.

Scenario I (Adult, On Site Future Construction/Remediation) - a construction worker exposure scenario was assumed for potential exposure to surface soils at the sludge lagoon in the event of future remediation or construction activities. For this scenario, it was assumed that an individual could come into contact with surface soils on a daily basis (250 days/year; 5 days/week for 50 weeks/year) for a period of 4 months (0.33 years) during future on-site construction or remediation activities (U.S., EPA, 1991). It also was assumed that this individual could have regular contact with surface soils at the sludge lagoon (3,875 cm^2; approximate exposed areas of forearms, hands, face, neck; U.S. EPA, 1992), and that such an individual incidentally may ingest 195 mg of soil per daily site work, according to conservative U.S. EPA assumptions for typical construction scenario (U.S. EPA, 1991). Inhalation of volatilized organics as well as inhalation of respirable particulates (dust) from exposed soil also was included in the calculation for Scenario I, due to the potential for airborne soils during work activities.

Scenario II (Adult, Industrial) - it was assumed that an adult may be directly exposed to contaminants in surface soil at the sludge lagoon for 50 days/year (1 day/week, 50 weeks/year) for 25 years (U.S. EPA, 1991) of 70 year lifetime (U.S. EPA, 1989). It was assumed for Scenario II that an individual would not spend more than 8 hours during a week (1 day/week) in "normal" work-related activities at the sludge lagoon site. It also was assumed that this individual could have dermal contact with surface soils at the lagoon (2,300 cm^2; approximate areas of forearms, hands and face; U.S.EPA, 1992), and that such an individual incidentally may ingest 50 mg of soil per day (U.S. EPA, 1991). Inhalation of volatilized organics from soil and respirable particulates (e.g., dust) from exposed surface soils at the lagoon site was included for Scenario II (inhalation rate - 20 m^3/day per U.S. EPA, 1991).

Figure III-1, Figure III-2, Figure III-3 present expressions with the assumptions which were employed for calculations involving oral, dermal and inhalation exposures to site soils, respectively.

· Groundwater

The installation of potable water wells on the Refinery site is not considered to be likely in the future. However, it is not possible to state with certainty that such wells would not be installed for non-potable uses (e.g., irrigation). While these potential situations are judged to be unlikely, it has been assumed for purposes of this assessment that such wells could be installed and that water could be used for irrigation purposes by future workers at the CZOR site. Therefore, Scenario III (Adult, On-Site Groundwater Future Irrigation) was assumed for potential exposure to groundwater at the CZOR site in the event of future irrigation activities. For this scenario it was assumed that an individual could come into contact with site groundwater on a daily basis (25 days/year; 1 hr/day) for a period of 25 years of 70 year lifetime. It also was assumed that this individual could have regular dermal contact with groundwater during his activity associated with

the irrigation (5,200 cm^2; approximate areas of hands, forearms, upper arms, neck, face, lower legs; U.S. EPA, 1992), and that such an individual incidentally may ingest 0.02 L of groundwater per day (U.S. EPA, 1989c). Potential inhalation exposure to contaminants which may be volatilized from groundwater during irrigation activities was also evaluated for this scenario.

Figure III-4, Figure III-5, Figure III-6 present calculations with the assumptions regarding dermal, oral and inhalation exposure to site groundwater during irrigation Scenario III, respectively.

If, in the future, some remediation activities are conducted at the Refinery site, these activities could lead to potential exposure of workers to contaminants in groundwater during construction or remediation activities. For Scenario I (Adult, Future Construction/Remediation), it was assumed that, during remediation activities, workers could be exposed to site groundwater on a reasonably regular basis, i.e. 2 hours/day; 50 day/year for 0.33 year of a 70 year lifetime (U.S. EPA, 1991). These workers could have dermal contact with groundwater during excavations associated with the construction or remediation (e.g., pits or trenches) (3,875 cm^2; approximate areas of forearms, hands, face, neck; U.S. EPA, 1992). Incidental ingestion of groundwater also was assumed to occur at the rate of 0.01 L/day (U.S. EPA, 1989c). Inhalation exposure to contaminants which may be volatilized from groundwater was also evaluated for this scenario.

Figure III-4, Figure III-5, Figure III-6 present calculations with the assumptions regarding oral, dermal and inhalation exposure to chemicals in site groundwater during construction/remediation activities for Scenario I, respectively.

Site-specific risk characterization and development of risk-based concentrations

Risk characterization combines toxicity assessment with exposure assessment in order to quantify risks posed by a contaminated site under a given set of conditions. Risk characterization is considered separately for carcinogenic and noncarcinogenic effects and includes the accompanying uncertainties.

A site-specific risk characterization is presented in Section V of this document to evaluate the present conditions at the sludge lagoon at the CZOR site under specific assumed conditions of exposure. The population at risk under existing or projected future conditions is assumed to include potential exposure to adults during construction/remediation (soil and groundwater) and industrial activities (soil), as well as exposure to adults from on-site groundwater during irrigation activities. As discussed in Section III-C, the scenarios and calculations are provided for the following specific potential contact conditions:

- **Scenario I** (Adult, On-site Future Construction/Remediation): occupational exposures to adults who may be exposed to surface soils and groundwater at the sludge lagoon at the CZOR site during potential construction or remediation activities. Exposure to soil was assumed to occur for 250 days/year for 0.33 year of a 70 year lifetime. Dermal exposure (3,875 cm^2) and oral exposure (195 mg/day) to soil and inhalation of volatilized organics and respirable particulates (dust) from exposed soils was assumed. Additionally, dermal exposure to groundwater and inhalation of contaminants volatilized from groundwater for 2 hours/day for 50 days/year for 0.33 year of a 70 year lifetime was included as well as incidental ingestion of groundwater (0.01 L/day) was assumed.

- **Scenario II** (Adult, Industrial): occupational exposure to adults who may be exposed to surface soils during their work-related activities at the sludge lagoon site (50 days/year for 25 years of a 70 year lifetime) through dermal contact with soils (2,300 cm^2), inhalation of surface soil particulates and volatilized organics from soil (inhalation rate - 20 m^3/day), and ingestion of 50 mg of soil per day.

- **Scenario III** (Adult, On-site Groundwater, Future Irrigation): exposure to adults who may be exposed to site groundwater on a daily basis (25 days/year; 1 hr/day) for a period of 25 years of 70 year lifetime. It was assumed that these individuals could have regular dermal contact with groundwater during their activities associated with the irrigation (5,200 cm^2), and that these individuals may have incidental consumption of groundwater (0.02 L/day). It also was assumed that these individuals may inhale chemicals volatilized from groundwater during irrigation activities.

These scenarios are considered to represent a reasonable range of upper bound assumptions for potential exposure of humans at the sludge lagoon at the CZOR site under present and projected future site conditions.

Potential noncarcinogenic risks for exposures at the CZOR site were evaluated by comparison of the estimated contaminant intakes with the U.S. EPA Reference Dose (RfD). Risks that may be associated with exposure to multiple, noncarcinogenic contaminants were evaluated according to the additive relationship which describes the Hazard Index (HI), defined by the following expression:

$$HI = (DCI_1/RfD_1) + (DCI_2/RfD_2) + (DCI_3/RfD_3) + ...+ (DCI_n/RfD_n),$$

where:

HI = Hazard Index (unitless);

DCI = Daily Contaminant Intake (mg/kg/day);

RfD = Reference Dose (mg/kg/day).

In case where the aggregate noncarcinogenic HI does not exceed unity (a value of 1), it typically is assumed that RfDs have not been exceeded and, thus, that no acute or chronic risks are likely to occur at the site.

A similar procedure may be used to estimate risks from multiple carcinogenic compounds. This relationship is expressed as follows [U.S. EPA, 1989a]:

$$Risk_t = \sum_{i=1}^{n} (Risk_i)$$

where:

$Risk_t$ = total cancer risk;

$Risk_i$ = risk estimate for the ith substance of a total of n substances.

Risks in range of 10^{-6} to 10^{-4} typically have been judged to be acceptable by regulatory agencies, including U.S. EPA [U.S. EPA, 1991].

One conclusion of risk characterization, if site conditions protect human health and the environment, could be that no remedial action is needed. Alternatively, if action is necessary to meet site-specific remedial goals (e.g., Risk-based Concentrations (RBCs)) are developed for selected environmental media. The final decision regarding whether (or to what extent) remediation is appropriate for a particular site typically is influenced by risk management considerations. These include the technical feasibility of cleanup, the likelihood of actual human exposure and the environmental persistence of a compound or compounds that may be present at the site. Media-specific RBCs were calculated for each indicator chemical in soil and groundwater at the sludge lagoon at the CZOR.

Calculations of RBCs for noncarcinogenic chemicals were conducted using the U.S. EPA RfDs as the maximum acceptable contaminant intake levels. In the calculation of risks and RBCs from dermal exposure, the oral RfD typically is used since no RfDs have been established for the dermal route of exposure. The dermal RfD values were calculated by multiplying the oral RfDs by the Dermal Equivalency Factors. The inhalation RfD values were calculated by multiplying the inhalation RfC by the inhalation rate and dividing by the body weight.

For each carcinogenic indicator chemical, the RBC was calculated using the Risk-specific Dose (RsD) as the maximum acceptable contaminant intake level for individual routes (i.e., dermal, oral and inhalation), as well as for combined exposures by all routes. The RsD was based on the U.S. EPA Carcinogenic Potency Factor (CPF) and a 1E-06 potential cancer risk as shown in the following expression:

$$\text{RsD (mg/kg/day)} = \text{1E-06/CPF (mg/kg/day)}^{-1}$$

The dermal CPF values were calculated by dividing the oral CPFs by the Dermal Equivalency Factors. The inhalation CPF values were calculated by multiplying the inhalation URFs by the body weight and dividing by the inhalation rate.

In this document, 1E-06 is used as a conservative point-of -departure. The RBCs calculated for 1E-05 and 1E-04 would be 10-fold and 100-fold less restrictive, respectively.

<u>Uncertainties associated with the Czechowice Oil Refinery site risk assessment assumptions</u>

Assumptions, calculations and conclusions that are presented in this risk assessment include uncertainties which may arise from a variety of sources. However, efforts were made to take a reasonable and conservative approach where possible.

The factors which may lead to either an overestimation or an underestimation of the potential adverse human health effects and associated environmental risks posed by exposure to analytes at the Czechowice Oil Refinery site, depending on the relationship of actual conditions to the assumptions employed in the calculations, include the following:

- although the sludge lagoon at the CZOR site has been characterized with respect to soil and groundwater in the areas of known or suspected analyte contamination, information regarding site conditions may be incomplete, possibly resulting in an underestimation or

overestimation of the actual quantities of the contaminant chemicals which are presented at the site. Lack of information on contamination of subsurface soil caused that surface soil data were used instead of subsurface soil data for Construction/Remediation Scenario. The sludge lagoon is only a small part of the Refinery area and it is difficult to separate risks from the sludge lagoon and the different sources of contamination. Lack of appropriate data made evaluation of risks to ecological (i.e., non-human) receptors impossible;

- assumptions regarding, for example, body weight, average lifetime, and other human factors were based on best estimates from available sources and may not be accurate for specific individuals whose characteristics may vary from the conservative general conditions which were assumed. However, standard assumptions were employed in those cases where they were available. In Poland there is lack of some statistical data needed for calculation of intakes and risk characterization, some of them could be regard as the same like in the United States, so for this risk assessment intake exposure parameter values and Risk-based Concentration exposure parameter values established by U.S. EPA were accepted after appropriate recognition;
- factors which affect the disposition of absorbed site contaminants, such as metabolism, distribution and excretion, were not explicitly considered in detail in the risk calculations or the RBC calculations. Rather, reasonable and conservative assumptions were employed regarding conditions which are unlikely to underestimate the true exposure conditions;
- the mechanism of action for toxicity of the site contaminants is not known with certainty in many cases, particularly regarding their putative carcinogenic effects. The rather specific nature of the carcinogenic effects suggests that any extrapolation to humans will be heavily dependent on the assumption of equivalent response in man, an assumption which often is not supported by the epidemiological data;
- non-quantifiable uncertainties are inherent in several different aspects of the estimation of potential human health effects and RBCs. Extrapolation of dose-response curves from high to low dose, from animals to humans and from one exposure route to another introduce uncertainty, intended to be conservative, at each step in the calculated results. The use in this document of established Carcinogenic Potency Factors which have been calculated by ostensibly conservative methods (e.g., the linearized multistage model) is unlikely to underestimate the true risk and may overestimate it by a margin which is not quantifiable at present;
- exposure to site contaminants was assumed to remain constant over time under the projected conditions of exposure, although the actual conditions on-site are more likely to reflect an intermittent or irregular exposure situation.
- actual toxicity that may be more or less than additive as a result of exposure to complex mixtures.

Toxicity Assessment

Note: Toxicological Progiles for the indicator chemicals: benzene, toluene, ethylbenzene, xylenes, cadmium, lead, arsenic, nickel were mostly based on quotations from "TomesPlus® System - Toxicology, Occupational Medicine & Environmental Series, Vol. 23. Expires 1/13/95. A Medical Economics Data Company, Micromedex, Inc. 1987-1995. CDRM 1234500" as well as data from "Richardson, M.L., Gangoli, S. (Eds.) - The Dictionary of Substances and their Effects. The Royal Society of Chemistry, 1992/1994" were used.

Toxicological Profile for Benzene

Environmental occurrence, fate and transport

Benzene (C_6H_6) is colorless to light-yellow, highly flammable liquid with characteristic aromatic odor (NIOSH, 1990; Budavari, 1989). Some selected physical/chemical properties of benzene are as follows:

- Molecular Formula: C_6H_6
- Molecular Weight: 78.11
- Melting Point: 5.5°C
- Boiling Point: 80.1°C
- Specific Gravity: 0.8786 at 20°C
- Vapor Pressure: 76 mm Hg at 20°C
- Solubility: Slightly soluble in water; miscible with alcohol, chloroform, diethyl ether, acetone
- Log K_{ow}: 2.13
- Conversion Factors: 1 ppm = 3.19 mg/m^3
1 mg/m^3 = 0.313 ppm
- Henry's Constant: 5.55×10^{-3} atm*m^3/mole
- Description: Colorless to light-yellow, highly flammable liquid with characteristic aromatic odor.

Originally, benzene was produced by coal carbonization, but now it mainly comes from petroleum or by cyclisation and aromatisation of paraffinic hydrocarbons. It dissolves fats, inks, oils, paints, plastics and rubber. Benzene is a starting material in chemical manufacture of resin, plastics, nylon-66, polyamides and styrene. It is used in production of detergents, explosives and pharmaceuticals (Verschueren, 1983).

Benzene enters the atmosphere primarily from fugitive emissions and exhaust connected with its use in gasoline. The current benzene content in gasoline ranges between 1.5% and 6% (Mehlman, 1991). Another important source is emissions associated with its production and use as an

industrial intermediate. In addition, there are discharges into water from industrial effluents and losses during spills.

If benzene is released to soil, it will be subject to rapid volatilization near the surface and that which does not evaporate will be highly to very highly mobile in soil and may leach to groundwater. The effective half-lives for volatilization without water evaporation from soil to benzene uniformly distributed to 1 and 10 cm in soil were 7.2 and 38.4 days, respectively (Jury et al., 1984). It may be subject to biodegradation based on reported degradation rates of 24% and 47% of the initial 20 ppm benzene in a base-rich soil in 1 and 10 weeks, respectively (Haider et al., 1974). It may be subject to biodegradation in shallow, aerobic groundwater, but less so under anaerobic conditions.

If benzene is released to surface water, it will be subject to rapid volatilization; the half-life for evaporation in a wind-wave tank with a moderate wind speed of 7.09 m/sec was 5.23 hrs (Mackay, Yeun, 1983); the estimated half-life for volatilization of benzene from a model river one meter deep flowing 1 m/sec with a wind velocity of 3m/sec is estimated to be 2.7 hrs at 20 ^{0}C. It will not be expected to significantly adsorb to sediment, bioconcentrate in aquatic organisms or hydrolyze. It may be subject to biodegradation based on a reported degradation half-life of 16 days in an aerobic river die-away test (Vaishnav and Babeu, 1987). In a marine ecosystem, biodegradation occurred in 2 days after an acclimation period of 2 days and 2 weeks in the summer and spring, respectively, whereas no degradation occurred in winter. Evaporation was the primary loss mechanism in winter in a mesocosm experiment which simulated a northern bay where the half-life was 13 days. In spring and summer the half-lives were 23 and 3.1 days, respectively. In these cases biodegradation plays a major role and takes about 2 days. However, acclimation is critical and this takes much longer in the colder water in spring (Wakeman et al., 1983).

According to one experiment, benzene has a half-life of 17 days due to photodegradation (Hustert et al., 1981) which could contribute to benzene's removal in situations of cold water, poor nutrients, or other conditions less conductive to microbial degradation.

If benzene is released to the atmosphere, it will exist predominantly in the vapor phase (Eisenreich et al., 1981). Gas-phase benzene will not be subject to direct photolysis but it will react with photochemically produced hydroxyl radicals with a half-life of 13.4 days calculated using an experimental rate constant for the reaction. The reaction time in polluted atmospheres which contain nitrogen oxides or sulfur dioxide is accelerated with the half-life being reported to be 4-6 hours (Korte and Klein, 1982). Products of photooxidation include phenol, nitrophenols, nitrobenzene, formic acid, and peroxyacetyl nitrate. Benzene is fairly soluble in water and is removed from the atmosphere in rain (Kato et al., 1980).

Human populations are primarily exposed to benzene through inhalation of contaminated ambient air, particularly in areas with heavy traffic and around filling stations. In addition, air close to manufacturing plants which produce or use benzene may contain high concentrations of benzene. Another source of inhalation exposure is from tobacco smoke (HSDB, 1991). 57 μg benzene is reported to be in the mainstream smoke of a cigarette containing 16 mg tar and

nicotine. A subject smoking 20 cigarettes per day would have a benzene intake of 1.25 mg/d (about 6 times the nonsmokers' intake; Ghittori et al, 1993).

Although most public drinking water supplies are free of benzene or contain <0.3 ppb, exposure can be very high from consumption of contaminated sources drawn from wells contaminated by leaky gasoline storage tanks, landfills, etc. (HSDB, 1991).

Although benzene has been detected in various food items, data are too scant to estimate exposure from ingestion of contaminated food (HSDB, 1991). Benzene occurs in both groundwater and surface public water supplies with higher levels occurring in groundwater supplies. Based upon federal drinking water surveys, approximately 1.3% of all groundwater systems are estimated to contain benzene at levels greater than 0.5 μg/L (HSDB, 1991).

The highest level reported in the surveys for groundwater was 80 μg/L. Approximately 3% of all surface water systems are estimated to be contaminated at levels higher than 0.5 μg/L. None of the systems are expected to contain levels higher than 5 μg/L (HSDB, 1991).

Ambient air samples from 44 sites in 39 US urban areas were collected on week days from 6 to 9 o'clock in the morning during June through September of 1984, 1985, and 1986. Not all sites were sampled all years. Benzene was present in every sample. Median concentrations by site and year ranged from 4.8 ppb to 35.0 ppb with the overall median being 12.6 ppb (HSDB, 1991). Investigations of ambient air contamination have been conducted in the vicinity of the Czechowice Oil Refinery in Czechowice-Dziedzice, Poland from May to October 1996 (Zeglin at al., 1996). Mean benzene concentrations in ambient air ranged from 5.7 (in May) to 11 $\mu g/m^3$ (in June).

Laboratory experiments using benzene adsorbed onto aquifer materials of low organic carbon content generated linear isotherms from which the following distribution coefficient was calculated: K(d) = 0.5 to 0.65 mL/g (Larsen et al., 1992).

Adsorption of benzene vapor on the surface of soils was less than 4% of the total adsorption. This result indicates that uptake was due mainly to condensation, rather than to partitioning or monolayer sorption. Uptake was greater for soils with higher organic carbon content (Li and Voudrias, 1993).

The diffusive transport of benzene was measured in air-dry soils to test the effect of non-linear sorption. The chemical followed the BET type sorption model. The increase of diffusivity with high initial chemical concentration produced higher-than-predicted emission rates (Shonnard et al., 1993).

Mammalian and human health effects

Absorption of benzene occurs rapidly by ingestion, inhalation, and dermal routes. In animals nearly 100% of benzene is absorbed orally (NTP, 1986; Avis and Hutton, 1993).

In mice, 20 to 40% of a 1 ppm exposure could be absorbed dermally (4 to 8 mg; Susten et al., 1985). It is estimated that an adult human exposed to 10 ppm would absorb 7.5 μL/hour from inhalation and 1.5 μL/hour from whole body exposure (Blank and McAuliffe, 1985). Absorption through the lungs is reported to be 46% of inhaled benzene (Avis and Hutton, 1993). Because of

the high lipid solubility of benzene, high levels may be found in the brain and body fat. Body fat better approximates blood levels than brain tissue (Avis and Hutton, 1993).

Benzene is metabolized extensively in the liver and excreted in the urine, with 51 to 87% excreted as phenol, 6% as catechol, and 2% as hydroquinone (Baselt et al., 1989). Benzene exhibits nonlinear kinetics at doses greater than 50 mg/kg in animals. At a dose of 0.5 mg/kg nearly all of a radiolabeled dose of benzene is excreted in the urine. At 300 mg/kg, about 60% is exhaled and 40% excreted in the urine (NTP, 1986). In humans, 12% of the dose is excreted unchanged by the lungs and 0.1% unchanged in the urine (Baselt et al., 1989).

100 ml is the estimated lethal dose. Benzene was formerly used in the treatment of leukemia in doses of 3 to 5 grams/day. Chronic therapy led to blood dyscrasias and death (NTP, 1986). The often-quoted adult lethal dose of pure benzene of 15 ml (12.99 grams) could not be documented. Acute ingestion of 10 to 14 ml (9 to 12 grams) of benzene was reported to cause serious collapse in 3 patients (Sollmann, 1957); however, the original references to this dated back to 1861 and 1889 and were not available for review. It has been reported that single exposures to 20,000 ppm in air were fatal within 5 to 10 minutes (Flury, 1928). Prior to 1986, there was little evidence that exposure to benzene at concentrations below 25 ppm caused blood dyscrasia of any kind (ACGIH, 1986). The TLV was established at 10 ppm, as a time-weighted average, to provide an added margin of safety (ACGIH, 1986). Recent research indicates that effects may be seen at less than 1 ppm. Exposures needed to be reduced to 0.1 ppm before no toxic effects were observed (Sax and Lewis, 1989). Brief exposure to concentrations in excess of 3,000 ppm is irritating to the eyes and respiratory tract; continued exposure may cause euphoria, nausea, a staggering gait, and coma. Inhalation of lower concentrations (250 to 500 ppm) produces vertigo, drowsiness, headache, and nausea (Proctor et al., 1988).

The published values for the LD_{50} (RTECS, 1991; Budavari, 1989; Sax and Lewis, 1989) are: LD_{50} (oral) rat - 930 mg/kg, LD_{50} (oral) rat - 3,400 mg/kg, LD_{50} (oral) rat - 3.8 mL/kg, LC_{50} (inhl) rat - 10,000 ppm/7hr, LD_{50} (IP) rat - 2,890 μg/kg, LD_{50} (oral) mouse - 4,700 mg/kg, LD_{50} (oral) mouse - 18,250 mg/kg/2yr-C, LD_{50} (skin) mouse - 48 mg/kg, LC_{50} (inhl) mouse - 9,980 ppm, LD_{50} (IP) mouse - 340 mg/kg, LD_{50} (IP) mouse - 990 μg/kg.

Exposure of rats to 50 ppm benzene vapor for several weeks led to a reduction in red and white blood cells and platelets; exposure to concentrations > 100 ppm produced leukopenia and aplasia (CDSS, 1988). In male mice fed 0-790 mg benzene/L of drinking water for 28 days, simulation of the hypothalamic-pituitary-adrenocortical axis and increased circulatory levels of corticosterone were observed at high dose levels (Hsieh, 1991).

Chronic exposure to benzene in humans at concentrations that produce changes in blood may result in leukemia, especially acute myelogenous leukemia (CDSS, 1988). Chronic lymphocytic leukemias are also common (Snyder, 1987).

Work exposure to 100 ppm resulted in 140 excess deaths from leukemia per 1000 exposed; 10 ppm resulted in 14 excess deaths (Landrigan and Rinsky, 1984). Risk assessment studies have reported estimated lifetime excess deaths due to leukemia of 14 to 104 per 1000 workers exposed to 10 ppm (Austin et al, 1988). Numerous other epidemiologic and case studies have reported an

increased incidence or a causal relationship between leukemia and exposure to benzene (IARC, 1982).

There is clear evidence of carcinogenity in mice and rats treated by gavage (103 weeks) 100 and 200 mg/L. Tumours have been reported in various tissues including adrenals, lung, liver, ovary, oral cavity, stomach and skin (Ashby, 1988). Benzene administered by gavage produced ovarian atrophy, cysts, hyperplasia and neoplasia in mice (Maronpot, 1988). Benzene is classified by the EPA and IARC as a human carcinogen (Mehlman, 1991).

Quantitative estimate of carcinogenic risk from oral exposure is as fellows (IRIS, 1996):

Oral Slope Factor -- 2.9E-2 per (mg/kg)/day

Drinking Water Unit Risk -- 8.3E-7 per (µg/L)

Extrapolation Method -- One-hit (pooled data)

Drinking Water Concentrations at Specified Risk Levels:

Risk Level	Concentration
E-4 (1 in 10,000)	1E+2 µg/L
E-5 (1 in 100,000)	1E+1 µg/L
E-6 (1 in 1,000,000)	1E+0 µg/L

Quantitative estimate of carcinogenic risk from inhalation exposure is as follows (IRIS, 1996):

Inhalation Unit Risk -- 8.3E-6 per (µg/m^3)

Extrapolation Method -- One-hit (pooled data)

Air Concentrations at Specified Risk Levels:

Risk Level	Concentration
E-4 (1 in 10,000)	1E+1 µg/m^3
E-5 (1 in 100,000)	1E+0 µg/m^3
E-6 (1 in 1,000,000)	1E-1 µg/m^3

Teratogenicity has been reported at high concentrations in rats, but there is no evidence of fetal malformations at concentrations which produce no maternal toxicity. Women are considered hypersusceptible to benzene, however there are no reports of teratogenic effects in women occupationally exposed to benzene (Maronpot, 1987; Fishbein et al., 1988).

1 ppm of benzene, inhaled in male mice, induced chromosomal aberrations in spermatocytes and sister chromatid exchange in spermatogonia (Au et al., 1990; Zhu, Yufen et al., 1989). Chromosomal aberrations in white blood cells and bone marrow in humans which could initiate leukemia have been reported, but there is no evidence of aberrations at exposure levels of 25 ppm or less (CDSS, 1988).

Toxicity to aquatic species

In result of bioassays on invertebrate species and fishes the following LC_{50} of benzene were calculated:

LC_{50} (96 hr) - grass shrimp - 20-27 ppm (Bringman, 1980; Verschueren, 1983)

LC_{50} (96 hr) - bass - 6 to 11 ppm (Verschueren, 1983)

LC_{50} (24-96 hr) - fathead minnow, bluegill sunfish, goldfish - 36-22 mg/L (Verschueren, 1983)

LC_{50} (1 hr) - brown trout yearlings - 12 mg/L, static bioassay (HSDB, 1991).

Based on bioaccumulation studies in pacific herring larvae, a bioconcentration factor of 3.5 - 3.9 was calculated for benzene (Verschueren, 1983). This value does not suggest a significant potential for bioaccumulation.

Summary of applicable regulatory guidelines

Polish guidelines values for benzene in soil and groundwater during remediation decision-making processes are presented in Table III-1.

Toxicological Profile for Ethylbenzene

Environmental occurrence, fate and transport

Ethylbenzene ($C_6H_5CH_2CH_3$) is a colorless liquid (Budavari, 1989) with an aromatic odor (Sax and Lewis, 1992). It is used as an intermediate in organic synthesis and a fuel additive, as well as in the manufacture of rubber products (Richardson and Gangolli, 1994). Ethylbenzene occurs in motor vehicle exhaust and cigarette smoke (Verschueren, 1983; Howard, 1989). Some selected physical/chemical properties of ethylbenzene are as follows:

- Molecular Formula: $C_6H_5CH_2CH_3$
- Molecular Weight: 106.16
- Melting Point: -95°C
- Boiling Point: 136°C
- Specific Gravity: 0.867 at 20°C
- Vapor Pressure: 10 mm Hg at 26°C
- Solubility: Practically insoluble in water; miscible with alcohols, ethers
- Log K_{ow}: 3.14
- Conversion Factors: 1mg/m^3 = 0.230 ppm
1 ppm = 4.34 mg/m^3
- Henry's Constant: 7.88×10^{-3} atm· m^3/mole
- Description: Colorless liquid with an aromatic odor.

Ethylbenzene enters the atmosphere primarily from fugitive emissions and exhaust connected with its use in gasoline. More localized sources will be emissions, waste water, and spills from its production and industrial use. Non-occupational exposure may result from indoor air containing cigarette smoke and ingestion of contaminated drinking water supplies (HSDB, 1992).

Ethylbenzene will be removed from the atmosphere principally by reaction with photochemically produced hydroxyl radicals (half-life of hours to 2 days) (HSDB, 1992).

When released into water, ethylbenzene will evaporate fairly rapidly into the atmosphere with a half-life ranging from hours to a few weeks. Biodegradation will also be rapid (half-life of 2 days) after a population of degrading microorganisms becomes established, which will depend on the particular body of water and the temperature. In one study, this acclimatization took 2 days and 2 weeks in summer and spring, respectively.

Some ethylbenzene will be adsorbed by sediment. There is evidence that ethylbenzene slowly biodegrades in groundwater. In cases where a large concentration persists in groundwater over a year after a spill, it is possible that resident microorganisms may be killed by high concentrations (HSDB, 1992).

When released onto soil, part of the ethylbenzene will evaporate into the atmosphere. It has a moderate adsorption in soil, but will probably leach into the groundwater, especially in soil with a low organic carbon content.

While there are limited direct data concerning its biodegradability in soil, it is likely that it will biodegrade slowly after acclimation (HSDB, 1992).

Ethylbenzene has very limited food chain concentration potential (CHRIS, 1992).

Mammalian and human health effects

Ethylbenzene is moderately toxic by the ingestion and intraperitoneal routes and mildly toxic by inhalation as well as skin contact. It is an eye, skin, and mucous membrane irritant (Sax and Lewis, 1992). Human exposure to high vapor concentrations may present primarily an irritation hazard, but secondarily also may cause central nervous system effects. It is absorbed through the skin at a low rate (Clayton and Clayton, 1981). Human systemic effects by inhalation are eye, sleep and pulmonary changes (Sax and Lewis, 1992). Ethylbenzene is an experimental teratogen and causes other experimental reproductive effects (Sax and Lewis, 1992). Human mutation data have been reported (Sax and Lewis, 1992). In high concentrations, ethylbenzene is narcotic (Budavari, 1989). The minimum lethal human exposure to this agent has not been defined.

In guinea pigs, exposure to 10,000 ppm caused immediate, intense eye and nose irritation, ataxia, narcosis, and death in 2 to 3 hours; 5000 ppm was lethal during or after 8 hours of exposure (Proctor et al, 1991). Exposure of guinea pigs to 1% concentration has been reported as causing ataxia, loss of consciousness, tremor of the extremities, and finally death through respiratory failure. The pathological findings were congestion of the brain and lungs with edema (Sax and Lewis, 1992).

Six human subjects exposed at 200 ppm of ethylbenzene experienced a transient irritation of the eyes; at 1000 ppm, there was eye irritation with profuse lacrimation, but tolerance developed

rapidly. At 2000 ppm, eye irritation and lacrimation were immediate and severe and were accompanied by moderate nasal irritation, constriction in the chest, and vertigo; 5000 ppm produced intolerable irritation to the eyes and nose (ACGIH, 1991; Sax and Lewis, 1992). For human chronic exposures exceeding 100 ppm, complaints included fatigue, sleepiness, headache, and mild irritation of the eyes and respiratory tract (Proctor et al., 1991).

The rate of absorption of ethylbenzene through the skin of the hand and the forearm in human subjects was 22 to 33 mg/cm^2/hour (Proctor et al, 1991).

Repeated oral administration of ethylbenzene to female rats, 5 days/week for a period of 6 months at doses of 13.6 or 136 mg/kg/day produced no effect in these animals (ACGIH, 1991). Repeated inhalation exposure at 400 ppm of ethylbenzene had no effect on guinea pigs, rabbits, and rhesus monkeys, but produced a slight increase in liver and kidney weights in both sexes of rats (ACGIH, 1991). Two drops of liquid in the eyes of a rabbit caused slight conjunctival irritation but no corneal injury. The liquid in contact with the skin of a rabbit caused erythema, exfoliation, and vesiculation (Proctor et al., 1991).

The published values for LD_{50} (Budavari, 1989; RTECS, 1992; Sax and Lewis, 1992) are as follows:

LD_{50} (oral) rat - 3500 mg/kg

LD_{50} (oral) rat - 5.46 g/kg

LD_{50} (IP) mouse - 2272 mg/kg

LD_{50} (skin) rabbit - 17,800 mg/kg.

The metabolic pathways for ethylbenzene in humans and rodents are different (Engstrom et al., 1984). Major metabolites in humans (mandelic acid and phenylglyoxylic acid) are minor metabolites in rats and rabbits (Kiese and Lenk, 1974). The major animal metabolites were not detected in the urine of exposed workers (Engstrom et al., 1984).

According to EPA weight-of-evidence classification system for carcinogenicity ethylbenzene is classified to D Group - not classifiable as to human carcinogenicity (IRIS, 1996). It is nonclassifiable due to lack of animal bioassays and human studies.

A chronic oral Reference Dose (RfD) for ethylbenzene have been established by U.S.EPA (IRIS, 1996):

Critical Effect	Experimental Doses*	UF	MF	RfD
Liver and kidney toxicity	NOEL:136 mg/kg/day (converted to 97.1 mg/kg/day)	1000	1	1E-1 mg/kg/day
Rat Subchronic to Chronic Oral Bioassay	LOAEL: 408 mg/kg/day (converted to 291 mg/kg/day)			

*Conversion Factors: 5 days/7 days; thus, 136 mg/kg/day x 5 days/7 days = 97.1 mg/kg/day Wolf et al., 1956

Confidence in this chosen study is low because rats of only one sex were tested and the experiment was not of chronic duration. Confidence in the supporting database is low because other oral toxicity data were not found. Low confidence in the RfD follows.

U.S.EPA has also established the inhalation Reference Concentration (RfC) for ethylbenzene (IRIS 1996):

Critical Effect	Exposures*	UF	MF	RfC
Developmental toxicity	NOAEL: 434 mg/m^3 (100 ppm) NOAEL(ADJ): 434 mg/m^3 NOAEL(HEC): 434 mg/m^3	300	1	1E+0 mg/m^3
Rat and Rabbit Developmental Inhalation Studies	LOAEL: 4340 mg/m^3 (1000 ppm) LOAEL(ADJ): 4340 mg/m^3 LOAEL(HEC): 4340 mg/m^3			

*Conversion Factors: MW = 106.18. Assuming 25°C and 760 mm Hg, NOAEL(mg/m3)= 100 ppm x MW/24.45 = 434 mg/m3. For developmental effects, this concentration is not adjusted; therefore, NOAEL(ADJ) = NOAEL. The NOAEL(HEC) was calculated for a gas:extrarespiratory effect, assuming periodicity was attained. Since b:a lambda values are unknown for the experimental animal species (a) and humans (h), a default value of 1.0 was used for this ratio.

NOAEL(HEC) = NOAEL(ADJ) x (b:a lambda(a)/lambda(h)) = 434 mg/m3. Andrew et al., 1981; Hardin et al., 1981

The RfC is given a low confidence rating.

Toxicity to aquatic species

In result of bioassays on invertebrate species and fishes, the following LC_{50} of ethylbenzene were calculated:

LC_{50} (24 hr) - grass shrimp - 10-14 mg/L (U.S.EPA, 1980)

LC_{50} (96 hr) - bahia shrimp - 88 mg/L (U.S.EPA, 1978)

LC_{50} (96 hr) - bluegill sunfish, goldfish, guppy, fathead minnow - 12-96 mg/L (Blum et al., 1991; Pickering et al., 1966).

Based on bioaccumulation studies, ethylbenzene bioconcentration factors of 15.5 and 4.7 were calculated for goldfish (Nunes et al., 1979) and Manila clams (Ogata et al., 1984). This indicates a very low bioaccumulation potential.

Summary of applicable regulatory guidelines

Polish guidelines values for ethylbenzene in soil and groundwater during remediation processes are presented in Table III-1.

Toxicological Profile for Toluene

Environmental occurrence, fate and transport

Toluene ($C_6H_5CH_3$) is colorless, flammable liquid with a sweet pungent, benzene-like odor (NIOSH, 1990; Budavari, 1989). It is a solvent for paints, lacquers, gums and resins. Toluene is used in the manufacture of benzoic acid, benzaldehyde, explosives, dyes and as a gasoline additives (Richardson and Gangoli, 1994).

Some selected physical/chemical properties of toluene are as follows:

- Molecular Formula: $C_6H_5CH_3$
- Molecular Weight: 92.13
- Melting Point: -95°C
- Boiling Point: 110.6°C
- Specific Gravity: 0.866 at 30°C
- Vapor Pressure: 36.7 mm Hg at 30°C
- Solubility: Very slightly soluble in water; miscible with alcohol, chloroform, ether, benzene
- Log K_{ow}: 2.75
- Conversion Factors: 1 mg/m^3 = 0.266 ppm
1 ppm (25°C) = 3.75 mg/m^3
- Henry's Constant: 6.64×10^{-3} atm*m^3/mole
- Description: Colorless, flammable liquid with a sweet pungent, benzene like odor.

Toluene, benzene, and higher aromatics have been detected in rainwater, the former two at concentrations of 0.1 to 0.5 µg/liter, and about twice the quantity in the ambient air (Clayton and Clayton, 1981). Toluene has been measured in urban air at 0.01 to 0.05 ppm, probably stemming from production facilities, automobile and coke oven emissions, gasoline evaporation, and cigarette smoke, and can occur in human respiratory air in smokers and nonsmokers (Clayton and Clayton, 1981). Investigations of ambient air contamination have been conducted in the vicinity of Czechowice Oil Refinery in Czechowice-Dziedzice, Poland from May to October 1996 (Zeglin at al., 1996). Mean toluene concentrations in ambient air ranged from 55.5 (in June) to

99 $\mu g/m^3$ (in October). Naturally occurring sources of toluene include volcanoes, forest fires, and crude oil (HSDB, 1991).

When released on land, toluene is lost by evaporation and microbial degradation. In one study, 94% of the chemical added to a clay loam was lost by these processes. Since it is relatively mobile in soil, it is possible that it will get into the groundwater and remain there where microbial degradation is slower or does not occur (HSDB, 1991).

When released into water, toluene will be lost by both volatilization to the atmosphere and biodegradation. The predominant process will depend on water temperature, mixing conditions and the existence of acclimated microorganisms at the site. The half-life will range from days to several weeks. Adsorption to sediment and bioconcentration will be low (HSDB, 1991).

When released to the atmosphere, toluene degrades moderately rapidly by reaction with photochemically produced hydroxyl radicals. Its half-life ranges from 3 hours to somewhat over a day. It is very effectively washed out by rain (HSDB, 1991). Biodegradation occurs both in soil and groundwater, but it is apt to be slow, especially at high concentrations which may be toxic to microorganisms. The presence of acclimated microbial populations may allow rapid biodegradation. Little bioconcentration into the food chain is expected (HSDB, 1991).

Mammalian and human health effects

Air pollution is the major source of exposure. 53% of an inhaled dose is absorbed (Flanagan et al., 1990). Peak blood concentrations occur 15 to 30 minutes after inhalation (Bergmen, 1979).

Gastrointestinal absorption of toluene is 100% (Baelum et al., 1993). Peak blood concentrations occur 1 to 2 hours after ingestion (Bergmen, 1979). As for dermal absorption immersion of the fingers or hands into toluene may result in significant blood levels (Bergmen, 1979).

Toluene is deposited in adipose tissue and in the central nervous system. Toluene uptake is directly proportional to the amount of body fat (Finkel, 1983). Toluene is extensively metabolized in the liver, with a hepatic extraction ratio approaching 1.0 (Baelum et al., 1993). Ethanol acutely inhibits toluene metabolism (Snyder, 1987). However, after repeated administration, ethanol enhances the metabolism of toluene in rats by inducing hepatic drug metabolizing enzymes (Snyder, 1987). Approximately 80% is metabolized to benzyl alcohol which is then oxidized to benzoic acid. Benzoic acid is then conjugated with glycine and excreted as hippuric acid (Ameno et al., 1989). Toluene clearance has been reported as 1.4 to 1.7 L/hour/kg after inhalation exposure (Wallen, 1986).

Toluene is an aromatic hydrocarbon solvent that produces narcosis. It is an irritant of skin and mucous membranes. There is some indication that toluene might interfere with the monoamine systems in the hypothalamic area, and the basal ganglia (Snyder, 1987).

The published values of LD_{50} (RTECS, 1991; Budavari, 1989) are as follows:

LD_{50} (oral) rat - 5,000 mg/kg,

LD_{50} (IP) rat - 1,332 mg/kg,

LD_{50} (IV) rat - 1,960 mg/kg,

LD_{50} (oral) rat - 7.53 g/kg,

LD_{50} rat - 6,900 mg/kg,

LD_{50} (IP) mouse - 640 mg/kg,

LD_{50} (IP) mouse - 1,120 mg/kg,

LD_{50} (SC) mouse - 2,250 mg/kg,

LD_{50} mouse - 2,000 mg/kg,

LD_{50} (skin) rabbit - 12,124 mg/kg.

Conflicting study results regarding the carcinogenic potential of toluene have been reported. However, when benzene contamination of the toluene is not present, it is unlikely that toluene exposure alone can be carcinogenic. There is conflicting information in the literature regarding the potential of toluene to cause DNA strand breaks. Toluene was not mutagenic in the Ames assay. Chromosome damage has been reported in some studies, but consistency in results is lacking.

Bosch et al. (1988) reported a case of myelofibrosis and focal segmental glomerulosclerosis in a patient who had been working in direct contact with toluene for 40 years, though other solvent exposure was not investigated.

The U.S. National Toxicology Program tested rats and mice for carcinogenic potential via inhalation. No evidence of carcinogenicity found in either species (NTP, 1992). According to EPA weight-of-evidence classification system for carcinogenicity toluene is classified to D Group - not classifiable as to human carcinogenicity (IRIS, 1996). Toluene did not produce positive results in the majority of genotoxic assays (IRIS, 1996).

Oral Reference Dose (RfD) for toluene have been established by U.S.EPA (IRIS, 1996):

Critical Effect	Experimental Doses*	UF	MF	RfD
Changes in liver and kidney weights	NOAEL: 312 mg/kg converted to 223 mg/kg/day	1000	1	2E-1 mg/kg/day
13-Week Rat Gavage Study	LOAEL: 625 mg/kg converted to 446 mg/kg/day			

*Conversion Factors: Dose adjusted for gavage schedule of 5 days/week. NTP, 1989

Confidence in this principal study (NTP, 1989) is high as a sufficient number of animals/sex were tested in each of six dose groups (including vehicle controls) and many parameters were studied. The same protocol was tested in both mice and rats, with rats being identified as the more sensitive species. The database is rated medium because it is supported by a 6-month oral study.

It is not higher than medium because there is no reproductive study. Also, the oral studies are all subchronic, with the critical study being only 13 weeks in duration. Medium confidence in the RfD follows.

In humans, toluene is a known respiratory irritant with central nervous system (CNS) effects at high levels. As available studies could not provide subthreshold (NOAEL) concentrations for either of these effects, the LOAELs for both effects need to be considered while developing the RfC. Consequently, the study of Foo et al. (1990) was used for the CNS effects, and that of the National Toxicology Program (NTP, 1990) for the irritant effects. Because the CNS effect was judged to be a more severe and relevant endpoint, the LOAEL for this effect was used to derive RfC. Further, this effect is supported by a number of other occupational studies that show effects around 100 ppm.

Results of the studies are summarized below (IRIS 1996):

Critical Effect	Exposures*	UF	MF	RfC
Neurological effects**	NOAEL: None	300	1	4E-1 mg/m^3
Occupational Study**	LOAEL: 332 mg/m^3 (88 ppm) LOAEL(ADJ): 119 mg/m^3 LOAEL(HEC): 119 mg/m^3			
Degeneration of nasal epithelium***	NOAEL: None			
2-Year Rat Chronic Inhalation Study***	LOAEL: 2261 mg/m^3 (600 ppm) LOAEL(ADJ): 437 mg/m^3 LOAEL(HEC): 79 mg/m^3			

*Conversion Factors: MW = 92.15. **Foo et al., 1990, *** NTP, 1990

The study of Foo et al. (1990) indicates adverse neurological effects of toluene in a small worker population. These effects are consistent with more severe CNS effects of atabusive toluene concentrations and could not have been confounded by alcohol as the control and exposed populations did not use alcohol. However, the paucity of exposure information and identification of only a LOAEL is not sufficient to warrant a higher confidence than medium for this study. Other studies indicate that irritation may occur at around the same concentration, 100 ppm (Baelum et al., 1985; Echeverria et al., 1989). In regard to this effect, the NTP (1990) rat chronic inhalation study was well conducted, established the rat as the most sensitive species, examined an adequate number of animals, and performed histopathology on all major organs, including the brain and the respiratory tract. The sensitive endpoint was the concentration-dependent degeneration of the nasal epithelium characterized by the erosion of the olfactory epithelium and degeneration of the respiratory epithelium in male rats. The NTP study is also given medium confidence, however, as it did not establish a NOAEL. Although this database has a complement of chronic laboratory animal studies, long-term data in humans are not available for either the neurotoxicity or irritation endpoints. The reproductive/developmental studies in three species were not comprehensive in endpoint evaluation but do identify the rabbit

as the most sensitive species. The database is thus given a medium confidence rating. A medium confidence rating for the RfC follows.

Toxicity to aquatic species

In result of bioassays on invertebrate species and fishes the following LC_{50} of toluene were calculated:

LC_{50} (24 hr) - *Palaemonetes pugio, Artemia salina, Nitocra spinipes* - 17.2, 33, 24.2-74.2 mg/L, respectively (Little, 1980; Potera, 1975)

LC_{50} (96 hr) - juvenile striped bass, bluegill sunfish - 0.0054, 24 mg/L, respectively (Palawski et al., 1985; Pickering et al., 1966)

LC_{50} (48 hr) - goldfish - 58 mg/L (Bridie et al., 1979)

LC_{50} (96 hr) - pink salmon, striped bass, fathead minnow, bluegill sunfish - 6.41, 7.3, 12.6, 13.0 mg/L, respectively (Korr et al., 1979; Verschueren 1983; Pearson et al. 1979; Buccafaso 1981)

LC_{50} (24 hr) - *Artemia salina* (brine shrimp) - 33 mg/L (HSDB, 1991)

LC_{50} (96 hr) - *Palaemonetes pugio* (grass shrimp) - 9.5 ppm (HSDB, 1991)

LC_{50} (96 hr) - *Crangon franciscorum* (shrimp) - 4.3 ppm

LC_{50} (24 hr) - *Nitocra spinipes* (copepod) - 24.2 to 74.2 mg/L.

Summary of applicable regulatory guidelines

Polish guidelines values for soil and groundwater toluene in remediation process are presented in Table III-1.

Toxicological Profile for Xylenes

Environmental occurrence, fate and transport

Xylene [$C_6H_4(CH_3)_2$), also known as xylol and dimethyl benzene is usually present as a mixture of ortho, meta, and para isomers, with the meta isomer being the most prevalent (usually 75 to 85%). Xylene is used as a solvent in paints, degreasers, and pesticides. At present, when used industrially, commercially, or in the home, the most harmful effect on the health of the user occurs during spray painting (Clayton and Clayton, 1981). Xylene may be contaminated with benzene, which, if it constitutes more than 0.02% (200 ppm), may cause benzene toxicity. Some selected physical/chemical properties of xylenes are as follows:

· Molecular Formula:	$C_6H_4(CH_3)_2$
· Molecular Weight:	106.16
· Melting Point:	
· o-xylene	-25°C
· m-xylene	-47.4°C
· p-xylene	13 - 14°C
· Boiling Point:	
· o-xylene	144°C
· m-xylene	139.3°C
· p-xylene	137 - 138°C
· Specific Gravity:	
· o-xylene	0.8801 at 20°C
· m-xylene	0.8642 at 20°C
· p-xylene	0.8610 at 20°C
· Vapor Pressure:	
· o-xylene	6.6 mm Hg at 25°C
· m-xylene	39 mm Hg at 25°C
· p-xylene	87 mm Hg at 25°C
· mixed isomers	6.72 mm Hg at 21°C
· Solubility:	Practically insoluble in water; miscible with absolute alcohol, ether and many other organic liquids
· Log Kow:	
· o-xylene	3.13
· m-xylene	3.20
· p-xylene	3.17
· Conversion Factors:	1 mg/m3 = 0.230 ppm 1 ppm = 4.34mg/m3
· Henry's Constant:	
· o-xylene	5.19 x 10-3 atm•m3/mole
· m-xylene	7.34 x 10-3 atm•m3/mole
· p-xylene	7.66 x 10-3 atm•m3/mole
· Description:	Clear, colorless, aromatic liquids.

Xylenes will enter the atmosphere primarily from fugitive emissions and exhaust connected with their presence in gasoline. Industrial sources include emissions from petroleum refining and their use as solvents and chemical intermediates. Discharges and spills on land and waterways result from their use in diesel fuel and gasoline, and storage and transport of petroleum products (HSDB, 1991). The primary source of exposure is from air, especially at occupational sites where xylenes are used and in areas with high automobile traffic. Investigations of ambient air contamination have been conducted in the vicinity of Czechowice Oil Refinery in Czechowice-Dziedzice, Poland from May to October 1996 (Zeglin at al., 1996). Mean p-xylene concentrations in ambient air ranged from 1 (in October) to 2.4 $\mu g/m^3$ (in May).

When released into the atmosphere, xylenes may degrade by reaction with photochemically produced hydroxyl radicals (half-life of 1.0 to 1.7 hours in summer and 10 to 18 hours in winter). However, ambient levels are detected because of large emissions (HSDB, 1991).

Xylenes are moderately mobile in soil and may leach into groundwater where they are known to persist for several years, despite some evidence that they biodegrade in both soil and groundwater. Bioconcentration is not expected to be significant (HSDB, 1991).

When spilled on land, xylenes will volatilize and leach into the ground. Xylenes may be degraded during their passage through soil. Xylenes have low to moderate adsorption to soil. The extent of the degradation will undoubtedly depend on their concentration, residence time in the soil, the nature of the soil, and whether resident microbial populations have been acclimated (HSDB, 1991).

In surface waters, volatilization appears to be the dominant removal process (half-life of 1 to 5.5 days). Some adsorption to sediment will occur. Although xylenes are biodegradable and have been observed to degrade in sea water, there are insufficient data to assess the rate of this process in surface waters. Although they have been observed to degrade in groundwater in one study, they are known to persist for many years in groundwater at least at sites where the concentration might have been quite high. In a field study of an oil spill from the Trans-Alaskan Pipeline which leaked into the Atigun River on June 10, 1979, aromatic hydrocarbons including xylenes were absent from the 40-km-long river in the contaminated area 18 days after the spill (HSDB, 1991).

Mammalian and human health effects

Xylene is rapidly absorbed following inhalation or ingestion. It is less well absorbed through intact skin. Peak blood concentrations occur 15 to 30 minutes after inhalation and 1 to 2 hours after ingestion (Bergmen, 1979). Experimentally, m-xylene was absorbed by healthy human subjects with one or both hands immersed, at an approximate rate of 2 _g/cm ^{2}. Immersion of both hands in m-xylene for fifteen minutes equals an estimated pulmonary retention at 100 ppm (Clayton and Clayton, 1981). Xylene is quite soluble in blood and fat (Snyder, 1987). Chronic poisoning may be associated with the presence of xylene traces in all organs, particularly the suprarenal glands, bone marrow, spleen, and nerve tissue (ILO, 1983). Xylene is metabolized by oxidation of a methyl group to the corresponding o-, m-, or p-toluic acid. The corresponding toluic acid is then excreted in the form of a glycine conjugate as o-, m-, or p-methyl hippuric acid (Baselt, 1988). Approximately 95% of absorbed xylene is biotransformed and excreted in the urine, less than 5% is excreted unchanged through the lungs (Snyder, 1987).

The lowest published human lethal dose (oral route) is 50 mg/kg (RTECS, 1991). The published values of LD_{50} or LC_{50} (RTECS, 1991) are:

LD_{50} (oral) rat - 4,300 mg/kg,

LC_{50} (inhl) rat - 5,000 ppm/4h,

LD_{50} (IP) rat - 2,459 mg/kg,

LD_{50} (SC) rat - 1,700 mg/kg,

LD_{50} (IP) mouse - 1,548 mg/kg.

According to EPA weight-of-evidence classification system for carcinogenicity xylene is classified to D Group - not classifiable as to human carcinogenicity (IRIS, 1996). Orally administered technical xylene mixtures did not result in significant increases in incidences in tumor responses in rats or mice of both sexes.

Studies indicate that xylene isomers, technical grade xylene or mixed xylene are not mutagenic in tests with *Salmonella typhimurium* (Florin et al., 1980; NTP, 1986; Bos et al., 1981) nor in mutant reversion assays with *Escherichia coli* (McCarroll et al., 1981). Technical grade xylene, but not o- and m-xylene, was weakly mutagenic in Drosophila recessive lethal tests. Chromosomal aberrations were not increased in bone marrow cells of rats exposed to xylenes by inhalation (Donner et al., 1980). There is ample evidence of embryotoxicity in mice and rats, manifested as reduced weight, retarded ossification and kidney development, and extra ribs. A variety of abnormalities have been found, including internal and external anomalies and fetal death (Council on Scientific Affairs, 1985).

The oral Reference Dose (RfD) for mixed xylenes (60.2% m-xylene, 13,6% p-xylene, 17.0% ethylbenzene and 9.1% o-xylene) is based on the National Toxicology Program study (NTP 1986; IRIS 1996):

Critical Effect	Experimental Doses*	UF	MF	RfD
Hyperactivity, decreased body weight and increased mortality (males)	NOAEL: 250 mg/kg/day (converted to 179 mg/kg/day)	100	1	2E+0 mg/kg/ day
Chronic Rat Gavage Study	FEL: 500 mg/kg/day (converted to 357 mg/kg/day)			

*Conversion Factors: Dose adjusted for gavage schedule (5/days/week).

The NTP (1986) study was given a medium confidence level because it was a well-designed study in which adequately sized groups of two species were tested over a substantial portion of their lifespan, comprehensive histology was performed, and a NOAEL was defined; but clinical chemistries, blood enzymes, and urine analysis were not performed. The data base was given a medium confidence level because, although supporting data exist for mice and teratogenicity and fetotoxicity data are available with positive results at high oral doses, a LOAEL for chronic oral exposure has not been defined. Medium confidence in the RfD follows.

The Reference Concentration (RFC) for chronic inhalation exposure of xylenes is being reviewed by the EPA work group.

Toxicity to aquatic species

In result of bioassays on fishes the following LC_{50} of xylenes were calculated:

LC_{50} (24 hr) - Goldfish, 13 mg/L (HSDB, 1991)

LC_{50} (96hr) - Rainbow trout - 13.5 mg/L (HSDB, 1991)

LC_{50} (96hr) - *Carassius auratus* (goldfish) - 16.9 ppm (HSDB, 1991)

LC_{50} (48hr) - golden orfe - 110 mg/L (di Vincenzo et al., 1974).

Summary of applicable regulatory guidelines

Polish guidelines values for xylenes in soil and groundwater during remediation processes are presented in Table III-1.

Toxicological Profile for Arsenic

Environmental occurrence, fate and transport

Arsenic (As) is a chemical element of Group V of the Mendeleyev Periodic system. It is a nearly tasteless (HSDB, 1993), gray or silver-gray solid (Budavari, 1989; ACGIH, 1991); in water it is colorless (OHM/TADS, 1993). Naturally occurring arsenic is made up of one stable isotope As^{+5}. Artificially produced arsenic has a number of isotopes, the most important of which are As^{+4}, As^{+5}, As^{+6}. Arsenic can be found in several allotrophous modifications. The so-called metallic arsenic is the most stable of them under normal conditions. The so-called yellow arsenic is formed at rapid vapor condensation on the surface cooled by liquid. The most important inorganic arsenic compounds are tri- and pentavalent arsenic in combination with oxygen and their respective acids: arsenous anhydride As_2O_3 (arsenous oxide III, white arsenic) and arsenic anhydride As_2O_5 (arsenic oxide V) (IRPTC, 1982). Arsenic is insoluble in water (Budavari, 1989), in caustic and non-oxidizing acids (HSDB, 1993).

Some selected physical/chemical properties of arsenic are as follows:

· Molecular Formula:	As
· Molecular Weight:	74.92
· Melting Point:	817°C at 36 atm
· Boiling Point:	subl. at 612°C
· Specific Gravity:	5.724 at 14°C
· Vapor Pressure:	10 mm Hg at 437°C
· Solubility:	
· As (O)	insoluble in water
· As (V)	658 g/L at 20°C
· As (III)	379 g/L at 20°C
· Log K_{ow}:	Not applicable
· Conversion Factors:	Not applicable
· Henry's Constant:	Not applicable
· Description:	Grey or silver-gray, tasteless solid; in water - colorless.

Arsenic compounds are used or found in the following industries: agriculture, forestry, mining or smelting, glass manufacture, semiconductors, among others.

Arsenic as a free element (0-oxidation state) is rarely encountered in natural waters. Soluble inorganic arsenate (+5-oxidation state) predominates under normal conditions since it is thermodynamically more stable in water than arsenite (+3 oxidation state) (HSDB, 1993).

Arsenic is strongly held by soils and long in moving through the soil column. Concentrations in water as low as 1 mg/L may injure some plants. Concentrations in excess of 75 ppm will damage foliage. Arsenic typically does not exceed 328 ppm in the top 12 inches of soil (OHM/TADS, 1993). Soil polluted with arsenic (391 to 459 mg/kg dry soil) showed that fungi are more tolerant to arsenic than bacteria and actinomycetes. The microbial population was more drastically affected in patty fields than in upland fields (Hiroki, 1993). Although mining activity ceased in 1961, leached mine waste still delivers about 3.5 Mg/y of arsenic to Moira Lake in Canada. The arsenic concentration averages about 545 µg/g in the top sediment and 1000 µg/g at depths between 23 to 27 cm. Acidification of the overlaying water might release large amounts of arsenic to the lake (Azcue and Nriagu, 1993). Arsenic is a widespread soil contaminant because of past use of arsenic-containing pesticides. Average arsenic content in top soils worldwide ranges from 0.2 to 16 ppm; in Poland from 0.5 to 15 ppm with an average value of 2 ppm in sandy soils and from 1.4 to 10 ppm with average value of 4.5 ppm in clay soils (Kabata-Pendias, Pendias, 1999). Worldwide rsenic concentrations of up to 2,500 ppm are reported in contaminated soils in regions with metallurgical and chemical industry as well as large urban agglomerations (Kabata-Pendias, Pendias, 1999). In Poland, arsenic content in soils contaminated by metallurgical

industry ranges from 150 to 2,000 ppm (Kabata-Pendias, Pendias, 1999). Arsenic content of soils in Louisiana ranged from near 0 to 73 mg/kg, with a mean value of 23.2 mg/kg (Ori et al., 1993).

Arsenic is bioaccumulated in organic form by fresh water and marine aquatic organisms (CHRIS, 1993).

Mammalian and human health effects

Acute arsenic ingestion generally produces symptoms within 30 minutes but may be delayed for several hours if ingested with food. Orally, arsenic can cause severe gastrointestinal damage, including vomiting, diarrhea, and shock. Facial swelling, muscle cramps, heart irregularities, anemia, lowered white blood cell count, and enlargement of liver have also been produced in acute oral exposures (EOSH, 1982). These effects can be immediate or delayed (EOSH, 1982). Other delayed effects include peripheral nervous disturbances involving both sensory and motor dysfunction (EOSH, 1982). In general the pentavalent arsenic compounds are absorbed more rapidly than the trivalent ones by the oral route (HSDB, 1993).

Acute inhalation exposures have resulted in irritation of an upper respiratory tract. Inhalation - arsenic can cause damage to mucous membranes and skin, and is a severe nose, eye, and respiratory irritant (EOSH, 1982). Cough, breathing difficulty, chest pain, and severe damage to a respiratory system can occur from acute inhalation exposures (Friberg et al., 1986). Arsenic trioxide is generally the most commonly encountered industrial arsenic compound by the inhalation route, unless arsine gas is a hazard for a particular industrial setting. The toxicity of arsine is quite different than that of other arsenic compounds. Inhalation of arsine gas causes hemolytic anemia (breakdown of red blood cells) and results in anemia, jaundice, and kidney failure.

After absorption, arsenic may cause delayed effects: multi-organ failure by inhibiting sulfhydryl-containing enzymes within cells. The primary target organs are initially a gastrointestinal tract, heart, brain, and kidneys. Eventually skin, bone marrow, and a peripheral nervous system may be significantly damaged.

In general inorganic arsenic compounds are poorly absorbed through skin, with the trivalent being more rapidly absorbed than pentavalent compounds (HSDB, 1993). The effects of acute exposure solely to skin are not well described in the literature, but may include severe skin irritation and possibly any or all the effects described for oral and inhalation exposures. Chronic inhalation of inorganic arsenic compounds is the most common cause of industrial poisoning. The sequence of chronic poisoning involves weakness, anorexia and gastrointestinal complaints, followed by conjunctivitis and irritation of throat and a respiratory tract, perforation of nasal septum, hyperkeratosis, hyperpigmentation, eczemoid and allergic dermatitis. Effects on mucous membranes, skin, nervous and circulatory systems (EOSH, 1982) and cirrhosis, of a liver (ACGIH, 1986) have also been reported from chronic inhalation of arsenic compounds. However, cancers of a respiratory tract would be the most serious of various chronic effects. A hoarse voice is common in arsenic workers, and a perforated nasal septum is a common result of prolonged inhalation of white arsenic dust or fume. The final phase consists of peripheral sensory neuritis of hands and feet, and sometimes, motors paralysis. As little as 3 to 4 mg of

arsenic per day can cause chronic poisoning (HSDB, 1993). The trivalent form is eliminated less rapidly than the pentavalent, and can thus cause cumulative toxicity (HSDB, 1993). Chronic arsenic poisoning appears to be more common from non-industrial exposures, and cases of poisoning from ingestion of arsenic-based herbicides still occur (Kelafant et al., 1993).

Evidence for chronic effects from oral intake of arsenic comes from its use in human medicine for treatment of psoriasis. A peculiar hyperpigmentation of skin occurs, particularly on palms of hands and soles of feet (Friberg et al., 1986). So-called blackfoot disease (gangrene), anemia, and cirrhosis of liver (perhaps complicated by alcohol intake in winery workers) have also been reported from chronic oral intake of arsenic (EOSH, 1982).

Some arsenic compounds are contact allergens (HSDB, 1993) and can cause papular eczema or follicular swelling and pustules, warts, increased or decreased pigmentation (so-called raindrop pigmentation) which can develop into skin cancer. Skin lesions can be delayed and may occur from other routes of exposure (Friberg et al., 1986). Other effects on skin are transverse lines on nails (Mees' lines), which appear 4 to 6 weeks after exposure (HSDB, 1993).

Similar systemic effects may occur from chronic exposure to arsenic regardless the route of exposure. The major target organs for the toxicity of arsenic are nerves, heart, blood/bone marrow, and liver. Nervous damage can be both central (encephalopathy) and peripheral. Early symptoms of peripheral nerve damage include pain, numbness, tingling, or a pins-and-needles sensation in the extremities, loss of touch, sensation, foot or wrist drop, and muscle cramps. Arsenic can depress formation of all blood elements in bone marrow, causing aplastic anemia (HSDB, 1993).

Arsenic trioxide in a solubilized form becomes sodium arsenite, which is more toxic than in an unsolubilized form. Approximately 200 milligrams of arsenic trioxide ingested acutely by an adult may be lethal (Baselt and Cravey, 1989). One milligram/kilogram of ingested arsenic may be lethal for a child (Alexander, 1964; Woody and Kometani, 1948). As little as 20 milligrams of arsenic may produce life-threatening toxicity (Zaloga et al., 1970; Schoolmeester and White, 1980; Hutton and Christians, 1983). Estimates of acute oral toxic doses of arsenic compounds range from 1 milligram to 10 grams. Acute ingestion of 9 to 14 milligrams of arsenic trioxide by a 16-month-old female produced classic GI signs and symptoms of arsenic poisoning (Watson et al., 1981). A 30-year-old male survived an ingestion of 6 ounces of "Blue Ball Rat Killer" containing 1.5% arsenous oxide (2,150 milligrams metallic arsenic per 6 ounces), ethanol, and intranasal cocaine use with aggressive therapy (fluid resuscitation, chelation therapy, and hemodialysis) (Fesmire et al., 1988).

Trivalent arsenic (arsenite) is more toxic for animals than the pentavalent forms (arsenates) by several orders of magnitude. However, significant toxicity may occur with large amounts of pentavalent salts for humans. Pentavalent arsenic may be converted *in vivo* to trivalent arsenic. In one case, about 91 percent of 149 cases of poisoning by sodium arsenate-containing ant killer occurred via a bait station. Most cases were children 3-years-old or younger. Symptoms of self-limiting episodes of vomiting and diarrhea were observed in 3 children (Kingston et al., 1989). Despite limited or no symptoms (e.g., transient emesis) in children with a history of sodium arsenate ant killer ingestion, significant elevations in 24-hour urine arsenic levels occurred, in the range of 3500 to 5350 µg/L (Scalzo et al., 1989). In another case, decreases in hemoglobin

and hematocrit values were the only sequelae associated with an acute ingestion of approximately 1.2 grams of arsenic as sodium arsenate in a 44-year-old female (Chan and Mathews, 1990).

The published values of LD_{50} (Lewis, 1992; RTECS, 1993) are as follows:

LD_{50} (oral) rat - 763 mg/kg,

LD_{50} (IP) rat - 13,390 µg/kg,

LD_{50} (oral) mouse - 145 mg/kg,

LD_{50} (IP) mouse - 46,200 µg/kg.

According to the EPA weight-of-evidence classification system for carcinogenicity arsenic is classified to A Group – known human carcinogen (IRIS, 1996). This classification is largely on the basis of observations of increased lung cancer mortality in exposed populations, primarily through inhalation, and of increased numbers of skin cancers in several populations consuming drinking water with high arsenic concentrations.

Studies on populations of smelter workers (Tacoma, WA; Magma, UT; Anaconda, MT; Ronnskar, Sweden; Saganoseki-Machii, Japan) have showed the association between occupational arsenic exposure and lung cancer mortality (Enterline and Marsh, 1982; Lee-Feldstein, 1983; Axelson et al., 1978; Tokudome and Kuratsune, 1976; Rencher et al., 1977). Both proportionate mortality and cohort studies of pesticide manufacturing workers have shown an excess of lung cancer deaths among exposed persons (Ott et al., 1974; Mabuchi et al., 1979). The study of the population living near a pesticide manufacturing plant revealed that it was also exposed to the risk of lung cancer (Matanoski et al., 1981). Case reports of arsenical pesticide applicators have demonstrated an association between arsenic exposure and lung cancer (Roth, 1958). A cross-sectional study of 40,000 Taiwanese exposed to arsenic in drinking water found significant excess of skin cancer prevalence by comparison to 7500 residents of Taiwan and Matsu who consumed relatively arsenic-free water (Tseng et al., 1968). This study design limited its usefulness to risk estimation. Arsenic-induced skin cancer has also been attributed to water supplies in Chile, Argentina and Mexico (Borgono and Greiber, 1972; Bergoglio, 1964; Cebrian et al., 1983). No excess skin cancer incidence has been observed in U.S. residents consuming relatively high levels of arsenic in drinking water (Morton et al., 1976; Southwick et al., 1981). The results of these U.S. studies, however, are not necessarily inconsistent with the existing findings from the foreign populations. The statistical powers of the U.S. studies are considered to be inadequate because of the small sample size.

A follow-up study (Tseng, 1977) of the population living in the same area of Taiwan, where arsenic contamination of water supplies was endemic, significantly elevated standard mortality ratios for cancer of bladder, lung, liver, kidney, skin and colon were found. This study of bladder, liver and lung cancer cases in the endemic area proved a significant association with arsenic dose-related exposure. The association of arsenic ingestion and cancer of various internal organs has also been cited in a number of case reports (Chen et al., 1985; 1986). Persons treated with arsenic-containing medicines have also been shown to be at a risk of skin cancer (Sommers and McManus, 1953).

There has not been consistent demonstration of arsenic carcinogenicity in test animals for various chemical forms administered by different routes to several species (IARC, 1980). There is some data to indicate that arsenic may produce animal tumors if retention time in lungs is increased (Pershagen et al., 1982; 1984).

Sodium arsenate has been shown to transform Syrian hamster embryo cells (Di Paolo and Casto, 1979) and to produce sister-chromatid-exchange in DON cells, CHO cells and human peripheral lymphocytes exposed *in vitro* (Wan et al., 1982; Ohno et al., 1982; Larramendy et al., 1981; Andersen, 1983; Crossen, 1983). While arsenic compounds have not been shown to mutate bacterial strains, it produces preferential killing of repair deficient strains (Rossman, 1981).

Quantitative estimate of carcinogenic risk from oral exposure is based on Tseng et al. (1977) study, which reported increased prevalence of skin cancers in humans as the consequence of arsenic exposure to drinking water, a unit risk of 5E-5 per µg/L was proposed (IRIS, 1996). A recent memorandum by the Administrator of the EPA recommended that the above unit risk is to be adopted.

Quantitative estimate of carcinogenic risk from inhalation exposure is as fellows (IRIS, 1996):

- Inhalation Unit Risk 4.3E-3$(\mu g/m^3)^{-1}$
- Extrapolation Method absolute-risk linear model

Air Concentrations at Specified Risk Levels:

Risk Level	Concentration
E-4 (1 in 10,000)	2E-2 $\mu g/m^3$
E-5 (1 in 100,000)	2E-3 $\mu g/m^3$
E-6 (1 in 1,000,000)	2E-4 $\mu g/m^3$

The oral Reference Dose (RfD) for arsenic has been established by U.S.EPA (IRIS 1996) as follows:

Critical Effect	Experimental Doses*	UF	MF	RfD
Hyperpigmentation, keratosis and possible vascular complications	NOAEL: 0.009 mg/L converted to 0.0008 mg/kg-day	3	1	3E-4 mg/kg-day
Human chronic oral exposure	LOAEL: 0.17 mg/L converted to 0.014 mg/kg-day			

Conversion Factors: NOAEL was based on the arithmetic mean of 0.009 mg/L to establish arsenic concentration of 0.001 to 0.017 mg/L. This NOAEL also included estimation of arsenic from food. Since experimental data was missing, arsenic concentrations in sweet potatoes and rice were estimated to be 0.002 mg/day. Other assumptions included consumption of 4.5 L water/day and 55 kg bw (Abernathy et al., 1989). NOAEL = [(0.009 mg/L x 4.5 L/day) + 0.002 mg/day] / 55 kg = 0.0008 mg/kg-day. The LOAEL dose was estimated using the same assumptions as the NOAEL starting with (Tseng, 1977) arithmetic mean of water concentration of 0.17 mg/L. LOAEL = [(0.17 mg/L x 4.5 L/day) + 0.002 mg/day] / 55 kg = 0.014 mg/kg-day. Tseng, 1977; Tseng et al., 1968

Confidence in this chosen study is considered medium. An extremely large number of people were included in the oral assessment (>40,000) but the doses were not well-characterized and other contaminants were present. The supporting human toxicity database is extensive but

somewhat flawed. Problems exist with all epidemiological studies. For example, the Tseng studies do not consider potential exposure from food or other sources. A similar criticism can be made of the Cebrian et al. (1983) study. The U.S. studies are too small in number to resolve several issues. However, the database does support the choice of NOAEL. It provides medium confidence. Medium confidence in the RfD follows.

Toxicity to aquatic species

In result of bioassays on invertebrate species and fishes the following LC_{50} of arsenic were calculated:

LC_{50} (96 hr) - knifefish - 31 mg/L (Ghosh et al., 1990)

LC_{50} (96 hr) - striped bass - 30 mg/L (Palacoski et al., 1985)

LC_{50} (48 hr) - *Aplexa hypnorum* - 24.5 mg/L (Holcombe et al., 1983)

Arsenic toxicity was also tested in a rainbow trout. Oral arsenic dose of 0.52 mg/kg/day (24 weeks) caused chronic inflammatory changes in subepithelial tissues of a gall bladder wall in 71% of the group (Cockell et al., 1991).

Bioconcentration factors (BCFs) ranging from 0 to 17 have been found for various forms of arsenic (trivalent, pentavalent and organic) in freshwater fish and invertebrates. However, a BCF of 350 was observed in marine systems, principally for the organic forms (ATSDR, 1991). These values do not indicate a strong bioaccumulative capacity for most forms of arsenic in fresh water systems; however, marine aquatic species are capable of accumulating organic arsenic to high concentrations (>150 mg/kg tissue). Seafood, especially shellfish, may have significant arsenic concentrations. Ingestion may result in urinary arsenic levels of 200 to 1700 µg/L within 4 hours (Baselt & Cravey, 1989).

Summary of applicable regulatory guidelines

Polish guidelines values for arsenic in soil and groundwater during remediation processes are presented in Table III-1.

Toxicological Profile for Cadmium

Environmental occurrence, fate and transport

Cadmium (Cd) is a soft, silvery, ductile metal. It is most often encountered in combination with other elements such as oxygen (cadmium oxide) or chlorine (cadmium chloride).

Some selected physical/chemical properties of cadmium are as follows:

- Molecular Formula: Cd
- Molecular Weight: 112.41
- Melting Point: 321°C
- Boiling Point: 769°C
- Specific Gravity: 8.65°C
- Vapor Pressure: 1 mm Hg at 394°C
- Solubility: Insoluble in water
- Log K_{ow}: Not applicable
- Conversion Factors: Not applicable
- Henry's Constant: Not applicable
- Description: Silvery, ductile metal.

The properties of cadmium complexes may differ substantially from those of the elemental form.

The largest uses of cadmium are in electroplating, pigments, plastic stabilizers, and batteries (USDI, 1985). Cadmium is produced as a by-product during the processing of zinc-bearing ores, as well as from smelting operations of lead and copper ores (U.S. EPA 1985; ATSDR, 1991; HSDB, 1992). Cadmium enters the environment is a limited extent from the natural weathering of minerals, but to a much greater degree from sources such as discarded metal-containing products, phosphate fertilizers and emissions from fuel combustion activities (ATSDR, 1991).

The atmosphere provides an important route for environmental cadmium transfer (Keitz, 1980), and the industrial emissions. The atmospheric cadmium particulate produced by fossil fuel combustion typically are in the respirable range (>10 µm), with an atmospheric residence time of one to ten days. These may be transported from 100 to several thousand kilometers before settling. Larger atmospheric cadmium particulate from industrial emissions are removed more rapidly from the atmosphere by gravitational settling, with substantial deposition in areas immediately downstream of the pollutant source (ATSDR, 1991). Typical atmospheric concentrations of cadmium range from about 1 to 5 ng/m^3 in rural areas, as compared to between 5 and 40 ng/m^3 in urban areas (Elinder, 1985).

Several processes, such as sorption to mineral matter and clays, and binding to humic substances, typically tend to keep the concentrations of soluble cadmium low in groundwater (ATSDR, 1991). Cadmium concentrations in unpolluted natural waters generally are less than 1 µg/L (Dunnick and Fowler, 1988).

In soil, cadmium may be present as unbound cadmium complexes or in dissolved ionic form in soil pore water. It also may be bound to soil minerals or to organic constituents by cation exchange, in which case it is not readily leached from the soil by rainwater (ATSDR, 1991). Typical soil levels of cadmium range from about 100 to 1,000 µg/kg, with an average value of about 260 µg/kg for most areas (Carey, 1979). Average cadmium content in top soils worldwide

ranges from 0.2 to 1.05 ppm. Average cadmium concentrations worldwide are reported to be 0.5 ppm and 0.2 ppm in Poland. (Kabata-Pendias, Pendias, 1999). In Poland, soil cadmium concentration from metal mining and processing regions ranges from 6 to 270 ppm (Kabata-Pendias, Pendias, 1999). The geometric average content of cadmium in agricultural soils in the Katowice province amounted to 1.06 mg/kg and exceeded the geometric average cadmium content in soils of the whole country (0.22 mg/kg) (Terelak at al., 1997). The highest average cadmium concentration in agricultural soils of the Katowice province was 22.88 mg/kg (Stawiany, 1998).

Mammalian and human health effects

Humans are exposed to cadmium via food, water, air, and dust. Cadmium inhalation is at least 60 times as toxic as cadmium ingestion (Macfarland, 1960). Average oral absorption of cadmium is 3 to 7% (Friberg et al., 1985). Symptoms occur within 1/2 to 3 hours after ingestion. Inhalation absorption may be as high as 50%. Air concentrations of 0.02 to 0.05 mg cadmium/m^3 result in inhalation of 150 to 400 µg/7.5 hours (Elinder, 1986). Oral or inhaled cadmium is transported to the liver where it induces metallothionein, which binds and detoxifies cadmium. A slow release of this complex produces cadmium-methiothionein complex in all organs, particularly the kidney and liver. Half of a non-smoker's body burden of 15 to 30 mg cadmium is in the liver and kidneys. The placenta provides a barrier for cadmium, at least during the last trimester. Cadmium is rapidly cleared from the plasma, but after repeated exposure some can be found in red cells combined with hemoglobin and low-molecular-weight proteins. Most tissue cadmium is bound to metallothioneins.

In mice, a dose of 790 µmol Cd/kg produced mortality in 82% of the animals and produced tissue damage (by histology) most notably in the testes, ventricle, and duodenum as well as damage in the liver, kidney, and ileum (Andersen et al., 1986).

Acute toxicity most notably occurs after cadmium ingestion or inhalation of cadmium fumes. Poisoning from inhalation is relatively rare but dangerous. Initial signs/symptoms of cadmium poisoning resemble those of the flu ("metal fume fever").

Following acute inhalation, the lung is the target organ, although symptoms may not begin for up to 12 hours (Beton et al., 1966). Chest pain, a cough, dyspnea, bronchitis, and pneumonitis have all been noted in acute poisonings (Tibbits & Milroy, 1980). Respiratory toxicity may progress, over 1 to 4 days, to pulmonary edema which may persist for months. Respiratory pneumonitis with persistent restrictive ventilatory defect may result (Barnhart and Rosenstock, 1984).

Acute cadmium chloride inhalation produced immunosuppression in mice (Krzystyniak et al., 1987).

Following acute oral ingestion, the target organ is the gastrointestinal tract. Acute poisoning produces severe nausea, vomiting, diarrhea, abdominal pain and cramping, as well as substernal pain, and gastroenteritis (Taylor et al., 1984).

Studies in mice indicate decreased peristalsis leading to retention and increased absorption of cadmium following oral ingestion (Andersen et al., 1986).

Liver damage can occur in acute or chronic cadmium poisoning because the liver contains high levels of metallothionein. Involvement of the liver does not occur as often as with the kidney (Gosselin et al, 1984).

Chronic exposure to cadmium can produce proteinuria, kidney damage, and chronic obstructive lung disease. Toxicity is usually a product of chronic industrial exposure, although acute and subchronic exposure may damage these organs as well. The predominant effect of chronic exposure is proximal renal tubule damage evidenced by enzymuria and proteinuria. Several epidemiological studies have suggested increased proteinuria at cumulative exposures below 500 $\mu g/m^3$/year (equivalent to PEL of 11.1 $\mu g/m^3$ over 45 working years). The effect is irreversible and may worsen despite termination of exposure (Elinder, 1985; Roels et al., 1989; Thun et al., 1991; Roels et al., 1991; Iwata et al., 1992). Glycosuria, B2 microglobulinuria and aminoaciduria can result from chronic poisoning (Shaikh and Smith, 1984; Takebayashi et al., 1987). In severe cases, higher molecular weight proteins such as albumin may be present. Chronic workplace cadmium exposure was associated with radiographic emphysema and decreased carbon monoxide transfer, which is correlated with cumulative cadmium exposure. None had a history of acute cadmium pneumonitis (Davison et al., 1988; Leduc et al., 1993). Out of 34 nickel-cadmium battery workers, all reported neurological-type problems, including headaches, weakness, lassitude, and dizzy spells. Six workers who complained of severe headaches had brain atrophy as shown on CT scans (Bar-Sela et al, 1992).

Chronic exposure to cadmium has been also associated with microfractures, osteomalacia, radiological decreases in bone density, and disturbances in calcium metabolism (ACGIH, 1986; Gosselin et al., 1984).

It has been suggested that renal damage due to cadmium exposure leads to decreases in serum vitamin D levels and increases in serum parathyroid hormone levels. The more marked changes in women as opposed to men may play a role in the development of sex-related differences in cadmium-induced bone injury (Tsuritani et al., 1992; Kido et al., 1990). Cadmium may act directly on the bone collagen in rats, causing acceleration of collagen catabolism and demineralization (Gosselin et al, 1984).

Spermatid and spermatocyte damage has been suggested in humans. Although no adverse effects have been reported on human female reproductive function, female rat reproductive function may be suppressed by 10 mg/kg cadmium chloride daily (AMA, 1985). Testicular necrosis resulting in creatinuria has been seen in cadmium poisoned rats (Gray et al., 1986). Offspring of women receiving industrial exposure to 0.16 to 35 mg soluble cadmium salts/m^3 weighed less than controls (AMA, 1985). These effects may be secondary to cadmium placental toxicity (Reproductive Toxicology, 1986).

In a study of non-smoking pregnant women exposed to low levels of smelter-derived cadmium and a group of non-exposed women, it was shown that a higher mean placental cadmium level was found in the exposed women. However, no association was found between placental cadmium and birth weight (Loiacono et al., 1992). IARC has classified cadmium as an animal carcinogen based on several animal studies, but recently the ACGIH has upgraded cadmium to a suspect human carcinogen (ACGIH, 1986). An increased risk for lung cancer may exist in chronic cadmium exposures. Cadmium workers exposed to 0.3 mg cadmium/m^3 may be at increased risk

for lung and prostatic cancer (Elinder, 1986). However, other studies have failed to demonstrate an increase risk of prostatic cancer (Armstrong and Kazantzis, 1985; Armstrong and Karantzis, 1983; Sorahan and Waterhouse, 1985).

Increased sister chromatid exchange was not seen in cultured lymphocytes from people exposed to cadmium nor in lymphocytes of non-exposed humans after addition of cadmium sulfate to the culture (Nogana et al., 1986; Bassendowska-Karska and Zawadzka-Kos, 1987).

U.S. EPA has categorized cadmium as a Class B1 carcinogen (probable human carcinogen) by the inhalation exposure route and has established a Cancerogenic Potency Factor (CPF) of 6.1E+00 $(mg/kg/day)^{-1}$ for cadmium (U.S. EPA, 1991). A summary of risk estimates is as fellows (IRIS, 1996):

- Inhalation Unit Risk 1.8E-3 $(\mu g/m^3)^{-1}$
- Extrapolation Method Two stage; only first affected by exposure; extra risk

Air Concentrations at Specified Risk Levels:

Risk Level	Concentration
E-4 (1 in 10,000)	6E-2 $\mu g/m^3$
E-5 (1 in 100,000)	6E-3 $\mu g/m^3$
E-6 (1 in 1,000,000)	6E-4 $\mu g/m^3$

An oral Reference Dose (RfD) for cadmium have been established by U.S.EPA (IRIS 1996) as follows:

Critical Effect	Experimental Doses	UF	MF	RfD
Significant proteinuria	NOAEL (water): 0.005 mg/kg/day(water)	10	1	5E-4 mg/kg/ day
Human studies involving chronic exposures	NOAEL (food): 0.01 mg/kg/day (food)	10	1	1E-3 mg/kg/ day

U.S. EPA, 1985

Cd is unusual in relation to most, if not all, of the substances for which an oral RfD has been determined in that a large quantity of both human and animal toxicity data are available. The RfD is based on the highest level of Cd in the human renal cortex (i.e., the critical level) that is not associated with significant proteinuria (i.e., the critical effect). A toxicokinetic model has been used to determine the highest level of exposure associated with the lack of a critical effect. Since the fraction of ingested Cd that is absorbed appears to vary with the source (e.g., food vs. drinking water), it is necessary to allow for this difference in absorption when using the toxicokinetic model to determine an RfD.

The choice of NOAEL does not reflect the information from any single study. Rather, it reflects the data obtained from many studies on the toxicity of cadmium in both humans and animals.

These data also permit calculation of pharmacokinetic parameters of cadmium absorption, distribution, metabolism and elimination. All of this information considered together gives high confidence in the database. High confidence in either RfD follows as well.

Toxicity to aquatic species

Cadmium is more mobile in aquatic environments than most other heavy metals (ATSDR, 1991). Freshwater acute values for cadmium are available for species in 44 genera and range from 1.0 µg/L for rainbow trout to 28,000 µg/L for a mayfly (U.S. EPA, 1986).

Chronic tests have been conducted on cadmium with 12 freshwater fish species and four invertebrate species with chronic values ranging from 0.15 µg/L for *Daphnia magna* to 156 µg/L for the Atlantic salmon. Acute-chronic ratios are available for eight species and range from 0.9 for the Chinook salmon to 433.8 for the flagfish (U.S. EPA, 1986).

Bioconcentration factors (BCFs) for cadmium in fresh water range from 164 to 4,190 for invertebrates and from 3 to 2,213 for fishes (U.S. EPA, 1986).

Shellfish, such as mussels, scallops, and oysters, may be a major source of dietary cadmium, and may contain 100 to 1,000 µg/kg. Shellfish accumulate cadmium from the water; it subsequently binds to cadmium-binding peptides in the shellfish (Klaassen et al., 1986).

Summary of applicable regulatory guidelines

Polish guidelines values for cadmium in soil and groundwater during remediation processes are presented in Table III-1.

Toxicological Profile for Lead

Environmental occurrence, fate and transport

Lead (Pb) is an element which occurs naturally in all compartments of the biosphere. The extent of occurrence of lead in the earth's crust is about 0.002% (15 g/ton) (Budavari, 1989). Lead is found in the environment in the +2 and +4 oxidation states, with the former more common in the environment (Cotton and Wilkinson, 1972).

Some selected physical/chemical properties of lead are as follows:

- Molecular Formula: Pb
- Molecular Weight: 207.2
- Melting Point: 327.4°C
- Boiling Point: 1740°C
- Specific Gravity: 11.34 at 20°C
- Vapor Pressure: 1.77 mm Hg at 1000°C
- Solubility: Insoluble in water
- Log K_{ow}: Not found
- Conversion Factors: Not applicable
- Henry's Constant: Not applicable
- Description: Bluish-white, silver gray metal; highly lustrous when freshly cut, tarnishes upon exposure to air.

Lead may enter the environment via mining, ore processing, smelting, refining use, recycling, or disposal. Generally, the initial means of entry is via the atmosphere. Lead is a common air contaminant (HSDB, 1993; Lewis, 1992). Lead may also enter the atmosphere from the weathering of soil and volcanoes, but these sources are minor compared with anthropogenic ones. Generally, the form of lead that enters the atmosphere is not determined. However, metallic lead may be released from smelting and refining plants (HSDB, 1993). When released to the atmosphere, lead will generally be in dust form or adsorbed to particulate matter. It will be subject to gravitational settling and be transformed to the oxide and carbonate. General lead exposure occurs from ambient air, especially in areas with high automotive traffic and sites near industrial sources (HSDB, 1993).

Lead occurs in water in either dissolved or particulate form. At low pH, lead is more easily dissolved. Chemical treatment to soften water increases the solubility of lead (Lewis, 1992). Lead enters water from atmospheric fallout, runoff, or wastewater. Little is transferred from natural ores. Lead is a stable metal and adherent films of protective insoluble salts form that protect the metal from further corrosion. That which dissolves tends to form ligands (HSDB, 1993). Lead is effectively removed from the water column to the sediment by adsorption to organic matter and clay minerals, precipitation as insoluble salt (the carbonate or sulfate, sulfide), and reaction with hydrous iron and manganese oxide. Under most circumstances, adsorption predominates. Lead does not appear to bioconcentrate significantly in fish but does in some shellfish, such as mussels (HSDB, 1993). Due to its very low vapor pressure and insolubility, volatilization of lead from soil or water will be negligible. However, relatively volatile tetramethyl lead can be formed in anaerobic lake sediment and loss of lead via volatilization can subsequently occur (HSDB, 1993). Elevated levels of lead in drinking water usually result from distribution systems containing lead pipe (HSDB, 1993).

Geochemical background for lead in top soil usually ranges from 25 to 40 ppm; the average natural lead content in Polish soils amounts to 18 ppm (Kabata-Pendias, Pendias, 1999). In Poland lead concentration in soils metal mining or processing regions ranged from 770 to 12,750 ppm (Kabata-Pendias, Pendias, 1999). The geometric average content of lead in agricultural soils in the Katowice Province amounted to 50.9 mg/kg and exceeded the overall national geometric average lead content in soils (13.8 mg/kg) (Terelak at al., 1997). The highest average lead concentration in agricultural soils of the Katowice province was 544.57 mg/kg (Stawiany, 1998).

If released or deposited in soil, lead will be retained in the upper 2 to 5 cm of soil, especially soils with at least 5% organic matter or a pH of 5 or above. Leaching is not important under normal conditions, although there is some evidence to suggest that lead is taken up by some plants. Generally, the uptake of lead from soil into plants is not significant. Effluent holding 173 mg/L lead has been noted to undergo a 98% reduction in 3 inches of soil (OHM/TADS, 1993). It is expected to slowly undergo speciation to the more insoluble sulfate, sulfide, oxide, and phosphate salts (HSDB, 1993). Lead concentrations should not exceed 2 ppm as the soluble form in the soil solution for phytotoxic considerations (OHM/TADS, 1993).

Mammalian and human health effects

For the general population, exposure to lead occurs from inhaled air, dust of various types, and food and water with an approximate 50/50 division between inhalation and ingestion routes. Adults absorb about 5 to 15% of ingested lead and retain less than 5%. Children absorb about 50% and retain about 30% (Lewis, 1992). The principal route of exposure to lead is via ingestion, but these are usually environmental and presumably controllable sources that produce excess exposure. These sources include lead in air from combustion of lead-containing auto exhausts or industrial emissions, lead-based paint, hand-to-mouth activities of young children living in polluted environments, and, less commonly, lead dust brought home by industrial workers on their clothes and shoes, and lead-glazed earthen ware (HSDB, 1993). The highest intake of lead typically is from food and water. Concentrations in food may be elevated due to surface contamination of fresh fruits and vegetables. Food in soldered-tin cans may contain particularly high levels of lead (HSDB, 1993).

Poisoning from organic lead compounds (tetraethyl and tetramethyl lead) may occur in the manufacture, transport and industrial handling of these compounds. Since lead has been removed from paints and gasoline the mean of blood lead levels in U.S. children has dropped from 17 µg/dL (1970s) to 6 µg/dL (1992) (Schoen, 1993).

Lead is absorbed primarily through the gut. Absorption is augmented in the presence of iron, zinc, and calcium deficiency (Mahaffey, 1981). When lead is ingested, much of it passes through the body unabsorbed, and is eliminated in the feces. The greater portion of the lead that is absorbed is sequestered by the liver and excreted, in part, in the bile. For this reason, larger amounts of lead are necessary to cause toxic effects by this route, and a longer period of exposure is usually necessary to produce symptoms (Lewis, 1992).

Absorption from the lungs is likely if the inhaled dust is in a fine particulate state. However, absorption takes place easily from the respiratory tract and symptoms tend to develop more quickly than from absorption via ingestion. In industry, inhalation is typically more important

than is ingestion (Lewis, 1992). All of the inhaled dose is eventually absorbed or transferred to the gastrointestinal tract, where it would mostly be eliminated in the feces (Friberg et al., 1986). Estimates of the actual absorbed dose by inhalation have varied, but a figure of 30% seems to be reasonable in most cases (Friberg et al., 1986). Many factors can affect the absorption of lead by the inhalation route. Smoking can increase the absorption (O'Donaghue, 1985), possibly by providing more surface area for adsorption or by causing irritation. Age, nutritional status, presence of infectious disease, and other factors including exposure to other metals and chemicals play a role in determining the ability of each individual to absorb lead.

Absorption through the skin has been reported only with lead acetate application to diseased skin. Prolonged absorption of lead or its inorganic compounds results in severe gastrointestinal disturbances and anemia; with more serious intoxication, there is neuromuscular dysfunction; the most severe lead exposure may result in encephalopathy (Hathaway et al, 1991).

Human systemic effects by ingestion and inhalation are: loss of appetite, anemia, malaise, insomnia, headache, irritability, muscle and joint pains, tremors, flaccid paralysis without anesthesia, hallucinations and distorted perceptions, muscle weakness, gastritis and liver changes. The major organ systems affected are the nervous system, blood system, and kidneys (Lewis, 1992). Low levels of lead impair neurotransmission and immune system function and may increase systolic blood pressure (Lewis, 1992).

A syndrome called acute lead encephalopathy occurs mostly in children and involves the central nervous system. It is accompanied by the so-called classical triad of symptoms: ataxia (loss of coordination), coma, and convulsions. The acute aspect of this toxicity of lead really refers to the acute nature of the illness and not to the results of acute or single exposures to lead. Typically these symptoms would develop in a child (and more rarely in adults) when the blood lead level (PbB) is greater than 90 µg/100 mL (O'Donaghue, 1985). Although it is possible that this PbB could be achieved from some massive acute exposure, it is more likely to occur as the result of a more intense exposure superimposed on a pattern of chronic intake.

Once in the body, >90% of the lead initially equilibrates between the blood and soft tissues, with a half-life of less than one month (O'Donaghue, 1985). Eventually >90% of the total body burden of lead is deposited in the bone, where it has a half-life of far greater than 20 years (O'Donaghue, 1985). An adult can take in a total of approximately 0.6 mg of lead per day without increasing the body burden. When chronically exposed to levels of lead which will result in intake greater than this, a person will steadily increase his or her body burden of lead. In general the body burden of lead increases throughout life. Effective treatment of acute exposure to lead may avoid permanent damage. In one recently reported follow-up case of a patient who was dusted with powdered white lead as an infant in 1889, the patient went on to lead a normal life and was still alive at the age of 93 (Fraser & Hawarth, 1991). Blood lead levels were not available to confirm that lead poisoning actually occurred, however.

The effects of chronic exposure to high levels of lead are well defined in humans, but as the exposures become lower and lower the effects are less well understood. The earliest signs of chronic exposure are effects in the blood-forming system. The various effects of lead on the blood-forming system produce a characteristic pattern of lead toxicity in the hematological picture involving lowered levels of ALA-D, elevated levels of free erythrocyte porphyrin and

zinc protoporphyrin, and lower levels of heme and hemoglobin. These effects on the blood produce a typical anemia. These effects on the blood are always present in the so-called classical lead poisoning (EOSH, 1982). While high exposure to lead is known to affect kidney function, one group of workers with median blood lead values of 1.54 µmol/L had no abnormal signs of kidney function. This study does not rule out the possibility that reversible kidney damage may have occurred in the past, when exposures were higher (Gerhardsson et al, 1992).

The Centers for Disease Control has revised its level of concern for blood lead in children to 10 µg/dL, a value once considered to be in the "normal" range (CDC, 1991). The basis for this concern is the widespread exposure of children to lead in the environment, with high-risk groups being children in inner cities and those living in old houses containing lead-based paint, and the neurodevelopmental deficits associated with low blood lead levels in a dose-related fashion. Children are at increased risk of developmental toxicity (decreased IQ, hearing, and growth) if the level in the blood is over 10 µg/dL (CDC, 1991). Even middle- and upper-class children have been found to perform more poorly on neuropsychological and IQ tests, in relation to elevated blood lead levels at 24 months of age (Bellinger et al, 1992). Adults are at increased risk of developing symptoms and signs with levels above 40 µg/dL (OSHA) although effects at lower levels have been observed (Wang et al, 1985). In cases of severe lead poisoning, the amount of lead found in the blood is frequently in excess of 0.07 mg/100 mL of whole blood. The urinary lead excretion generally exceeds 0.1 mg/L of urine (Lewis, 1992). Subtle, often subclinical, neurologic effects have been demonstrated in workers with relatively low blood lead levels, below 40 to 60 µg/100 mL blood (Hathaway et al, 1991).

Lead is a suspected carcinogen and an experimental teratogen. Human mutation data have been reported (Lewis, 1992). Reproductive effects from lead exposure have been documented in animals and human beings of both sexes (Hathaway et al, 1991). Severe toxicity can cause sterility, abortion and neonatal mortality and morbidity (Lewis, 1992).

The carcinogenic potential of lead salts (primarily phosphates and acetates) administered via the oral route or by injection has been demonstrated in rats and mice by more than 10 investigators (IRIS, 1996). The most characteristic cancer response is bilateral renal carcinoma. Rats given lead acetate or subacetate orally have developed gliomas, and lead subacetate also produced lung adenomas in mice after i.p. administration. Most of these investigations found a carcinogenic response only at the highest dose. The lead compounds tested in animals are almost all soluble salts. Metallic lead, lead oxide and lead tetralkyls have not been tested adequately. Studies of inhalation exposure have not been located in the literature. Rats exposed to lead acetate at 500 ppm lead (25 mg/kg/day) in the diet for 2 years had statistically increased incidences of kidney tumors (Azar et al., 1973). No kidney tumors were seen at the next lower dietary level, 100 ppm.

Lead acetate induces cell transformation in Syrian hamster embryo cells (DiPaolo et al., 1978) and also enhances the incidence of simian adenovirus induction. Lead oxide showed similar enhanced adenovirus induction (Casto et al., 1979). Under certain conditions lead compounds are capable of inducing chromosomal aberrations in vivo and in tissue cultures. Lead has been shown, in a number of DNA structure and function assays, to affect the molecular processes associated with the regulation of gene expression (U.S. EPA, 1986).

U.S. recently has classified lead as a Probable Human Carcinogen (Group B2) (IRIS, 1996). U.S. EPA noted that the available data provide an insufficient basis to regulate carcinogenic lead salts, and a quantitative estimate of the excess cancer risk is not available. U.S. EPA has established an ambient air quality standard for lead of 1.5 $\mu g/m^3$ and a Maximum Contaminant Level (MCL) for drinking water of 5.0E+01 µg/L (U.S. EPA, 1992); both of these standards are currently undergoing review by U.S. EPA. The U.S. EPA Office of Drinking Water has proposed an MCLG of 15 µg/L for lead in unrestricted drinking water supplies (ATSDR, 1991), which presently is in place as an Action Level throughout the U.S.

Toxicity to aquatic species

The primary mechanism of acute toxicity of lead to freshwater organisms is unknown. As dissolved oxygen levels decrease, lead becomes more toxic to fish (OHM/TADS, 1993). Soft water also increases toxicity (OHM/TADS, 1993).

In acute assays, invertebrate species are generally more sensitive than vertebrate species. At water hardness of 50 mg/L, the acute sensitivity of 10 freshwater species ranged from 142.5 mg/L to 236 mg/L. For saltwater species the range was 315 µg/L to 27 mg/L. Limited chronic data for saltwater species have identified a no effect level as $\leq$ 37 µg/L lead (U.S. EPA, 1986a). The lowest maximum allowable toxicant concentration (MATC) reported from chronic studies is 19 µg/L of lead for rainbow trout at a water hardness of 128 mg/L $CaCO_3$ (Davies et al., 1976). Equivalent MATC data for marine species were not found. A whole-body bioconcentration factor of 45 was reported using a natural small lake population of bluegills (Atchison et al., 1977). This value is typical for edible tissues of fishes (U.S. EPA, 1986b).

Summary of applicable regulatory guidelines

Polish guidelines values for lead in soil and groundwater during remediation processes are presented in Table III-1.

<u>Toxicological Profile for Nickel</u>

Environmental occurrence, fate and transport

Nickel (Ni) is a naturally occurring, shiny, light-colored metal with high electrical and thermal conductivity. It is resistant to corrosion by air, water and alkalis, but reacts with dilute oxidizing agents.

Some selected physical/chemical properties of nickel are as follows:

- Molecular Formula: Ni
- Molecular Weight: 58.69
- Melting Point: 1547-1555°C
- Boiling Point: 2837°C
- Specific Gravity: 8.90 at 25°C
- Vapor Pressure: 1 mm Hg at 1810°C
- Solubility: Insoluble in water
- Log K_{ow}: Not applicable
- Conversion Factors: Not applicable
- Henry's Constant: Not applicable
- Description: Shiny, light-colored metal.

Nickel is used in nickel-plating, for various alloys such as new silver, Chinese silver, and German silver; for coins, electrotypes, lighting-rod tips, electrical contacts and electrodes, spark plugs, machinery parts. It is used as a catalyst for hydrogenation of organic substances, in manufacturing of Monel metal, stainless steels, and nickel-chrome resistance wire as well as in alloys for electronic and space applications (Merck, 1983). Abundance of nickel in the Earth's crust is 0.018%. It occurs free in meteorites. Nickel was found in many ores as sulfides, arsenides, antimonides, oxides or silicates (Richardson and Gangoli, 1994).

The atmosphere is a major conduit for nickel as particulate matter. Contributions to atmospheric loading come from both natural sources and anthropogenic activity, with input from both stationary and mobile sources. Various dry and wet precipitation processes remove particulate matter as rain out, wash out or fallout from the atmosphere with transfer to soils and waters.

Soil borne nickel may enter waters by surface runoff or by percolation into ground water. Once nickel is in surface and ground water systems, physical and chemical interactions (complexation, precipitation/dissolution, adsorption/desorption, and oxidation/reduction) occur that will determine its fate and that of its constituents (U.S. EPA, 1983).

Soils and volcanoes are the major sources of airborne nickel representing 40-50% of natural sources. From man-made sources combustion of oil and incineration of waste contribute 70% and nickel mining and refining - 17% (Richardson and Gangoli, 1994). Food processing methods apparently add to the nickel levels already present in foodstuffs via leaching from nickel containing alloys in food processing equipment made from stainless steel, the milling of flour, and catalytic hydrogenation of fats and oils by use of nickel catalysts (U.S. EPA, 1980).

Typical average levels of airborne nickel are: 0.00001-0.003 $\mu g/m^3$ in remote areas; 0.003-0.03 g/m^3 in urban areas having no metallurgical industry; 0.07-0.77 $\mu g/m^3$ in nickel processing areas (NRCC, 1981). Aerial fallout from a nickel smelter at Port Colborne, Ontario, Canada, resulted in accumulation of nickel ranging from 600 to 6455 mg/kg in the organic soil of a farm (U.S. EPA, 1983). Soils derived from serpentine rock may contain up to 25,000 mg Ni/kg,

although a more typical value is 1,000 mg/kg. Accumulations of Ni in soil exceeding 1000 mg/kg occur within 1-2 km of large nickel smelters. Uncontaminated agricultural soils in Canada generally contain less than 30 mg Ni/kg (NRCC, 1981). Average nickel content in agricultural soils of Poland is reported to be 6 ppm with the range from 0.1 to 328 ppm (Kabata-Pendias, Pendias, 1999). The geometric average content of nickel in agricultural soils in the Katowice Province is reported to be 13.3 mg/kg and exceeded the overall national geometric average nickel content in soils (6.4 mg/kg) (Terelak at al., 1997).

Mammalian and human health effects

Nickel itself is an micronutrient. It is used in many enzymatic reactions. Nickel carbonyl inhibits synthesis of ribonucleic acid. Nickel carbonyl can pass across the alveolar membrane in either direction without metabolic alteration (CMBEEP, 1975). Once absorbed, nickel carbonyl is slowly broken down to carbon monoxide and nickel.

Nickel is distributed to the lungs, kidney, and less readily to the brain, stomach, and intestinal tissue (CMBEEP, 1975). Subcutaneous, intravenous, or intraperitoneal routes of nickel carbonyl produce a similar pulmonary picture. In human serum, nickel is 34% albumin bound, 26% nickeloplasmin bound and approximately 40% bound to ultrafilterable fractions (Webster, 1980). Parenterally administered nickel is 90% excreted in the urine (CMBEEP, 1975). Most orally ingested nickel is excreted in the feces. Rezuke et al (1987) reported significant biliary excretion of nickel and suggested that biliary excretion may be a significant route for elimination of nickel in humans. The way in which nickel is consumed may greatly affect its bioavailability. Sunderman et al. (1989) demonstrated that 27+/-17% of the nickel in drinking water was absorbed by healthy humans, whereas only 0.7+/-0.4% of the same dose of nickel ingested in food was absorbed (a 40-fold difference).

Adult oral toxicity of nickel is low, and is similar to zinc, chromium, and manganese (Errera, 1980). The usual adult oral intake of nickel is approximately 300 to 600 µg/day. Hogetveit et al. (1978) has recommended a plasma level of 10 µg/L be set as the maximum tolerated dose for nickel refinery workers.

Acute toxicity of nickel and nickel carbonyl in animals is as follows (Sunderman, 1981):

Nickel (colloidal and powdered):

Intravenous	Dogs	LD = 10 to 20 mg/kg
Acute Oral	Dogs	Tolerated: 1 to 3 g/kg

Nickel Carbonyl - $Ni(CO)_4$:

Inhalation	Mice	LC_{50} = 0.067 mg/L for 30 minutes
Inhalation	Rats	LC_{50} = 0.24 mg/L for 30 minutes
Inhalation	Cats	LC_{50} = 1.9 mg/L for 30 minutes
Intravenous	Rats	LD_{50} = 22 + 1.1 mg/kg
Subcutaneous	Rats	LD_{50} = 21 + 4.2 mg/kg
Intraperitoneal	Rats	LD_{50} = 13 + 1.4 mg/kg

Comparative acute toxicity of 4 nickel compounds after inhalation by rats indicated the following toxicity ranking: Ni_3S_2, $NiSO_4$, and $NiCl_2$ were much more toxic than NiO (Benson et al., 1986).

Routes of nickel intake for man and animals are inhalation, ingestion, and percutaneous (U.S. EPA, 1980).

Oral exposures to elemental nickel are generally not very dangerous. However, large doses taken orally may cause nausea, vomiting, abdominal pain, and diarrhea (Sunderman et al., 1988). Workers who accidentally drank water contaminated with 1.63 g Ni/L developed lassitude, headache, giddiness, cough and shortness of breath (Sunderman et al., 1988). Nickel carbonyl gas is seldom ingested. Parenteral exposures may occur from prostheses, stainless steel needles, or contaminated dialysate material. Dermatitis may come from varied sources, both internal and external. Costume jewelry was found to be one of the main causes of nickel dermatitis especially in children of 10 to 19 years old, mainly female.

Inhalation exposures usually are due to nickel carbonyl, but other oxides and sulfides, as well as powdered nickel, may cause some reactions. Nickel inhalation toxicity is divided into an early and late phase.

Exposure to nickel carbonyl is much more dangerous than exposure to nickel metal or nickel alloys.

Following acute inhalation exposure, injury occurs in two phases consisting of immediate effects (nonproductive cough, headache, vertigo, weakness, chest pain), followed by delayed effects (tachypnea, dyspnea, ARDS) (Kurta et al., 1993). Late changes include pulmonary edema and interstitial fibrosis. Alveolar walls are replaced with connective tissue which resolves slowly (Barnes and Denz, 1951). Autopsy shows hemorrhage, atelectasis, necrosis, and infiltration of connective tissue. Early neurologic symptoms after inhalation are dizziness, giddiness, weakness, dysphoria, blurred vision, and numbness (Sunderman and Denz, 1954; Zhi-Cheng, 1986). Second phase symptoms may include cold and clammy skin, cerebral edema (Jones, 1973), and sleeplessness (Sunderman, 1971). Weakness and somnolence can persist 3 to 6 months after exposure (Zhi-Cheng, 1986).

Nickel contact dermatitis is the most common reaction to nickel. It is estimated that 5% of all eczemas are nickel reactions (Sunderman, 1981). These dermal reactions may occur to a number of nickel containing objects encountered externally or internally (Lacroix et al, 1979). Nickel sulfide dermally may cause asthma (McConnell, 1973). Chronic exposure to nickel dust may

cause Loefflar's syndrome (pulmonary eosinophilia) (Sunderman, 1981). Zhi-Cheng et al. (1986) reported a significant decrease in serum monoaminoxidase (SMAO) and EEG abnormalities in workers chronically exposed to nickel carbonyl.

An oral Reference Dose (RfD) for nickel has been established by U.S.EPA (IRIS, 1996) as follows:

Critical Effect	Experimental Doses*	UF	MF	RfD
Decreased body and organ weights	NOAEL: 100 ppm diet (5 mg/kg/day)	300	1	2E-2 mg/kg/ day
Rat Chronic Oral	LOAEL: 1000 ppm diet (50 mg/kg/day)			

*Conversion Factors: 1 ppm = 0.05 mg/kg/day (assumed rat consumption). Ambrose et al., 1976

This chronic study (Ambrose et al., 1976) was properly designed and provided adequate toxicological endpoints; however, high mortality occurred in the controls (44/50). Therefore, a low confidence is recommended for the study. The database provided adequate supporting subchronic studies, one by gavage and the other in drinking water. A medium confidence level in the database is recommended since there are inadequacies in the remaining reproduction data.

Nickel carbonyl produced increases in the number of cases of nasal and lung cancer in nickel workers (Sunderman and Kincaid, 1954). Epidemiological studies confirmed that there is a strong correlation between exposure time and the cancer risk (Grandjean et al., 1988). An inhalation risk assessment for nickel is under review by an EPA work group.

Occupational groups such as nickel workers and other workers handling nickel comprise the individuals at the highest risk. Women, particularly housewives, are at special risk to nickel induced skin disorders because of the greater than average contact with nickel containing materials. Approximately 47 million individuals, comprising the smoking population of the United States, are potentially at risk for possible co-factor effects of nickel in adverse effects on the respiratory tract (U.S. EPA, 1980). Highest risk of mortality from cancer of respiratory tract is found among nickel mine workers involved in roasting, smelting and electrolysis (Venugopal and Luckey, 1978).

The International Agency for Research on Cancer concluded, in 1989, that some nickel compounds are carcinogenic to humans (Group 1) and metallic nickel is possibly carcinogenic to humans (Group 2B) (WHO, 1991). Nickel has been evaluated by the U.S. EPA for evidence of human carcinogenic potential. This does not imply that this agent is necessarily a carcinogen. The evaluation for this chemical is under review by an inter-office Agency work group.

Toxicity to aquatic species

No data were found to suggest that nickel is involved in any biological transformation in the aquatic environment (Callahan et al. 1979).

Nickel toxicity in aquatic invertebrates varies considerably, according to species and abiotic factors. A 96-h LC_{50} of 0.5 mg nickel/L was found for *Daphnia* spp. while, in molluscs, 96-h LC_{50} values of around 0.2 mg/L were found for two freshwater snail species and of 1100 mg/L for a bivalve (WHO, 1991). In fish, the 96-h LC_{50} values generally fall within the range 4-

20 mg nickel/L, but they can be higher in some species. Long-term studies on fish and fish development demonstrated some effects on rainbow trout in soft water at levels as low as 0.05 mg nickel/L (WHO, 1991).

Polish guidelines values for nickel in soil and groundwater during remediation processes are presented in Table III-1.

Toxicological Profile for Mercury

Environmental occurrence, fate and transport

Mercury is one of least abundant elements in the earth's crust. Although greater than trace amounts are found in at least 30 ores, only one, cinnabar, has a mercury concentration sufficient to justify commercial extraction. Mercury is extracted from cinnabar by firing the ore in retorts with lime or iron (Magos, 1988). The world production is about 8,000 tons/year (Magos, 1988). Exploitable deposits are almost exclusively located in the Mediterranean, the Himalayas and Circumpacific mercuriferous belts.

A major use of mercury has been as a cathode in the electrolytic preparation of chlorine and caustic soda. Electrical apparatus (lamps, arc rectifiers and mercury battery cells), industrial and control instruments (switches, thermometers and barometers), and general laboratory applications represent other major mercury uses. Antifouling applications; mildew proofing paints; mercury treatment of seeds, bulbs, plants and vegetation; as well as dental amalgams; catalysts; pulp and paper manufacture; pharmaceuticals and metallurgy represent the remainder of commercial mercury demand (Wallace et al., 1971; NAS, 1977).

The primary source of environmental mercury is the natural degassing of the earth's crust, including land areas, rivers, and the ocean, and is estimated to be on the order of 25,000 to 150,000 tons per year (WHO, 1976; Goldwater and Stopford, 1977; NRCC, 1979). Metallic mercury in the atmosphere represents the major pathway for the global transport of mercury. Although anthropogenic sources of mercury have reached about 8,000 to 10,000 tons per year since 1973, nonanthropogenic sources remain the predominant contributors. The average atmospheric mercury concentration is 1.5 ng/m^3 in the lower troposphere, 3-9 ng/m^3 over remote nonmineralized areas, and up to 50 ng/m^3 over mineralized or urban area (Magos, 1988).

Natural mercury content in top soils ranges from 0.05 to 0.3 ppm worldwide with average natural content estimated to be 0.1 ppm (Kabata-Pendias, Pendias, 1999). In Poland mercury content in different types of soils ranges from 0.02 to 0.16 ppm and in soils contaminated by municipal wastes and sewage from 0.12 to 0.35 ppm (Kabata-Pendias, Pendias, 1999).

The average concentration of mercury in the open ocean has been reported to range from approximately 3.0 ng/L to <10.0 ng/L while the concentration in coastal water has been reported to range from 5.0 to <20.0 ng/L (Magos, 1988; Fitzgerald, 1979). In an area seriously affected by pollution, (e.g., Minamata Bay, Japan) concentrations as high as 3.6 µg/L have been recorded. Oceanic mercury generally is present as mercuric chloride, which does not easily bind to particulate substances and settle out as do mercury compounds found in fresh water (Wallace et al., 1971).

Regardless of the source, both organic and inorganic forms of mercury may undergo environmental transformation. Metallic mercury may be oxidized to inorganic divalent mercury, particularly in the presence of organic material such as in the aquatic environment. Divalent inorganic mercury may be reduced to metallic mercury when conditions are appropriate for reducing reactions to occur. This cycling is important in terms of the global budget of mercury and represents a potential source of mercury vapor that may be released to the atmosphere. A second potential conversion of divalent mercury is methylation to methyl mercury by anaerobic bacteria, although requirements for methylation by sediment microorganisms are strict and occur only within a narrow pH range. These compounds may diffuse into the atmosphere and return as methyl mercury in rainfall. The organic form of mercury readily enters the food chain with concentration factors as great as 3,000 in fish. If taken up by fish in the food chain, it may eventually cycle through to humans.

The rate of synthesis of methyl mercury also depends on the redox potential, composition of the microbial population, availability of Hg^{2+}, and temperature of sediments. However, the conversion rate for inorganic mercury to methyl mercury under ideal conditions is less than 1.5 percent/month (Jensen and Jernelov, 1969). Despite the transformation process discussed, little or no methyl mercury is found in sediments. Conversion of inorganic mercury to methyl mercury results in its desorption from sediment particles at a relatively fast rate. In addition, demethylation by sediment microorganisms occurs at a rapid rate when compared to methylation.

Mercury may be transported to aquatic ecosystems via surface runoff and through the atmosphere. It is complexed to both organic and inorganic particles. Sediments with high sulfur content generally will strongly bind with mercury. Fulvic and humic acids usually are associated with the mercury that is not bound to particles.

Several investigators have estimated blood levels of mercury at which the identifiable symptoms of mercury intoxication occur. These levels may be attained with a steady mercury intake in the range of 4-14 µg/kg/day. This would be ~240 to 840 µg/day for adults and 80 to 280 µg/day for children. It is estimated that a normal diet contributes about 10 µg/day mercury. Thus, with a daily intake of 10 µg from food and a conservative estimate of 4 µg from water (2 µg/L x 2 L/day), it appears that there is a considerable margin of safety. However, those individuals who regularly consume fish from contaminated areas may exceed the normal dietary intake.

Selected physical/chemical properties of mercury as cited in ATSDR (1992) are as follows:

- Molecular Formula: Hg
- Molecular Weight: 200.59 g/mole
- Melting Point: -38.87°C
- Boiling Point: 356.72°C
- Specific Gravity: 13.53
- Vapor Pressure: 2.0E-03 mm Hg at 25°C
- Solubility (H_2O): 5.6E-02 mg/L at 25°C
- Log K_{ow}: Not applicable
- Conversion Factors: Not applicable
- Henry's Law Constant: Not applicable
- Description: Silver white, heavy, mobile liquid metal.

Mammalian and human health effects

The toxicity of mercury depends on the specific compound in question. Alkyl mercury compounds (e.g., methyl mercury) are extremely toxic in comparison to the inorganic mercury compounds. Absorption of inorganic mercury salts from the gastrointestinal tract typically is less than 10% in humans, whereas absorption of methyl mercury exceeds 90%. The pattern of distribution in the mammalian body also differs between alkyl and inorganic forms of mercury. The red blood cell/plasma ratio for inorganic forms generally is less than 2, while for organic forms it is ~10, indicating a longer body half-life for the latter. Inorganic mercury tends to localize in the kidneys as a result of filtration and reabsorption, while organic mercury exhibits a preference for the brain and, to a lesser extent, the kidneys. Excretion may be in both urine (minor) and feces (major), depending upon the form of mercury, the magnitude of the dosage and the time post-exposure (Klaassen et al., 1986). Investigations of the metabolism of mercury and its various compounds have been reviewed by Takeuchi (1972), particularly the comprehensive studies in Japan and Sweden which include investigations of the biological reactions and pathological changes in human beings and animals caused by organic mercury contamination.

Metallic mercury exposure is infrequent, and ingestion of oral doses of 100-500 grams has occurred in humans with little effect other than diarrhea. The toxicity of the inorganic salts of mercury is related to their comparative absorption rates. Insoluble mercurous salts, such as calomel (Hg_2Cl_2; mercurous chloride), are relatively nontoxic in comparison to the mercuric salts. The immediate effects of acute poisoning with mercuric chloride ($HgCl_2$) are due to primary irritation, coagulation necrosis and superficial corrosion of the exposed tissues. Chronic oral effects for the mercuric salts include kidney damage, intestinal hemorrhage and ulceration. Inhalation exposure to mercuric chloride may cause proteinuria, which is suggestive of early renal tubular dysfunction.

Metallic mercury and inorganic mercury salts are limited contributors to the environmental mercury contamination problem. The principal problem of mercury intoxication is related to methyl mercury compounds (which may accumulate in fish), and to ingestion of treated grains or meat from animals which have been fed grain treated with alkyl mercury compounds (Lu et al., 1972).

Methyl mercury becomes available in the food chain through the aquatic transformation of inorganic mercury into organic mercury by microorganisms or other biological alkylating systems under aerobic and anaerobic conditions in aquatic sediments. Specific data on human absorption and excretion of methyl mercury were derived from studies with orally administered [^{203}Hg] methyl mercuric nitrate in which over 90% was absorbed. Maximum blood levels were reached 3-6 hours after ingestion. The biologic half-life was estimated to be 70-74 days (Ekman et al., 1968; Aberg et al., 1969; Falk et al., 1971).

Blood concentrations of mercury generally represent recent exposure to methyl mercury, while hair concentrations reflect average intake over a long period. The mercury concentrations in successive segments of hair over the period of its formation can indicate the degree of past absorption of mercury compounds (NAS, 1982).

The factors that determine the biotransformation of mercurials, their passage through barriers in the body, and the ultimate action on cellular mechanisms are only beginning to be understood, though these compounds have been used as pharmacologic agents for many years. For mercury, taking the half-life of excretion in man as 70 days, a steady state will be reached in approximately one year. Once attained, this steady state concentration of mercury becomes proportional to the daily intake. Studies of methyl mercury in humans support this conclusion (Goldwater and Stopford, 1977).

The Swedish Commission on Evaluating the Toxicity of Mercury in Fish (Berglund, 1971) recommended the use of an "allowable daily intake" (ADI) for mercury on the basis that clinically manifest poisoning of sensitive adults may occur at a whole blood concentration of 0.2 mg/kg. These concentrattions may be achieved by exposure to about 0.3 mg methyl mercury per day, or about 4 µg/kg/day (4E-03 mg/kg/day). A safety factor of 10 was applied to this value and it was concluded that the ADI of methyl mercury through fish would correspond to about 0.03 mg of mercury (as methyl mercury), or about 0.4 µg/kg of body weight (4E-04 mg/kg/day). Subsequent evaluations by WHO (1976) and U.S. EPA have resulted in a slightly more conservative interpretation of these data, and the current U.S. EPA (1991a) RfD has been set at 3E-04 mg/kg/day. However, it should be noted that this value applies to methyl mercury, an organic form of mercury rather than the inorganic forms. An MCL (U.S. EPA, 1991b) for mercury has been established for drinking water supplies at 2 µg/L.

Toxicity to aquatic species

Acute toxicity to invertebrate species occurs at divalent mercury concentrations as low as 2.2 µg/L (*Daphnia* sp.), compared with a higher limit of 30 µg/L in vertebrates (*Lebistes* sp.). Although few data are available, organomercurials are more toxic and generally exhibit toxicity at levels 4-30 times lower than inorganic mercury compounds. Methyl mercury is chronically toxic at less than 0.1 µg/L in several aquatic vertebrate species (*Daphnia* sp., *Salmo* sp.), compared

with a chronic value of ~0.3 µg/L for inorganic mercury compounds in life cycle and early life-stage experiments (U.S. EPA. 1986). Based on bioaccumulation studies in *Pimephales promelas*, a bioconcentration factor of over 81,000 was calculated for methyl mercury. From this evidence, a 4-day average concentration of 0.012 µg/L was established as the level beyond which some testing of edible fish should be performed to ensure that fish flesh in the area is not unacceptably contaminated (≥1 mg/kg).

Methyl mercury in surface waters is rapidly accumulated by aquatic organisms; concentrations in carnivorous fish at the tops of freshwater and salt water food chains (e.g., pike, tuna and swordfish) are biomagnified on the order of 10,000 to 100,000 times those concentrations found in ambient waters (Callahan et al., 1979).

Summary of applicable regulatory guidelines

Polish guidelines values for mercury in soil and groundwater during remediation processes are presented in Table III-1.

Toxicological Profile for Polycyclic Aromatic Hydrocarbons (PAHs)

Environmental occurrence, fate and transport

Polycyclic aromatic hydrocarbons (PAHs), also known as polynuclear aromatic hydrocarbons, are organic chemicals consisting of two or more fused benzene rings in linear, angular and cluster arrangements. The compounds include different numbers of rings in structural arrangements which result in a variety of physical, chemical and biological properties. The study of these compounds is of environmental and toxicological significance due to their carcinogenicity and widespread occurrence. Of primary environmental concern are those relatively mobile PAHs which have two to seven fused rings (molecular weight, 128 to about 300; Eisler, 1987).

Common PAHs include acenaphthene, acenaphthylene, anthracene, benzo(a)anthracene, benzo(a)pyrene, benzo(b)flouranthene, benzo(g,h,i)perylene, benzo(k)flouranthene, chrysene, dibenzo(a,h)anthracene, indeno(1,2,3-cd)pyrene, naphthalene, phenanthrene and pyrene.

At normal temperatures (20-30°C) and pressure (1 atm) PAHs are in the solid state. They have low vapor pressures and low water solubilities, both of which usually decrease with increasing molecular size. Water solubility typically ranges from about 30 mg/L for the 2 ring structures, to 1 µg/L or less for the structures with 5 or more rings (Knutzen, 1987). PAHs generally do not burn easily and typically will persist in the environment for months to years (ATSDR, 1989).

PAHs are formed by a variety of mechanisms (Larsson, 1986; Anderson et al., 1986; Knutzen, 1987) including:

- the rapid, incomplete combustion (i.e., pyrolysis) of organic materials at high temperatures (above 400°C) followed by rapid recombination of the resulting free radicals to form a number of relatively stable polycyclic compounds (pyrosynthesis);
- the very slow (e.g., millions of years) rearrangement and transformation of organic materials at increased temperature (100-300°C) and pressure to form fossil fuels;

- the relatively rapid (e.g., days to years) transformation of natural or synthetic organic compounds with polyaromatic base structures, from various plants and animals, to PAHs under anaerobic conditions in soil and sediment; and
- direct biosynthesis of PAHs.

Selected physical/chemical properties of representative PAHs are as follows:

	Pyrene	Benzo(a)pyrene
Molecular Formula:	$C_{16}H_{10}$ (4 rings)	$C_{20}H_{12}$ (5 rings)
Molecular Weight:	202.3 g/mole	252.3 g/mole
Melting Point:	156°C	179°C
Boiling Point:	393°C	495°C
Specific Gravity:	1.27	1.35
Vapor Pressure:	6.8E-06mm Hg at 25°C	5.5E-09 mm Hg at 25°C
Solubility (H_2O):	0.135 mg/L	0.0038 mg/L
Log K_{OW}:	5.11	6.11
Conversion Factors:	1 ppm=8.26 mg/m^3 1 mg/m^3 = 0.12 ppm	1 ppm=10.3 mg/m^3 1 mg/m^3 = 0.097 ppm
Henry's Law Constant:	1.10E-05 (atm•m^3/mole)	1.13E-06 (atm•m^3/mole)
Description:	Colorless, white or pale yellow solid.	Colorless, white or pale yellow solid.

Sources of PAHs in the environment are both anthropogenic and natural. Two principal sources are related to the use of fossil fuels and the high-temperature, incomplete combustion of organic matter in other processes. Forest fires and volcanic eruptions are natural sources which contribute to the ubiquitous environmental occurrence of these substances. Anthropogenic sources of PAHs provide a much greater release volume of PAHs than natural sources, as a result of both domestic and industrial activities. Domestic activities that produce significant quantities of PAHs include: exhaust from internal combustion engines, cigarette smoking, incineration of wastes (burning), and the broiling and smoking of foods. The largest single anthropogenic source of PAH release to the environment in the U.S. is home heating with wood or fossil fuels (ATSDR, 1989; Anderson et al., 1986). Significant industrial PAH production and release are

associated with the iron and steel industries, petroleum refining, coal liquefaction or gasification, and the production of coke, coal tar, pitch, creosote, asphalt and road and roofing tar.

Some PAHs are used in the production of pharmaceuticals, organic dyes and pigments, plastics, pesticides, explosives, insulating materials, and pipe and storage tank lining materials. Petroleum products containing PAHs include gasoline, kerosene, diesel fuel, some heating oils and motor oil. Phenanthrene, chrysene and anthracene, which are refined from coal-derived chemicals, are the main PAHs of commercial significance. Many PAHs are used as reagents in organic syntheses (ATSDR, 1989; Eisler, 1987; Archer et al., 1979; Guerin, 1978).

PAHs are widely distributed in the environment and have been detected in animal and plant tissues, sediments, soils, air, surface water, groundwater and industrial effluents. Most PAHs do not occur alone in the environment, but rather are found as mixtures of two or more PAHs. The most extensively studied compound, benzo(a)pyrene (BaP), generally constitutes 1-5% of the total detected PAHs for any specific sample.

Most direct releases of PAHs to the environment are to the atmosphere, the primary source being incomplete combustion of wood and fossil fuels (NRC, 1983; Perwak et al., 1982). Background levels of PAHs in the air typically are 0.02-1.2 ng/m^3 in rural areas, compared with 0.15-19.3 ng/m^3 in urban areas (ATSDR, 1989). Estimates in the early 1970s suggested that approximately 2,000 tons of BaP were emitted into the U.S. atmosphere each year (NAS, 1972).

Unsubstituted PAHs and their alkyl substituted homologs are distributed widely in soils and aquatic environments (Andelman and Snodgrass, 1974; Harrison et al., 1976). PAHs enter surface waters primarily from wet and dry atmospheric deposition, but also may occur in industrial effluents, municipal wastewater discharge, urban storm water runoff, oil spills and erosion of contaminated soil (ATSDR, 1989; Landrum et al., 1987; Knutzen, 1987; Bulman et al., 1987). Typical rain water PAH content is 0.1-10 µg/L. In pristine areas, surface water, groundwater and seawater generally contain less than 0.1 µg/L total PAHs (Knutzen, 1987). PAHs have been found in some drinking water supplies in the U.S., with background levels typically ranging from 4-24 ng/L (ATSDR, 1989).

Aquatic sediment PAH concentrations span several orders of magnitude from polluted to remote areas. Background levels in aerobic sediments typically contain less than 0.2-0.5 mg/kg dry weight, while anaerobic sediments tend to contain higher levels (Knutzen, 1987).

Concentrations of BaP in clean regions of Poland ranged mostly from 2 to about 30 µg/kg and seldom exceeded 70 µg/kg (Górski and Górska, 1980; Maslowski, 1981; Dutkiewicz, 1988; Dziewiêcka et al., 1993).

Mammalian and human health effects

In the two centuries since PAHs were first associated with cancer in chimney sweeps in 1775 (Eisler, 1987), they have been the subject of numerous investigations resulting in a massive amount of literature dealing with PAHs absorption, metabolism and distribution, as well as acute and chronic health effects, especially carcinogenesis. Of the hundreds of identified PAH compounds, BaP, a potent carcinogen, is the most widely researched. The health effects of

PAHs as a group have traditionally been based primarily on the effects of BaP, though an increasing body of information suggests that BaP is among the most toxic of the PAHs.

PAHs can be taken into the mammalian body by inhalation, skin contact, or ingestion, although they typically are poorly absorbed from the gastrointestinal tract (Eisler, 1987). PAHs are readily absorbed by inhalation of PAH vapors or from PAHs attached to dust and other particles. Exposure from soil may occur in areas where coal, wood, gasoline and other products have been burned.

Tissue distribution and accumulation of PAHs have not been studied in humans. However, predominantly from rodent studies, it is known that once absorbed, these compounds are distributed to a wide variety of tissues. Because PAHs are hydrophobic, they can readily cross cell membranes and become concentrated in those organs with a high lipid content (Enzminger and Ahlert, 1987; Williams and Burson, 1985). PAHs tend to concentrate initially in the liver and kidney, where they are quickly metabolized into products that can be excreted via bile and urine, and eventually are deposited in organs containing or surrounded by fat such as the mammary glands and adrenals. Within these sites, the presence of PAHs can be detected at low levels for long periods of time (Zedeck, 1980). However, numerous studies show that despite their high lipid solubility, PAHs show little tendency for long-term bioaccumulation in the fatty tissues of animals or man (Lee et al., 1972; Ahokas et al., 1975). This observation is not unexpected in light of convincing evidence that PAHs are rapidly and extensively metabolized (ATSDR, 1989; Eisler, 1987).

BaP orally administered to rats at a dosage of 0.004 mg/kg was distributed primarily to the protein fractions of the liver, lung and kidney, with concentrations gradually increasing with time (Yamazaki et al., 1987). In contrast, the lipid fractions of these tissues accounted for 70% of the administered dose at three hours, but subsequently decreased rapidly. The nucleic acid fraction maintained approximately 10% of the administered dose throughout the experiment. The authors concluded that protein binding of BaP in the lung and kidney may contribute to the cytotoxicity, mutagenicity and carcinogenicity of BaP and its metabolites, since these organs have low metabolic activity while the liver has high detoxification potential and can expedite the excretion of these toxic products.

Orally administered benzo(a)anthracene and chrysene also are distributed rapidly and widely in the rat (Bartosek et al., 1984). Maximum concentrations in well-perfused tissues like the liver, blood and brain were achieved within 1-2 hours after administration.

PAH metabolism has been studied extensively *in vitro* and *in vivo*, primarily in the rat liver microsomal fraction, as well as in cells and cultured tissues from other animals and humans (ATSDR, 1989).

Since, in many cases, humans are exposed to mixtures of PAHs, such as in automobile exhaust and cigarette smoke, rather than to individual agents, the total biologic effect clearly will depend on the composition and concentration of each PAH in the source of exposure. Exposure to PAH mixtures may result in synergism or inhibition (i.e., toxicity of mixtures that is more or less than additive) of the expected response in comparison to a single PAH (Zedeck, 1980). In fact, many chemicals are known to modify the action of carcinogenic PAHs in experimental animals,

including other PAHs that are weakly carcinogenic or noncarcinogenic. For example, benzo(a)anthracene, a weak carcinogen, when applied simultaneously with dibenzo(a,h)anthracene, inhibited the carcinogenic action of the latter in mouse skin. A similar case is made for benzo(a)pyrene or dibenz(a,h)anthracene applied to mouse skin prior to initiation with 7,12-dimethylbenzo(a)anthracene or 3-methylcholanthrene (DiGiovanni and Slaga, 1981). Other PAH combinations are cocarcinogenic, such as benzo(e)pyrene, pyrene, and fluoranthene when applied repeatedly with BaP to mouse skin (DiGiovanni and Slaga, 1981). Effective inhibitors of PAH-induced tumor development include natural or added constituents of foods such as flavenoids, selenium, vitamins A, C and E, phenolic antioxidants, and additives like BHT and BHA (Eisler, 1987; Williams and Burson, 1985).

There is no direct information available concerning PAH excretion processes in humans. Animal studies show that the main routes of elimination of PAHs and their metabolites are the hepatobiliary system and the gastrointestinal tract (Sims and Overcash, 1983).

Absorption and elimination of BaP from rat and mouse lungs is very rapid. Eighty-five percent of a single intratracheal instillation of 2.5 mg/kg BaP was cleared from the lungs of a mouse after 24 hours (Schnizlien et al., 1987). In the rat lung, 40% of a BaP dose was cleared within five minutes, and greater than 94% was cleared within six hours (Weyand and Bevan, 1986).

Generally, acute PAH toxicity occurs only with very high doses, making acute systemic toxicity, which is observable in some animal tests, an unlikely occurrence in humans (Williams and Burson, 1985). Non-cancer adverse health effects associated with PAH exposure have been observed in animals, but with the exception of adverse hematological and dermal effects, generally not in humans (ATSDR, 1989).

There have been no reports of death in humans following exposure to PAHs. The intraperitoneal LD_{50} in mice for phenanthrene, pyrene, anthracene, chrysene and BaP is 700, 680, >430, >320, and 250 mg/kg body weight, respectively (Gerarde, 1960; Salamone et al., 1981).

It has been suggested that PAHs may contribute to the pathogenesis of atherosclerosis in humans. Arterial smooth muscle cell proliferation, collagen synthesis, lipid accumulation and cellular necrosis all are involved in the pathogenesis of atherosclerosis. *In vitro* studies conducted using bovine, rabbit and human arterial smooth muscle cells demonstrated that BaP affects some of these processes (Stavenow and Pessah-Rasmussen, 1988).

Anthracene has been associated with gastrointestinal toxicity in humans. Humans that consumed laxatives containing anthracene for prolonged periods were found to have an increased incidence (73.4%) of melanosis of the colon and rectum in comparison to those who did not consume anthracene-containing laxatives (26.6%; Badiali et al., 1985). Given the selectivity of PAHs for rapidly proliferating tissues such as gastrointestinal mucosa, oral exposure to PAHs by humans could lead to adverse gastrointestinal effects (ATSDR, 1989).

Adverse hematological effects also have been observed in humans and animals following PAH exposure. Hematopoietic toxicity was observed in humans with primary liver cancer or metastatic breast cancer who were treated intermittently with anthracene-containing chemotherapeutics by intravenous injection for nine weeks. Myelosuppression, represented by

cumulative leukopenia and thrombocytopenia, was the primary effect observed (Falkson et al., 1985).

No adverse hepatic effects explicitly attributable to PAHs have been reported in humans. However, hepatic effects have been observed in animals after short-term oral, intraperitoneal, or subcutaneous administration of various PAHs. These effects include the induction of preneoplastic cells in the liver, an increase in liver weight and stimulation of hepatic regeneration (Gershbein, 1975; Robinson et al., 1975; Shubik and Porta, 1957). More serious effects indicative of hepatic injury also have been observed in animals. An acute intraperitoneal injection of phenanthrene to rats resulted in liver congestion with a distinct lobular pattern and alterations in serum chemistry (Yoshikawa et al., 1987). Dibenzo(a,h)anthracene injected subcutaneously weekly for 40 weeks and pyrene incorporated in the diet were associated with pale, soft and enlarged livers that showed evidence of fatty degeneration and iron deposition (Hoch-Ligeti, 1941; White and White, 1939).

It has been acknowledged that the skin is susceptible to PAH-induced toxicity in humans and in animals. Regressive verrucae were reported following subchronic application of BaP to human skin. BaP application also apparently exacerbated the severity of skin lesions in patients with pre-existing skin conditions (*pemphigus vulgaris* and *xeroderma pigmentosum*) (Cottini and Mazone, 1939). Workers exposed to substances that contain PAHs may experience chronic dermatitis and hyperkeratosis (ATSDR, 1989).

No adverse effects on the lymphoid system associated with PAH exposure have been reported in humans, but several accounts of lymphoid toxicity in animals are available. As noted previously, a single intraperitoneal injection of BaP to mice resulted in a small spleen with marked cellular depletion, prominent and edematous trabeculae and large lymphocytes (Shubik and Porta, 1957).

There are reports of immunotoxicity of PAHs following dermal, intraperitoneal and subcutaneous injection in animals, but immunotoxicity associated with PAH exposure has not been observed in humans.

No information was found regarding the short- or long-term neurotoxic effects of PAH exposure in humans or animals. However, studies of acute, intermediate or chronic duration which have been conducted in animals indicate that none of the tested PAHs show evidence of neurotoxicity (ATSDR, 1989).

No studies were located regarding reproductive effects in humans or animals following dermal exposure to PAHs. PAHs or their metabolites can pass transplacentally to the fetus and can also be delivered via the mammary gland to the newborn animal (Rossi and Neff, 1978; Enzminger and Ahlert, 1987). The placental transfer of BaP following oral and intravenous exposure of dams has been demonstrated in mice (Shendrikova et al., 1974), and in rats following intratracheal administration (Srivastava et al., 1986). Oral exposure of pregnant mice to BaP produced resorptions and fetal malformation (Legraverend et al., 1984) and decreased fertility and total sterility in F1 mouse progeny (Mackenzie and Angevine, 1981). Intraperitoneal injection of BaP to pregnant mice produced stillbirths, resorptions and malformations (Shum et al., 1979). Testicular changes in males included atrophy of seminiferous tubules with lack of spermatids and spermatozoa. Adverse effects observed following subcutaneous injection of BaP included

increased fetal resorptions in rats (Wolfe and Bryan, 1939) and lung tumor induction in mice (Nikonova, 1977).

Other PAHs, such as anthracene, benzo(a)anthracene, chrysene and dibenzo(a,h)anthracene, have been tested for developmental effects via parenteral routes. Of these compounds, only dibenzo(a,h)anthracene produced fetolethal effects in rats (Wolfe and Bryan, 1939), while chrysene produced liver tumors in mouse progeny (Grover et al., 1975). Teratogenic effects were not observed.

Results of *in vitro* and *in vivo* studies indicate that several PAHs have genotoxic potential at sufficient concentration or dosage and that a mammalian metabolic activation system is necessary for activation in most cases. BaP is genotoxic in a large number and a wide variety of assays. Several types of cultured human tissue cells demonstrated positive results for BaP-induced genotoxicity, as evidenced by the induction of chromosomal aberrations, sister chromatic exchange and binding of BaP to DNA. BaP also produced several different types of genotoxic effects (e.g., DNA binding and damage, sister chromatid exchange, chromosomal aberrations and cell transformation) in non-human *in vitro* systems, in bacterial systems and in mammalian cell culture (ATSDR, 1989).

The results of *in vivo* studies indicate that BaP produces many of the same types of genotoxic effects observed in *in vitro* studies in intact mice, rats and hamsters. BaP induces genotoxic effects in both somatic and germ cells of intact exposed animals; however, it is not known whether BaP is capable of producing these effects in human germ cells (ATSDR, 1989).

Both benzo(a)anthracene and dibenzo(a,h)anthracene exhibited mutagenic potential (Barfknecht et al., 1982; Rocchi et al., 1980) and produced DNA damage in cultured cells (Martin et al., 1978). A preponderance of test results in non-human systems also were positive for genotoxic potential.

The evidence implicating PAHs as inducers of precancerous and cancerous lesions is strong, and this class of substances has been suggested to represent a significant contributor to the observed progressive increase in cancer rates reported for industrialized nations (Cooke and Dennis, 1984). Several PAHs have been shown to produce tumors in skin and in most epithelial tissues of practically all animal species tested; malignancies may be induced by acute exposures to microgram quantities.

Oral Reference Doses (RfDs) have been established by the U.S. EPA for six PAHs (U.S. EPA, 1992a; U.S. EPA, 1993):

PAH	RfD
acenaphthene	6.0E-02 mg/kg/day
anthracene	3.0E-01 mg/kg/day
fluoranthene	4.0E-02 mg/kg/day
fluorene	4.0E-02 mg/kg/day
naphthalene	4.0E-02 mg/kg/day
pyrene	3.0E-02 mg/kg/day

The oral RfD of 4.0E-02 mg/kg/day for naphthalene as cited in U.S. EPA (1992a) currently is under review (U.S. EPA, 1993).

Numerous carcinogenicity studies have been carried out on many of the different PAHs using various test animals and routes of exposure. Most PAHs are found in the environment as mixtures of two or more PAHs. It has been common practice to estimate the carcinogenic risk of complex mixtures of PAHs by assuming that all carcinogenic PAHs are equivalent in potency to BaP. This practice has little scientific support, and ICF (1987) developed an alternate method for estimating the cancer risk associated with exposure to mixtures of PAHs. ICF (1987) proposed the use of a relative potency approach that takes into account the differing potencies of carcinogenic PAHs and, therefore, should yield a more realistic estimate of risk.

This approach recently has been proposed by U.S. EPA in the following manner regarding relative potency (U.S. EPA, 1992c):

PAH	Relative Potency	Oral Carcinogenic Slope Factor	Inhalation Slope Factor
Benzo(a)pyrene	1.0	7.3 $(mg/kg/day)^{-1}$	6.1 $(mg/kg/day)^{-1}$
Benzo(a)anthracene	0.1	0.73 $(mg/kg/day)^{-1}$	0.61 $(mg/kg/day)^{-1}$
Benzo(b)fluoranthene	0.1	0.73 $(mg/kg/day)^{-1}$	0.61 $(mg/kg/day)^{-1}$
Benzo(k)fluoranthene	0.01	0.073 $(mg/kg/day)^{-1}$	0.061 $(mg/kg/day)^{-1}$
Chrysene	0.001	0.0073 $(mg/kg/day)^{-1}$	0.0061 $(mg/kg/day)^{-1}$
Dibenzo(a,h)anthracene	1.0	7.3 $(mg/kg/day)^{-1}$	6.1$(mg/kg/day)^{-1}$
Indeno(1,2,3-c,d)pyrene	0.1	0.73 $(mg/kg/day)^{-1}$	0.61 $(mg/kg/day)^{-1}$

The carcinogenicity of the PAHs has been investigated by all three major routes of exposure: inhalation, oral and dermal. The chronic study of Thyssen et al. (1981) provides clear cut evidence of a dose-response relationship between inhaled BaP particles and respiratory tract

tumorigenesis in hamsters. Respiratory tract tumors were induced in the nasal cavity, pharynx, larynx and trachea. Tumors also were observed in the esophagus and forestomach, presumably as a consequence of mucociliary clearance and subsequent ingestion of the particles. These tumor types consisted of papillomas, papillary polyps and squamous cell carcinomas (Thyssen et al., 1981).

A relationship between the ingestion of BaP and the development of benign and malignant tumors has been documented in several mouse studies (Hartwell, 1951; Klein, 1963; Shubik and Hartwell, 1957; Thompson, 1971; Tracor-Jitco, 1973a; Tracor-Jitco, 1973b). Acute and intermittent intragastric doses of BaP also have been shown to elicit pulmonary adenomas and forestomach papillomas in mice (Sparnins et al., 1986; Wattenburg and Bueding, 1986; Wattenburg and Leong, 1970). Mice fed BaP in the diet exhibited gastric neoplasms, in the study which is now used by the U.S. EPA to estimate BaP cancer risk (Neal and Rigdon, 1967). Hamsters also have been observed to develop papillomas and carcinomas of the alimentary tract in response to gavage or dietary exposure to BaP (Chu and Malmgrem, 1965). Huggins and Yang (1962) induced mammary tumors in rats with a single large oral dose of BaP. McCormick (1981) also reported an increased incidence of mammary tumors after a single oral dose of BaP in rats.

Mixtures of PAHs that included BaP were shown to be dermal carcinogens as early as 1918 (Yamagiwa and Ichikawa, 1918). Many studies have reported a dose-dependent relationship between dermal BaP application and the development of skin tumors, including skin papillomas and squamous cell carcinomas (Cavalieri et al., 1988; Shubik and Porta, 1957; Wynder and Hoffman, 1959a; Habs et al., 1984; Warshawsky and Barkley, 1987).

Papillomas and carcinomas were observed by Wynder and Hoffman (1959b) after the dermal application of benzo(b)fluoranthene to mice. Habs et al. (1980) also found that dermal application of benzo(b)fluoranthene produced a significant carcinogenic response. Dermal application of chrysene to the backs of mice resulted in an increased incidence of papillomas and carcinomas (Hecht et al. 1974; Wynder and Hoffman, 1959a).

Toxicity to aquatic species

PAHs vary substantially in their toxicity to aquatic organisms. In general, significant acute toxicity from PAHs in water is limited to two and three ring compounds and their methylated derivatives at relatively high concentrations.

Toxicity is most pronounced among crustaceans and least pronounced among teleost fishes. In all but a few cases, concentrations of PAHs that are acutely toxic to aquatic organisms are several orders of magnitude higher than concentrations found in even the most heavily polluted waters, excepting circumstances of oil spills. Sediments from polluted regions, however, may contain PAH concentrations similar to those which are acutely toxic, but their limited bioavailability apparently renders them substantially less toxic than PAHs in aqueous solution (Neff, 1979).

It was demonstrated that anthracene is acutely toxic (100% mortality; Landrum et al., 1987) to juvenile bluegill sunfish at 12 µg/L in less than nine hours, presumably through generation of photoproducts. This toxicity is more than 400 times greater than the previously reported no-

effect concentrations for the parent compound. *Daphnia pulex* are more sensitive (LT_{50} = 13 min at 1.2 µg/L).

Many reports exist of high incidences of cancer-like growths and developmental anomalies in natural populations of aquatic biota in areas of high sediment concentrations of PAHs (Eisler, 1987). The induction of cancer by exposure of aquatic animals to environmentally realistic levels of carcinogenic PAHs in the water column, diet or sediments has not been convincingly demonstrated (Neff, 1982).

Most studies on fish and mussels indicate that relatively high concentrations are needed to produce adverse effects on growth or reproduction from PAHs. However, a variety of histopathological and physiological responses have been observed, especially in mussels, after injection of PAHs or exposure via food. Concentrations as low as 2 µg/L naphthalene in water resulted in gill hyperplasia. Concentrations as low as 24 µg/L BaP resulted in reduced hatching of fish eggs and various morphological abnormalities (Winkler et al., 1983). In copepods, a total concentration of about 10 µg/L naphthalene and its methylated derivatives caused reduced lifespan and reproduction (Knutzen, 1987).

In many cases, aquatic organisms from PAH-contaminated environments have a higher incidence of tumors and hyperplastic diseases than those from unpolluted environments. An unusually high prevalence of oral, dermal and hepatic neoplasms has been observed in bottom-dwelling fish from heavily polluted sediments containing elevated PAH levels (Couch and Harshbarger, 1985). Abnormalities including cataracts, skin lesions and abnormal fin shapes have been observed in fishes inhabiting waters with highly PAH-contaminated sediments (Bender et al., 1988).

Teratogenic or carcinogenic responses have been induced in sponges, planarians, echinoderm larvae, teleosts, amphibians and aquatic plants by exposure to carcinogenic PAHs (Neff, 1979; Neff, 1982). Tumors and tumor precursors have been observed in flatworms, amphibians and fish after various types of exposure to carcinogenic PAHs (Knutzen, 1987). Concentrations as low as 0.5 µg/L BaP for 48 hours resulted in chromosome damage and abnormal cell division in embryos of sea urchins (Hose et al., 1983). Increased chromosomal aberrations in the common mussel after exposure to 5-10 µg/L BaP have been reported (Al-Sabti and Kurelec, 1985).

Hepatic microsomes of fish are capable of transforming PAHs into mutagenic metabolites. The covalent binding of BaP metabolites to macromolecules has been demonstrated in the laboratory with copepods (Reichert et al., 1985) and fish (Knutzen, 1987). Damage to DNA in the liver of mosquito fish after exposure to 100 µg/L BaP has been reported (Batel et al., 1985). However, coexistence of a mixture of PAHs, which is the usual situation, may suppress formation of hazardous metabolites due to competitive inhibition from non-carcinogenic PAHs for the enzyme sites effecting transformation of PAHs to the hazardous intermediates (Knutzen, 1987).

Although many individual PAHs have shown effects on growth and cell division in the 1-100 µg/L range in individual cultures, consequences on the community level have been difficult to demonstrate due partly to the difficulty in isolating PAH effects from those of other pollutants at the same locality.

The U.S. EPA Ambient Water Quality Criteria or Lowest Effect Concentration (LEC) values for protection of freshwater and marine aquatic organisms based on acute toxicity are as follows (U.S. EPA, 1993):

PAH	Freshwater	Marine
Acenaphthene	Not Found	Not Found
Acenaphthalene	Not Found	300 µg/L (LEC)
Anthracene	Not Found	300 µg/L (LEC)
Benzo(a)anthracene	Not Found	300 µg/L (LEC)
Benzo(b)fluoranthene	Not Found	300 µg/L (LEC)
Benzo(k)fluoranthene	Not Found	Not Found
Benzo(g,h,i)perylene	Not Found	300 µg/L (LEC)
Benzo(a)pyrene	Not Found	300 µg/L (LEC)
Chrysene	Not Found	300 µg/L (LEC)
Dibenzo(a,h)anthracene	Not Found	300 µg/L (LEC)
Fluoranthene	4,000 µg/L	40 µg/L (LEC)
Fluorene	Not Found	300 µg/L (LEC)
Indeno(1,2,3-cd)pyrene	Not Found	300 µg/L (LEC)
Phenanthrene	30 µg/L	7.7 µg/L (LEC)
Pyrene	Not Found	300 µg/L (LEC)

Although listed under the heading of Water Quality Criteria by the U.S. EPA, a discussion of many of these values by U.S. EPA (1993) indicates that the values noted as LEC are the lowest effective concentration found in the literature. These LEC values are not criteria, but are given when the minimum data to derive water quality criteria are not available.

Additionally, chronic criteria are available for fluoranthene (16 µg/L for marine aquatic species) and phenanthrene (6.3 µg/L for freshwater aquatic species; 4.6 µg/L for marine aquatic species; U.S. EPA, 1993).

Summary of applicable regulatory guidelines

Polish guidelines values for polycyclic aromatic hydrocarbons in soil and groundwater during remediation processes are presented in Table III-1.

Risk Characterization

Introduction

This section summarizes the contribution by the major constituents from among the selected indicator chemicals to the calculated risks in surface soils and groundwater for the sludge lagoon at the CZOR site.

Risks from exposure to surface soils

Potential noncarcinogenic risks

A summary of the 95% upper confidence limit concentrations for indicator chemicals in the sludge lagoon surface soils is presented in Table V-1. Table V-2 and Table V-3 present intake and risk values for the oral, dermal and inhalation routes of exposure along with RfD values for Scenario I and II, respectively.

· oral exposure

The expression describing potential exposure to surface soils by ingestion is presented in Figure III-1. Substituting appropriate values into that expression for the noncarcinogenic indicator chemicals yields results as summarized in Table V-2 for Scenario I and in Table V-3 for Scenario II. The oral HI value under an assumption of the 95% upper confidence limit for surface soils concentration is 6.8E-02 for Scenario I (Table V-2) and 3.5E-03 for Scenario II (Table V-3) .

· dermal exposure

The expression describing potential exposure to surface soils by dermal contact is presented in Figure III-2. Substituting appropriate values into that expression for the noncarcinogenic indicator chemicals yields results as summarized in Table V-2 for Scenario I and in Table V-3 for Scenario II. The dermal HI value under an assumption of the 95% upper confidence limit for surface soils concentration is 5.9E-03 for Scenario I (Table V-2) and 4.2E-04 for Scenario II (Table V-3).

· inhalation exposure

The expression describing potential exposure to surface soil particulates by inhalation is presented in Figure III-3. Substituting appropriate values into that expression for the noncarcinogenic indicator chemicals in surface soil particulates yields results as summarized in Table V-2 for Scenario I and in Table V-3 for Scenario II. The inhalation HI value under an assumption of the 95% upper confidence limit for surface soils concentration is 7.1E-02 for Scenario I (Table V-2) and 1.2E-02 for Scenario II (Table V-3).

· summary

With respect to the U.S. EPA guidelines regarding acceptable noncarcinogenic exposure (i.e., that the Hazard Index value should not exceed 1.0), surface soils in the sludge lagoon in the CZOR site are judged to not represent a potential noncarcinogenic risk under Scenario I and Scenario II, based on available sampling data. This conclusion is based on fact that the aggregate HI value for

surface soils is 1.4E-01 for Scenario I (Table V-2) and 1.6E-02 for Scenario II (Table V-3) for 95% UCL concentrations.

Potential carcinogenic risks

Table V-2 and Table V-3 present intake and potential carcinogenic risk values for the oral, dermal and inhalation routes of exposure along with CPF values for Scenario I and II, respectively.

· oral exposure

The expression describing potential exposure to surface soils by ingestion is presented in Figure III-1. Substituting appropriate values into that expression for the potentially carcinogenic indicator chemicals in surface soils yields results as summarized in Table V-2 for Scenario I and in Table V-3 for Scenario II. The product of the estimated intake and CPF describes calculation of the potential carcinogenic risk by ingestion. Potential Carcinogenic Risk from ingestion exposure to surface soils under an assumption of the 95% upper confidence limit for surface soils concentration is 6.4E-07 and 2.5E-06 for Scenario I and Scenario II, respectively. Benzo(a)pyrene and arsenic are the main contributors to oral carcinogenic risk in both scenarios.

· dermal exposure

The expression describing potential exposure to surface soils by dermal contact is presented in Figure III-2. Substituting appropriate values into that expression for the potentially carcinogenic indicator chemicals in surface soils yields results as summarized in Table V-2 for Scenario I and in Table V-3 for Scenario II. The product of the estimated intake and CPF describes calculation of the dermal potential carcinogenic risk. Potential Carcinogenic Risk from dermal exposure to surface soils under an assumption of the 95% upper confidence limit for surface soils concentration is 2.2E-07 and 1.2E-06 for Scenario I and Scenario II, respectively. Benzo(a)pyrene is the main contributor to dermal carcinogenic risk in both scenarios.

· inhalation exposure

The expression describing potential exposure to surface soil particulates by inhalation is presented in Figure III-3. Substituting appropriate values into that expression for the potentially carcinogenic indicator chemicals in surface soil particulates yields results as summarized in Table V-2 for Scenario I and in Table V-3 for Scenario II. The product of the estimated intake and CPF describes calculation of the inhalation potential carcinogenic risk. Potential Carcinogenic Risk from inhalation exposure to surface soil contaminants under an assumption of the 95% upper confidence limit for surface soils concentration is 5.3E-09 and 7.7E-08 for Scenario I and Scenario II, respectively. Benzene and benzo(a)pyrene are the main contributors to inhalation carcinogenic risk in the both scenarios.

· summary

With respect to typical conservative guidelines regarding acceptable risks (e.g., range 1E-05 to 1E-06), surface soils in the sludge lagoon at the CZOR site pose a limited potential carcinogenic risk under Scenario II. This conclusion is based on the fact that the potential combined risk for surface soils under the assumption of 95% UCL concentrations is 3.7E-06 (Table V-3). The main portion of this risk is contributed by potential oral exposure to benzo(a)pyrene in surface soils.

The potential combined risk under assumptions of Scenario I is 8.6E-07 (Table V-2) and does not exceed the 1E-06 point-of-departure.

Risks from exposure to groundwater

Potential noncarcinogenic risks

A summary of the 95% upper confidence limit concentrations for indicator chemicals in the sludge lagoon groundwater is presented in Table V-4. Table V-5 and Table V-6 present intake and risk values for the oral, dermal and inhalation routes of exposure along with RfD values for Scenario I and III, respectively.

· oral exposure

The expression describing potential exposure to groundwater by ingestion is presented in Figure III-4. Substituting appropriate values into that expression for the noncarcinogenic indicator chemicals yields results as summarized in Table V-5 for Scenario I and in Table V-6 for Scenario III. The oral HI value under an assumption of the 95% upper confidence limit for groundwater concentration is 6.2E-04 for Scenario I (Table V-5) and 6.2E-04 for Scenario III (Table V-6).

· dermal exposure

The expression describing potential exposure to groundwater by dermal contact is presented in Figure III-5. Substituting appropriate values into that expression for the noncarcinogenic indicator chemicals yields results as summarized in Table V-5 for Scenario I and in Table V-6 for Scenario III. The dermal HI value under an assumption of the 95% upper confidence limit for groundwater concentration is 2.9E-02 for Scenario I (Table V-5) and 9.8E-03 for Scenario III (Table V-6).

· inhalation exposure

The expression describing potential exposure to groundwater by inhalation is presented in Figure III-6. Substituting appropriate values into that expression for the noncarcinogenic indicator chemicals in groundwater yields results as summarized in Table V-5 for Scenario I and in Table V-6 for Scenario III. The inhalation HI value under an assumption of the 95% upper confidence limit for the groundwater is 1.6E-01 for Scenario I (Table V-5) and 1.4E-01 for Scenario III (Table V-6).

· summary

With respect to the U.S. EPA guidelines regarding acceptable noncarcinogenic exposure (i.e., that the Hazard Index value should not exceed 1.0), groundwater in the CZOR site are judged to not represent a potential noncarcinogenic risk under Scenario I and Scenario III, based on available sampling data. This conclusion is based on fact that the aggregate HI value for groundwater is 1.9E-01 for Scenario I (Table V-5) and 1.5E-01 for Scenario III (Table V-6) for 95% UCL concentrations.

Potential carcinogenic risks

Table V-5 and Table V-6 present intake and potential carcinogenic risk values for the oral, dermal and inhalation routes of exposure along with CPF values for Scenario I and III, respectively.

· oral exposure

The expression describing potential exposure to groundwater by ingestion is presented in Figure III-5. Substituting appropriate values into that expression for the potentially carcinogenic indicator chemicals in surface soils yields results as summarized in Table V-5 for Scenario I and in Table V-6 for Scenario III. The product of the estimated intake and CPF describes calculation of the ingestion potential carcinogenic risk. Potential Carcinogenic Risk from ingestion exposure to groundwater under an assumption of the 95% upper confidence limit for groundwater concentration is 9.3E-09 and 6.9E-07 for Scenario I and Scenario III, respectively. Benzene is the main contributor to oral carcinogenic risk in the both scenarios.

· dermal exposure

The expression describing potential exposure to groundwater by dermal contact is presented in Figure III-6. Substituting appropriate values into that expression for the potentially carcinogenic indicator chemicals in groundwater yields results as summarized in Table V-5 for Scenario I and in Table V-6 for Scenario III. The product of the estimated intake and CPF describes calculation of the dermal potential carcinogenic risk. Potential Carcinogenic Risk from dermal exposure to groundwater under an assumption of the 95% upper confidence limit for groundwater concentration is 1.7E-07 and 4.3E-06 for Scenario I and Scenario III, respectively. Benzene is the main contributor to dermal carcinogenic risk in the both scenarios.

· inhalation exposure

The expression describing potential exposure to groundwater by inhalation is presented in Figure III-7. Substituting appropriate values into that expression for the potentially carcinogenic indicator chemicals in groundwater yields results as summarized in Table V-5 for Scenario I and in Table V-6 for Scenario III. The product of the estimated intake and CPF describes calculation of the inhalation potential carcinogenic risk. Potential Carcinogenic Risk from inhalation exposure to groundwater under an assumption of the 95% upper confidence limit for groundwater concentration is 3.8E-08 and 2.4E-06 for Scenario I and Scenario III, respectively. Benzene is the main contributor to inhalation carcinogenic risk in the both scenarios.

· summary

With respect to typical conservative guidelines regarding acceptable risks (e.g., range 1E-05 to 1E-06), groundwater at the CZOR site is judged to represent a limited potential carcinogenic risk under Scenario III, based on available sampling data. This conclusion is based on the fact that the aggregate potential risk for groundwater under the assumption of 95% UCL concentrations is 7.4E-06 (Table V-6) for Scenario III. The main portion of this risk is contributed by potential dermal and inhalation exposure to benzene in groundwater. The potential combined risk under assumption of Scenario I is 2.2E-07 (Table V-5) and does not exceed the 1E-06 point-of-departure.

Proposed Risk-Based Concentrations (RBCs)

Introduction

Risk-based concentrations were calculated for the purpose of guiding remediation activities at the CZOR sludge lagoon site. This section describes proposed RBCs of all indicator chemicals for individual environmental media, based on specific exposure scenarios and exposure assumptions, as discussed in Section III. The expressions describing the RBCs calculations have been provided in detail, so that other assumptions may be employed in the calculations if appropriate.

Calculation of Risk-based concentrations (RBCs) for soils

Risk-based concentrations for surface soils at the CZOR sludge lagoon site were calculated for potential combined exposure by oral, dermal and inhalation routes. A summary of the expressions and the assumptions which were employed in the development of RBCs for soils is presented in Figure III-1, Figure III-2 and Figure III-3.

The RBCs were calculated for each noncarcinogenic indicator chemical in order to achieve circumstances where the combined Hazard Indices for each route of exposure would not exceed a Hazard Index of 1.0. The RBC equation for soils was derived as follows:

$$\textbf{Hazard Index (HI; 1.0)} = CI/RfD_0 + AD/RfD_d + PI/RfD_i$$

or:

$$1.0 = [(CS \times EF \times ED \times FC \times IR_0 \times CF_1)/ BW \times AT \times RfD_0)] + [(CS \times EF \times ED \times FC \times SA \times AF \times DA \times CF_1)/ BW \times AT \times RfD_d)] + [(CS \times EF \times ED \times FC \times IR_i \times (1/PEF + 1/VF)/ BW \times AT \times RfD_i)]$$

The equation was then rearranged to solve for the appropriate contaminant concentration in soils (CS equivalent to the RBC):

$$CS = BW \times AT / EF \times ED \times FC \times (A + B + C)$$

where:

$$A = 1/RfD_0 \times IR_0 \times CF_1$$

$$B = 1/RfD_d \times SA \times AF \times DA \times CF_1$$

$$C = 1/RfD_i \times IR_i \times (1/PEF + 1/VF)$$

The terms RfD_0, RfD_d, and RfD_i represent the oral, dermal and inhalation RfD values, respectively.

The RBC equation for potential noncarcinogenic effects, based on oral, dermal and inhalation exposure to chemicals in soil as well as the assumptions regarding oral, dermal and inhalation exposure to site surface soils for Scenarios I and II are presented in Figure VI-1, VI-2 and VI-3, respectively. Figure VI-4 presents RBC equation based on combined oral, dermal and inhalation exposure to chemicals in soil. Table VI-1 and Table VI-2 summarize the proposed RBCs for the

selected noncarcinogenic indicator chemicals in surface soils for Scenario I and Scenario II, respectively.

For carcinogenic indicator chemicals, Risk-specific Dose (RsD) values (i.e., 1E-06/CPF) were employed in place of the RfD values. Thus, for carcinogenic chemicals the following equation was used for RBC calculation:

$$\mathbf{RBC = 1E\text{-}06 \times BW \times AT / EF \times ED \times FC \times (A + B + C)}$$

where:

$$\mathbf{A = CSF_0 \times IR_0 \times CF_1}$$

$$\mathbf{B = CSF_d \times SA \times AF \times DA \times CF_1}$$

$$\mathbf{C = CSF_i \times IR_i \times (1/PEF + 1/VF)}$$

The RBC equation for potential carcinogenic effects, based on oral, dermal and inhalation exposure to chemicals in soil as well as the assumptions regarding oral, dermal and inhalation exposure to site surface soils for Scenarios I and II are presented in Figure VI-1, VI-2 and VI-3, respectively. Figure VI-4 presents RBC equation based on combined oral, dermal and inhalation exposure to chemicals in soil. Table VI-1 and Table VI-2 summarize the proposed RBCs for the selected carcinogenic indicator chemicals in surface soils for Scenario I and Scenario II, respectively.

Based on a comparison with the RBCs which were calculated using the direct exposure assumptions cited, the concentrations of indicator contaminants which were detected in surface soils at the sludge lagoon of the CZOR site represent a potentially limited health risk to humans under specific present conditions. This conclusion is based on the fact that the mean and maximum detected concentrations of benzo(a)pyrene exceed the calculated RBCs for surface soils for Scenario II (Industrial). In addition, under the Scenario II, the maximum detected concentration of benzo(b)fluoranthene and arsenic exceed the calculated RBCs for surface soils. The maximum detected concentration of benzo(a)pyrene exceed the calculated RBCs for surface soils under the Scenario I (Construction /Remediation).

<u>Calculation of Risk-based concentrations (RBCs) for groundwater</u>

Risk-based concentrations for groundwater at the CZOR sludge lagoon site were calculated for potential combined exposure by oral, dermal and inhalation routes. A summary of the expressions and the assumptions, which were employed in the development of RBCs for soils, is presented in Figure III-4, Figure III-5 and Figure III-6.

The RBCs were calculated for each noncarcinogenic indicator chemical in order to achieve circumstances where the combined Hazard Indices for each route of exposure would not exceed a Hazard Index of 1.0. The RBC equation for groundwater was derived as follows:

$$\textbf{Hazard Index (HI; 1.0)} = CI/RfD_0 + AD/RfD_d + PI/RfD_i$$

or:

$$1.0 = [(CW \times EF \times ED \times FC \times IR_0)/ BW \times AT \times RfD_0)] + [(CW \times EF \times ED \times FC \times ET \times SA \times PC \times CF_1)/ BW \times AT \times RfD_d)] + [(CW \times EF \times ED \times FC \times ET \times CF_2 \times IR_i \times (1/GW_v)/ BW \times AT \times RfD_i)]$$

The equation was then rearranged to solve for the appropriate contaminant concentration in groundwater (CW equivalent to the RBC):

$$CW = BW \times AT / EF \times ED \times FC \times (A + B + C)$$

where:

$$A = 1/RfD_0 \times IR_0$$

$$B = 1/RfD_d \times ET \times SA \times PC \times CF_1$$

$$C = 1/RfD_i \times ET \times CF_2 \times IR_i \times (1/GW_v)$$

The terms RfD_0, RfD_d, and RfD_i represent the oral, dermal and inhalation RfD values, respectively.

The RBC equation for potential noncarcinogenic effects, based on oral, dermal and inhalation exposure to chemicals in soil as well as the assumptions regarding oral, dermal and inhalation exposure to site groundwater for Scenarios I and III are presented in Figure VI-5, VI-6 and VI-7, respectively. Figure VI-8 presents RBC equation based on combined oral, dermal and inhalation exposure to chemicals in groundwater. Table VI-3 summarizes the proposed RBCs for the selected noncarcinogenic indicator chemicals in groundwater.

For carcinogenic indicator chemicals Risk-specific Dose (RsD) values (i.e., 1E-06/CPF) were employed in place of the RfD values. Thus, for carcinogenic chemicals the following equation was used for RBC calculation:

$$RBC = 1E\text{-}06 \times BW \times AT /EF \times ED \times FC \times (A + B + C)$$

where:

$$A = CSF_0 \times IR_0$$

$$B = CSF_d \times ET \times SA \times PC \times CF_1$$

$$C = CSF_0 \times ET \times CF_2 \times IR_i \times (1/GW_v)$$

The RBC equation for potential carcinogenic effects, based on oral, dermal and inhalation exposure to chemicals in groundwater as well as the assumptions regarding oral, dermal and inhalation exposure to site groundwater for Scenarios I and III are presented in Figure VI-5, VI-6 and VI-7, respectively. Figure VI-8 presents RBC equation based on combined oral, dermal and

inhalation exposure to chemicals in groundwater. Table VI-3 summarizes the proposed RBCs for the selected carcinogenic indicator chemicals in groundwater.

Based on a comparison with the RBCs which were calculated using the direct exposure assumptions cited, the concentrations of indicator contaminants which were detected in groundwater at the sludge lagoon of the CZOR site represent a potentially limited health risk to humans under specific present or future conditions. This conclusion is based on the fact that the mean and maximum detected concentrations of benzene exceed the calculated RBCs for groundwater for Scenario III (Irrigation). In addition, under the Scenario III, the maximum detected concentration of benzo(a)pyrene and indeno(1,2,3-cd)pyrene exceeds the calculated RBCs for groundwater at the 1E-06 risk level. Under the Scenario I (Construction/Remediation) the maximum detected concentration of benzene exceeds the calculated RBCs for groundwater.

Summary

The risk assessment process is a part of the project conducted at the CZOR in Czechowice-Dziedzice, Poland. The project is coordinated and conducted by the joint team consisting of representatives of: the U.S. Department of Energy (DOE), the Ames Laboratory (Ames), the Westinghouse Savannah River Company (WSRC), the Florida State University (FSU), and the Institute for Ecology of Industrial Areas (IETU) in Katowice, Poland.

The risk assessment process is an integral part of the remedial investigation/feasibility study, conducted at the contaminated sites in the U.S. Risk assessment is designed to evaluate the potential for adverse effects on humans and the environment from existing conditions, and to establish health-based remediation goals for appropriate environmental media (e.g., soils, groundwater).

The CZOR was selected as the demonstration site for this project. The CZOR is situated in the southern part of the Katowice Province, Poland, approximately 45 km from the City of Katowice. The Refinery is located in a small town, where land uses include residential, recreational, agricultural and industrial.

The Refinery is about 100 years old. It uses catalytic cracking process to refine crude oil. Waste after acid refinery process historically has been disposed in the lagoons. Waste product in the lagoons is a viscous semi-liquid hydrocarbon mixture, which is not completely characterized.

Risk assessment, performed as a part of the CZOR Project, is based on the U.S. experiences in this field. The procedure, which was used for this risk assessment, encompasses the following areas:

- site characterization;
- selection of indicator chemicals;
- toxicity assessment for carcinogenic and non-carcinogenic substances;
- human exposure assessment under site-specific exposure scenarios;
- risk characterization; and
- development of remedial goals.

The first step - *Site Characterization* - was performed by the Ames Laboratory and their IETU counterparts. It was conducted using the Expedited Site Characterization (ESC) System, which is an innovative approach to site characterization that integrates data from several disciplines to provide more efficient and cost-effective results. During the site characterization historical information, data on: geography and local land use, geology, hydrology and ecology were gathered. Characterization mainly focused on groundwater and soil affected by refinery activities in the vicinity of petroleum waste lagoons. Field data were collected and analyzed, moreover vertical/horizontal extent of contaminants was determined. Data collection and evaluation involved also gathering and analyzing the site data relevant to the human health evaluation and identification the substances present at the site that are the focus of the risk assessment process.

In addition, toxicological data needs and the regulatory requirements for remediation activity were identified.

The second step was the *Selection of Indicator Analytes,* which are representatives of the toxicity and environmental behaviors of contaminants at the site. Indicator analytes are selected as an initial step in a site-specific risk assessment in order to focus the assessment activities on those compounds that are judged to pose the most significant potential risks based on their inherent toxicity. For the CZOR site benzene, ethylbenzene, toluene, xylenes (BETX), six polycyclic aromatic hydrocarbons (PAHs) and nine heavy metals were gathered. For these chemicals information on environmental occurrence, physical/chemical properties, fate and transport in the environment (e.g., biodegradation, evaporation, and hydrolysis) were gathered.

The next step in the risk assessment process is the *Toxicity Assessment*. This step evaluates toxicity and potential adverse effects of the chemicals of concern. Toxicity assessment is based on available scientific data on adverse effects in humans and nonhuman species (e.g., mammalian and human health effects, toxicity to aquatic species). Toxicological characteristics of each chemical of concern included identification of important measures of toxicity, i.e., reference doses to evaluate non-carcinogenic effects and slope factors for carcinogens.

The next step of the risk assessment process is the *Exposure Assessment*. Exposure assessment includes: determination of exposure scenarios, determination of factors associated with each scenario (e.g., exposure frequency, exposure duration, life expectancy, inhalation rate, etc.), and collection of data to support each factor. Exposure scenarios are based on standard U.S. exposure considerations and are modified to reflect conditions unique to the CZOR site. For the purposes of this risk assessment surface soils and groundwater in the sludge lagoon at the CZOR were evaluated with regard to the potential risks that they may pose to humans. Ingestion, inhalation and dermal exposure routes were considered. The CZOR site is currently classified as industrial and land use of the site is not expected to change in the future. For the defined land use category, for the purposes of estimating contaminant intakes at the site, the following three exposure scenarios were developed for the CZOR lagoon site:

- **Scenario I** (Adult, On-site Future Construction/Remediation): occupational exposures to adults who may be exposed to surface soils and groundwater at the sludge lagoon at the CZOR site during potential construction or remediation activities. Exposure to soil was assumed to occur for 250 days/year for 0.33 years of a 70 year lifetime;
- **Scenario II** (Adult, Industrial): occupational exposure to adults who may be exposed to surface soils during their work-related activities at the sludge lagoon site (50 days/year for 25 years of a 70 year lifetime); and,
- **Scenario III** (Adult, On-site Groundwater, Future Irrigation): exposure to adults who may be exposed to site groundwater on a daily basis (25 days/year; 1 hr/day) for a period of 25 years of 70-year lifetime.

The next step is the *Risk Characterization,* which combines toxicity assessment with exposure assessment in order to quantify risks posed by a contaminated site under a given set of conditions. Risk characterization is considered separately for carcinogenic and non-carcinogenic

effects and includes the accompanying uncertainties. Potential noncarcinogenic risks for exposures at the CZOR site were evaluated by comparison of the estimated contaminant intakes with the U.S. EPA Reference Dose (RfD). The estimated carcinogenic risks were compared with the risk of 1E-06, used as conservative point-of-departure for carcinogenic risk. Surface soils in the sludge lagoon at the CZOR site pose a limited potential carcinogenic risk under Industrial Scenario (3.7E-06). The main portion of this risk is contributed by potential oral exposure to benzo(a)pyrene in surface soils. Groundwater at the CZOR site is judged to represent a limited potential carcinogenic risk under the Irrigation Scenario (7.4E-06). The main portion of this risk is contributed by potential dermal and inhalation exposure to benzene in groundwater.

Media-specific RBCs were calculated for each indicator chemical in soil and groundwater at the sludge lagoon at the CZOR for the purposes of guiding remediation activities. RBCs were calculated for combined oral, dermal and inhalation exposure to chemicals. The calculated RBCs were compared with the concentrations of indicator contaminants that were detected in surface soils and groundwater at the sludge lagoon of the CZOR site. The mean detected concentration of benzo(a)pyrene exceeds the calculated RBCs for surface soils under Industrial Scenario. The mean detected concentration of benzene exceeds the calculated RBCs for groundwater under Irrigation Scenario.

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Chapter 4

Treatability Studies

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Treatability Studies

Introduction

Determining and demonstrating the ability of an environment to be biostimulated or bioaugmented to effect the remediation of a contaminant is critical to the successful application of bioremediation. Treatability studies need to determine the 1) biodegradability or biotransformability of the contaminants both anaerobically and aerobically, 2) effectiveness of the proposed amendments, 3) compatibility of the proposed amendment additions with the soil and groundwater matrix at the site, 4) abiotic losses, (e.g., volatilization, sorption, leaching) and 5) final toxicity of the environmental material (USEPA, 1989). All of these determinations will require collection of a large number of representative field samples. Field sample collection is critical to validate the process chosen and may require aseptic and anoxic sampling techniques for terrestrial subsurface sediments and immediate access to laboratory facilities. A number of treatability study protocols have been published by EPA for different types of contaminants and environmental conditions (USEPA, 1989). The reactor, flask, pan, or soil column chosen for the treatability study must mimic in so far as possible the environmental conditions of the site. They must also be of sufficient size to minimize "bottle effect" and sub-sampling errors. The systems used must also provide simultaneous testing of positive (inoculated), negative (sterile), and no-treatment controls of the treatability protocol (Nelson et al., 1994). The types of systems chosen will be largely dependent on the historical data and process knowledge from the site, and the initial characterization. In addition, the contaminants at the site may have been "weathered", (i.e., exposed to leaching, low level biodegradation or biotransformation, and soil chemical reactions for extended periods of time), resulting in a contaminant chemical composition that is quite unique. These problems have contributed greatly to the unreliability of treatability studies to predict bioremediation in the field (Nelson et al., 1994).

Measurements of degradation kinetics are also critical to accurate prediction of the amendments needed, their concentrations, rate of application and time necessary to reach the clean-up goals for the site. These measurements can be made indirectly by modeling the mass balance through time, by direct measurement of enzyme activities or organism density changes in the reaction vessel, or by real-time measurements of terminal electron acceptor concentrations. This last technique has been increasing in popularity in recent years, especially when less volatile contaminants are being considered and the desired effect is complete mineralization. These measurements are made with micro-respirometers which can measure very small changes in carbon dioxide, oxygen, and methane in reaction vessels in real-time (Pietro et al., 1992). This allows calculations of respiration rates for controls and amendments and, if appropriate controls can be done, a calculation of the rate of carbon dioxide or methane production from the contaminant (Hazen, 1997).

Data from the expedited site characterization phase of the project indicated that the refinery soils and surface waters were low in nitrogen and available phosphorous. Water and soil samples were collected from the process waste lagoons and transferred to the IETU for microcosm studies which were to compare aeration (water samples only), nutrient addition and buffering. These laboratory investigations were used to examine parameters necessary for the optimal biodegradation of material originating from the refinery process waste lagoons.

Materials and Methods

Microcosm Set Up

Two different types of petroleum contaminated soils (humic and clay containing soils), soil with high leaf litter content (leaf litter) and water samples from and adjacent to the process waste lagoons were collected from the Czechowice Oil Refinery in Czechowice-Dziedzice, Poland and transported at 4°C to the IETU in Katowice, Poland. Water samples containing petroleum (1 L) were placed into six separate stirred tank reactors (Virtis, New Jersey, USA). A control was set up in which the water sample was not aerated. Formaldehyde (1.5% v/v) was added to another reactor containing petroleum contaminated water and served as a killed aerated control. In the other four aerated reactors, varying concentrations phosphorous and nitrogen were added using a stock salt solution containing NO_3, NH_4, and PO_4. Leaf litter and soil samples (70 g) were placed into 500 mL screw cap Erlenmeyer flasks. Soil and leaf litter microcosms were amended with dolomite ($CaMgSO_4$) and compost in a ratio of 7:2:1. Formaldehyde (14 %v/w) was added to amended soil and leaf litter microcosms for killed controls. All microcosm experiments, water, soil and leaf litter were incubated at room temperature for three weeks. All experiments were performed in triplicate.

Chemical Analysis

Soil BTEX- 3 g of the soil material was collected from the columns and transferred to a 20 ml preweighed crimped vial with a teflon-lined septa containing 6 ml deionized water Supelco, Poland). During transport and storage vials were kept at 4°C upside down. In the lab, vials were weighed to calculate the exact amount of collected soil sample. Before analyses, samples were equilibrated by heating vials at 90°C in a water bath for 2 hours. Every 10 minutes, vials were shaken. BTEX standards were prepared in a similar manner; using a crimp vial with 6 ml of deionized water. An equivalent volume of BTEX standard was injected through the septum with a syringe. Five standards were used during the calibration of gas chromatograph. 100 µL of headspace phase was removed with a gas tight syringe from the vial and injected into a gas chromatograph. No noticeable changes in the response were seen after 3 - 4 injections from a vial. Determination of BTEX was done with a Varian 3400CX chromatograph and a SATURN3 GC/MS (USA) equipped with SPI injector and capillary column DB-5/MS, (ID = 0.25 mm, thickness of the stationary phase 0.25µm, 30 m long). The parameters of the GC run were as follows: collected mass 50 - 150; ion trap temperature 170°C; transfer line temperature 200°C; and injector temperature 200°C. The oven was heated to 45°C and held for 18 minutes isothermally, ramped from 45 - 150°C at a rate of 20 °C/min for 5.25 minutes, and then held at 150°C for 6.75 minutes isothermally. The results of BTEX determination in soil samples are expressed in µg/kg of fresh (wet) weight. Relative Standard Deviation was determined for blank samples spiked with BTEX at 0.1µg/kg each (Varian, 1989).

BTEX in Water- Water (6 ml aliquot) was collected from the bioreactors into 20 ml crimp vials. The subsequent procedures were the same as those for determination of BTEX in soil samples above. The results of BTEX determination in water samples were expressed in µg/L.

Soil TPH - The extraction procedure of soil samples was based on procedure 5520 C, "Partition-Infrared Method" (APHA, 1992) with some modifications. 2 - 5 g of fresh soil sample is mixed with anhydrous sodium sulfate at a ratio 1: 1.5 v/v. The content was quantitatively transferred to a paper thimble and extracted in a Soxhlet apparatus for 4 h with carbon tetrachloride. The

volume of the extract was adjusted to 25 ml for low concentration or 100 ml for a high concentration of TPH in soil material. The absorbance was measured and the obtained result was the sum of TPH itself and of some interfering polar substances, and was expressed in g/kg of fresh soil weight. The second measurement was done after removing the polar substances with Florisil and the results are given as g of TPH/kg of fresh soil weight.

TPH in Water- Water samples were fixed with hydrochloric acid 1:1 (v/v) at pH = 2. The sample (50 ml aliquot) was shaken with 25 ml of carbon tetrachloride and after discarding water the organic layer was dried over anhydrous sodium sulfate. The drying medium was removed by passing through a glass filter. The absorbance of the sample is measured twice (as in TPH determination in soil) before and after removing of the polar interfering substances and result are given in mg/L of TPH and polar substances and in mg TPH/L respectively.

Soil preparation for determination of nitrate, nitrite, phosphate, and ammonium-The method was based on ISO 14256 (Soil quality - Determination of nitrate, nitrite and ammonium in field moist soils using potassium chloride as extractant). The field moist soil was extracted in polyethylene bottles with 1M KCl at a 1:5 ratio on a shaker for 1 h. After filtration through cellulose filter paper (0.45µm pore diameter), supernatant was used for measurement of nitrate, nitrite, ammonium and phosphates.

Nitrite-The nitrite was measured according to ISO 14256 colorimetrically in extracts directly by forming diazo compounds through reaction with Griess-Ilosvay reagent. The absorbance of this product was measured at a wavelength of 543 nm.

Sum of nitrate and nitrite-After reduction of nitrate in the column filled with cadmium catalyst, the sum of the original nitrite and that formed from nitrate was determined colorimetrically. The content of nitrate was calculated from the difference between nitrite concentration after and before the reduction process. The final result was a mean value from replicate determination that should differ no more than 10%.

Ammonium-Ammonium was determined according to PN-76/C-04576/01 "Water and waste water tests for nitrogen: Determination of ammonium nitrogen by colorimetric indophenol blue method". Ammonium in extract forms at high pH and in the presence of hypochlorite ions monochloramine, which reacts with phenol to form an indophenol blue complex. The absorbance of this complex was measured at a wavelength of 630 nm. The final result was a mean value from replicate determination that should differ no more than 10%.

Phosphates-Phosphate determination in soil extract was performed according to ISO 14256. Phosphate was reacted to form an antimony-phosphate-molybdate complex which was reduced with ascorbic acid to produce a deep colored blue complex. The absorbance was measured at 880 nm for 30 min after color development.

Total KJELDAHL Nitrogen in Soil- 1 g of fresh soil was digested in Büchi 426 Digestion Unit (Büchi, Switzerland) with 10 ml of concentrated sulfuric acid, 0.5 g catalyst mixture (1:2:74 w/w metallic selenium: copper sulphate: potassium sulphate) until a clear solution was obtained. The resulting ammonium was distilled in Büchi Distillation Unit B-323 (Büchi, Switzerland) into 25 ml of absorption solution 0.1 M hydrochloric acid with Taschiro indicator. The absorbed ammonium was titrated with 0.1M sodium hydroxide solution. The final result was given in mg of nitrogen for 1 kg of fresh soil sample. The final result was a mean value from two parallel determinations which should differ no more than 100 mg/kg. Determination was done in

accordance with BN-90/9103-10 "Determination of nitrogen content in compost made from municipal wastes".

Microbial activity- Microbial activity was measured by oxygen uptake using an Orion model 830 O_2 meter (Orion, Germany) and CO_2 production was measured using NaOH trapping and titration.

Microbial identification- Microbial strains were identified by plating on selective media and presumptively identified microscopically (Zeiss Axioscope, Germany). A mineral salts agar supplemented with petroleum vapors incubated in a dessicator was used to isolate bacteria capable of degrading petroleum. Fungi and yeasts were isolated using Sabouraud agar. Microorganisms were stained with FITC (bacteria) or Calcafluor White (fungi) to facilitate microscopic identification (Sparkes, et al., 1994). Yeasts were identified by morphology microscopically.

Results

Water Microcosms

The contaminated water samples were assayed in the IETU laboratories. The pH of the water was found to be 2.69. Total BTEX concentrations were 2.1mg/L, while TPH levels were 5.93 mg/L. The dissolved oxygen concentration in the aerated water microcosm was 7.4 mg O_2/L, while that of the unaerated water microcosm was approximately 5.5 mg O_2/L. In the water microcosm studies that were incubated in the stirred tank reactors, CO_2 production ranged between 2.71-7.6 mg CO_2/L/hr and oxygen uptake was measured between 0.024-0.104 mg O_2/L/hr. During the course of this study, the pH in both aerated and unaerated waters increased from 2.69 to pH 4.00. TPH and BTEX reduction after three weeks in the N and P amended waters were found to be over 80% and 78% respectively. A 10% to 25% addition of the N and P containing stock solution was found to optimize TPH and BTEX degradation in contaminated surface water. During the experiment abundant growth of *Clonothrix sp*., a filamentous iron oxidizing bacteria, and algae (species not identified) was noted in the unamended nonaerated microcosm. However in the aerated and amended contaminated surface waters the prevalent microbial genera was found to be composed of motile gram-negative rod bacteria and yeasts. No microorganisms were seen in the killed controls.

Soil and Leaf Litter Microcosms

The highest TPH concentration was measured in the leaf litter soil while the highest BTEX concentrations were seen in clay soils. Clay soil and leaf litter soil were found to be extremely acidic while the humic soils were found to be circumneutral (Table 4.1). Soil humidity was between 21-34%. The amendment of the leaf litter soil, humic soil and clay with dolomite and compost elevated the final pH of the microcosms to 6.9, 7.4, and 6.7, respectively. This effect has been in part attributed to the buffering effect of the dolomite. It was determined that 60% of the measured CO_2 recovered was a result of the reaction of the acidic soils with the dolomite. The highest microbially generated CO_2 was measured to be 40 µl CO_2/ g soil/h in the microcosm containing the amended clay soil. This may be attributed to the addition of nutrients (compost), buffering (dolomite) and modification of the soil structure (compost and dolomite). Alternatively, this may have occurred because the petroleum in the clay was strongly sorbed and was not as weathered (recalcitrant) as the petroleum in the other samples. This later hypothesis is further suggested by the much higher TPH concentrations in the clay. Microbial populations in the

amended soils were found to be composed of bacteria and fungi and some yeast. In the amended leaf litter, fungal populations were found to predominate. However, lower numbers of microorganisms were measured in the unamended microcosms. No viable microorganisms were seen in the killed controls. The highest levels of BTEX and TPH reduction were seen in the amended clay microcosm. As seen earlier, this was also the microcosm set that demonstrated the greatest microbial diversity and activity.

Summary

The microcosm studies were used to determine the biodegradative potential of contaminated soils, leaf litter and surface waters from or adjacent to the process waste lagoons. It was determined that when the pH of the microcosms were near neutrality (dolomite or bacterial metabolites) and they were supplemented with nutrients (compost or N and P), indigenous microorganisms could be stimulated for optimal biodegradation of BTEX and TPH. These data support the use of bioremediation, via stimulation of indigenous microorganisms, for the treatment of the acidic process waste at the Czechowice Oil Refinery.

References for Methods Used in Treatability Studies

DETERMINATION OF PAHs IN SOIL SAMPLES

ISO 11464 Soil quality - Pretreatment of samples for physico-chemical analyses.

ISO/FDIS 13877:1998 Soil quality - Determination of polynuclear aromatic hydrocarbons - Method using high-performance liquid chromatography

DETERMINATION OF PAHs IN WATER SAMPLES

J.T. Baker's Application Note ENV 103 Extraction of PAHs from water samples using a double phase SPE column

Disposition nr 7 of the Central Inspector of Environmental Protection Introducing a method of PAHs content measurement in water and waste water, PIOS (Poland) 1993

DETERMINATION OF TPH IN WATER SAMPLES

PN-82/C-04564.01 Water and wastewater; Tests for petroleum and its components. Determination of non-polar aliphatic hydrocarbons by infra-red spectrophotometry

DETERMINATION OF TPH IN SOIL SAMPLES

Method 5520 E Extraction method for sludge samples, pp 5-28 - 5-29 from Standard Methods for the Examination of Water and Wastewater 18th Edition, American Public Health Association 1992

PN-V-04007 Soil protection - Tests for petroleum and ists components content. Determination of non-polar aliphatic hydrocarbons by infra-red spectrophotometry

DETERMINATION OF COD IN LEACHATE

PN-74/C-04578.03 Water and waste water. Tests for chemical oxygen demand and organic carbon content. Determination of chemical oxygen demand (COD) by dichromate method

DETERMINATION of the NITRATE, NITRITE, PHOSPHATES and AMMONIUM IN SOIL

ISO 11464 Soil quality - Pretreatment of samples for physico-chemical analyses

ISO 14256 Soil quality - Determination of nitrate, nitrite and ammonium in field moist soils using potassium chloride as extractant

PN-76/C-04576.01 Water and waste water. Tests for nitrogen; Determination of ammonium nitrogen by colorimetric indophenol method

PN-88/C-04537.04 Water and waste water. Tests for content of phosphorus compounds. Determination of dissolved orthophosphates by molybdate colorimetric method with ascorbic acid as reductant

DETERMINATION of the SPECIFIC ELECTRICAL CONDUCTIVITY

ISO 11265 Soil quality - Determination of the specific electrical conductivity

DETERMINATION of the SOIL pH

ISO 10390 Soil quality - Determination of pH

DETERMINATION of TOTAL KJELDAHL NITROGEN in SOIL

BN-90/9103-10 Determination of nitrogen content in compost made from municipal wastes

METHODS of HEAVY METALS DETERMINATION in SOIL

ISO 11464 standard Soil quality - Pretreatment of samples for physico-chemical analyses

ISO 11466 Soil quality - Extraction of trace elements from soils and related materials by aqua regia

As determination VGA-76 Vapor Generation Accessory - Operation Manual pp. 16, Publication No. 85 100577 00 March 1984 Rev. 1: February, 1989 Varian Australia Pty Ltd

Hg determination VGA-76 Vapor Generation Accessory - Operation Manual pp. 16, Publication No. 85 100577 00 March 1984 Rev. 1: February, 1989 Varian Australia Pty Ltd

METHODS of HEAVY METALS DETERMINATION in LEACHATE

EPA Method 3005 Rev. 0 September 1986 Acid digestion of waters for total recoverable or dissolved metals for analysis by FLAA or ICP spectroscopy

EPA Method 6010B Rev. 2 January 1995 Inductively coupled plasma - atomic emission spectroscopy As determination VGA-76 Vapor Generation Accessory - Operation Manual pp. 16, Publication No. 85 100577 00 March 1984 Rev. 1: February, 1989 Varian Australia Pty Ltd

Hg determination VGA-76 Vapor Generation Accessory - Operation Manual pp. 16, Publication No. 85 100577 00 Marc

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Table 4.1 Selected physico-chemical characteristics of water, soils, dolomite and compost used in the treatability study

Material	Water	Litter	Organic Soil	Clay	Dolomite	Compost
TPH[1]	5.93	245	1.34	42.0	0.04	0.12
TPOC[1]	12.7	273	2.9	53.2	0.04	0.12
BTEX[2]	2.7	292	92	1098	17	13
NEE[3]	ND	28.1	0.71	9.98	0.51	0.01
pH	2.69	4.7	6.9	3.0	8.93	6.75

[1] - mg/L or g/kg, [2] - µg/L or µg/kg, [3] - percent, ND - not done.

Chapter 5

Column Studies

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Column Studies

Introduction

Nutrient-limitation or availability of appropriate electron acceptors can hamper natural biodegradative processes at contaminated sites. In laboratory studies, high rates of biodegradation of refinery wastes are often reported. Unfortunately, this is due, in part, to the highly controlled and optimal conditions provided (pH, temperature, nutritional balance, ideal mixing etc.) in these laboratory systems. At many contaminated sites, including the Czechowice Refinery, the problem of varying soil structure, contaminant concentration and type of contaminants make the determination of bioremediation strategies difficult. These heterogeneities also lead to problems with mass transfer of the supply of appropriate nutrients (i.e., phosphate, nitrogen, oxygen, water, etc.). An intermediate step between batch laboratory degradation studies and actual field remediation is the use of soil columns containing contaminated soil from the site of interest. Use of this type of system can provide essential information in determining operational parameters (i.e., fine tuning), for control of engineering and construction of field scale systems to overcome problems with mass transfer and nutrient availability. Furthermore, data obtained from column studies can be applied to biodegradation simulation models that may be used and compared with actual data from field scale studies.

<u>Theory</u>

The stoichiometric relationship used (Manual. Principles and Practices of Bioventing. Volume II: Bioventing Design., EPA/540/R-95/534a, September 1995) to determine petroleum degradation rates is:

$C_6H_{14} + 9.5\ O_2 \rightarrow 6\ CO_2 + 7\ H_2O$

The biodegradation rate in terms of mg hexane-equivalent per kg of soil per day is estimated using the following equation:

$$-k_B = \frac{\frac{-k_o}{100}\theta_a \frac{1L}{1{,}000cm^3}\rho_{o_2}S}{\rho_k\left(\frac{1kg}{1{,}000g}\right)} = \frac{-k_o\theta_a\rho_{O_2}S(0.01)}{\rho_k}$$

where:

k_B = biodegradation rate (mg/kg-day)

k_O = oxygen utilization rate (%/day)

ϑa = gas-filled pore space (volumetric content at the vapor phase, cm^3 gas/cm^3 soil), assumed value: 0.25

ρ_{O2} = density of oxygen (mg/l), assumed value: 1,330 mg/l

S = mass ratio of hydrocarbons to oxygen required for mineralization, assumed in the manual as equal to 0.29

ρ_k = soil bulk density (g/cm^3), assumed value: 1.4 g/cm^3

Taking these values to above equation gives:

$k_B = -\ 0.68\ k_O$

However, the biopile contaminants are not only alkanes but also aromatics with side chains and polyaromatics. Contaminant composition influences the H:C atomic ratio in model particle taken as a representative in calculation of biodegradation rate. It is assumed that H:C ratio in a contaminant is m:n. So the stoichiometric relationship used to estimate the contaminant degradation is:

$$C_nH_m + \left(n + \frac{m}{4}\right)O_2 = nCO_2 + \frac{m}{4}H_2O$$

and mass ratio of the contaminant to oxygen is:

$$S = \frac{12n + m}{\left(n + \frac{m}{4}\right)32} = \frac{1}{8}\left(\frac{12 + \frac{m}{n}}{4 + \frac{m}{n}}\right)$$

As can be seen from the above equation, S depends on H:C atomic ratio only and changes over the whole range of hydrocarbons: for methane (a hydrocarbon richest in hydrogen) S = 0.25 and this is the lowest value for S, whereas for pure carbon S = 0.375 which is the highest possible number for S . These extreme values differ by a factor of 1.5. It is assumed that in a model particle of contaminants, roughly half of the C atoms were in aromatic form (with H:C ratio as 1:1) and the second half in saturated aliphatic form (H:C ratio being 2:1) which gives an overall H:C ratio 1.5:1 and S becomes equal to 0.31. This value will be used in future calculations. The biodegradation rate is estimated using the following relationship:

$k_B = -\ 0.73k_O$

Soil Column Design

<u>Process Optimization for the Biopile Design</u>

The scale of the column experiments as compared to the biopile is approximately 1:1 in depth. Four, 2 meter by 30 cm diameter plexiglass columns filled with contaminated refinery soil were used. In three of the columns, an active ventilation system in which air is injected from the base of the column apparatus, were used. Air flow was controlled with airflow regulator/meters. In the fourth column, a passive air injection system via a Baro-Ball were employed (See Figure 5.1 for schematic of experimental set up). As with the preliminary biopile design, the first 20 cm of the column fill consisted of dolomite aggregate which serves two purposes; diffusion of the injected air (active system only) and as a pH buffering agent. The next 110 cm were composed

of a mixture of contaminated refinery soil and wood chips (10%v/v). The wood chips serve as a bulking agent to improve hydraulic conductivity and act as a moisture sink. The upper most 20 cm were filled with topsoil and possibly seeded with grass. Soil moisture was monitored using a soil moisture testing system with two sensors, one placed near the top and the other placed near the bottom of the column. Leachate water was recirculated to maintain soil moisture and reseeding of pollutant degrading microorganisms. A perforated PVC pipe underneath the topsoil layer supplying leachate minimizes the risk of aerosolization of microorganisms contained in the leachate (detail not shown). Five sampling ports will provide access for measurement of temperature and soil samples for chemical and microbiological examination (see Figure 5.2 for detail of single column and 5.3 for a photograph of the completed column).

Surfactant screening

Three, 2 meter by 30 cm plexiglass columns filled with contaminated refinery soil was used during surfactant screening experiments. Sawmill scrap (wood chips) were mixed 1:10 v/v with the refinery soil to improve structure. Dolomite ($CaMgCO_3$) was used as a natural buffering agent against the acidic leachate. A 20 cm layer of topsoil was laid over the top as cover. In all three of the columns, air was injected from the base of the column apparatus using a Model UN726.1.2 FTP air compressor (KNF Neuberger, Inc., Trenton, New Jersey, USA). Air flow was controlled with airflow regulator/meters (Cole Palmer, USA). Leachate water was recirculated to maintain soil moisture and delivery of surfactant. A piezometer constructed from perforated PVC pipe underneath the topsoil layer was used to supply leachate. Commercially available fertilizer, Polifoska, (Poland) was added as needed.

Experimental Plan

Approach

Soil columns were used to observe *in situ* biodegradation under controlled laboratory conditions to simulate the longitudinal cross-sectional operations of the biopile system. By using a smaller scale, potential design problems were seen and modified and multiple parameters were simultaneously tested. Additionally, optimization of certain operational parameters (e.g. airflow, moisture, hydraulic conductivity and nutrient amendments) was first established with the columns before actual implementation in the field. In this study the following treatments were investigated and their effects on biodegradation elucidated: 1) a comparison between air supply (passive vs. active aeration); 2) nutrient amendments (commercially available fertilizer, triethyl phosphate and ammonium phosphate, or synthetic reagents); and 3) screening the efficacy of two locally available surfactants. Constant measurement of contaminant concentration and microbial numbers and activity demonstrated direct evidence of column performance. Monitoring of column temperature is also useful, since as microbial activity increased, the temperature of the columns also increased. Measurement of soil gas composition was also very important and gave inferential evidence on efficiency of air supply. If methane was detected, increased airflow rates were necessary to overcome anaerobic conditions. Data from initial site characterization and column studies were imported to biodegradation modeling programs and later compared with results from actual biopile operations.

Analytical Methods and Materials

Chemical Analysis

Soil BTEX- 3 g of the soil material were collected from the columns and transferred to a 20 ml preweighed crimped vial with a teflon-lined septa containing 6 ml deionized water Supelco, Poland). During transport and storage vials were kept at 4°C upside down. In the lab, vials were weighed to calculate the exact amount of collected soil sample. Before analyses, samples were equilibrated by heating vials at 90°C in a water bath for 2 hours. Every 10 minutes, vials were shaken. BTEX standards were prepared in a similar manner; using a crimp vial with 6 ml of deionized water. An equivalent volume of BTEX standard was injected through the septum with a syringe. Five standards were used during the calibration of gas chromatograph. 100 µL of headspace phase was removed with a gas tight syringe from the vial and injected into a gas chromatograph. No noticeable changes in the response were seen after 3 - 4 injections from a vial. Determination of BTEX was done with a Varian 3400CX chromatograph and a SATURN3 GC/MS (USA) equipped with SPI injector and capillary column DB-5/MS, (ID = 0.25 mm, thickness of the stationary phase 0.25µm, 30 m long). The parameters of the GC run were as follows: collected mass 50 - 150; ion trap temperature 170°C; transfer line temperature 200°C; and injector temperature 200°C. The oven was heated to 45°C and held for 18 minutes isothermally, ramped from 45 - 150°C at a rate of 20 °C/min for 5.25 minutes, and then held at 150°C for 6.75 minutes isothermally. The results of BTEX determination in soil samples are expressed in µg/kg of fresh (wet) weight. Relative Standard Deviation was determined for blank samples spiked with BTEX at 0.1µg/kg each (Varian, 1989).

Leachate BTEX Leachate (6 ml aliquot) was collected from the columns into 20 ml crimp vials. The procedures that followed were the same as those used during determination of BTEX in soil samples. The results of BTEX determination in water samples were expressed in µg/L.

Soil PAH Soil samples were dried overnight at 40°C and after passing through a 0.25 mm sieve, a 10 g aliquot was extracted in SOXTHERM 2000 Automatic (Gerhardt, Germany) with dichloromethane during 3.5 h. The extract was evaporated to near dryness and was then cleaned and filled with Florisil. 2 µL of cleaned extract is injected on HPLC chromatograph Series 1050 Hewlett-Packard (USA) equipped with a fluorescence detector 1046A Hewlett-Packard (USA) and Bakerbond PAH 16-Plus column (3 mm x 25 cm). The mobile phase was a mixture of methanol and water, and gradient profile was 75% methanol and 25% water during 6 min and then 100% methanol. The changes of excitation and emission wavelengths were programmed and optimized for detection of 6 PAHs. The chromatograph was calibrated with 5 PAH standards. Final results are expressed in mg/kg dry weight.

Leachate PAH The pH of water samples was neutralized (pH = 7) and mixed with 10 % (v/v) of isopropanol. The PAHs were extracted, concentrated and cleaned with a Baker's SPE column filled with modified silica gel (cyanoNU2 or amino silica gel over C18 silica gel layer) and a Baker 12G accessory. PAHs were selectively eluted from SPE column with dichloromethane. Clean extract was injected and treated in the same way as PAH determinations in soil material. Final results are expressed in ng/L.

Sample preparation for TPH measurements Soil and leachate samples were extracted with carbon tetrachloride and interfering substances were removed by passing extract through a column filled with Florisil. The extract was quantitatively measured with an IR

spectrophotometer after calibration with 5 standards. The TPH standard was a mixture of 37.5 % (v/v) n-hexadecane, 37.5 % (v/v) isooctane and 25.0 % (v/v) benzene, and the spectrum was recorded between 3000 and 2800 cm^{-1} range. The absorbance value was measured at 2926 cm^{-1} with the IR spectrophotometer UNICAM SP1000 (UNICAM, UK), a measure of TPH content related to the number of CH_2 groups. A standard mixture was prepared according to PN-82/C-04564.01 "WATER AND WASTEWATER; Tests for Petroleum and its Components. Determination of Non-polar Aliphatic Hydrocarbons by infra-red spectrophotometry"

Soil TPH The extraction procedure of soil samples was based on procedure 3520E "Extraction Method for sludge samples pp 5-28 to 5-79" from "Standard Methods for the Examination of Water and Wastewater 18th Edition" (1992) with some modifications. 2 - 5 g of fresh soil sample were mixed with anhydrous sodium sulfate at a ratio of 1: 1.5 v/v. The contents were quantitatively transferred to a paper thimble and extracted in a Soxhlet apparatus for 4 h with carbon tetrachloride. The volume of the extract was adjusted to 25 ml for low concentrations or 100 ml for high concentrations of TPH in soil material. The absorbance was measured and the obtained result was the sum of TPH itself and the sum of interfering polar substances, and is expressed in g/kg dry weight. The second measurement was done after removing the polar substances with Florisil and the results are given as g of TPH/kg dry weight.

Leachate TPH Leachate samples were fixed with hydrochloric acid 1:1 (v/v) at pH = 2. The sample (50 ml aliquot) was shaken with 25 ml of carbon tetrachloride and after discarding water the organic layer was dried over anhydrous sodium sulfate. The drying medium was removed by passing it through a glass filter. The absorbance of the sample was measured twice (as in TPH determinations for soil) before and after removing the polar interfering substances and the results are reported as mg/L of TPH and polar substances and in mg TPH/L, respectively.

Leachate Chemical Oxygen Demand (COD) Determination of COD was based on PN-74/C-04578.03 based on the dichromate method". 20 ml of determined sample was boiled 10 min under reflux with 0.2 g of mercury sulfate, 10 ml of 0.025N potassium dichromate and 40 ml of concentrated sulfuric acid with dissolved silver sulfate (10 g /L) as a catalyst. Volumes of the sample and sulfuric acid varied depending on the estimated COD values, and the amount of mercury sulfate corresponded with chloride content in the sample. The sample was titrated with ferrous-ammonium sulfate in the presence of 0.025M 1,10-phenanthroline-ferrous sulfate complex solution as an indicator. The result was calculated as mg of oxygen used for oxidation of organic substances per volume of the sample [mg O_2/L]. The final result is a mean value from two parallel determinations, which should differ no more than 10%.

Determination of Nitrate, Nitrite, Phosphates, and Ammonium This method was based on ISO 14256 (Soil quality - Determination of nitrate, nitrite and ammonium in field moist soils using potassium chloride as extractant). The wet soil was extracted in a polyethylene bottle with 1M KCl at a 1:5 ratio on a reciprocating shaker for 1 h. After passing through a dense filter, paper filtrate was used for measurement of nitrate, nitrite, ammonium and phosphates.

Nitrite plus Nitrate Nitrite was measured according to ISO 14256 colorimetrically in extract directly by forming diazo compounds in reaction with Griess-Ilosvay reagent. Its absorbance was measured at a wavelength of 543 nm. After reduction of nitrate in the column filled with cadmium catalyst, the sum of the original nitrite and that formed from nitrate was determined colorimetrically. The content of nitrate was calculated from the difference between nitrite

concentration after and before the reduction process. The final result was a mean value from two parallel determinations, which should differ no more than 10%.

Ammonium Ammonium was determined according to PN-76/C-04576.01 "Water and waste water. Tests for nitrogen; Determination of ammonium nitrogen by colorimetric indophenol method" Ammonium in extract form at high pH and in the presence of hypochlorite ions monochloramine, which reacts with phenol to an indophenol blue complex. The absorbance of the complex was measured at a wavelength of 630 nm. The final result was a mean value from two parallel determinations that should differ no more than 10%.

Phosphates Phosphate determinations in soil extracts were performed according ISO 14256. Phosphate reacted to form an antimony-phosphate-molybdate complex, which was reduced with ascorbic acid to produce a deep-colored blue complex. The absorbance was measured at 880 nm for 30 min after color development. The final result was a mean value from two parallel determinations that should differ no more than 20%.

Total Kjeldahl Nitrogen in Soil 1g of fresh soil was digested in Büchi 426 Digestion Unit (Büchi, Switzerland) with 10 ml of concentrated sulfuric acid, 0.5 g catalyst mixture (1:2:74 w/w metallic selenium : copper sulfate : potassium sulfate) until clear solution was obtained. The formed ammonium was distilled in a Büchi Distillation Unit B-323 (Büchi, Switzerland) into 25 ml of absorption solution 0.1M hydrochloric acid with Taschiro indicator. The absorbed ammonium was titrated with 0.1M sodium hydroxide solution. The final result was given in mg of nitrogen on 1 kg dry weight. The final result was a mean value from two parallel determinations that should differ no more than 100 mg/kg. Determination was done according to BN-90/9103-10 "Determination of nitrogen content in compost made from municipal wastes"

Specific conductance in soil Air-dried soil was extracted in polyethylene bottles with water at a 1:5 ratio on a reciprocating shaker for 30 min. After passing through a dense paper filter the filtrate was used for measurement of the conductivity. The result of the conductivity was temperature corrected at 25°C. The measurements were done with a CX731 conductivity meter (Elmetron, Poland) with a glass cell and temperature compensation probe. The final result was a mean value from two parallel determinations that should differ no more than 10%. These measurements were done in accordance with ISO 11265 "Soil quality - Determination of the specific electrical conductivity".

Soil pH- Air-dry soil was extracted in a polyethylene bottle with water at a 1:5 ratio (v/v) on a reciprocating shaker for 5 min. After at least 2 hours the measurement of pH was repeated. The read-out was done when the reaction varied not more than 0.02 pH unit over a period of five seconds. The measurements were done with CX731 pH-meter (Elmetron, Poland) with a combined electrode and a temperature compensation probe. The same procedure was used for determination of soil pH with 1M potassium chloride and 0.01M calcium chloride as extractant. Determination was done in accordance with ISO 10390 "Soil quality - Determination of pH"

Pretreatment of soil samples for heavy metals analysis The air-dry soil was passed through a 0.25mm (60 mesh) sieve and then 1 g of soil sample was digested with 10 ml of *aqua regia* in a closed pressurized vessel lined with Teflon. Subsequently the 1g aliquot of soil sample was dried for a period of 8 hours in an oven at 105°C for the determination of moisture content. The final result was recalculated on dry weight. The digestion process was controlled with a computerised microwave system MDS 2000 (CEM). The digested sample was quantitatively transferred and filtered to a 50 ml volumetric flask. The final volume was adjusted with deionized water. The

metal content was determined with AAS or ICP spectrometer; Varian SpectrAA 300 or Varian Liberty 220, respectively. The soil was prepared according to ISO 11464 standard "Soil quality - Pretreatment of samples for physico-chemical analyses". The principle of the method was based on ISO 11466 (Soil quality - Extraction of trace elements from soils and related materials by *aqua regia*) with some changes in acid extraction procedure where a closed system was used instead of an open system.

Arsenic was determined with AAS and VGA 76 Vapour Generation Accessory after reduction of As^{V} to As^{III} with KI solution. The hydride was formed in reaction with sodium borohydride (0.6% $NaBH_4$ in 0.5% NaOH).

Mercury was determined with AAS and VGA 76 Vapour Generation Accessory by cold vapour method with stannous chloride (25% $SnCl_2$ in 20% v/v HCl) as a reducing agent. The spectrometer was calibrated with five standards.

Other metals Cadmium, chromium, cobalt, copper, lead, nickel and zinc were determined with ICP spectrometer. The spectrometer was calibrated with four standards.

Leachate heavy metals After homogenization of water samples, a 25 ml aliquot was acidified with 0.25ml of concentrated nitric acid to pH 2. Samples were left standing overnight and then were passed through a dense paper filter (Whatman, USA) prior to metal determination. Such a procedure was used due to the small volume of a leachate, especially during column experiments. The metal content was determined with AAS or ICP spectrometer; Varian SpectrAA 300 or Varian Liberty 220 respectively. Determination of cadmium and lead was done with an ICP spectrometer equipped with ultrasonic nebulizer U-6000AT^{+} Cetac Technologies Inc. (Omaha, USA). The method was based on EPA 3005 (TR, TO) and EPA 6010B (ICP).

QA/QC of heavy metal analysis- During heavy metal determination in soil material, quality control was used in agreement with the Internal Quality Assurance Programme. The QA/QC program encompasses the entire analytical process from beginning to end including the computing of final results. For each batch of samples that were analysed, 20% of the batch was used as QA/QC samples and was verified accordingly. For a given analytical method the blank and matrix spike sample recovery were determined.

Calculation of Critical Micellar Concentration. Critical micelle concentrations (CMC) were measured by dissolving 1ml of each surfactant in 50 ml of de-ionized water. Appropriate dilutions were prepared and their surface tensions measured with a tensiometer (Stalagmeter, University of Silesia, Poland).

Leachate toxicity. Toxicity of leachate originating from the column studies were assessed using:

A. **Inhibition of Filamentous Fungi** (after Ulfig, 1999) Filamentous fungi were cultivated on malt extract agar. Leachate was applied to the surface of the plates and the fungi were inoculated. Average fungal colony diameters were measured and compared to those challenged with leachates

B. ***Daphnia magna*** (18th edition of Standard Methods For the Examination of Water and Wastewater) Wild *Daphnia sp.* were collected from freshwater ponds in Ruda Slaska and cultivated aerated moderately hard reconstituted water (Table 8010 I, Standard Methods) at room temperature. *Daphnia magna* were separated from *Daphnia pulex* and separately cultured. Dehydrated milk powder was supplied as food. Tanks were cleaned weekly and

replenished with fresh reconstituted water. Only young *Daphnia magna* were used in the study. Daphnia magna were tested using 100%, 10%, 1% and 0.1% leachate v/v with reconstituted water. Leachate from the biopile was applied to test organisms. LC_{50}s were calculated graphically via Probit analysis.

C. ***Lemna minor*** (18th edition of Standard Methods For the Examination of Water and Wastewater). *Lemna minor* was collected from the same ponds as the Daphnia. *Lemna* were cultivated in aerated moderately hard reconstituted water supplemented with Duckweed nutrient solution (Table 8211:I, Standard Methods). Toxicity tests were carried out using method 8211 C. *Lemna minor* were tested using 100%, 10%, 1% and 0.1% leachate v/v with reconstituted water. Probit analysis was used to determine LC_{50} values.

Microbiological Analysis

4, 6 Diamindino 2 phenylindole (DAPI) Staining

DAPI provided a direct estimate of the total number of bacteria in the environment, regardless of ability to grow on any media that might be used. Samples were preserved in phosphate buffered formalin. Samples (1 to 3 grams) were extracted three times with a non-ionic homogenizing detergent to remove bacteria from the sediment particles. Homogenates are cleared by low speed centrifugation and the supernatants pooled. Ten microliters of supernatant were spotted onto each well of a toxoplasmosis microscope slide, stained with 0.5 µg/ml DAPI, then rinsed with distilled water. The number of cells stained with DAPI was counted by epifluorescence microscopy. The number of cells per sample was normalized by dividing by the dry weight of the sediment. Counts were reported as cells per gram weight (Kepner and Pratt, 1994). A comparison of acridine orange (AODC) stained samples and DAPI stained samples of soil obtained earlier from the refinery site showed that DAPI gave superior results.

Calcofluor White (CFW) Staining

CFW provided a direct estimate of the total number of fungi in the environment, regardless of ability to grow on any media that might be used. Samples were preserved in phosphate buffered formalin. Samples (1 to 3 grams) were extracted three times with a non-ionic homogenizing detergent to remove bacteria from the sediment particles. Homogenates were cleared by low speed centrifugation and the supernatants pooled. Ten microliters of supernatant were spotted onto each well of a toxoplasmosis microscope slide, stained with Calcofluor White, then rinsed with distilled water. The number of cells stained with CFW was counted by epifluorescence microscopy. The number of cells per sample was normalized by dividing by the dry weight of the sediment. Counts were reported as cells per gram weight.

Naphthalene and Crude Oil Enrichment

This method provided an estimate of the total number of viable microbes capable of living in an enriched naphthalene and crude oil soil. Successful bioremediation of TPH/PAH can also be measured in terms of increased microbial activity, increased biomass; particularly biomass which contains TPH degrading enzymes, increased biomass capable of consuming TPH as evidence of stimulation by treatments. Minimal salts media (MSM) were used (Fogel et al., 1986). The plates for naphthalene were incubated in an enclosed environment with naphthalene vapors available to the bacteria as a source of carbon for metabolism. This count was also in colony forming units per gram dry weight. As naphthalene was the only carbon source available, this

was a count of these degraders only. For crude oil degraders MSM was placed in 96 well microtiter plates. Samples were diluted 10 fold across 8 wells in triplicate and a drop of crude oil placed in each well. After incubation each well was scored for turbidity and oil emulsification to obtain a most probable number (MPN) density per gram dry wt or per ml.

Since the actively aerated parts of the biopile could reach high temperatures due to high rates of biodegradation (composting type conditions), enrichments from the active aeration side were incubated both at 25°C and at 45°C. This ensured that changes in temperature adaptation were documented and that thermophilic degraders were not under estimated.

Microbial Dehydrogenase Activity - TTC

Oxidation of petroleum by microbes, like other types of organic oxidation under aerobic conditions, is linked to the electron transport system (ETS) of the cell. The enzymes of the ETS include a number of dehydrogenases; thus dehydrogenase activity can be used as an overall measure of activity in the soil. Triphenyltetrazolium chloride (TTC) is used as an artificial electron acceptor to estimate dehydrogenase activity since the reduction of TTC to triphenyl formazan (TTF) causes a color change that can be quantified using a spectrophotometer. Soil samples were incubated with TTC (1.5g/100ml) for 24 h. The samples were then extracted with acetone and the extract measured at 546 nm using a spectrophotometer (Alef and Nannipieri, 1995). Values were presented as TPF µg/gdw.

Respiration Rates

Columns were aerated for 24 hrs and sealed with a specially designed gas-tight top from which the piezometer tip protruded. The piezometer also served as a port for sampling soil gases relevant to respiration. When not in use, the port was sealed with a viton septum. Over the course of three days, nine measurements were taken. Respiration rates were calculated from CO_2 production and O_2 uptake as measured by the Landtec landfill gas measurement device (Landfill Technologies, CA USA).

Materials

Surfactants. Surfactants used in all experiments were commercially obtained (Chemical Factory Rokita, Brzeg Dolny, Poland). Rokafenol N-8, a Triton N-102 analogue, and Rokanol L-4, a BRIJ –30 analogue, were chosen for their water solubility, biodegradability and their ability to increase the apparent solubility of the HOCs when their concentrations were above the CMC.

Fertilizers. (Flovit or Polifoska) containing nitrogen as ammonium - 4%, phosphorus as P_2O_5 - 12%, potassium as K_2O - 18%, magnesium as MgO - 7%, calcium as CaO - 10% as well as micro-elements and biologically active substances).

Other Chemicals. Triethyl phosphate was purchased from Eastman Chemical, Rochester, NY, USA). Ammonium nitrate and ammonium phosphate was purchased from Plock Chemicals, Gliwice, Poland.

Results

Nutrient and Aeration Optimization

In three of the columns (A, B and C), an active ventilation system with air up-flow forced by a compressor was used, and in the fourth column a passive air injection system via Baroball™ was employed. At the beginning of the experiment, the air flow rate ~200 ml/min was maintained for 12 hr a day in each of the active columns. Column A and D were fertilized with a commercially available garden fertilizer (Flovit, containing nitrogen as ammonium - 4%, phosphorus as P2O5 - 12%, potassium as K_2O - 18%, magnesium as MgO - 7%, calcium as CaO - 10% as well as micro-elements and biologically active substances), whereas in column B a mixture of NH_4NO_3 and TEP, and in column C a mixture of NH_4NO_3 and $(NH_4)_3PO_4$ were used as sources of nitrogen and phosphorus.

Initially, leachate was recirculated at rate 500 ml per week. 100 ml of water were added weekly to the columns to compensate for evaporation losses. In June, the time in which the compressor was on increased by 8 hr a day to 20 hr a day for each of the active columns, but the flow rate of ~200 ml/min was maintained. Another 100 ml of water was added weekly to the columns to compensate for losses caused by increased temperature and airflow. An additional 200 ml of water per week was added to the column starting in July to compensate losses due to increased ambient temperature. Samples of soil and leachate were taken every other week from each column for microbiological and chemical examination.

During the course of the aeration and nutrient optimization experiments, microbial activity increased over time, generally independent of the form of nutrient addition used. Addition of reagent grade NH_4NO_3 and $(NH_4)_3PO_4$ in column C was found to exhibit the greatest increase in microbial activity (33%) over the commercial fertilizer or TEP and NH_4NO_3. However, the costs of utilizing reagent grade chemicals outweighed the benefits of using locally available commercial fertilizers such as Flovit or Polifoska. These data are summarized in Table 5.1. Microbial activity was found to be lowest in the column passively aerated by the Baroball™.

Shifts in the composition of the microbial community were seen during the column operation. The general trend for the aerated columns was influenced by seasonal changes and also by the bioavailability of the remaining contaminant. Population levels for fungi were inversely proportional to that of the microbial numbers indicating that fungal populations have a competitive disadvantage until the bioavailability of the contaminants becomes limiting (Figure 5.4).

Furthermore, during temperature shifts that were encountered either from effects of seasonal or increased metabolic activity, indigenous populations of soil microorganisms capable of degrading napthalene were not influenced. However, overall populations of petroleum degrading organisms decreased when temperatures were raised from 20°C to 37°C.

However, when comparing temperature, greater microbial numbers of both napthalene and petroleum degraders originating from column leachate were found at 20°C rather than at 37°C. When comparing the data in Figures 5.5 and 5.6, it was determined that the indigenous populations of both napthalene and petroleum degrading organisms with varied temperature optimas were able to compensate and adapt to temperature changes through shifts in population dynamics or other physiological mechanisms.

By nutrient treatment, no great difference was observed in the level of TPH removal as seen in Figure 5.7. However, the total TPH reduction was found to be greater in actively aerated columns than in the passively aerated column under the same nutrient treatment. No difference in BTEX and napthalene removal was seen between both aeration means or nutrient type (Figures 5.8 and 5.9). However, more time was necessary to degrade other PAH by passive aeration than with active aeration.

Respiration tests were conducted to calculate biodegradation rates in the soil columns as a result of the different nutrient application. Although higher biodegradation rates (middle of section) were seen in columns in which reagent grade nutrients were used, changes in the overall contaminant inventory as seen from previous figures remained the same. Biodegradation rates and TPH levels over time indicate decreased availability of readily utilizable substrates. In the top level of the columns, biodegradation rates may reflect the influence of leachate application.

Estimation of the Toxicity of the Leachates by Lemna minor*,* Dapnia magna *and Filamentous Fungi.*

Only juvenile *Daphnia magna* were used in the study. Daphnia magna were tested using 100%, 10%, 1% and 0.1% leachate to screen for toxicity ranges v/v with reconstituted water. Only Daphnia in 100% leachate perished. Results indicated that a tighter concentration grouping was required. Daphnia were challenged with 100%, 75%, 50% 25% and 10% leachate. From the data, the LC_{50} was calculated graphically via Probit analysis to be approximately 37% pure leachate. Similar results were obtained with leachate from the refinery.

Lemna were cultivated in aerated moderately hard reconstituted water supplemented with Duckweed nutrient solution. Toxicity tests were carried out using method 8211 C. *Lemna minor* were tested using 100%, 10%, 1% and 0.1% leachate v/v with reconstituted water. Controls without leachate were performed.

At 100% leachate concentration, yellowing of *Lemna* was seen with minimal frond replication. No difference in reproduction was seen 0.1% as compared to the control. Decreased frond division was seen in 10% and 1% tests. The LC_{50} value for the leachate was found to be approximately 40%. Identical results were seen with refinery leachate. Floating plants, such as *Lemna*, may be more sensitive to hydrophobic materials such as the petroleum based contaminants than other aquatic plants.

Results from the toxicity tests with *Daphnia* and *Lemna* were similar. These data were used to determine the amount of dilution water necessary to be added to the column. A 1:1 dilution of leachate was suggested for use during the column nutrient optimization studies.

The filamentous fungal inhibition studies were carried out during the operation of the columns. The leachate from column B displayed the highest mean inhibition of fungal growth, while the leachate from column C and from the biopile had the lowest mean inhibition values. The TPH concentrations in the leachates were low. Polar compounds (products of the decomposition of petroleum hydrocarbons in soil) predominated in this environment. The highest mean TPOC concentration was observed in the leachate from column B, whereas the lowest was in the leachate from the biopile. TPOC versus inhibition range analysis was performed. For TPOCs lower than 0.2 g/l the mean inhibition of fungal growth was 37.79% with minimal and maximal values 0 and 100%, respectively. For TPOCs over 0.2 g/l the mean inhibition was 99.3% with minimal and maximal values 98.5 and 100%, respectively. The pH values in the leachates from

columns A, B and C ranged between 7.52-8.51. In the leachate from column D the pH range was 7.42-7.95. The pH values in the leachate from the biopile fluctuated between 6.54-7.89. No clear relationship was obtained between the inhibition of fungal growth/biomass production and pH. The mean values of radial growth inhibition and the mean TPH/TPOC concentrations in the leachates are presented in Table 5.2.

Surfactant Screening

Column experiment

The effectiveness of in situ bioremediation in many systems is constrained by low contaminant bioavailability due to limited aqueous solubility or a large magnitude of sorption. The presence of highly weathered hydrocarbon contaminants and the high portion of clay in soil causes the COR biopile to belong to this class of systems. Several attempts have been made to use solubility enhancers such as surfactants, to increase the rates of biodegradation of high molecule hydrocarbons, mostly PAHs. It was shown that surfactants, at certain concentrations, mobilize sorbed contaminants and increase the amount of soluble compounds available for microbial utilization. However, there is not much information in the literature on systems containing wastes from acid refining processes.

The objective of the column experiment was to determine the effects of adding surfactant to such a system with respect to the rate and extent of removal of contaminants.

The experimental system consisted of three parallel, 2 m long, 30 cm diameter Plexiglas columns, filled with contaminated soil from Czechowice Oil Refinery, mixed with wood chips (10% v/v). The scale of the experiment as compared to the biopile was approximately 1:1 in depth.

As with the biopile design, the first 20 cm of each column fill consisted of dolomite aggregate which serves two purposes: diffusion of the injected air and as a pH buffering agent. The next 110 cm was composed of a mixture of contaminated refinery soil and wood chips. The upper most 20 cm was filled with topsoil.

An active ventilation system, where air is injected from the base of the column apparatus, was used. Air was controlled with airflow regulator/meters and kept constant at the level. Three sampling ports (marked 2 for the top, 3 for the middle, and 4 for the bottom of each column) provide access for soil samples for chemical and microbiological examination. Analogous to the biopile soil and leachate, samples from columns were analyzed chemically and microbiologically.

Initial concentration of TPH and PAH in columns are shown in Table 5.3.

Rokanol L-4 and Rokafenol N-8 (counterparts of Triton N 101 and Brij 30 respectively) were chosen as surfactants for the column experiment. Both were produced in “Rokita” Chemical Factory, Brzeg Dolny, Poland.

After a four week initial period of intense watering of columns soil in order to saturate them with surfactant and nutrient solution, leachate circulation rate in columns was reduced.

Column experiment on the effects of surfactant addition to TPH contaminated soil was continued as follows:

Aeration - Air compressor was operated 2 hours on / 2 hours off with a constant air flow

rate of 100ml/min in each column. Total hours with compressor "on" during experiment: 1650.

Leachate circulation - amounts of water, nutrient, and surfactants added to the columns as well as the amount of leachate samples taken are summarized in Table 5.4. A saturated solution of Polifoska (a Polish commercial fertilizer containing 8% of soluble N, and 24% of soluble P_2O_5) was used as a nutrient in the experiment. Samples of soil and leachate were taken every other week *and analyzed for TPH concentration in column soil and TTC microbial activity.* TPH concentrations in the columns are shown in Table 5.5 and Figure 5.7 respectively. Data in Table 5.6 show that after an 8 week adaptation period, microbial activity increased significantly in all three columns. Attempts to correlate TTC data with other parameters including column soil water content, TPH and nutrient concentration in column leachate or rate of TPH removal from column soil were not successful. Also, the cause for distinctively lower microbial activity in column C is not clear so far.

The mean concentration of TPH (in grams per kilogram of dry soil) in soil at the beginning of the column experiment was 209.7 g/kg.

Overall TPH inventory changes in columns are shown in Figure 5.10 and Table 5.5. The plot was made assuming that at starting point TPH concentration throughout all columns was the same and equal to the average calculated above. Other points represent averages from measurements carried out in three levels of each column respectively.

As can be seen from Fig.5.10, there are practically no differences between columns in terms of TPH inventory changes and, consequently, in TPH removal rates. However, when the differences between levels rather than columns were analyzed, it was easily seen that TPH removal rate for level 2 (upper part of columns) was much higher than that for the two other levels (3 - middle and 4 - bottom of columns), see Fig.5.11.

The reason for that can be manifold - migration of contaminants downward of the columns, better aeration due to the vicinity of a more air-permeable layer of top soil, and/or higher microbial activity in the top soil. Most probably, the mechanism of TPH removal in this level differs from that in two other levels and is caused by other factors than the presence of surfactants.

In order to make the probable role of surfactant more distinct, TPH concentration changes in levels 3 and 4 only were compared (Fig.5.12).

In Figure 5.12, the differences between columns (however still not significant) are more distinct. The 20-week average TPH removal rate calculated from rate constants obtained were:

Column A 240 mg/kg day

Column B 320 mg/kg day

Column C 160 mg/kg day

These results can be treated as a suggestion, that in some circumstances, surfactants are able to accelerate the removal of TPH from soil contaminated with weathered petroleum product acid refining sludge.

In order to detect any differences in the removal of PAH and TPH, changes in ratio of PAH to TPH concentrations in column soil with time were analyzed. As the PAH/TPH ratio was constant

over time (see Fig.5.13) it was concluded that PAH and TPH fractions were removed proportionally to their concentrations in the soil.

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Figure 5.1. Schematic Soil Columns Experimental Set-up. Three actively aerated columns and one passively aerated column using BaroBalls™.

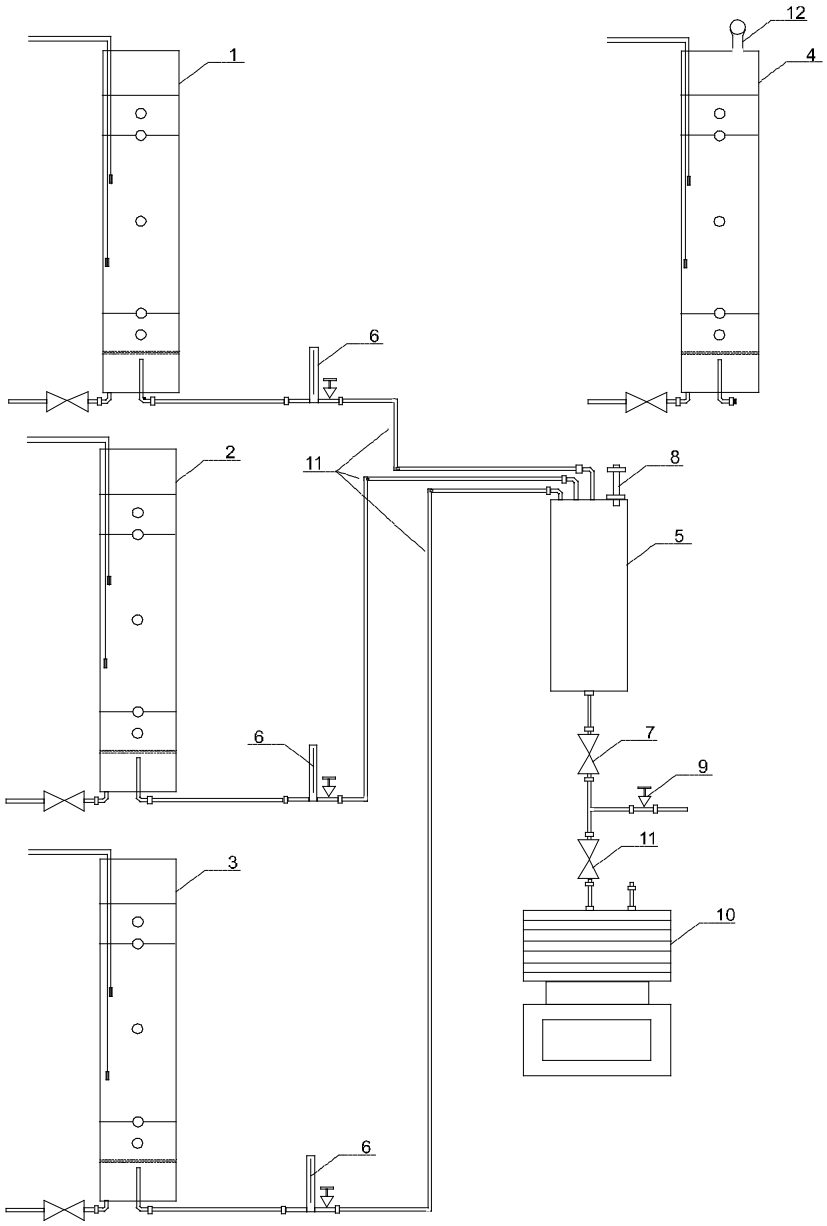


Figure Legend

1-3	Active Column Interrupter
4	Passive Column
5	Pressure Equalization Chamber
6	Air Flow Meters
7	Stop Valve
8	Blow-out Valve
9	Nutrient Amendment Inlet
10	Air Pump
11	Backflow
12	Baro-ball

Figure 5.2. Individual Column Set-up

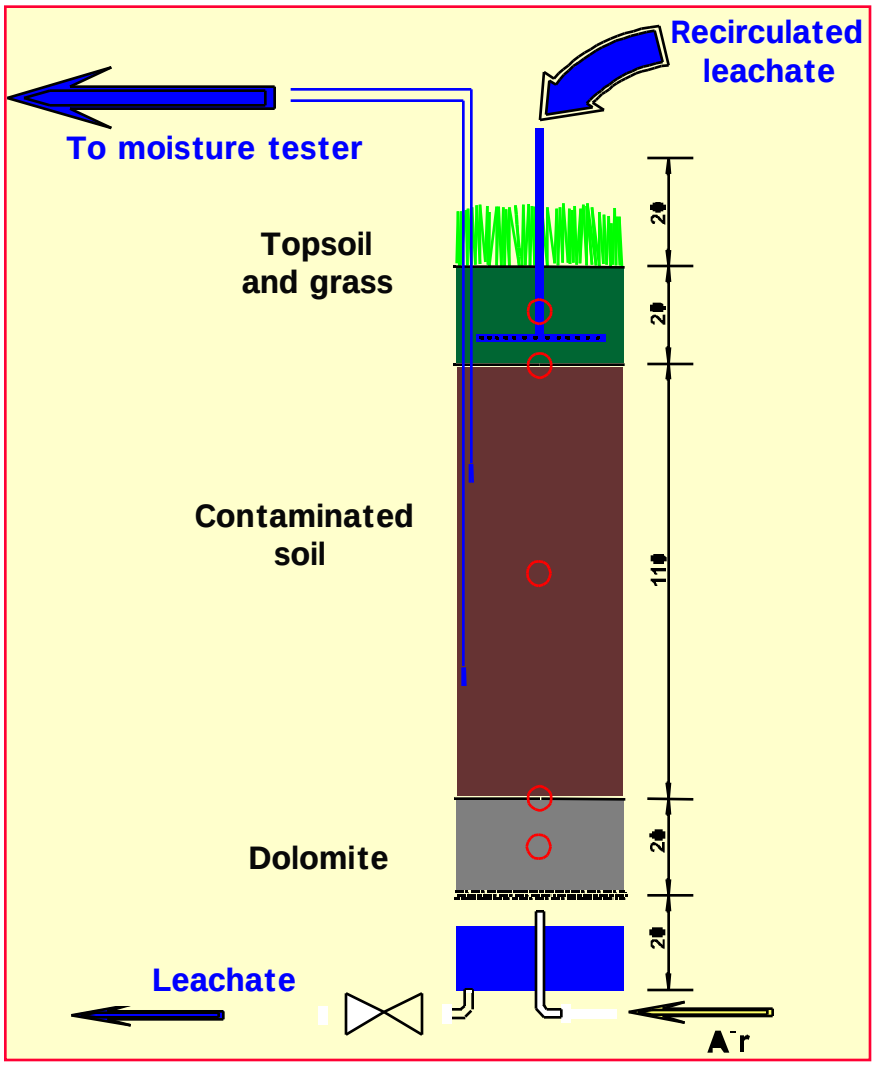


Figure 5.3 Column Experiment for Process Validation

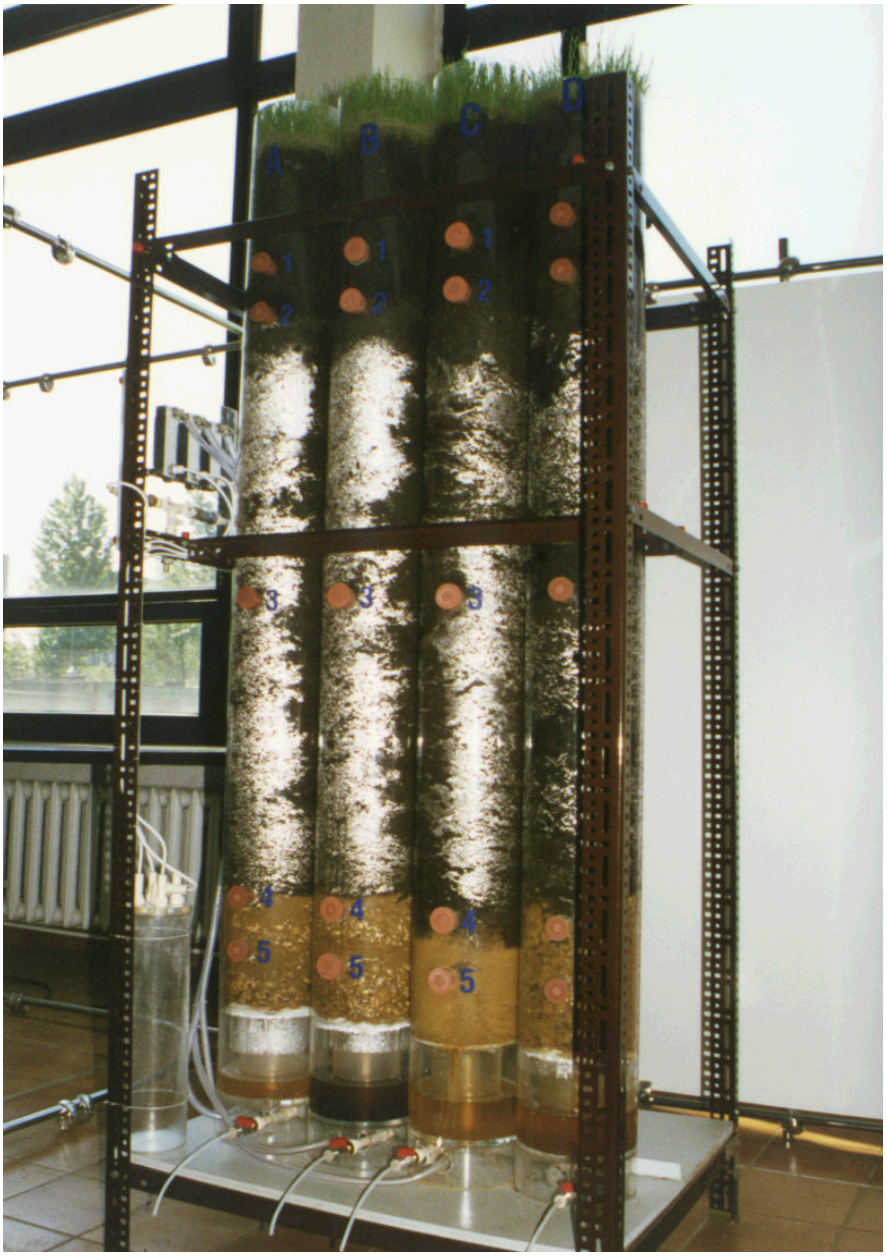
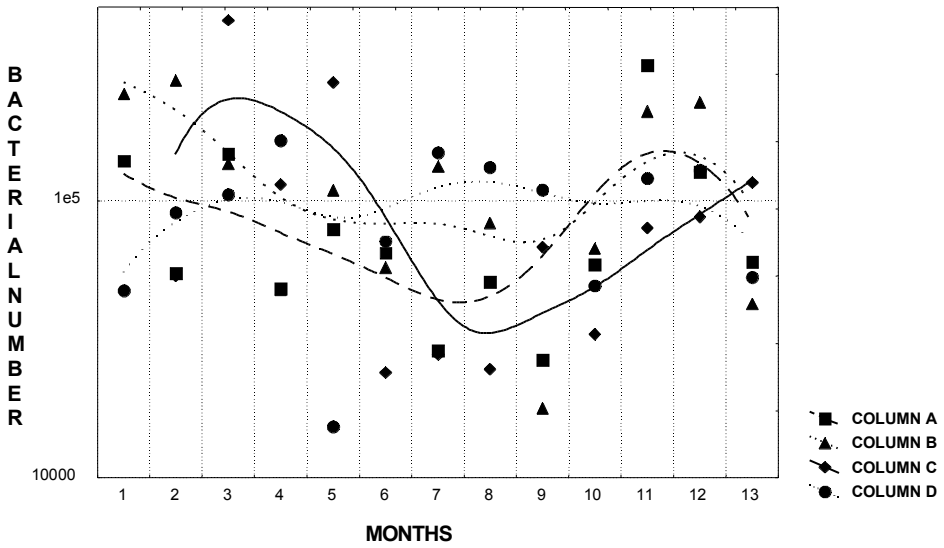
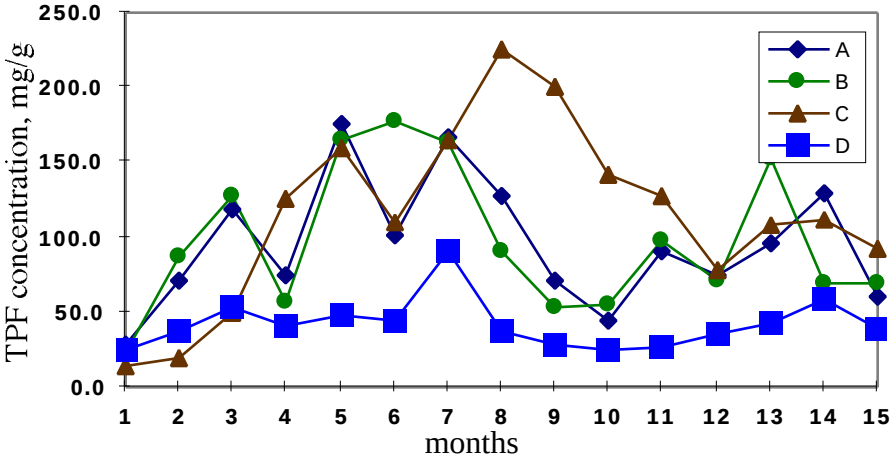


Figure 5.4 (A,B,C) Comparison of Nutirent Additon and Aeration (Active vs. Passive) on Microbial Activity in Columns Studies by measurement of Dehydrogenase Activity. Column A - aerated+Flovit Fertilizer, Column B-aerated, triethyl phosphate + ammonium phospate, Column C - aerated, ammonium phosphate + ammonium nitrate, Column D - passive aeration (Baroball) + Flovit Fertilizer.

A



B



Changes in fungal number during the column experiment

C

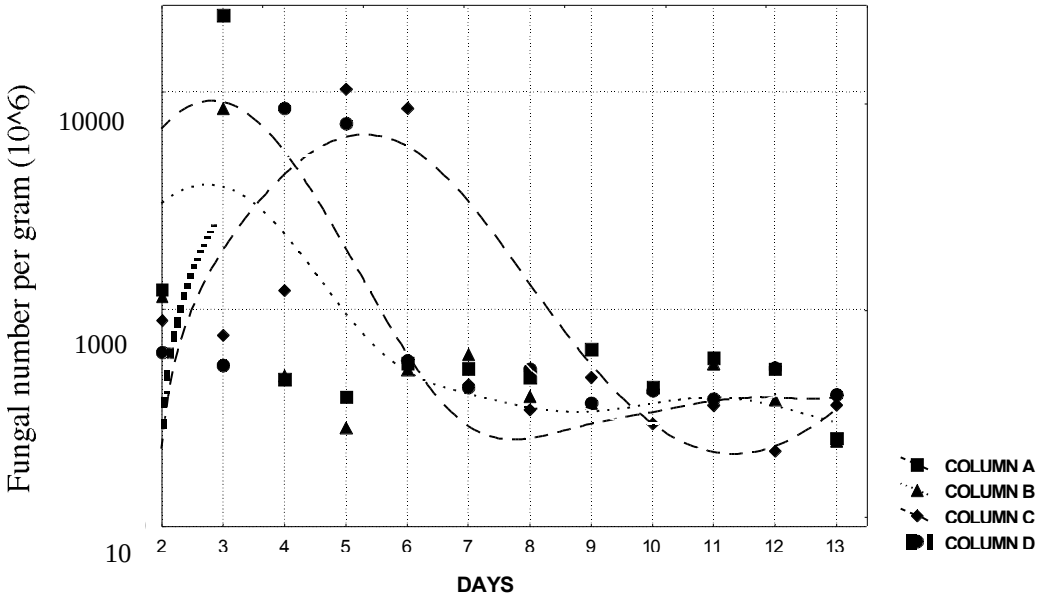


Figure 5.5. Use of Enrichment Cultures (MPN) to Estimate Relative Concentration of Naphthalene Degrading Organisms at 20°C and 37°C. Topsoil indicates the first 20 cm of cover. Clay refers to the contaminated soil from the refinery mixed with 10% woodchips.

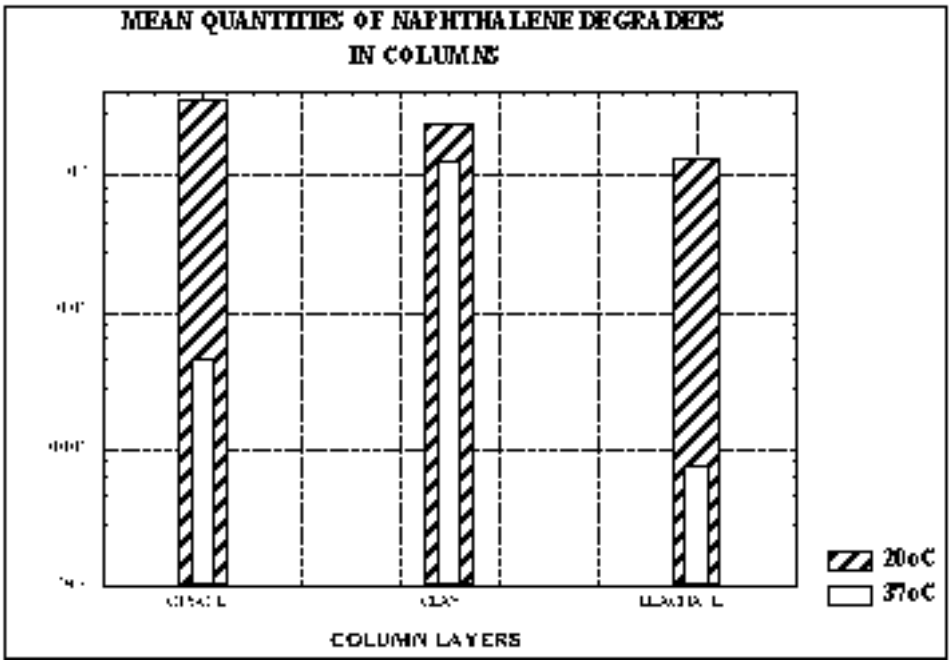


Figure 5.6 Use of Enrichment Cultures (MPN) to Estimate Relative Concentration of Petroleum Degrading Organisms at 20°C and 37°C. Topsoil indicates the first 20 cm of cover. Clay refers to the contaminated soil from the refinery mixed with 10% woodchips.

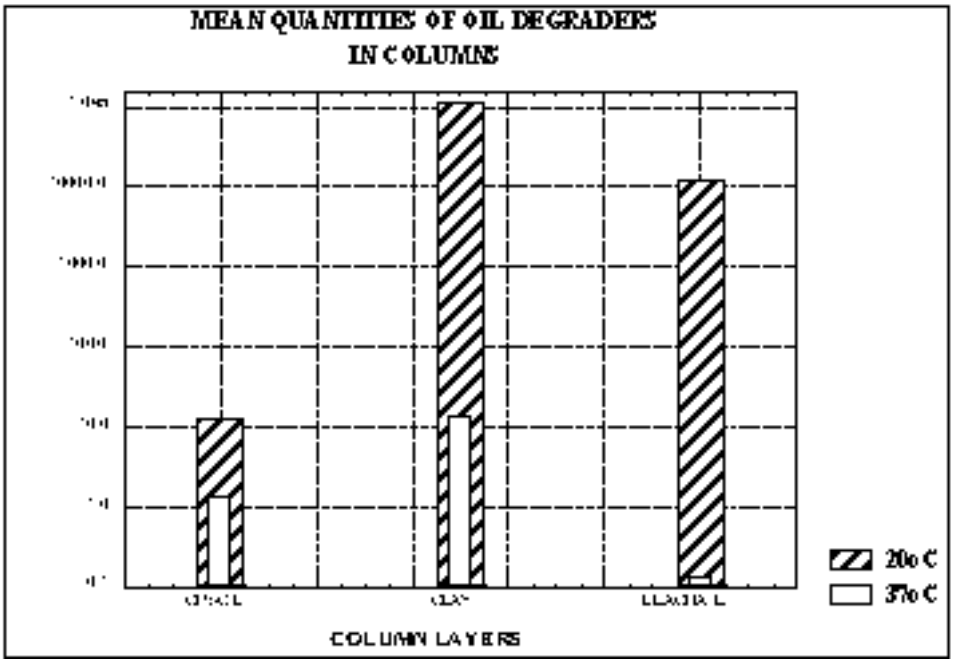


Figure 5.7 TPH concentrations in column by treatment. Column A –aerated+Flovit Fertilizer, Column B- aerated, triethyl phosphate + ammonium phosphate, Column C-aerated, ammonium phosphate+ammonium nitrate, Column D-passive aeration (BaroBall) +Flovit fertilizer.

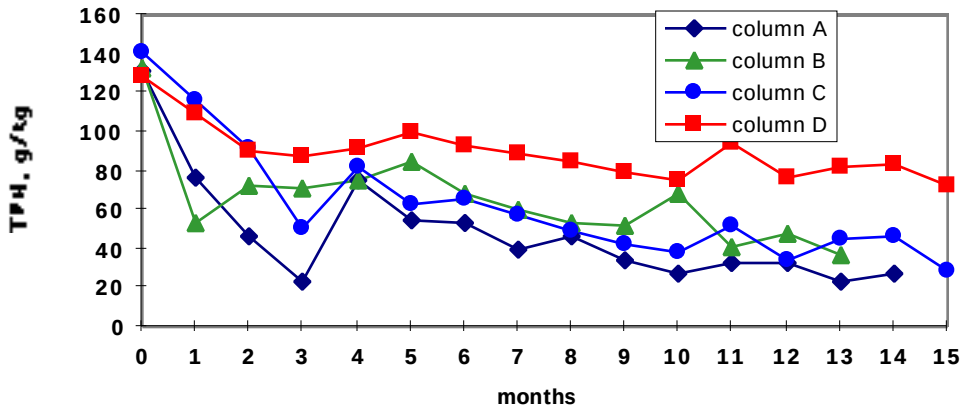


Figure 5.8 Total BTEX Levels by Treatment.

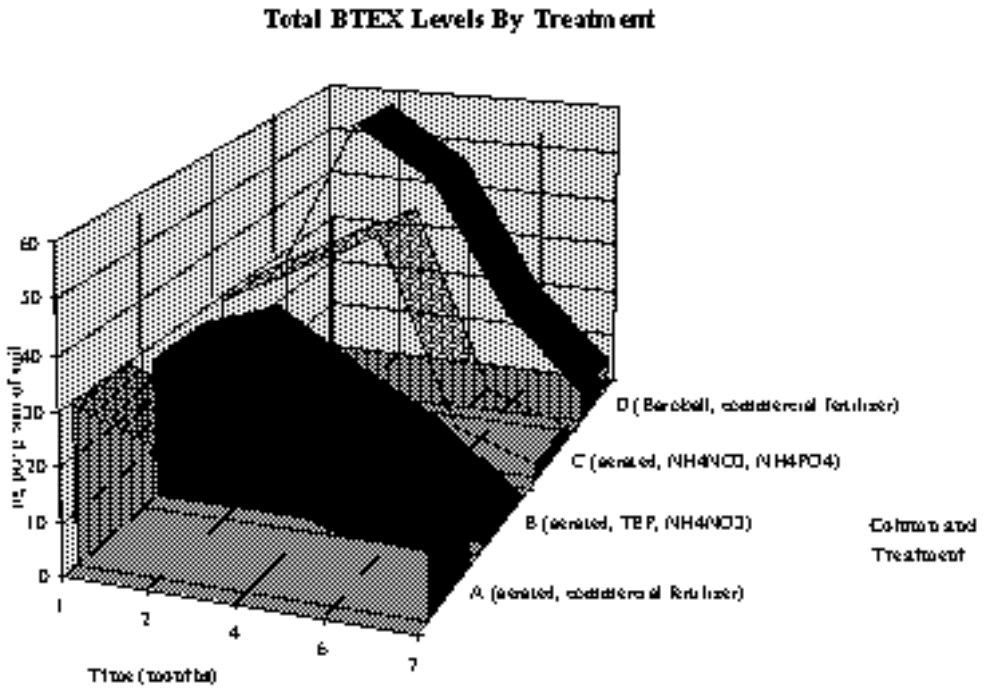


Figure 5.9 PAH degradation in Columns.

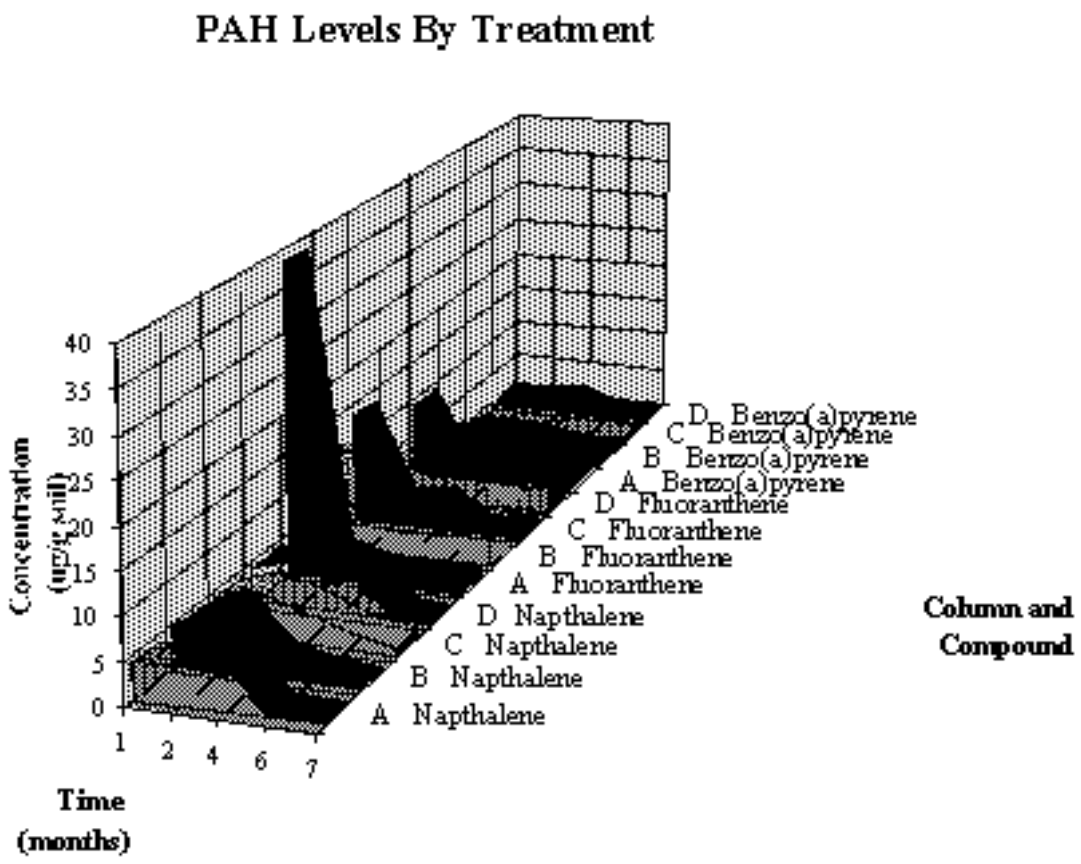


Fig. 5.10. Overall TPH inventory changes in Columns.

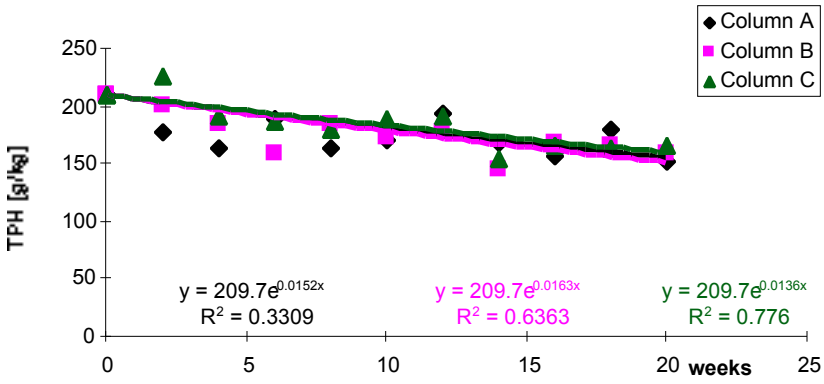


Fig.5.11. TPH inventory changes in various column levels.

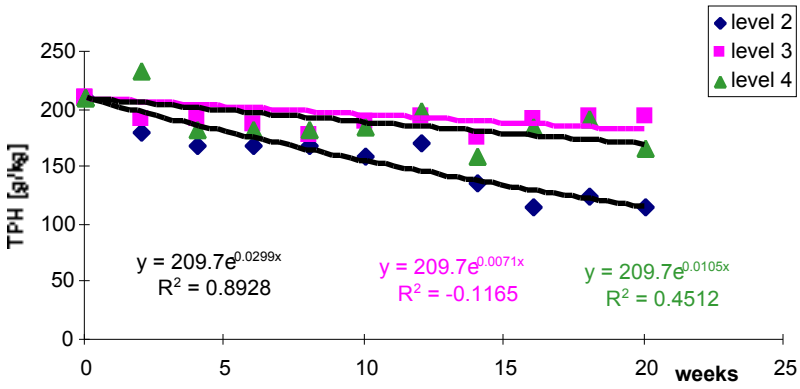


Fig. 5.12. TPH inventory changes in levels 3 and 4.

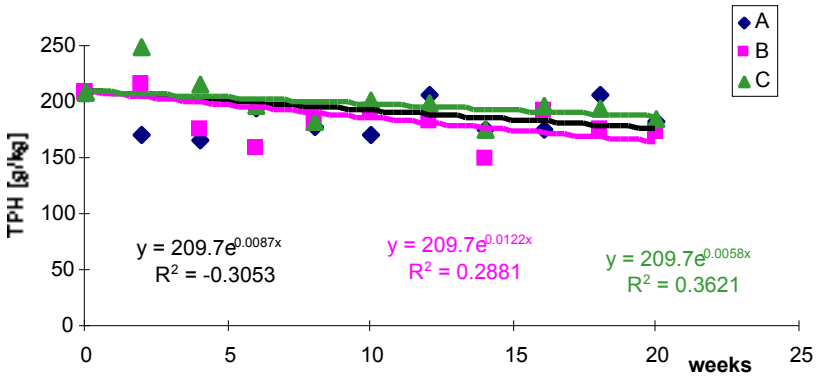


Fig. 5.13. PAH/TPH concentrations ratio in columns

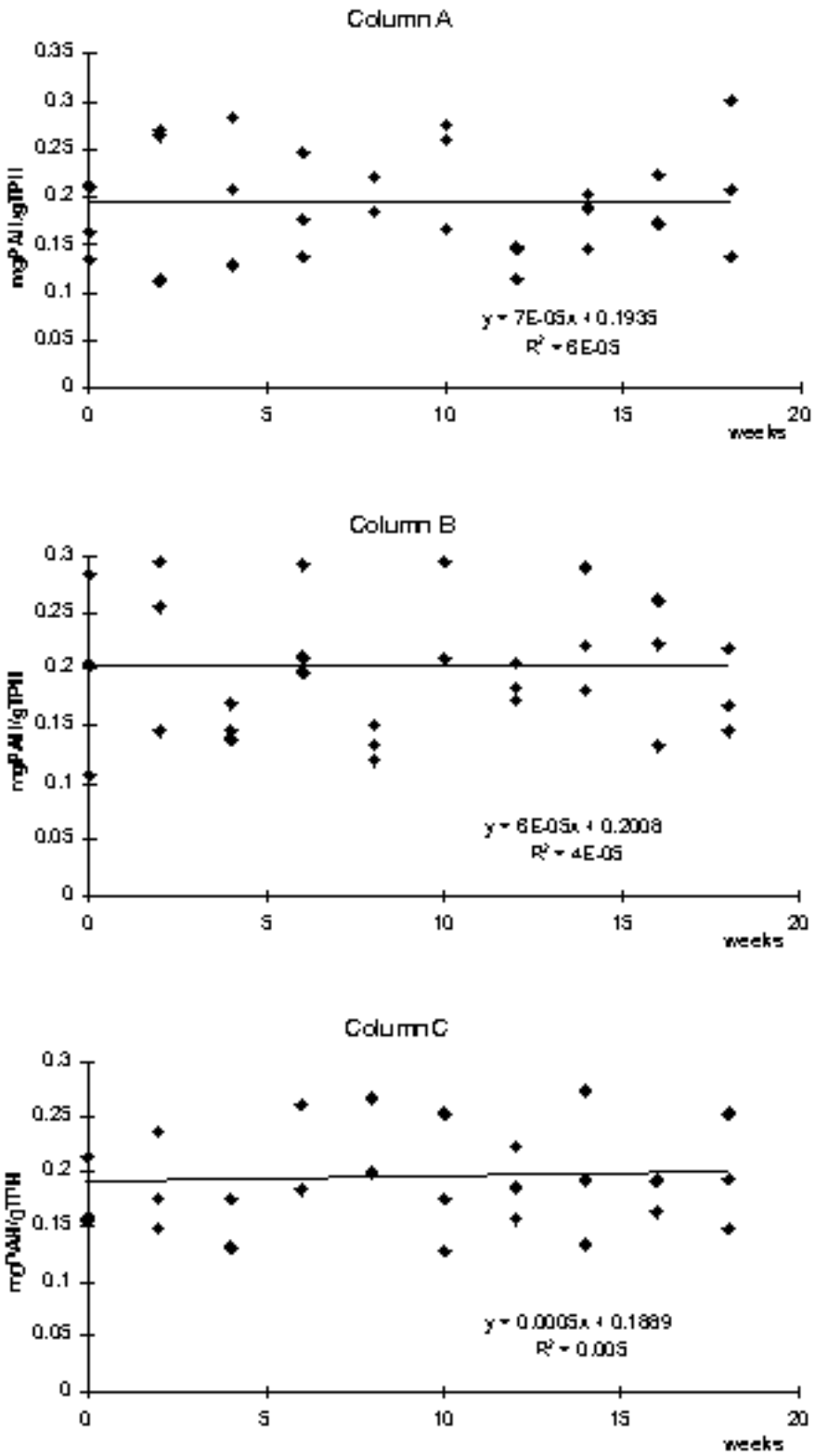


Table 5.1 Degradation rates based upon respiration tests within the columns by treatment and sampling level.

Date	Column	Treatment	Level	Degradation Rate (mg/kg/day)
Dec. 97	A	Active	Top	0.88
			Middle	-
Feb. 98			Top	3.9
			Middle	24.3
May 98			Top	2.2
			Middle	9.54
Dec. 97	B	Active	Top	2.3
			Middle	-
Feb. 98			Top	4.4
			Middle	34.4
May 98			Top	2.1
			Middle	25.2
Dec. 97	C	Active	Top	1
			Middle	-
Feb. 98			Top	6.1
			Middle	42.7
May 98			Top	4.3
			Middle	28.4
Dec. 97	D	Passive	Top	0
			Middle	-
Feb. 98			Top	1.1
			Middle	3.4
May 98			Top	2.1
			Middle	7.3

Table 5.2. Fungal Inhibition by Column Leachates

Parameter	Leachate from				
	Column A	Column B	Column C	Column D	Column E
Inhibition of fungal growth (%)	64.36	99.29	45.7	60.72	50.37
TPH (g/dm^3)	0.0035	0.001	0.002	0.0013	0.0001
TPOC (g/dm^3)	0.1212	0.606	0.0895	0.0133	0.0047

Table 5.3. Initial TPH and PAH contents in columns

Column	Sampling point	TPH g/kg	TPH+POL g/kg	PAH mg/kg
A	A2	151.7	193.5	25.4
	A3	154.4	214.0	31.5
	A4	182.7	238.7	48.3
B	B2	142.1	197.4	36.1
	B3	192.0	214.5	68.0
	B4	192.4	239.6	25.7
C	C2	169.1	198.8	32.7
	C3	167.1	249.1	33.0
	C4	158.5	224.7	42.4

Table 5.4. Balance data

time weeks	Column A water ml	Rokanol L4 ml	fertilizer ml	samples ml
0	2000	2		
0-2	2700	16	500	-200
2-4	5315	9	300	-2500
4-6	490	4	200	-500
6-8	565	4.5	225	-500
8-10	165	1.5	25	-500
10-12	70	0.5		-500
12-14	70	0.5		-500
14-16	4000	8		-450
16-18	1530	4		-500
18-20	1680	0.5		-2820
Total	**18585**	**50.5**	**1250**	**-8970**

time weeks	Column B water ml	RokafenolN8 ml	fertilizer ml	samples ml
0	2000	1		
0-2	1640	8	500	-200
2-4	4790	4.5	300	-2100
4-6	410	2	200	-500
6-8	1035	2.25	225	-500
8-10	650	0.75	25	-500
10-12	310	0.25		-500
12-14	310	0.25		-500
14-16	4000	4		-500
16-18	700	2		-500
18-20	1550	0.25		-2950
Total	**17395**	**25.25**	**1250**	**-8750**

time weeks	Column C water ml	surfactant ml	fertilizer ml	samples ml
0	2000			
0-2	3120		500	-200
2-4	2500		300	-1900
4-6	2200		200	-500
6-8	1375		225	-500
8-10	850		25	-500
10-12	410			-500
12-14	410			-500
14-16	4000			-620
16-18	780			-500
18-20	1550			-2950
Total	**19195**	**0**	**1250**	**-8670**

Table 5.5. Overall TPH inventory in Columns, g/kg of dry soil.

weeks	Column A			Column B			Column C		
	A2	A3	A4	B2	B3	B4	C2	C3	C4
0	189.6	193.0	228.4	177.6	240.1	240.5	211.4	208.8	198.1
2	189.0	156.0	186.9	172.5	190.6	242.1	179.2	227.5	272.7
4	163.0	179.3	153.8	204.6	191.3	161.4	140.7	204.5	230.7
6	179.6	189.9	199.3	158.0	189.2	130.3	167.1	180.5	216.1
8	136.2	180.1	175.7	195.6	183.4	178.3	174.5	173.8	194.1
10	170.2	175.9	168.0	138.6	189.2	194.5	168.9	207.0	196.4
12	171.2	196.3	217.2	166.0	187.8	180.7	175.4	199.0	201.9
14	155.8	161.3	189.1	138.7	166.1	135.6	115.8	199.1	152.5
16	120.7	176.2	177.0	122.1	196.5	188.4	104.2	201.6	193.5
18	129.7	207.8	207.5	145.1	183.2	169.2	100.7	195.5	197.1
20	88.3	187.2	179.8	131.1	205.9	141.6	128.8	193.5	176.8

Table 5.6. Microbial activity in columns, TTC (μgTPF /g)

Time	COLUMN		
weeks	A	B	C
2	31.1	12.1	0
4	63.9	6.1	1.4
6	11.2	24.4	0
8	17	6.9	0
10	43.4	30.2	23.8
12	90.3	77.4	70.64
14	24.7	21.47	22.68
16	90.76	62.91	24.4
18	147.95	42.37	22.95
20	0	21.9	0

Chapter 6

Bioremediation

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Biopile

Introduction

Bioremediation is generally attempted by employing biostimulation, a process in which the conditions for microbial growth are optimized by supplying adequate amounts of electron acceptor(s), water, nutrients, in the form of nitrogen, phosphorus and trace elements, to the contaminated material. Because biodegradation rates for petroleum hydrocarbons are fastest under aerobic conditions, maintaining adequate oxygen levels and moisture control are two of the main objectives associated with this project.

The material selected for the technology demonstration contains petroleum sludges, soils contaminated with crude and processed oil, and other petroleum by-products and process waste from the refining of crude oil. The predominant contaminants of concern (COCs) are polycyclic aromatic hydrocarbons (PAHs) including benzo(a)pyrene, a known carcinogen. Also benzene, toluene, ethylbenzene and xylene known as BTEX and very recalcitrant high molecular weight molecules, the remnants and residue from tank bottoms of acid refining of crude oil. Although the high molecular weight molecules represent a portion of the total petroleum hydrocarbons (TPH) present in the waste material, it is of less concern to human health and the environment from a risk assessment stand point, due to their highly insoluble state and lack of mobility within a soil matrix. The bioremediation processes will however, reduce even the highly recalcitrant substances found in the waste material over time. The contaminated material presents several unique challenges to the remediation effort. The refinery and its associated lagoons are over one hundred years old, creating highly weathered conditions and material that will require special handling and preparation for the remediation process to be effective. The integrated bioremediation system (biopile), as designed, will provide the necessary stimulation needed to support the biological processes required to break down the recalcitrant hydrocarbon complexes to a more innocuous and stable material.

Wood chips (weathered) were selected as a bulking agent for the biopile because they provide the necessary porosity increase while utilizing an inexpensive waste product from a local lumber mill which otherwise would have to be disposed. [Wood chips are normally sold as feed stock for pressed wood manufacturing. However, weathered (i.e. old and dirty) chips are not usable and must be disposed of separately.] During the construction of the biopile, the refinery took the initiative in utilizing grass clippings, leaf litter, and chipped waste lumber or wood originating from the refinery property. This eliminated the need and associated costs for transporting wood chips from Kobior, located approximately 25 km from the refinery in Czechowice.

Dolomite was selected over other materials (e.g., gravel), as the leachate collection layer based on several factors including its ease of handling, relative low cost and availability, pH amelioration, and a direct and inexpensive transportation route via train from the quarry to the refinery. Dolomite is also available in a variety of screen sizes, which will be incorporated into the process design to ensure effective air distribution throughout the system.

The final site use, proposed by the refinery, for the lagoons is a “green zone” to serve as a buffer and visual barrier between the refinery installations and the city of Czechowice-Dziedzice. The green zone will have limited access by trained refinery and IETU personnel for scientific and research purposes and for continued monitoring of the biopile processes. The area is not

intended for recreational use by the general population or the refinery staff. No other regularly scheduled activities associated with the operations of the facility are planned for the site. The removal of the lagoon and the creation of the green zone have great public relations significance and greatly reduces the overall risk of the refinery to the city.

For the complete characterization see the physical conceptual site model and chemical site model prepared for the Expedited Site Characterization (Chapter 2, this document). For a complete description of risk drivers and contaminants of concern see the Risk Assessment (Chapter 3, this document).

Biopile Design

Biopile Description

This bioremediation demonstration project focused on the clean-up technique known as "biopiles". The biopile process is very similar to active bioventing, where air, as an oxygen source, and other amendments are forced through the vadose zone sediments either by vacuum extraction or by injection to stimulate the microbial oxidation of the hydrocarbons. As the name implies, biopiling is an ex situ process. The contaminated material is excavated and recombined or amended with other materials (e.g., nutrients, sand, sawdust, wood chips, compost or other similar bulking agents) as needed to improve permeability and moisture retention, and then placed in an engineered configuration, to support and stimulate the biological reactions necessary to oxidize the hydrocarbons. Typically, this is a composting process that utilizes forced air via injection or vacuum extraction, moisture control, nutrient addition and environmental monitoring. Using commercially available vacuum pumps, or blowers, leachate pumps, moisture probes, thermocouple temperature probes, and real time soil gas monitoring equipment provides a mature and effective technology base for the operation and monitoring of the biopile.

Biopile Design and Construction

The biopile was constructed utilizing contaminated soil amended with wood chips and other vegetative materials. The pile was constructed in the existing excavated lagoon as seen in Figure 6.1. The empty lagoon bottom was sloped toward a sump pump that was connected to the leachate collection piping. A leachate collection system consisting of perforated leachate collection piping was placed at the bottom of a dolomite base, approximately 1 ft (30.48 cm) deep. A cell divider (constructed of clay) was placed within the dolomite to create a separate active and passive section of the biopile. This design change was done at the request of the refinery to provide a direct comparison of an active and passive system. The conceptual schematic with all potential process flows is presented in Figure 6.2.

The sump and its associated pump (Figure 6.3), were used to recirculate any collected leachate to the top of the biopile. The high concentration of bacteria in the leachates (>108/ml served as a source of inoculum for the biopile. In addition, make-up water from the existing wastewater treatment facility at the refinery, was used to ensure that an adequate supply of moisture was available.

As described by the USEPA (EPA/540/R-95/534a), one driving force behind the development of bioventing was the difficulty of delivering oxygen in situ. Many contaminants, especially petroleum hydrocarbons, are biodegradable in the presence of oxygen. Enhanced bioreclamation processes use water to carry oxygen or an alternative electron acceptor to the contaminated zone.

This process was common, whether the contamination was present in the ground water or in the unsaturated zone. Media for adding oxygen to contaminated areas have included pure-oxygen-sparged water, air-sparged water, hydrogen peroxide, and air (Table 6.1). In all cases where water is used, the solubility of oxygen is the limiting factor effecting mass transfer. At standard conditions, a maximum of 8 mg/L to 10 mg/L of oxygen can be obtained in water when aerated. The stoichiometric equation 5.2.2.1 shown below is an example that can be used to calculate the quantity of water that must be delivered to provide sufficient oxygen for biodegradation.

$$\text{Eq. 5.2.2.1} \qquad C_6H_{14} + 9.5\ O_2 _ 6CO_2 + 7H_2O$$

An example of the mass of water that must be delivered for hydrocarbon degradation to occur is shown below. Based on Equation 5.2.2.1, the stoichiometric molar ratio of hydrocarbon to oxygen is 1:9.5 or, to degrade 1 mole of hydrocarbon, 9.5 moles of oxygen must be consumed. On a mass basis:

$$\frac{1 \text{ mole } C_6H_{14}}{9.5 \text{ moles } O_2} \times \frac{1 \text{ mole } O_2}{32 \text{ g } O_2} \times \frac{86 \text{ g } C_6H_{14}}{1 \text{ mole } C_6H_{14}} = \frac{86 \text{ g } C_6H_{14}}{304 \text{ g } O_2} = \frac{1 \text{ g } C_6H_{14}}{3.5 \text{ g } O_2}$$

Given an average concentration of 9 mg/L of oxygen dissolved in water, the amount of air-saturated water that must be delivered to degrade 1 g of hydrocarbon is calculated as follows:

$$\frac{3.5 \text{ g } O_2 \text{ required}}{\frac{9 \text{ mg } O_2}{1 \text{ L } H_2O} \times \frac{1 \text{ g}}{1{,}000 \text{ mg}}} = \frac{390 \text{ L } H_2O}{1 \text{ g } C_6H_{14}}$$

or, to degrade 1 lb:

$$\frac{390 \text{ L } H_2O}{1 \text{ g } C_6H_{14}} \times \frac{1{,}000 \text{ g}}{2.2 \text{ lb}} = 178{,}600 \text{ L } H_2O / 1 \text{ lb } C_6H_{14}$$

Based on findings from the IETU treatability study, and an understanding of the mass transfer limitations of air-saturated water as an oxygen delivery system and the costs and safety concerns associated with pure oxygen generation, air injection was selected for the biopile electron acceptor delivery system. Clearly, the goals established by the risk assessment for the clean-up criteria and the final end use of the site were met with this process.

Previous field demonstrations at SRS have shown that direct air injection is an acceptable method of delivering oxygen to the subsurface microbiota. Additionally, a recent demonstration at a local municipal landfill (Columbia County, GA), has shown that air can be delivered via the leachate collection piping without adversely impacting the collection of leachate. This dual use of the leachate collection system (Figures 6.4, 6.5, 6.6) was also applied to the construction of the biopile. A regenerative blower has been obtained to provide the necessary airflow for the biopile. The Columbia County Landfill demonstration has shown that air injected into the perforated leachate collection piping is distributed to the entire cell via the leachate drainage layer (i.e. dolomite) (Figure 6.7).

Approximately 1 meter of amended biopile material was placed above the leachate collection system. The composition of the mixture was approximately 80% to 90% contaminated materials, and 10% to 20% wood chips as a bulking agent. Results from the column studies for permeability conducted by IETU indicated 10% wood chips (V/V) to be adequate.

Immediately above the amended biopile material was a 20 to 30 cm silty topsoil cover. The cover was planted with a mixture of clover and local grasses that provide protection from erosion, support of a green zone and a biofilter for any gaseous substances that may reach the surface of the biopile. The refinery additionally planted a mixture of deciduous conifer and beech trees and also some evergreen pines for landscaping purposes.

Atop of the biopile, a trickle system for water application was installed to maintain soil moisture between 20-80% of the biopile's field capacity. The target range was 30-40%. The water supply came from the leachate collection sump with make-up water coming from the refinery's process water sources including treated wastewater.

System Performance

Biodegradation of petroleum hydrocarbons in soil (petroleum land farming) has been used by the oil industry for more than 30 years as an efficient way to destroy oil sludges (Bartha and Bossert, 1984). By applying oil to the soil surface, adding fertilizer (P & N), water, and then tilling to aerate (oxygenate), the soil microbes have been shown to completely degrade large quantities of oil. A demonstration of this technology using waste oil was done at the Savannah River Site near Central Shops in 1980 (Watts and Corey, 1982).

Until recently, the state-of-the-art approach to soil remediation was excavation and disposal at a secure landfill. Changes in liability concerns, increasing costs, and regulatory constraints have decreased the popularity of excavation and disposal as a soil cleanup alternative. Landfill disposal of contaminated soil does not remove the future liability of its generator, who will be held jointly liable with the landfill operator for any future associated contamination. Thus, on site permanent solutions must be sought whenever possible.

At this time, it has been estimated, based on previous work performed by WSRC and others, that the removal of BTEX was between 90-99.9% with a reduction in TPH of 65-90% and PAH removal of 50-75%. Sims (1986) reported 50-100% reduction of fossil fuels in soil after only 22 days. St. John and Sikes (1988) reported that a prepared bed system, complete with fugitive air emissions control, at a Texas oil field was able to reduce volatile organic carbon by >99% after 94 days, with semivolatiles being reduced by more than 89%. In California, Ross et al. (1988) reported that four acres of soil 15 in (38 cm) deep, contaminated with diesel and waste motor oils were decreased from 2,800 ppm TPH to less than 380 ppm in only four weeks. He also reported that at another site owned by a heavy equipment manufacturer, 7,500 m^3 were reduced to <100 ppm TPH after nine weeks and an additional 9,000 m^3 with 180 ppm TPH were reduced to <10 ppm after only five weeks. Another site in California had 600 m^3 reduced from 1000 ppm TPH to <200 ppm in 35 days. Molnaa and Grubbs (1989) report other sites in California where similar results were obtained, (e.g., a site in which 2000 m^3 with 2800 ppm TPH were reduced to less than 38 ppm in 74 days; a truck stop where 15,000 m^3 were reduced from 3000 ppm TPH to less than 30 ppm TPH in 62 days; and a site contaminated with lubricating oils at which 25,000 m^3 were reduced from 4800 ppm down to 125 ppm in 58 days). Based on the initial concentrations (> 200,000 mg/kg TPH in litter) reported by Ulfig, et al. (1996), the rates of removal should range between 10 to 80 mg/kg of soil per day for TPH and could exceed 120 mg/kg of soil per day, based on similar work by Reisinger, et al. (1996). Reisinger experienced a 41% removal of TPH over the first two quarters (180 days) of biopile operations, based on respiration test data. Seasonal variations and other system parameters will also impact removal rates.

Experimental Plan

Criteria for Success

There were three primary criteria by which the overall success of this demonstration was evaluated:

1. Demonstrate the application of bioventing/biosparging as a viable cost-effective process to remediate contaminated sites to reduce risk to man and environment and resulting in a green zone. The ability of the remediation process to degrade high molecular weight compounds (PAHs) was evidenced by utilizing state-of-the-art monitoring equipment, analytical techniques and treatability studies to determine the rate and volume reduction in the starting concentrations of the contaminants.

2. Evidence of biological destruction (biodegradation) of petroleum (PAH, TPH and BTEX) from the contaminated material. Since a major advantage of bioremediation is destruction, it is important and significant to demonstrate that biodegradation is occurring. The evidence is expected to come primarily from comparison of the biopile material and soils analysis taken before, during and after the material is subjected to the treatment process (nutrient addition, aeration, pH adjustment and moisture control) to stimulate microbial activity and thus biodegradation of the contaminants.

3. Relatively simple and trouble-free operation. A critical assumption for the successful demonstration of the technology is that the system, as designed, will function with little or no down time and provide operating conditions that minimize fugitive air emissions and maximize biodegradation rates. The proposed project has no precedence in Poland and as such represents new technology for the country. However, since several other nations have demonstrated similar technologies, it represents a relative low risk and should have high public acceptance. The simplistic design contributes direct benefits associated with the ease of management and operation. A minimal staff will be required to operate the equipment, again adding to the low risk factor by limiting exposure to operations personnel.

Process Monitoring

Monitoring of the system (see Table 6.2) was accomplished in a variety of ways. Soil gas piezometers were installed in the biopile to monitor carbon dioxide (CO_2), oxygen (O_2), methane (CH_4), volatile organic hydrocarbons (VOCs) and semi-volatile organic hydrocarbons (sVOCs). Water and soil samples were analyzed for polycyclic aromatic hydrocarbons (PAHs), nutrients, metals, and microbiological activity. Water quality of the leachate was tested for pH, dissolved oxygen (DO), specific conductance, temperature and other chemical and physical parameters like BOD and COD. The data gained from the monitoring program was used to calculate the biodegradation rates for PAH and total petroleum hydrocarbons (TPH). Respiration testing was conducted to monitor O_2 utilization during the remediation and helium tracer tests were performed to monitor the air flow, distribution and hydraulic conductivity with respect to the permeability of the contaminant mixture within the biopile during air injection. Moisture and temperature were measured by in situ moisture probes and thermocouples set next to each of the vadose zone piezometers.

Monitoring Equipment

The products and manufacturers used on this project are listed in this document, and are meant as guidance for environmental managers and consulting engineers.

The Brüel & Kjær (B&K) Multi-gas Monitor, Type 1302 is a highly accurate, reliable and stable quantitative gas analyzer that is microprocessor controlled. Its measurement principle is based on the photoacoustic infrared detection method. In effect, this means that the B&K 1302 can be used to measure almost any gas that absorbs infrared light. The 1302's detection threshold is gas-dependent but typically in the 10^{-3} ppm region (Brüel & Kjær, 1996). In this project, the B&K served a dual role. First, the instrument was used for personnel occupational health and safety monitoring. Initial environmental sampling indicated the presence of benzene, a known human carcinogen. The instrument assigned to this project was set-up and calibrated for benzene monitoring. The second role of the instrument was for process monitoring of soil gases. The B&K was set-up to selectively measure the concentration of up to five component gases and water vapor in any air sample. For this project, the instrument monitored benzene, toluene, xylene(s) and naphthalene as well as CO_2 and water vapor.

The Landtec GEM-500 Gas Extraction Monitor is a highly reliable gas-monitoring unit originally designed for the detection of landfill gases. The Landtec GEM-500 is designed to detect CH_4, CO_2 and O_2 concentrations in soil gas. Because the biopile was designed to be an aerobic system the GEM-500 was employed to monitor the production of CO_2 and the depletion of O_2 and in this case, the lack of presence of methane indicating aerobic conditions exist in the subsurface of the biopile. The lack of CH_4 production and the presence of CO_2 indicate the system is providing an adequate O_2 supply for the aerobic biological processes to take place. The instrument's detection ranges are 0-100% for methane, 0-50% for carbon dioxide and 0-25% for oxygen with a resolution of 0.1 for all gases.

In a former acid refining process used for the manufacture of motor oil, large quantities of sulfuric acid (H_2SO_4) were used in the processing operation. The H_2SO_4 was disposed of in the waste lagoons creating a potential health hazard when the materials are mixed or disturbed. In order to monitor the airborne concentrations of H_2SO_4 during the construction and operation of the biopile system a Single Point Monitor (SPM) manufactured by Zellweger Analytics was deployed. The SPM combines the Chemcassette™ Detection System and microprocessor control to achieve optimum detection speed, accuracy, and specificity. It responds quickly to hazardous releases, yet ignores other commonly used chemicals.

Soil moisture was monitored with multiple gypsum moisture blocks installed throughout the biopile at approximately the same locations as the soil piezometers. The soil moisture blocks consist of two concentric electrodes cast into gypsum blocks. When the blocks are placed within the biopile, the moisture content of the gypsum approaches equilibrium with the moisture content of the biopile material. When the electrodes of the moisture block are connected to a moisture meter, a current is passed between the electrodes and the resulting resistance is measure and converted to a meter display. The meter display can then be transformed to a percent of Available Soil Moisture. The moisture meter is a battery powered hand held device about the size of a scientific calculator. The moisture meter is carried between sample locations , the moisture block leads are connected to the meter, and the moisture measurement is displayed. The moisture blocks and moisture meter (Model KS-D1) utilized in this project were manufactured by Delmhorst Instrument Company, Towaco NJ.

Soil temperature was monitored using J Type or K Type thermocouples placed within the biopile at approximately the same locations as the piezometers and moisture blocks. Standard Grade Type J thermocouples employ an Iron Constantan (Copper nickel alloy) junction with a temperature range of -200 °C to 760 °C (-328°F to 1400°F). Standard Grade Type K thermocouples employ a Chromel (Chromium-nickel) Alumel (Aluminum-nickel) junction with a temperature range of -200°C to 1370°C (-328°F to 2498°F). When the junction of the thermocouple is subjected to a temperature, a current is produced which is indicative of the temperature at the junction. Thermocouples are usually supplied with Type K minimal plugs which are compatible with the thermometer (readout device) and orient the thermocouple leads to the correct polarity. The thermometer is also a battery powered hand held device about the size of a scientific calculator. The thermometer is carried between sample locations, the thermocouple plug is inserted into the thermometer and the temperature of the thermocouple location is displayed within moments. The readout device used on this project was a Fluke Model 52 K/J Thermometer manufactured by the John Fluke Manufacturing Co. Inc., Everett, WA.

Sampling and Analysis

Soils were collected during the Expedited Site Characterization (ESC), the initial phase of the remediation demonstration and again for post demonstration characterization for analysis of VOCs, microbial counts, physical parameters, and miscellaneous parameters. The amount of soil sampling conducted at a site has a tremendous impact on the cost of the project. Minimizing soil sampling makes a remediation effort much more cost-effective. Since the biopile contaminated soil is being mixed with wood chips, the soil matrix should be much more homogeneous than the native soil, thus random soil sampling of the passive and active zones should provide a reasonable estimate of soil parameter changes during interim sampling intervals. With biopile systems, in situ respiration testing can also indicate when the site is clean and, therefore, when to collect final soil samples.

Periodic soil gas monitoring was conducted to ensure that the biopile system is well oxygenated. Initially, soil gas was monitored weekly until the site became fully aerated. Once full aeration was achieved, system operation was optimized. After this initial period, soil gas monitoring normally was conducted bi-monthly for the first year, during the warmest and coldest months, and monthly thereafter. If conducting an in situ respiration test during different seasons was not possible, then it was conducted during the same seasons as the initial test. In situ respiration testing were used as a preliminary indicator for site closure. A good indication that the site was remediated and that final soil sampling was conducted was an in situ respiration rate in the contaminated area similar to that in the uncontaminated area. In situ respiration testing to determine remediation success was economically significant because soil sampling was not relied upon as the sole indicator of site remediation, thus eliminating the high cost of intermediate soil sampling.

Soil Sampling Protocol

Soils for organic and inorganic analysis were collected using a hand auger, and placed in a Whirl-Pak bag or other clean container. Samples were placed in a cooler on ice and managed according to the hold times as seen in Table 6.2. Prior to sample analysis, samples were weighed to determine the mass of the sample. Core specimens for microbial analysis were obtained directly from the soil sampler. Cores were sectioned with sterile spatulas and the outermost layer

scraped off using a sterile scoopula. The sample was then placed in a sterile Whirl-Pak bag and transported to the laboratory on ice for immediate analysis according to this test plan. Laboratory analyses were performed by personnel at the IETU laboratory.

Soil Gas Sampling Protocols

The following protocol was utilized for sampling soil gases. First, a magnehelic gage or other measuring device (the Landtec GEM 500 is equipped with an electronic pressure gauge) was attached to the quick connect fitting for measurement of pressure. Second, a high volume pump approximately 5 liters per minute (l/min) was attached to the quick connect and the well gas was evacuated until oxygen readings have stabilized indicating that one is monitoring soil gas rather than well gases. Third, the Landtec GEM-500 or equivalent was attached to a side stream of the vacuum pump and measurements of O_2, CO_2, and CH_4 were taken. Fourth, the Brüel & Kjær multi-gas monitor was used for the detection and analysis of VOCs including benzene, toluene and xylene(s) and the sVOC naphthalene. Later, in order to streamline soil gas sampling, use of the external sampling pump was abandoned. Soil gases were sampled using the Landtec's internal pump with a split fitting before the inlet port where a side stream was supplied to the Brüel & Kjær multi-gas monitor. Laboratory and field analyses as seen in Table 6.2 were performed by personnel at the IETU laboratory.

Helium tracer tests and vadose zone respiration measurements were done using a Marks Helium Detector Model 9821(or equal) helium detector using the Bioventing Respiration Test protocols of EPA (EPA/540/R-95/534a).

Leachate Sampling Protocols

A sampling port, pump or bailer was used to collect leachate samples from the leachate recirculation system. Water was filtered in the field, if required, with 45 µm mesh filters. Field water parameters including dissolved oxygen, oxidation-reduction potential (ORP), pH, specific conductivity, and temperature, were monitored using the Hydrolab. The Hydrolab Surveyor probes used for estimation of dissolved oxygen and pH were calibrated prior to each use. All other probes on the Hydrolab were calibrated monthly.

Laboratory and field analyses were performed by personnel at the IETU laboratory. Analytical methods (organics and inorganics) for leachate samples were utilized as noted for soils. Total VOC and carbon dioxide in leachate samples were prepared and analyzed as follows. Leachate samples were acidified in a serum bottle with a crimp seal septa. Thirty milliliters of leachate were added to an amber serum bottle, capped and crimped in the field and held on ice until analyzed. One milliliter of concentrated hydrochloric acid was added to serum bottles with a syringe, allowed to equilibrate, and then 2.5 ml of headspace was injected into a GC with a thermal conductivity detector (TCD). Standards were made with sodium bicarbonate solutions (EPA Method 524.2).

The assays were performed by the IETU with EPA approved methods or Polish Standard Methods. Soluble reactive phosphate concentrations were measured by the ascorbic acid colorimetric determination method (EPA 365.2). Total Phosphorus was determined by the persulfate digestion and ascorbic acid colorimetric determination (EPA 365.2). Total Nitrogen was determined using a thermal conductivity detector (TCD) which includes free-ammonia. Organic nitrogen was determined colorimetrically following digestion, distillation and Nesslerization method (EPA 351.3). Ammonia as distilled ammonia nitrogen was determined

colorimetrically following distillation and Nesslerization method (EPA 350.2). Nitrate, Nitrite, and Sulfate was determined by the ion chromatography method (EPA 300.0). BOD and COD were determined by 5-day BOD test 5210 B APHA (1992) and the 5220B Open Reflux COD method APHA (1995).

Analytical Procedures

The EPA 8000 series analytical procedures found in Table 6.3 were used in the analysis of soil samples. The use of these methods is now nearly universal in public and private sector laboratories. Each of these methods has an associated list of target compounds for which it was specifically developed and evaluated. These methods use gas chromatography (GC) and mass spectrometers (MS) or a combination of both GC/MS techniques to detect organic compounds. These instruments are well known for their excellent sensitivity and selectivity for specific target compounds.

Detection of complex hydrocarbon mixtures is best achieved using a GC with a flame ionization detector (GC-FID). GC-FID analysis provides a more accurate representation of the degree of hydrocarbon contamination. EPA Method 418.1 does not provide information on the type of hydrocarbon contamination and the low boiling point components are easily lost. This method was only used for screening purposes and final disposal was governed by GC analysis.

The procedures outlined in Table 6.3 list different methodologies for the low to medium boiling point hydrocarbons (gasoline) and the high boiling point hydrocarbons (diesel motor fuels and light heating fuels). A purge and trap or headspace is preferred for the more volatile contaminants whereas the high boiling point contaminants are to be analyzed using a GC-FID. The gas chromatographic analysis is equivalent to the well known "California Method" for testing TPHs for the Underground Storage Tank Program. For highly contaminated samples, a waste dilution technique was used and documented with the analytical results.

Microbiological Procedures

Microbiological analyses were done on a monthly basis. The soil samples from the biopile were collected and processed on the same day the sampling was done. The first test gave total direct cell counts in the soil, utilizing DAPI (4, 6 Diamindino 2 phenylindole). This provided a total bacterial cell count, expressed in cells per gram dry weight. The second analysis performed was a viable count, this gave the total number of organisms that can be cultured on an oligotrophic media. This number was expressed in colony forming units per gram dry weight. The third analysis was an enrichment for TPH. Bacteria were grown on a minimal salts media with trace metals and TPH vapors as the only carbon source.

· 4, 6 Diamindino 2 phenylindole (DAPI)

DAPI provided a direct estimate of the total number of bacteria in the environment, regardless of ability to grow on any media that might be used. Samples were preserved in phosphate buffered formalin. Samples (1 to 3 grams) were extracted three times with a non-ionic homogenizing detergent to remove bacteria from the sediment particles. Homogenates were cleared by low speed centrifugation and the supernatants pooled. Ten microliters of supernatant were spotted onto each well of a toxoplasmosis microscope slide, stained with 0.5 µg/ml DAPI, then rinsed with distilled water. The number of cells stained with DAPI were counted by epifluorescence microscopy. The number of cells per sample was normalized by dividing by the dry weight of

the sediment. Counts were reported as cells per gram weight (Kepner and Pratt, 1994). A comparison of acridine orange (AODC) stained samples and DAPI stained samples of soil obtained earlier from the refinery site showed the DAPI gave superior results (Ulfig, 1997)

· Calcofluor White (CFW)

CFW provided a direct estimate of the total number of fungi in the environment, regardless of the ability to grow on any media that might be used. Samples were preserved in phosphate buffered formalin. Samples (1 to 3 grams) were extracted three times with a non-ionic homogenizing detergent to remove bacteria from the sediment particles. Homogenates were cleared by low speed centrifugation and the supernatants pooled. Ten microliters of supernatant were spotted onto each well of a toxoplasmosis microscope slide, stained with Calcofluor White, then rinsed with distilled water. The number of cells stained with CFW were counted by epifluorescence microscopy. The number of cells per sample was normalized by dividing by the dry weight of the sediment. Counts were reported as cells per gram weight.

· Naphthalene and Crude Oil Enrichment

This method provided an estimate of the total number of viable microbes capable of living in an enriched naphthalene and crude oil soil. Successful bioremediation of TPH/PAH can also be measured in terms of increased microbial activity, increased biomass; particularly biomass which contains TPH degrading enzymes, increased biomass capable of consuming TPH as evidence of stimulation by treatments. Minimal salts media (MSM) were used (Fogel et al., 1986). The plates for naphthalene were incubated in an enclosed environment with naphthalene vapors available to the bacteria as a source of carbon for metabolism. This count was also in colony forming units per gram dry weight. As naphthalene was the only carbon source available, this was a count of these degraders only. For crude oil degraders MSM was placed in 96 well microtiter plates. Samples were diluted 10 fold across 8 wells in triplicate and a drop of crude oil was placed in each well. After incubation, each well was scored for turbidity and oil emulsification to obtain a most probable number (MPN) density per gram dry wt or per ml.

Since the actively aerated parts of the biopile could reach high temperatures due to high rates of biodegradation (composting type conditions), enrichments from the active aeration side were incubated both at 25°C and at 45°C. This insured that changes in temperature adaptation were documented and that thermophilic degraders were not under estimated.

· Microbial Dehydrogenase Activity - TTC

Oxidation of petroleum by microbes, like other types of organic oxidation under aerobic conditions, is linked to the electron transport system (ETS) of the cell. The enzymes of the ETS include a number of dehydrogenases, thus dehydrogenase activity can be used as an overall measure of activity in the soil. Triphenyltetrazolium chloride (TTC) was used as an artificial electron acceptor to estimate dehydrogenase activity since the reduction of TTC to triphenyl formazan (TTF) causes a color change that can be quantified using a spectrophotometer. Soil samples were incubated with TTC (1.5 g/100 ml) for 24 h. The samples were then extracted with acetone and the extract measured at 546 nm using a spectrophotometer (Alef and Nannipieri, 1995). Values are presented as TPF µg/gdw.

· Respiration Rates

Laboratory respiration rate measurements were taken as another source for the detection of carbon utilization by the TPH degraders. Alef and Nannipieri(1995) methods for soil respiration

were used to calculate the production of CO_2 over a given period of time. Soil was placed in a closed flask with a small solution of NaOH to act as CO_2 trap. After incubation for several hours or more the NaOH was fixed with $BaCl_2$, colored with phenolphthalein and titrated with a weak solution of HCl to determine the amount of CO_2 produced. The results were reported as mg CO_2/h/gdw. This has already been demonstrated to work well for the refinery soils (Ulfig et al., 1997).

· Risk Assessment

When conditions for bioremediation were not optimal, sometimes more toxic by-products were formed. In the original Biopile design, a holding lagoon was designed to contain leachates from the contaminated soil for reapplication on to the biopile. Toxicity experiments were used to assess the risk to freshwater organisms, in case a breach were to occur, and the concentration of leachate to be reapplied to the biopile

Inhibition of Filamentous Fungi (after Ulfig, 1999) Filamentous fungi are cultivated on malt extract agar. Leachate was applied to the surface of the plates and fungi inoculated. Average fungal colony diameters were measured and compared to those challenged with leachates from the soil column experiments.

Daphnia magna (18th edition of Standard Methods For the Examination of Water and Wastewater) Wild *Daphnia* sp. were collected from freshwater ponds in Ruda Slaska and cultivated in aerated moderately hard reconstituted water (Table 8010 I, Standard Methods) at room temperature. *Daphnia magna* were separated from *Daphnia pulex* and separately cultured. Dehydrated milk powder was supplied as food. Tanks were cleaned weekly and replenished with fresh reconstituted water. Only young *Daphnia magna* were used in the study. Toxicity of leachate to *Daphnia magna* were used for testing of 100%, 10%, 1% and 0.1% leachate v/v with reconstituted water. Leachate from the soil column experiment was applied to test organisms. LC50s were calculated graphically from methods described by Weber et al. (1988).

Lemna minor (18th edition of Standard Methods for the Examination of Water and Wastewater). *Lemna minor* were collected from the same ponds as the *Daphnia Lemna* were cultivated in aerated moderately hard reconstituted water supplemented with Duckweed nutrient solution (Table 8211:I, Standard Methods). Toxicity tests were carried out using method 8211 C. Toxicity of leachate on *Lemna minor* were tested using 100%, 10%, 1% and 0.1% leachate v/v with reconstituted water.

Results

<u>Operating Campaign 1 – Startup and Mobilization</u>

This operational campaign began on 25 September 1997 and lasted until 27 January 1998.

Operation Plan: The Operation Plan for the First Operating Campaign assumed continuous airflow and no nutrient amendments. Internal biopile temperature was limited to 40 – 50°C and controlled by airflow rates.

Actual sampling and operation details: Aeration of the biopile started at the end of September. Until the middle of November, air was blown through the biopile 2 hours every other day with the full capacity of the blower (i.e., 500 m^3/hr). The air distribution was highly uneven, but airflow was confirmed at each piezometer of the active part of the biopile. When the ambient temperature dropped to below 0°C, the blower began experiencing problems (e.g., abnormally

high power consumption, probably caused by some obstacles in the blower rotor movement). Because of this, from the middle of November until the end of January the blower was only turned on sporadically, when weather permitted. During this campaign, the site also experienced large amounts of precipitation, this caused the biopile soil to be constantly saturated with water. Temperature of the biopile was uneven, ranging from ambient at the top, to 3 – 11°C above zero at the measuring points.

Issues / Resolutions

1. The reason for blower stoppages was not found. However, the blower and connections were examined by the refinery maintenance personnel. A cover was also built over the blower to protect it from ice.

2. It was decided to install a valve on the main of leachate collection / aeration system in the active part of the biopile, in order to improve air distribution.

3. Tracer tests and respiration test were not done during this campaign because of the unequal air distribution, problems with blower operation and procurement issues with the Helium.

<u>Operating Campaign 2 – Air</u>

Operating Campaign 2 lasted from February 1, 1998 until April 15, 1998.

Operation Plan: The Operation Plan for the Second Operating Campaign assumed continuous airflow in the active part of the biopile, an no nutrient amendments. Internal biopile temperature was limited to 40 – 50°C and was controlled by airflow rates.

Actual sampling and operation details: Aeration of the biopile was continued. The blower was disassembled and operated flawlessly afterwards. On average, the blower was on 8 hours a day with the full capacity (500 m^3/hr) which gave about 4,000 m^3 of air, (i.e., more than three soil pores volume exchanges, per day. A valve was installed on the leachate collection system main to control airflow. Pressure measured at the outlet of the blower dropped from about 0.3 atmosphere to about 0.1 atm, which is indicative for lower resistance to airflow through the biopile. Pressure measurements carried out on each piezometer showed better air distribution throughout the active part of the biopile. However, a respiration test with helium as a tracer showed that some differences in airflow through the biopile still remained. During this campaign, the site also experienced large amounts of precipitation (120 mm), which caused the biopile soil to be constantly saturated with water. Temperature of the biopile was fairly even, ranging from 4.5 to 7°C.

Issues / Resolutions

1. A valve on the main of the leachate collection/aeration system was installed in order to improve air distribution in the active part of the biopile.

2. Because tracer tests and respiration tests carried out during this campaign showed that the unequal air distribution remained, it was decided that some piezometers should be reinstalled or flushed.

Respiration and Tracer Tests.

A tracer test was carried out during the campaign using helium as a tracer. The test confirmed uneven air distribution in the active part of the biopile. Piezometers 13, 14, 15, 18, and 20 indicated almost no airflow.

Respiration tests carried out immediately after tracer tests generally showed very low rates of oxygen usage throughout the active part of the biopile. As an example, results from the piezometer no. 16, showing the highest decrease in oxygen concentration during the test, are presented below (Fig. 6.8).

The biodegradation rate calculated from this data is 2.9 mg/kg/day, which is about two orders lower than the rate calculated from inventory change data.

Operating Campaign 3 – Air and fertilizer

This operating campaign ran from April 16, 1998 until June 30, 1998.

Operation Plan: The Operation Plan for the Third Operating Campaign assumed continuous airflow and nutrient amendments in the active part of the biopile.

Actual sampling and operation details: Aeration of the biopile was continued. It cannot be determined accurately how much time the air blower was actually on. A watt/h meter was installed in late May to monitor air blower operation. After heavy rains, the blower should be turned off, while a leachate release valve must be manually opened for approximately 1- 2 hrs. Immediately after this procedure, the valve must be manually closed and the pump manually restarted. Quite often, refinery personnel forgot to restart the pump. During this campaign, the site experienced large amounts of precipitation, this caused the biopile soil to be constantly saturated with water. Temperature of the biopile was constantly increasing from 7°C to nearly 19°C at the end of this campaign. Active side average soil temperatures were consistently higher than those of the passive side.

Issues / Resolutions

1. The Watt/h meter was installed on May 15 to properly track air blower operations. Refinery personnel were informed again on the importance of restarting the blower after leachate draining after heavy rains.

2. Fertilizer application was too low (100 kg) because of competition between surface cover and soil microbes. The solution was to utilize the new leachate recirculation system to dissolve fertilizer for uniform application under the rhizosphere layer. The system was designed and was deployed before the start of the next campaign.

3. Plugged piezometers, 13, 14, 15, 18, 20 were flushed and reinstalled before the next campaign to insure accurate soil gas readings.

Operating Campaign 4 – Leachate recirculation

This Operating Campaign began 1 July 1998 and ended 30 September 1998.

Operation Plan: The Operation Plan for the Fourth Operating Campaign assumed continuous air flow in the active part of the biopile, nutrient amendments and leachate recirculation in both active and passive parts of the biopile.

Actual sampling and operation details: Aeration of the biopile was continued. A leachate recirculation system was built. The aim of the system was to maintain proper moisture level in soil, dissolve fertilizer and apply it uniformly throughout the whole biopile avoiding competition for nutrients between surface plant cover and soil microbes. The system consists of a pump, a container vol 1.5 m^3 , a 50 meter long main, and 10 parallel perforated pipes each 40 meters long. Perforated pipes are inserted in trenches about 30 cm deep to avoid direct contact of leachate with rhizosphere. A respiration test with helium used as a tracer was carried out. Results showed rather uneven air distribution throughout the biopile. Landfill gases (CH_4, CO_2, O_2) were measured each week in both the active and passive parts of the biopile. In some points characterized by water-logged soils, high methane concentrations were measured. CO_2 concentrations were generally high, (particularly in the shallow part) which can be explained as result of high biopile activity.

Moisture measurement showed some places in the upper part of the biopile with a low content of water. Moisture content in the lower part of the biopile was constantly above 90%, except for a few spots. The average temperature in the active section of the biopile was consistently 10°C higher that in the passive section.

Issues / Resolutions

1. During a start-up procedure it was found that the leachate was not distributed evenly throughout the biopile surface. There were some spots located far from the system feeding point which were not watered at all. It was decided to replace the main with a larger pipe (1 inch ID). An inspection of the system showed that water distribution throughout the biopile was satisfactory.

2. Plugged piezometers were flushed and reinstalled.

<u>Operating Campaign 5 – Surfactants</u>

This operating campaign ran from July 4, 1999 until Sept 29, 1999.

Operation Plan: The Fifth Operating Campaign tested the use of a Triton N-101 analogue (Rokafenol N-8) to increase biodegradation within both active and passively aerated sections of the biopile.

Actual sampling and operational details: The air blower supplying air to the active section was operated for eight hours a day. The air supply to the passive sections was dependent on changes in atmospheric pressure to operate BaroBalls. Leachate from the biopile was held in a collection sump and 1.5 m^3 of leachate was pumped into an above ground tank and mixed with approximately 30 kg of surfactant. The mixture was pumped on to the surface of the contaminated soil into specially dug trenches beneath the topsoil layer. Thirteen applications of surfactant/leachate were planned during the three-month test period. Meteorological data (average rainfall of 133 mm of rain) was used to calculate the amount of surfactant necessary to produce three times the CMK. Polifoska fertilizer (200 kg) mixed with leachate was also applied to the biopile at the start of the experiment. A total of 380 kg of Rokafenol N8, a counterpart of Triton N 101, was applied to the biopile. After three months of surfactant treatment, nearly 44% and 61% of the remaining TPH were respectively biodegraded from the passively and actively aerated sections of the biopile. Concurrently, microbial activity, measured by dehydrogenase measurements with TTC, also was shown to increase.

Respiration tests in June prior to the start of OC5 showed a good rate of respiration, indicating high biological activity (Figure 6.9). Just after fertilizer application and recirculation of leachate with surfactants the respiration in the biopile was measured again (Figure 6.10). The much lower respiration rate observed suggests that the initial increase and nutrients and/or the surfactants may have decreased the biodegradation rate at first.

Issues/Resolutions

1. The time necessary for surfactant application shortened from 7 h to 1.5 h. The original hose (0.5 inch ID) was found to be too small in diameter to efficiently distribute the surfactant/leachate. A replacement hose (1-inch ID) was purchased and substituted.

<u>Overall changes and comparison</u>

Physical Parameters

· Weather (rainfall, temperature, barometric pressure)

Temperature at the demonstration site ranged from –10 to 27°C during the demonstration. Rainfall was highest during OC3, OC4 and before the start of OC5. The end of OC5 was also a drought period. Oversaturation of the soil during OC3 and OC4 could have significantly reduced the aerobic biological activity during the demonstration due to water logging of the soil and decreased ability of oxygen to diffuse into pore spaces to promote aerobic respiration. The drought period at the end of OC5 could also have reduced the biological activity due to moisture limitations (Figure 6.11). The drying effect was collaborated by the drop in soil moisture observed for all treatment areas during OC5 (see soil moisture below). Barometric pressure ranged from 950 mm to 990 mm and could be rapid over a 2 or 3 day period, previous studies have shown this range of pressure fluctuations should provide good barometric pumping into the biopile over a maximum of 2-3 day intervals (Rossabi, 1999).

· Temperature, (i.e. soil/leachate)

Soil temperature for the passive and active sides of the biopile were usually 5-10°C above the ambient air temperature (Figure 6.12). The actively injected part of the biopile was also usually 1-5°C warmer than the passive side. This suggests that biodegradation was more active on the air injection side of the biopile, since the only way that more heat could have been created is by the increased respiration, a phenomena well known in composting.

· pH

The pH in the soil ranged from 5.8 to 7.7 during the demonstration. Passive, active, shallow, and deep zones all increased in pH during the OC2 and OC3, declined or increased slightly during OC4 and decreased from OC4 to the end of OC5. This is consistent with air addition, which increases aerobic activity, thereby decreasing reducing agents produced under anaerobic and less active conditions. Leachate recirculation during OC4 and surfactant recirculation during OC5 released adsorbed acidic contaminants in the subsurface thereby decreasing the pH slightly. The observed pH changes were not significantly different between active and passive or between shallow and deep (Figure 6.13)

· Moisture

Moisture in the soil was generally high and changed very little during the demonstration regardless of aeration strategy or depth. The lowest moisture observed at all sites was during

OC5 due to a drought (Figure 6.11). The moisture at any site in the study area was not limiting at any time (Figure 6.14)

· Humidity

Relative humidity ranged from 91% to 100% in the soil for the entire demonstration. Though the shallow passive area had consistently lower humidity than the other areas it was still well above any soil gas humidity that would indicate the soil was dry and that water could be limiting to biological activity (Figure 6.15).

Contaminant Parameters

· Leachate toxicity.

LC50 values for leachate using *Daphnia magna* and *Lemna minor* at the start of OC1 generally agree with values obtained from column studies (See Chapter 5) LC50 values for the leachate were 40% and 37% respectively. For the filamentous fungal tests, leachate from the biopile produced a 50% inhibition in fungal colony diameter. Results indicate the potential risk of leachate to aquatic and fungal organisms.

· TPH

Total Petroleum Hydrocarbon (TPH) concentrations decreased by more than 50% in both deep and shallow active aeration zones by the end of the second operating campaign. TPH declined more slowly in the passive aeration area but had also declined by more than 50% by the end of OC3. Very little change was observed during OC4; however, another significant decrease was observed at all sites after surfactants were added during OC5. By the end of OC5 all areas had experienced more than an 80% drop in TPH concentrations (Figure 6.16).

· TPH Polar

Polar Total Petroleum Hydrocarbon (TPH Polar) showed the same pattern as TPH: concentrations decreased by more than 50% in both deep and shallow active aeration zones by the end of the second operating campaign. TPH Polar declined more slowly in the passive aeration area but also declined by more than 50% by the end of OC3. Very little change was observed during OC4; however, another significant decrease was observed at all sites after surfactants were added during OC5. By the end of OC5 all areas had experienced more than an 80% drop in TPH Polar concentrations (Figure 6.17).

· B(a)P

The concentrations of Benzo (a) pyrene were less than 1 at all sites. A slight increase at the end of OC2 was apparently caused by a spill that caused leakage of oily waste from and the adjacent lagoon into the back of the active area and to a lesser extent of the passive area. However, even though there were significant inputs into the biopile all areas decreased by 50% or more by the end of the demonstration (Figure 6.18).

· Fluoranthene

Fluoranthene was low in all the areas but lower in the shallow passive section (Figure 6.19). Despite a slight increase during OC3 for the deep passive zone, fluoranthene for all other zones declined during the demonstration (Figure 6.19). All fluoranthene concentrations were less the 2 mg/kg by the end of OC5.

· Total PAH

Total PAH concentrations were generally low ranging from 0.20 to 0.75 mg/kg soil (Figure 6.20). The deep sections in both the passive and active areas had nearly twice the concentrations of the shallow areas initially. By the end of the demonstration all depths and areas had declined to less than 0.20 mg/kg. Significant differences between operating campaigns were only seen between OC4 and OC5 when total PAH concentrations dropped in all areas. The low concentrations do not allow an interpretation of differences between operating campaigns.

· Metals

The soil metal concentrations were well below maximum contaminant level guidelines for Polish industrial use sites at all times (Table 6.4). In general the metal concentrations changed very little; however all metals were markedly lower by the end of the demonstration. Indeed, cadmium declined by more than 90%, chromium by more than 30%, cobalt by 38%, lead by more than 70%, and mercury by 30%. Cadmium, lead and zinc were all greater than the guidelines for multi-use purposes at the beginning of the demonstration, by the end they were all well below the Polish multi-use guidelines (Table 6.4). Reduction in soil metal concentrations could have resulted from biological reduction, leachate recirculation, and surfactant additions. The greatest reductions occurred after surfactant addition, suggesting that surfactant mobilization of metals and subsequent dispersion could have caused the observed metal reduction.

Nutrient Parameters

· PO4

Phosphate concentrations were extremely low, except during a dramatic increase between OC4 and OC5 due to a major application of fertilizer at that time (Figure 6.21). This caused phosphate concentrations to also be significantly higher during OC5. Phosphate was limiting for all areas through OC4, but could have significantly increased biodegradation during OC5.

· Total Phosphorus

Total phosphorus concentrations were high, ranging from 100 to 800 mg/kg (Figure 6.22). The concentrations declined after OC2, probably as a result of nutrient depletion and leaching. After fertilizer application and leachate recirculation the total phosphorus levels more than doubled probably due to increased leaching caused by the surfactants added during OC5.

· NO2

Nitrite levels were low in all areas but declined even more during the demonstration (Figure 6.23). This suggests that the biopile was originally anaerobic which would allow accumulation of nitrite in the soil. Aerobic conditions that would deplete nitrite caused it to decline through the demonstration. This is further supported by the slower rate of decline in the passively aerated sections both shallow and deep.

· NO3

Nitrate concentrations were low in all areas but increased after fertilizer additions in the active parts of the biopile after OC2 and during OC5 (Figure 6.24). Fertilizer application in OC3 and OC5 undoubtedly caused this increase in nitrate concentration during these operating campaigns, though passively aerated areas showed only minor effects during OC3, they showed an equal response in OC5.

· NH4

Ammonium was low and increased during OC3 and OC4, but declined after the end of OC4 (Figure 6.25). Generally the ammonium concentrations were variable by depth and type of aeration.

· TKN

Total Kjeldahl Nitrogen increased during the first 3 operating campaigns but declined dramatically during OC4 while leachate was being recirculated (Figure 6.26). TKN increased from the end of OC4 until OC5. This suggests that denitrification was greatly enhanced during OC4 leachate recirculation.

· Leachate BOD and COD

The leachate BOD and COD increased slightly after leachate recirculation began and then again after surfactants were added (Table 6.5). Both increases were modest, however, it does suggest that the leachate recirculation and the surfactants increased the amount of oxidizable and biodegradable organics that were in the leachate, suggesting that more organics were being eluted off the soil matrix.

Biological Parameters

· TTC

Dehydrogenase activity increased dramatically during the first two operating campaigns then declined during OC3 (Figure 6.27). During OC4 leachate recirculation activity increased in all areas. The actively injected areas were higher in biological activity than the passive sections and the deeper sections of both the passive and active areas had a higher activity than their respective shallow sections. Since dehydrogenase activity is a total measurement of enzymatic activity in the soil, both fungal and bacterial, and the fungal densities declined when the bacterial densities increased.

· Fungal (CFW)

Fungal densities were highest prior to air injection when bacterial populations were stimulated. However, both deep areas showed an increase in fungal density during leachate recirculation in OC4 (Figure 6.28). Both shallow areas experienced an increase in fungi during OC3, because bacteria densities declined concomitantly. This would suggest that conditions in the shallow areas during the fertilizer addition favored fungi.

· DAPI

Bacteria densities increased as much as 3 orders of magnitude during OC1 and OC2 (Figure 6.29). Total bacterial numbers remained fairly stable once they had been stimulated, with a slight decline observed during OC3 in all areas. This decline could have been due to the water logging of the soil observed at this time due to above normal rainfall.

· MPN Petroleum

Petroleum degraders that grew at 20°C declined in both areas during the demonstration (Figure 6.30), while petroleum degraders that grew at 37°C increased in all areas with a decline during OC4 when leachate was being recirculated (Figure 6.31). This would indicate that a shift to more aerobic and thermotolerant organisms was occurring in all areas during the demonstration.

· MPN Naphthalene

Naphthalene degraders that grew at 20°C declined in both areas through OC3 and then rebounded during OC4 and OC5 (Figure 6.32), while naphthalene degraders that grew at 37°C increased in all areas through OC3 and then declined to their previous densities during OC4 and OC5 when leachate was being recirculated (Figure 6.33). This would indicate that leachate recirculation might have selected for less thermotolerant organisms during the demonstration.

· CO_2

Both deep areas had significantly higher concentrations of carbon dioxide due to their more anaerobic conditions (Figure 6.34). Carbon dioxide increased with fertilizer addition in OC3 and leachate recirculation and surfactant addition in OC4 and OC5, respectively. The carbon dioxide concentrations observed indicate active biodegradation was occurring in all areas.

· CH_4

Methane was generally low in all areas and variable (Figure 6.35). Methane concentrations were significantly higher in both deep areas, but highest in the deep passive area. This is to be expected since the deep passive zone should have the least air penetration and should be more conducive to anaerobic conditions where methane could be generated.

· O_2

Oxygen was generally near saturation in all areas and varied only slightly during the demonstration (Figure 6.36).

Spatial distribution of parameters in the Biopile

The spatial distribution of contaminants was different between the passive and active sides of the biopile (Figure 6.37-6.40). The active side of the biopile had higher contaminant concentrations initially than the passive side, but the differences between the shallow and deep areas of each side of the biopile were not significant. It is also obvious that during OC4 and OC5 there were leaks on the southern side of the active part of the biopile. By the end of the demonstration there were only trace concentrations of TPH and PAHs left in either the passive or active parts of the biopile.

The carbon dioxide concentrations were higher in the passive parts of the biopile and the deep parts of the biopile (Figures 6.41 and 6.42). Where air penetration was the poorest carbon dioxide concentrations were the highest, (e.g., passive and deep areas of the biopile). This coincides with more anaerobic conditions that would generate more carbon dioxide.

The dehydrogenase concentrations (TTC) gradually increased in the active parts of the biopile through OC4 (Figures 6.43 and 6.44). The deep parts of the active zone showed the highest TTC concentrations during OC2.

Additional parameters are presented here without significant discussion. These include benzo(a)pyrene (B(a)P); calcofluor white (CFW); 4, 6 diamindino 2 phenylindole (DAPI); and pH concentrations in shallow and deep layers (Figures 6.45 - 6.52).

By plotting changes in TPH concentrations together with changes in microbial activity (TTC), the relationship between reduction in contaminant and microbial activity becomes more obvious (Figures 6.53 and 6.54). The highest microbial activity areas, both shallow and deep, for the end of OC2 coincide nicely with the areas in the biopile that showed the greatest reduction in TPH concentration.

Correlations and other Statistics

The overall correlations for the soil parameters showed that the direct bacteria counts (DAPI) were significantly inversely correlated with total petroleum hydrocarbons (TPHTOT), polar total petroleum hydrocarbons (TPHPOL), and fluoranthene (FLORAN) (Table 6.6). This shows that over the entire demonstration, as the bacterial numbers increased the contaminant concentrations decreased, suggesting a direct relationship. Further inspection of the matrix also shows that as DAPI numbers increased the fungal numbers (CFW) decreased, suggesting that the microbial community shifted due to an inability of fungi to compete with the smaller and more metabolically active bacteria. The fungi also apparently played little if any role in the reduction in contaminants numbers since CFW was not significantly correlated with any of the contaminant parameters (TPHTOT, TPHPOL, FLORAN, BBFLUORA, BKFLUORA, BAPYRE, BOPERY, and I123CDY). DAPI numbers were also significantly correlated with enzymatic activity (TTC), so that as the bacterial numbers increased the total dehydrogenase enzyme activity in the soil also increased. The dependence of bacterial densities on adequate sources of phosphate was also indicated by the significant positive correlation between DAPI and PO4. The petroleum degrader enrichments at 20 and 37°C and the naphthalene degrader enrichments at 20 and 37°C appeared to be indicating the density of contaminant-tolerant microbial populations in the soil rather then degraders. This is suggested by the significant direct correlations between these parameters and the contaminants parameters (TPHTOT and TPHPOL), thus the higher the concentration of the contaminant the higher the density of these types of microbes. Both enrichments at 37°C had very few correlations to any of the other soil parameters, in part due to few measurements. The enrichment assays seem to be a poor index of biodegradation activity during the demonstration. Soil pH was also significantly inversely correlated with nearly all the contaminant parameters. This suggests that either the biostimulation process was increasing, the pH as the contaminants were being degraded, and/or the biodegradation of the contaminants was causing the soil pH to increase. It is likely to some extent that both processes were occurring since it is well known that oxidation processes tend to increase pH when anaerobic acidic environments are driven to be aerobic. The validity of the soil data matrix is supported by highly significant direct correlations between all the contaminant parameters and between the contaminants and total Kjeldahl nitrogen (TKN), a normal expectation since the contaminants are normal components of petroleum and petroleum is high in organic nitrogen.

Summary and Discussion

The Polish petroleum refinery biopile field demonstration had a number of significant findings. These were tied back to the criteria for success that were stated at the beginning of this section and in the original Test Plan for the demonstration (Altman et al., 1997).

<u>First criteria for the success of this demonstration.</u>

The first criteria for success was to demonstrate the application of bioventing/biosparging as a viable cost-effective process to remediate contaminated sites, to reduce risk to man and the environment, and resulting in a green zone. The ability of the remediation process to degrade high molecular weight compounds (PAHs) was evidenced by utilizing state-of-the-art monitoring equipment, analytical techniques and treatability studies to determine the rate and volume reduction in the starting concentrations of the contaminants.

Over the entire field demonstration more than 120 metric tons or 81% of the total petroleum hydrocarbons present were remediated(Table 6.7). By the end of the 20 month biopile demonstration, concentrations of TPH and all PAHs were below the Polish and US risk guidelines for even shallow soils (0.3-15 m) for sites with multi-uses (including residential). All the metal concentrations in the soil which were initially only acceptable for industrial use sites fell below the MCL guidelines for shallow multi-use sites because of the injection of nutrients and recirculation of leachates. This full scale demonstration simultaneously remediated the contaminants present in the soil to acceptable risk levels and created a permanent green zone with a park like atmosphere in less than 20 months. The comparison of passive with active aeration demonstrated that the Baroballs, a DOE patented technology, could be used effectively to provide aeration of biopile for petroleum remediation via barometric pumping. This comparison showed that passive air injection required 3-5 months longer to reach the same end point as blower injection of air. Passive injection could thus provide a significant cost savings whenever there is no urgency for remediation due to immediate risk to human health or the environment (or in areas where risk of damage or vandalism are high). The details of the cost comparison to baseline technologies is covered in chapter 7 on cost analysis.

New field instruments that were used to monitor physical and chemical parameters in the field had variable success. The landfill gas analyzer proved extremely robust for measuring changes in carbon dioxide, oxygen, and methane in the soil gas. These measurements helped verify the respiration rates, the degree of injected air penetration into the biopile and a measure of aerobic conditions in the biopile. The installed temperature and moisture blocks were not sensitive enough to indicate significant changes in either parameter, thus were of minimal value. However, the moisture blocks did provide evidence that the biopile was drying out in the later part of operating campaign 5. The photoacoustic infrared spectrophotometer proved difficult to operate and did not provide reliable data on soil gas concentrations in the later part of the demonstration. This was primarily due to humidity interferences from water vapor becoming entrained in the instrument. These measurements had to be eliminated from the final analytical data set due to these problems. The HydroLab surveyor worked well but was not of significant use due to the small quantity of leachate that that was measurable from the biopile system.

The five operating campaigns showed that initially air injection alone (OC1 & OC2) stimulated dramatic reductions of contaminants (>50%) in the biopile in less than 7 months (Table 6.7). Subsequent operating campaigns using the addition of fertilizer with the air (OC3) and leachate recirculation (OC4) removed only an additional 1% of the contaminant inventory in a similar period of time. However, the final operating campaign (OC5) which added surfactants, decreased the contaminant inventory an additional 30% and caused a significant reduction of all of the metals in the soil. These findings are verified by the biodegradation rates observed during the different operating campaigns (Table 6.8). The first two operating campaigns had high rates of biodegradation in the active injection areas and these fell off during OC3 and OC4, but were increased to their highest levels in any area during OC5. This suggests that surfactants make more of the strongly sorbed contaminants bioavailable. The passive section of the biopile responded in a similar manner but with about a 3-5 month lag and did not achieve the rates seen in the active aeration sections. The rates observed are similar for bioremediation of other petroleum contaminated soils, and quite good for similar biopile studies, {e.g., prepared beds (52-641 mg/kg soil/day), biopiles (20-60 mg TPH/kg soil/day), bioventing (2.5-10 mg TPH/kg soil/day)} (Bartha, 1986; Lombard and Hazen, 1994; Kastner et al., 1997). This demonstration suggests the combination of active aeration, fertilizer, and surfactants with leachate recirculation

will provide the fastest site remediation and substituting passive aeration will reduce the cost but increase the time to reach endpoint.

Second criteria for success of this demonstration.

The second criteria for success was to demonstrate evidence of biological destruction (biodegradation) of petroleum (PAH, TPH and BTEX) from the contaminated material. Since a major advantage of bioremediation is destruction, it is important and significant to demonstrate that biodegradation is occurring. The evidence is expected to come primarily from comparison of the biopile material and soils analysis taken before, during and after the material is subjected to the treatment process (nutrient addition, aeration, pH adjustment and moisture control) to stimulate biodegradation.

Multiple lines of evidence show that biodegradation of PAH and TPH occurred during the demonstration. BTEX compounds were undetectable in the soil after the first samples. The field photo-acoustic infrared spectrophotometer gave unreliable results of soil gas concentrations especially later in the demonstration when the humidity in the detection column became high. First, the contaminant inventory changes showed that large concentrations of petroleum contaminants were being removed at rates that could only have been attributed to rapid biodegradation (Table 6.7). Second, respiration studies showed that the oxygen demand in the active area corresponded to the rates of contaminant reduction observed. Third, over the entire demonstration there was a highly significant inverse correlation between bacterial density and contaminant concentration. Fourth, limiting nutrients like phosphate concentrations were directly correlated to bacterial density as were enzymatic activity measurements of soil (TTC). This suggests that bacteria were being biostimulated by the nutrient amendments being applied during the operating campaigns. The treatability and column simulation studies also verified in a like manner that biodegradation was responsible for reduction of contaminants and that the nutrient and surfactant amendments being applied in the field caused similar responses in the laboratory. Fifth, the aeration of the biopile soil created an aerobic environment conducive to aerobic biodegradation of petroleum contaminants. Sixth, all PAHs measured were also being degraded. Seventh, very active, low pH tolerant petroleum and PAH degraders could be isolated from the biopile that used petroleum and PAHs as their sole carbon and energy source. And eighth, the modeling studies of the field data showed that the biodegradation of the contaminants observed during the demonstration could be simulated by a kinetic model of contaminant biodegradation. The effects of each operating campaign were discussed in the previous section.

Third criteria for success of this demonstration.

The third criteria of success was to demonstrate a relatively simple and trouble-free operation. A critical assumption for the successful demonstration of the technology is that the system, as designed, will function with little or no down time and provide operating conditions that minimize fugitive air emissions and maximize biodegradation rates. This project had no precedence in Poland and as such represents new technology for the country. However, since several other nations have demonstrated similar technologies, it represents a relatively low risk and should have high public acceptance. The simplistic design contributes direct benefits associated with the ease of management and operation. A minimal staff will be required to operate the equipment, again adding to the low risk factor by limiting exposure to operations personnel.

The equipment and operation went through a number of delays during the initial 3 months of operation, due to differences in voltage, planning, weather and manpower delays from a variety of sectors in this multi-institutional and multi-national demonstration. However once these initial problems were solved, the operation was relatively simple and maintenance free. See the cost analysis for a complete description of costs and comparison to international differences. The simplistic design served the project well and helped make the project the success it was. The large number of tours, symposia, presentations and publications (see the Appendices for complete list) are also a direct index of the overall success of this project and its public out reach and acceptability.

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Figure 6.1 Refinery Lagoons

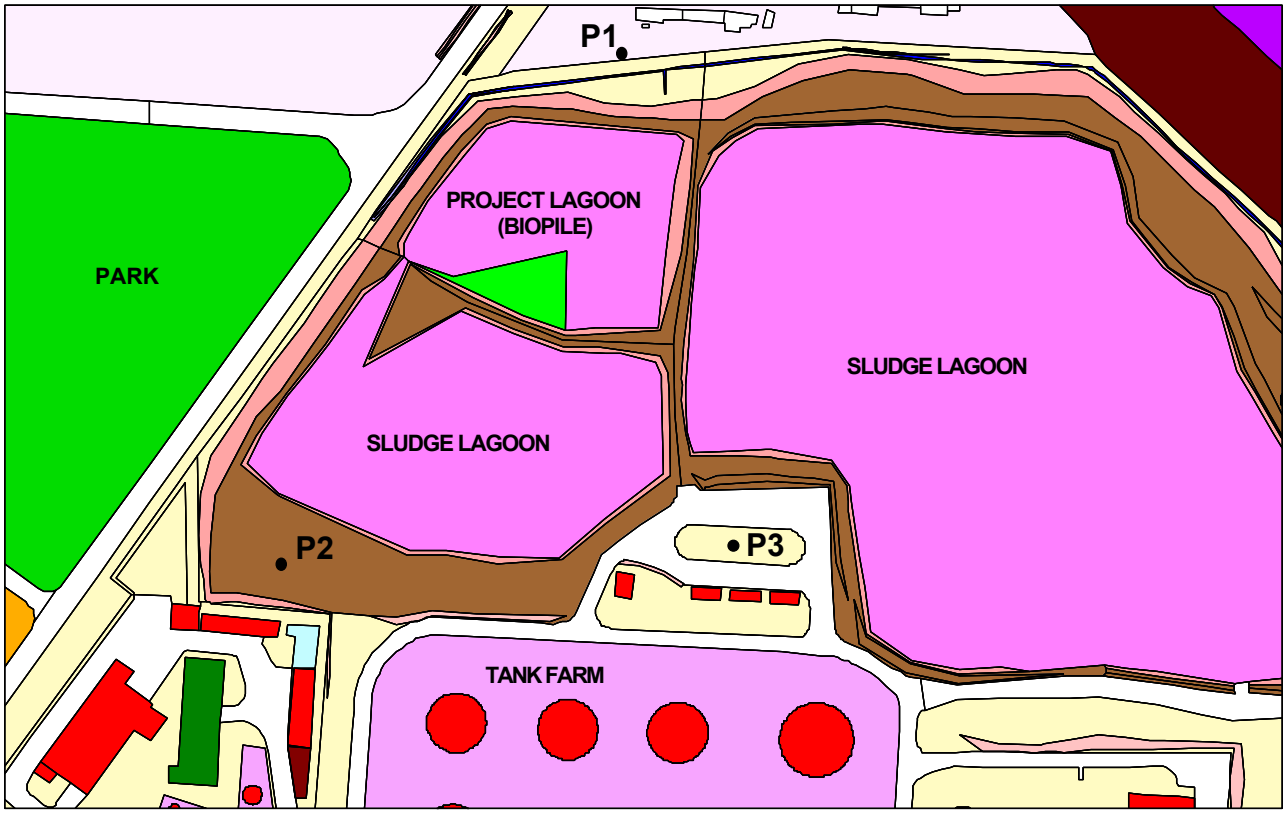

Figure 6.2 Conceptual Diagram

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Figure 6.3 Cross Section Design Drawing

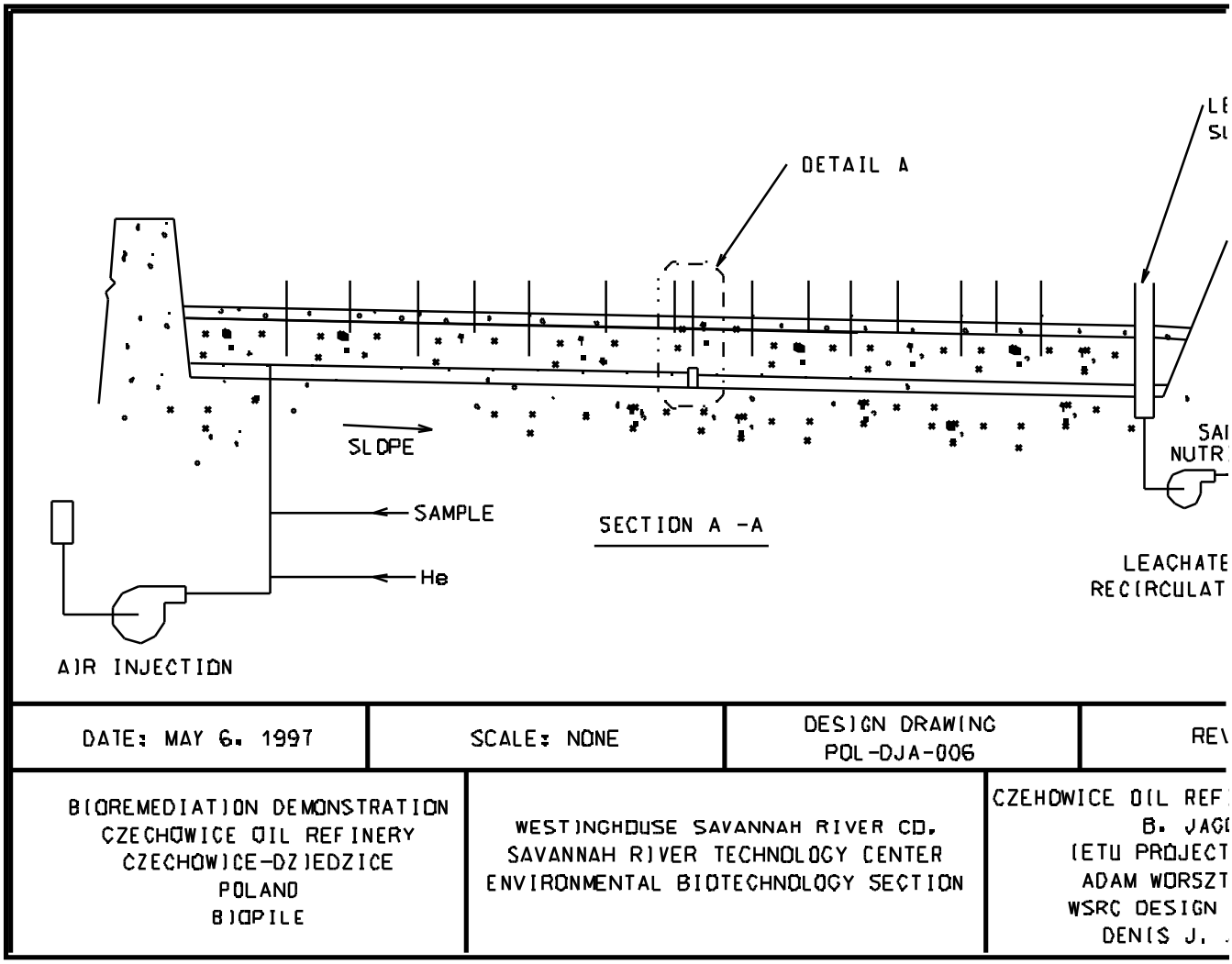


Figure 6.4 Plan View

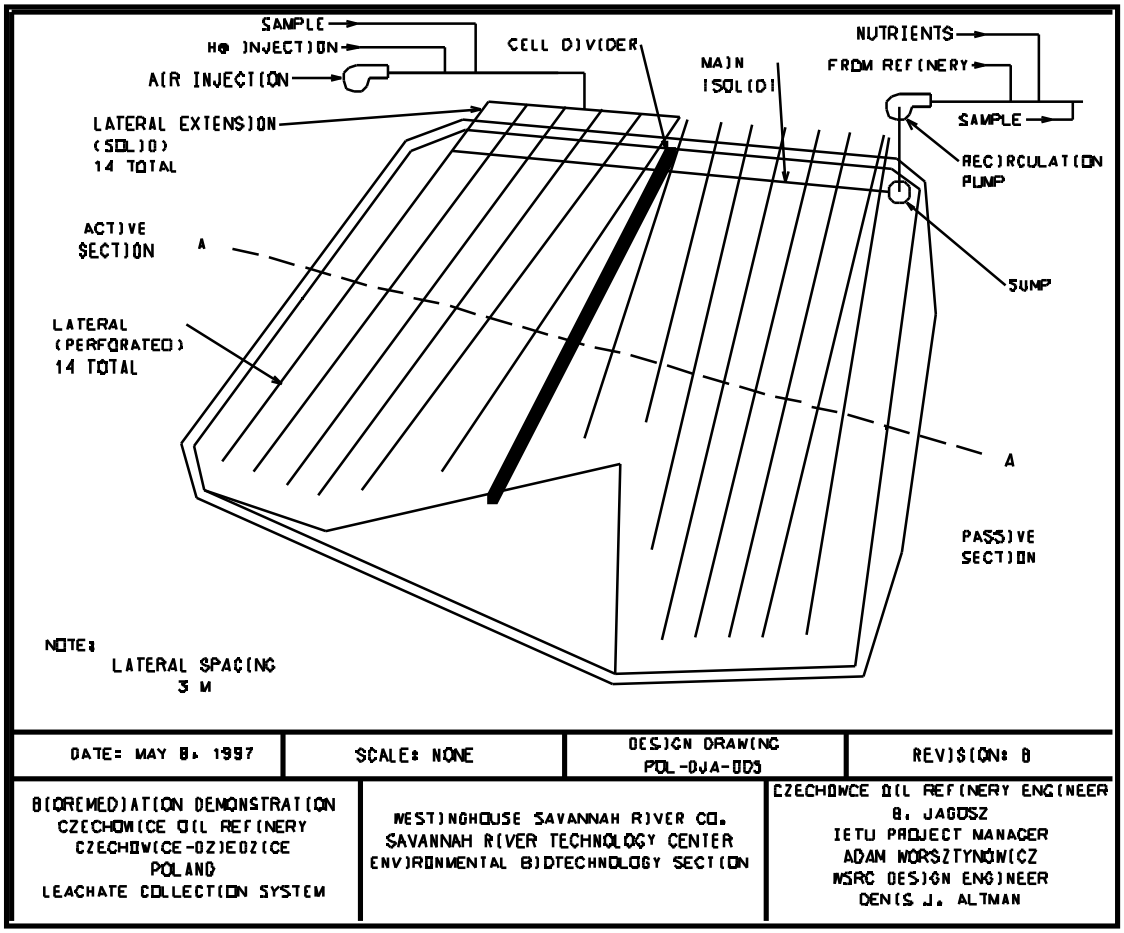


Figure 6.5 Monitoring Point Design

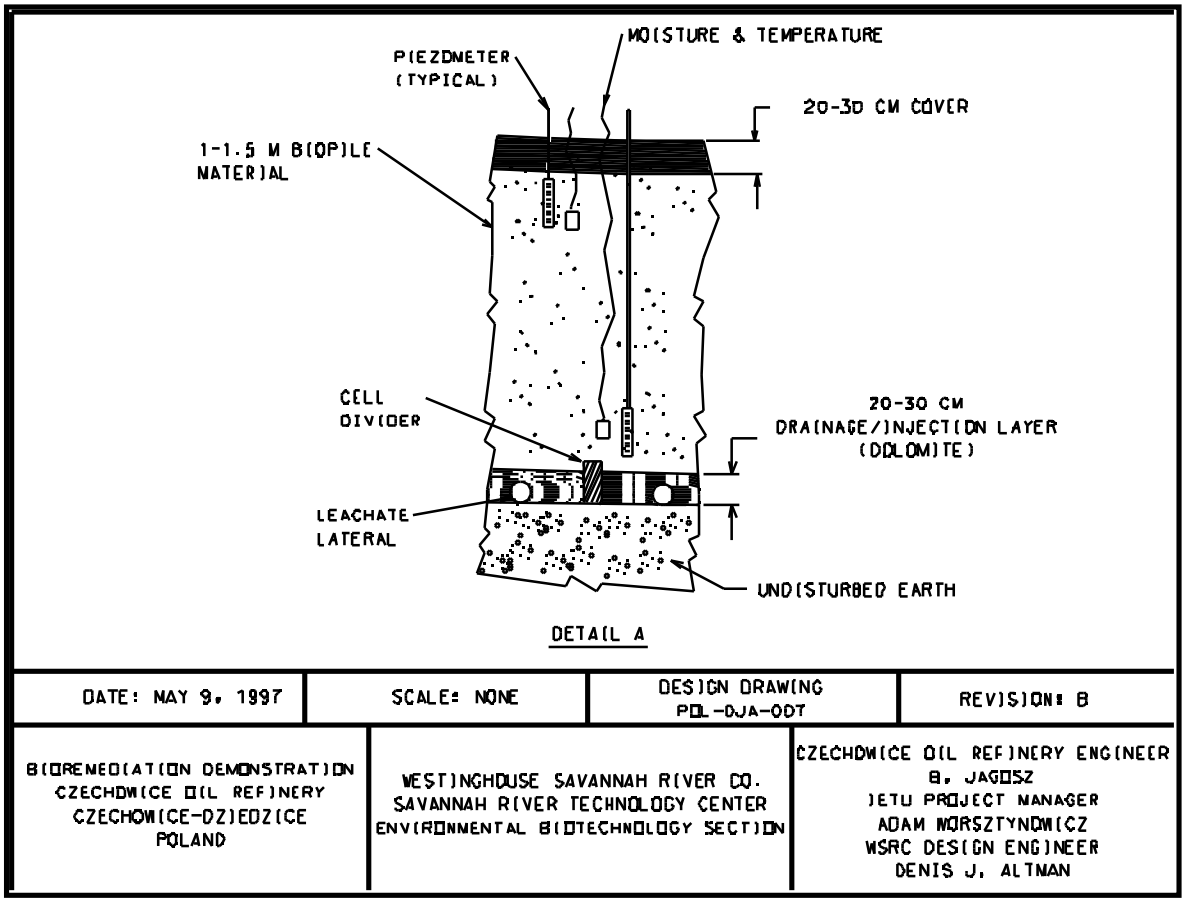


Figure 6.6 Injection Design

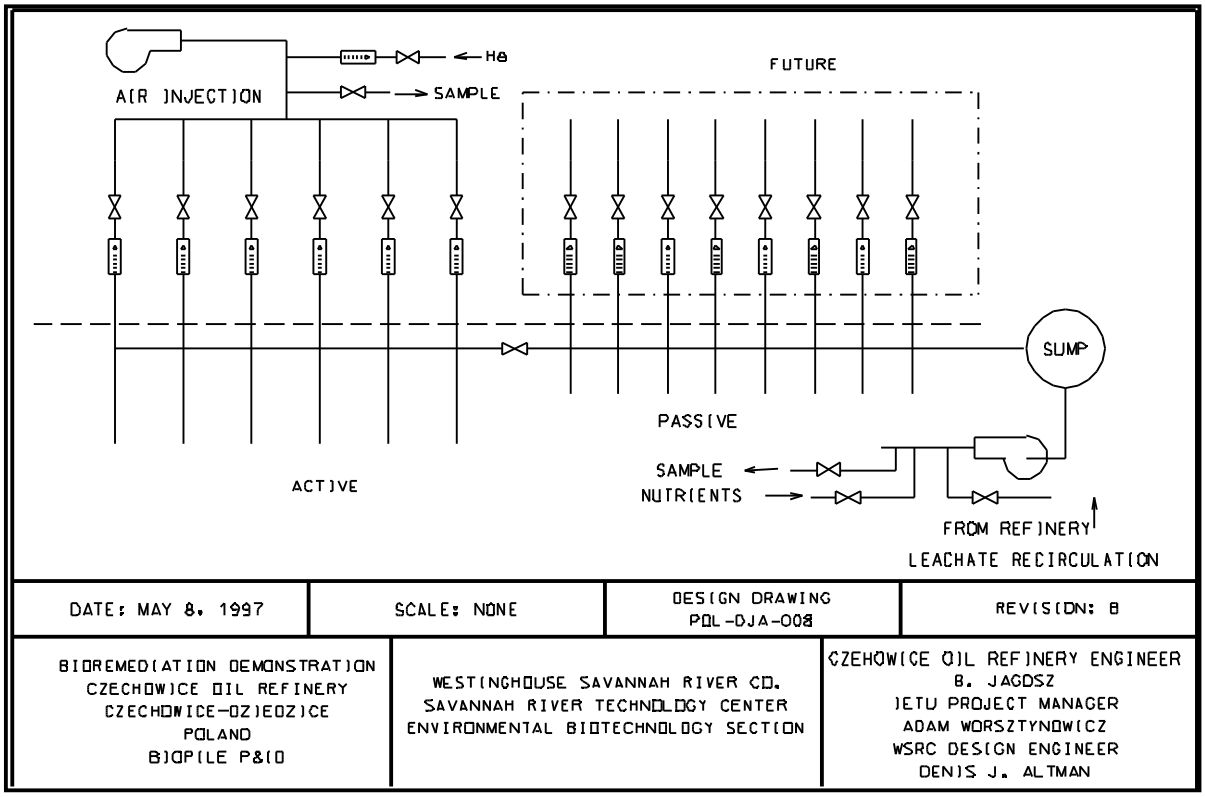


Figure 6.7 Vadose Zone Piezometer Design

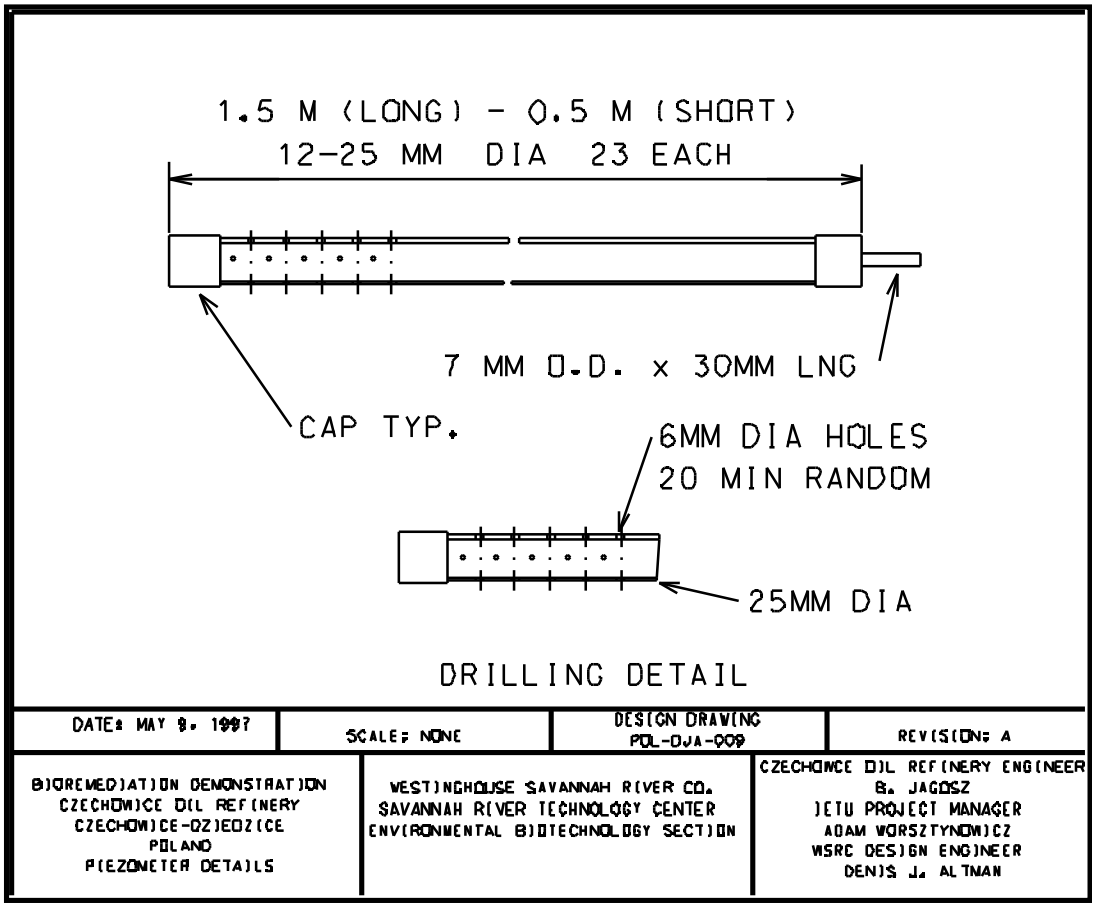


Figure 6.8 Biopile respiration test results.

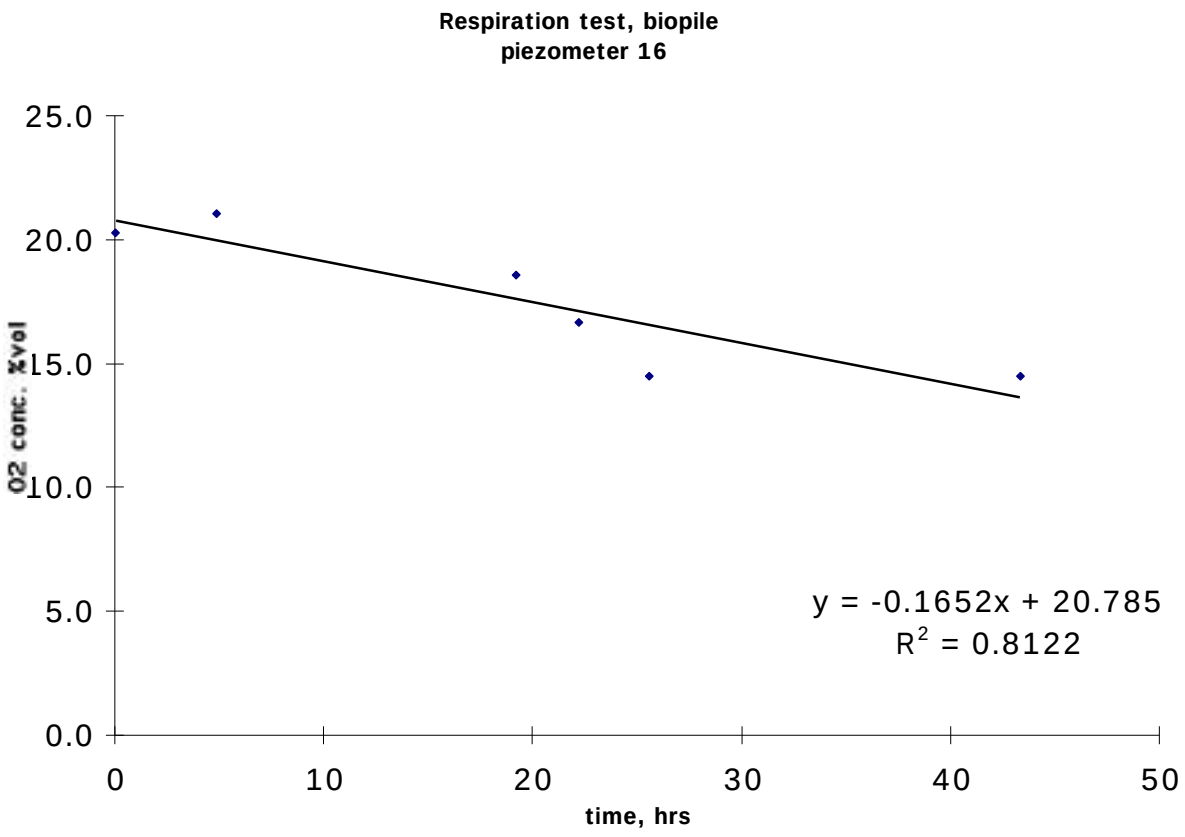


Figure 6.9 Respiration Test (June 15, 1999)

Figure Not Available

Figure 6.10 Respiration Test (July 13, 1999)

Figure Not Available

Figure 6.11 (A,B,C) Pressure, Temperature and Rainfall Over Time

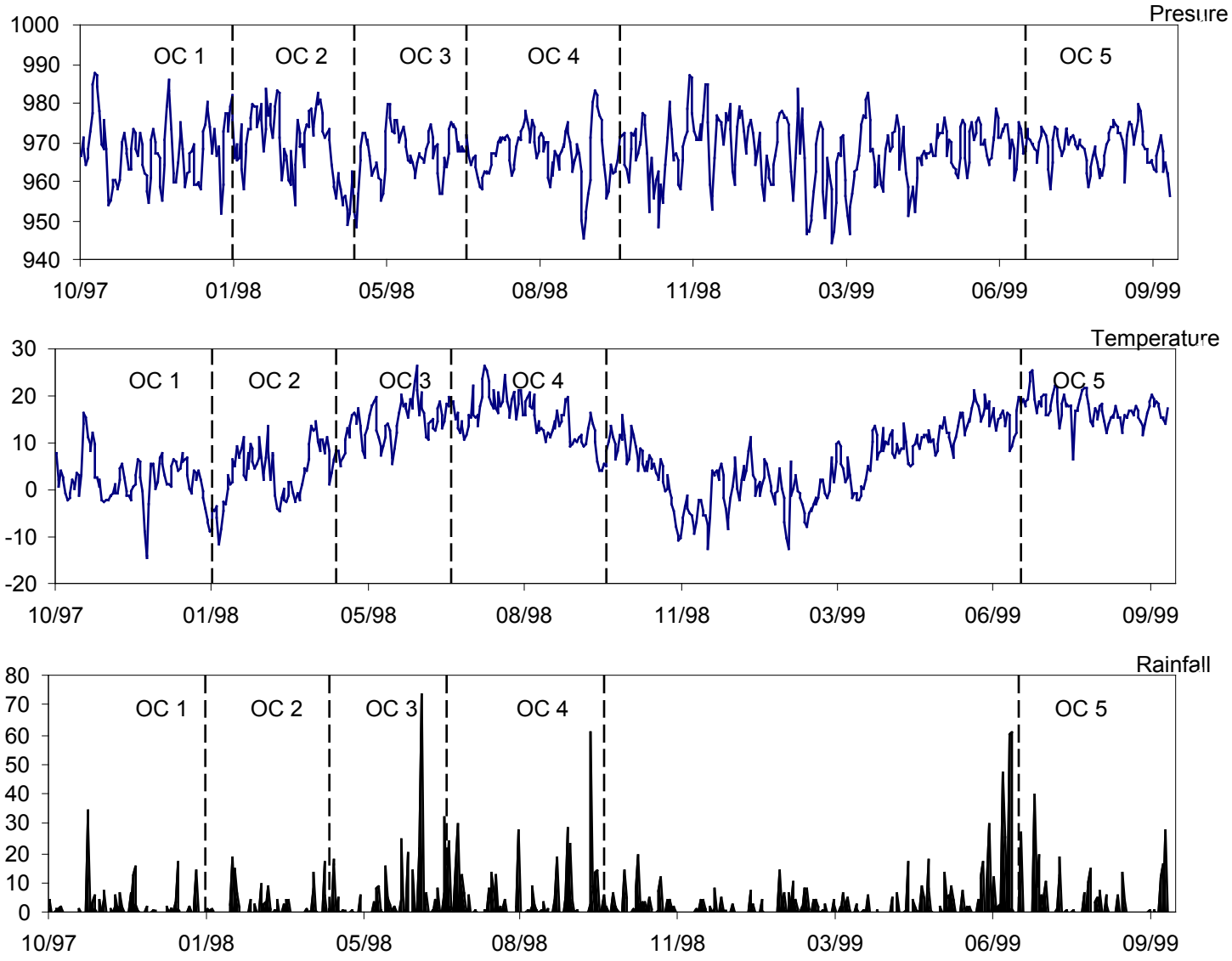


Figure 6.12 (A,B) Soil Temperature: Active & Passive

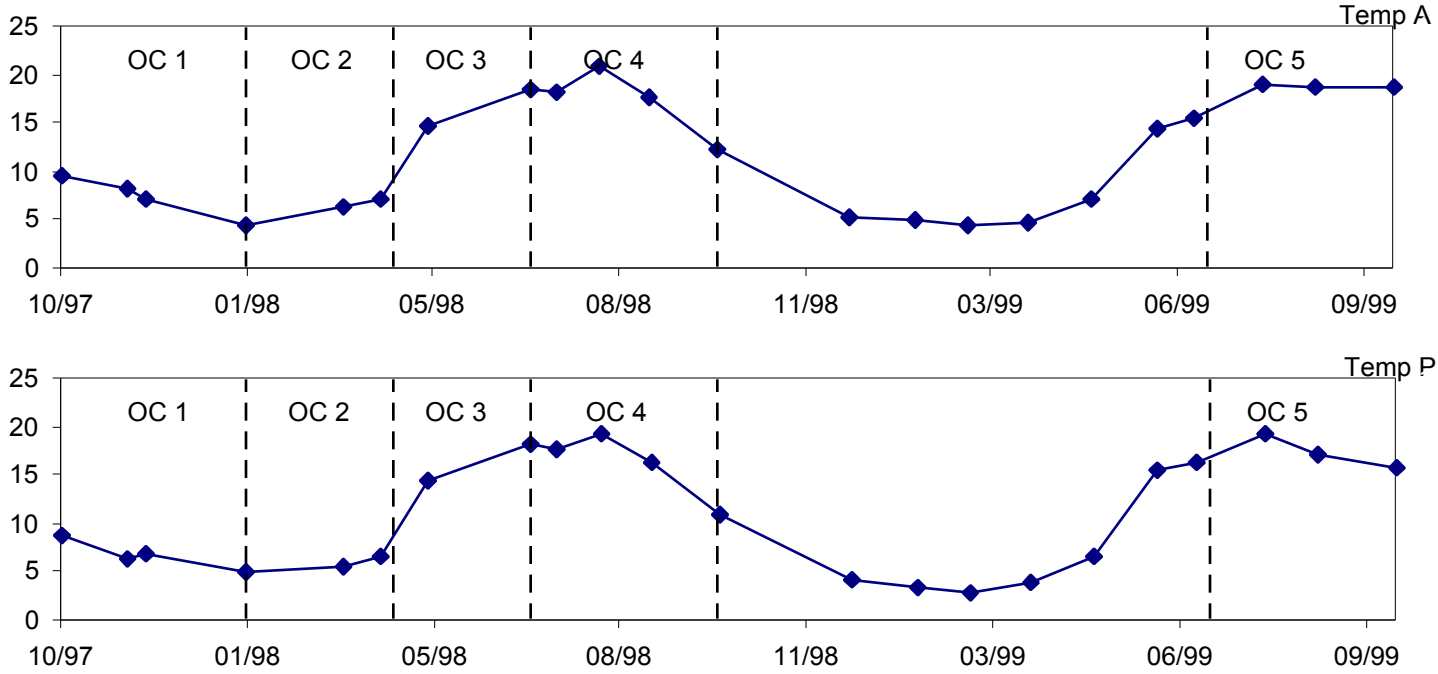


Figure 6.13 (A,B,C,D) pH: Active Deep, Passive Deep, Active Shallow, Active Deep

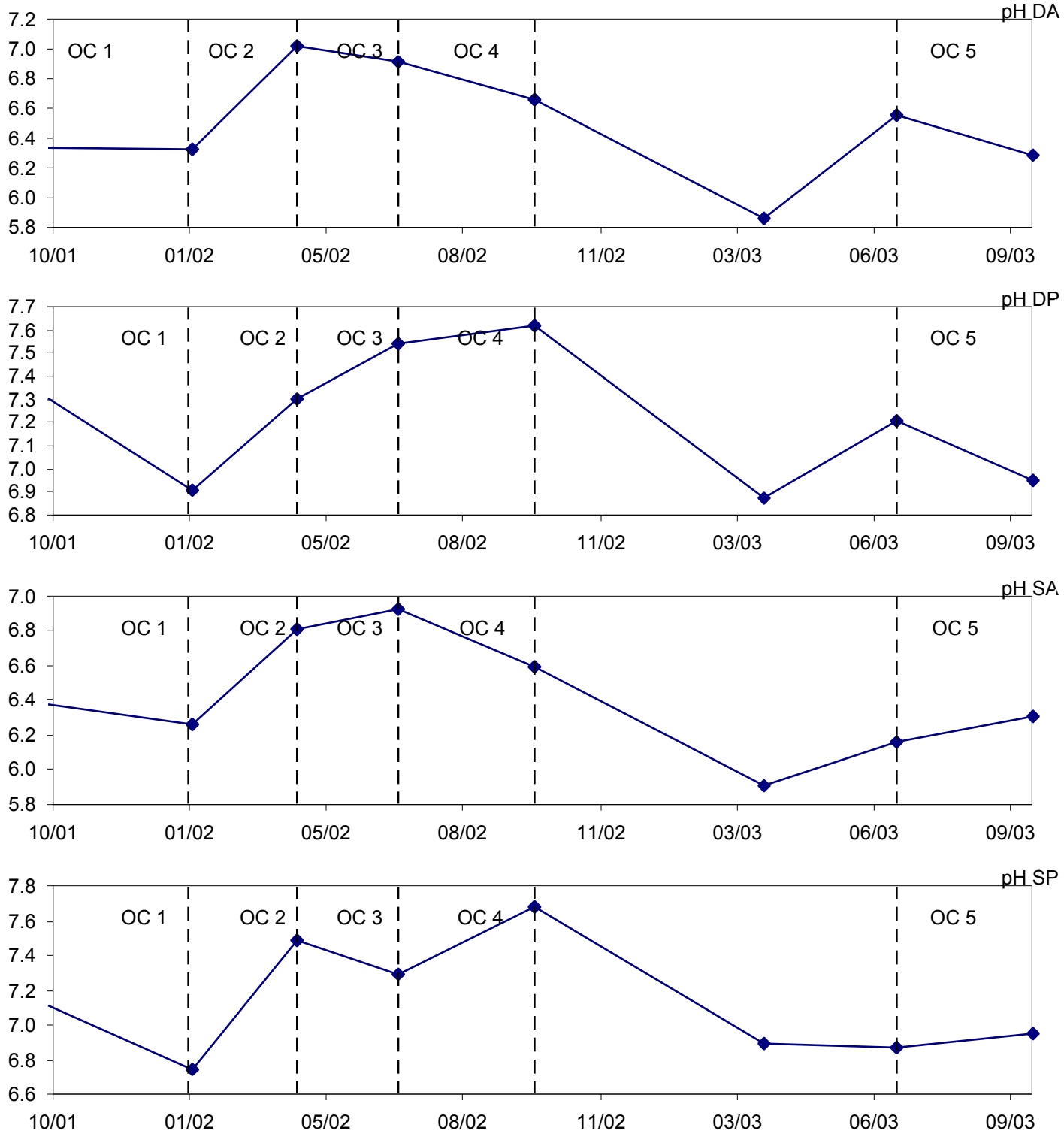


Figure 6.14 (A,B,C,D) Moisture: Active Deep, Passive Deep, Active Shallow, Passive Shallow

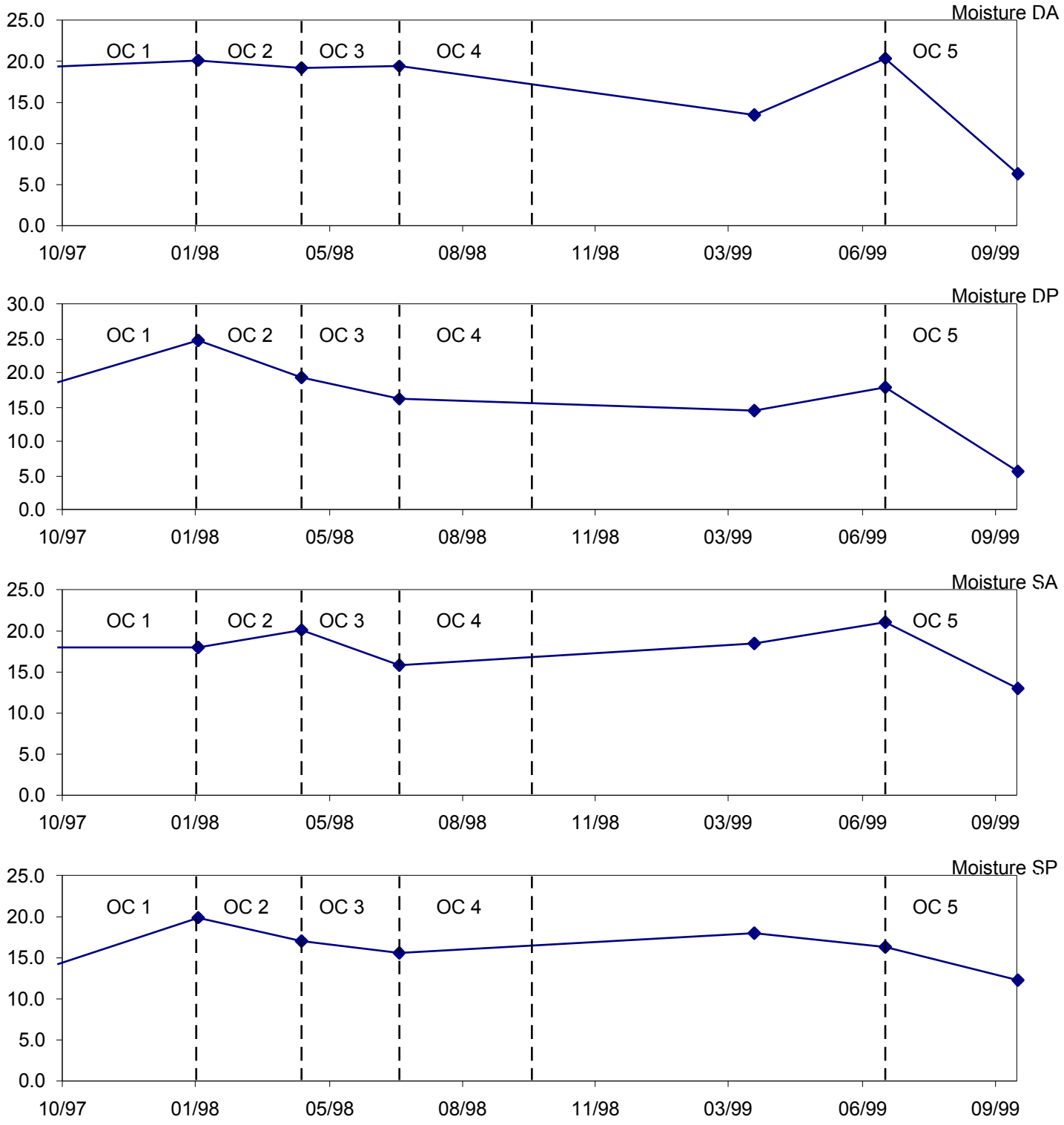


Figure 6.15 (A,B,C,D) Humidity: Active Deep, Passive Deep, Active Shallow, Passive Shallow

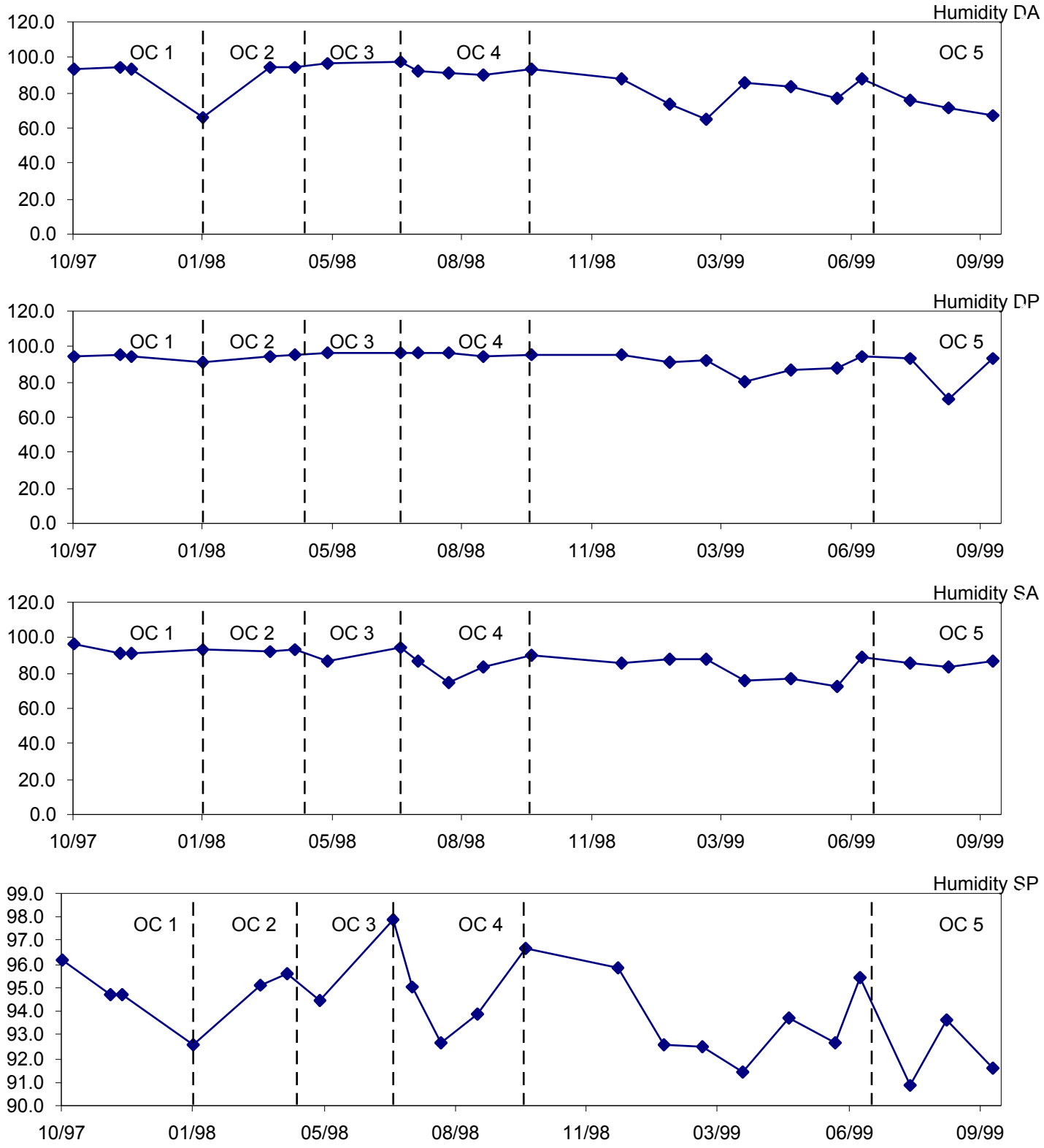


Figure 6.16 (A,B,C,D) Total TPH: Active Deep, Passive Deep, Active Shallow, Passive Shallow

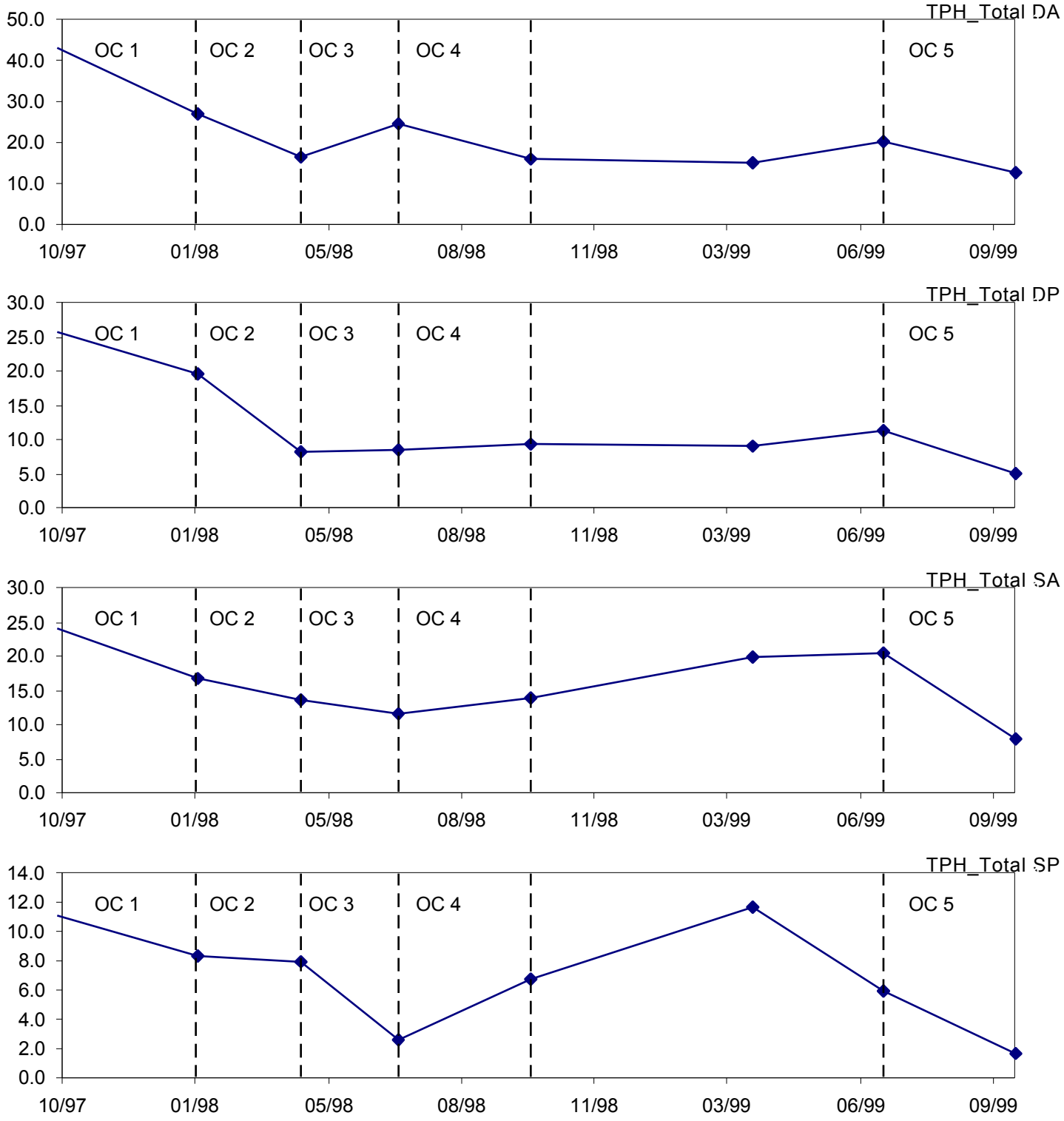


Figure 6.17 (A,B,C,D) TPH Polar: Active Deep, Passive Deep, Active Shallow, Passive Shallow

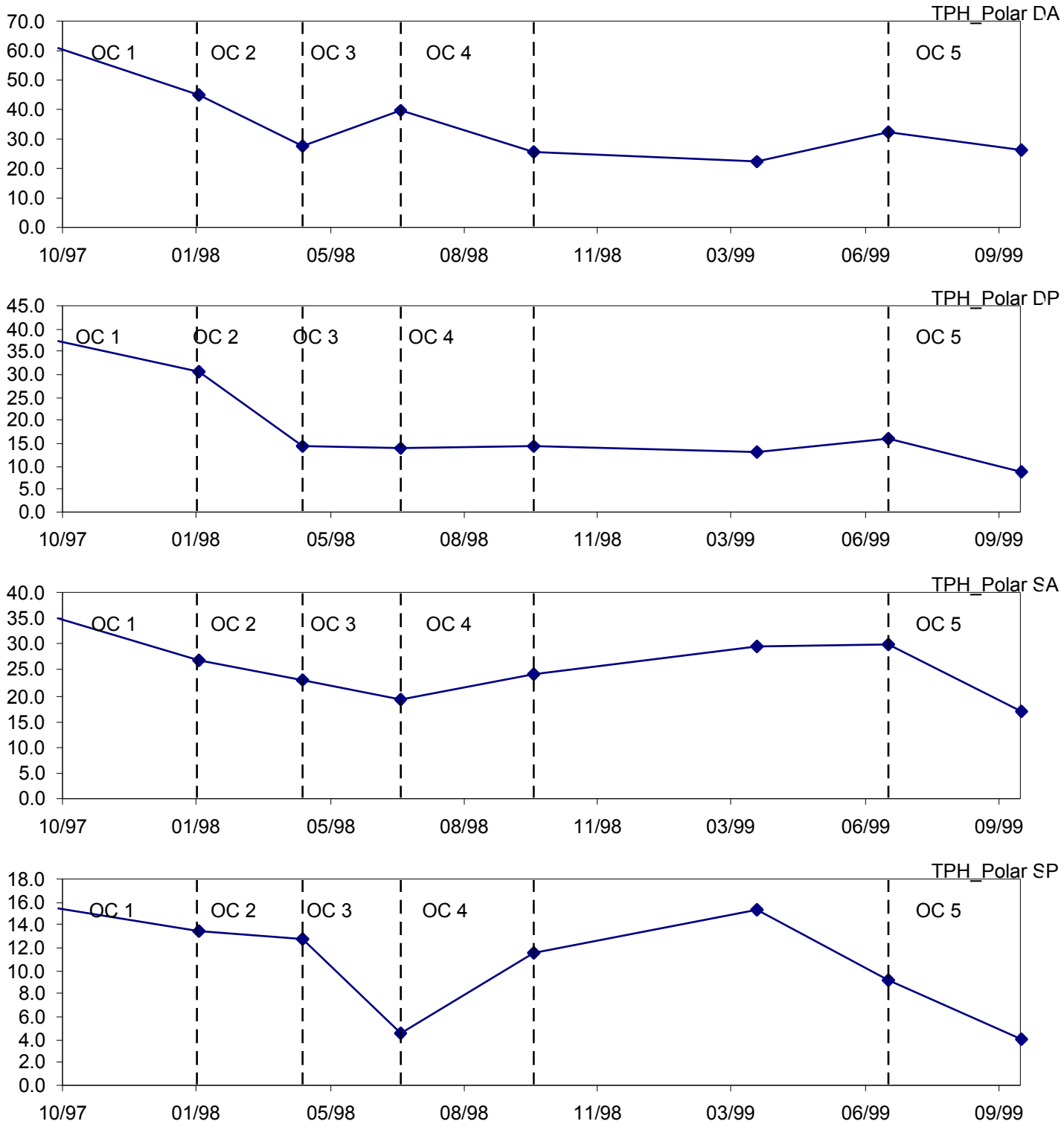


Figure 6.18 (A,B,C,D) Benzo(a)pyrene: Active Deep, Passive Deep, Active Shallow, Passive Shallow

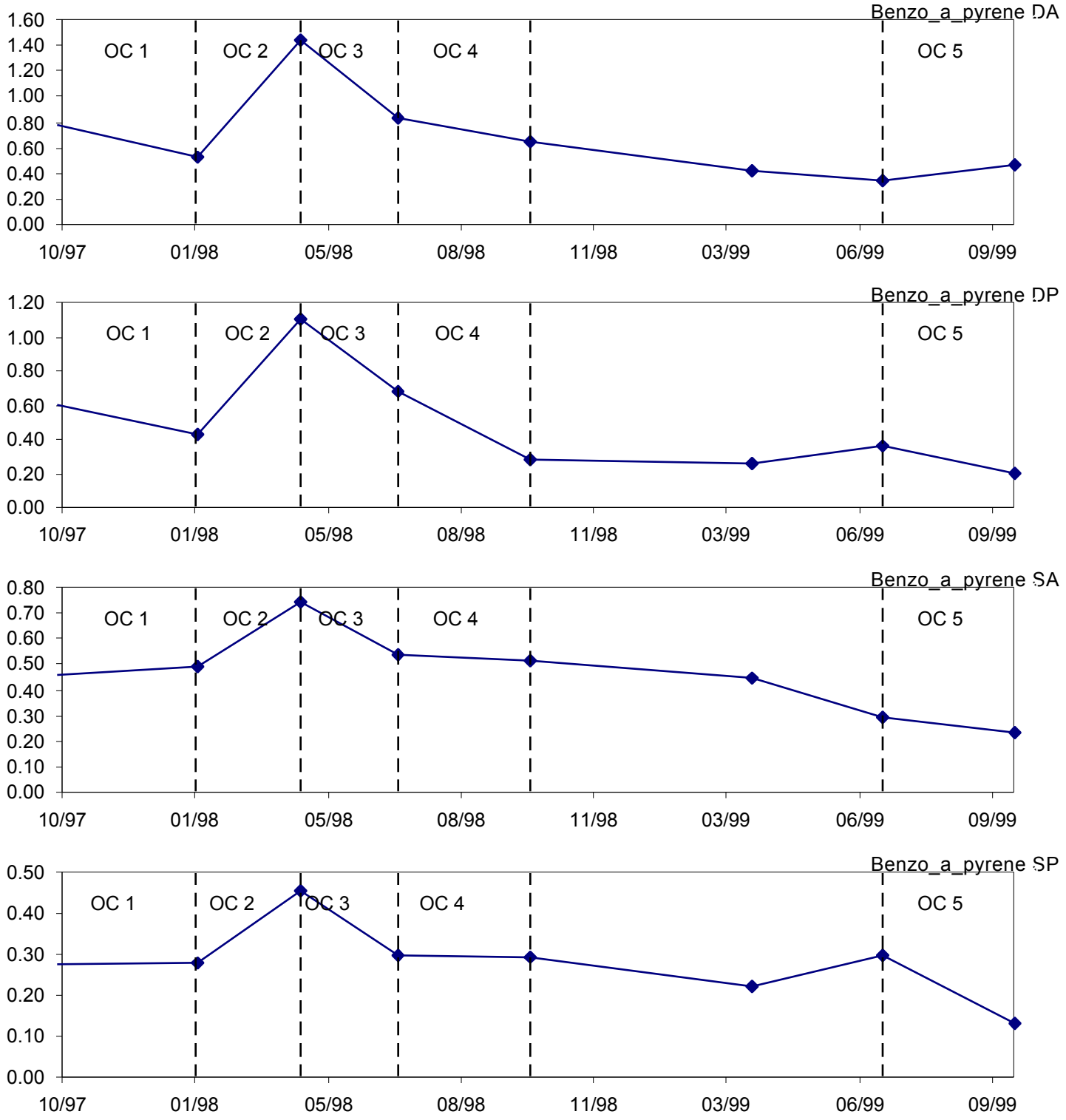


Figure 6.19 (A,B,C,D) Fluoranthene: Active Deep, Passive Deep, Active Shallow, Passive Shallow

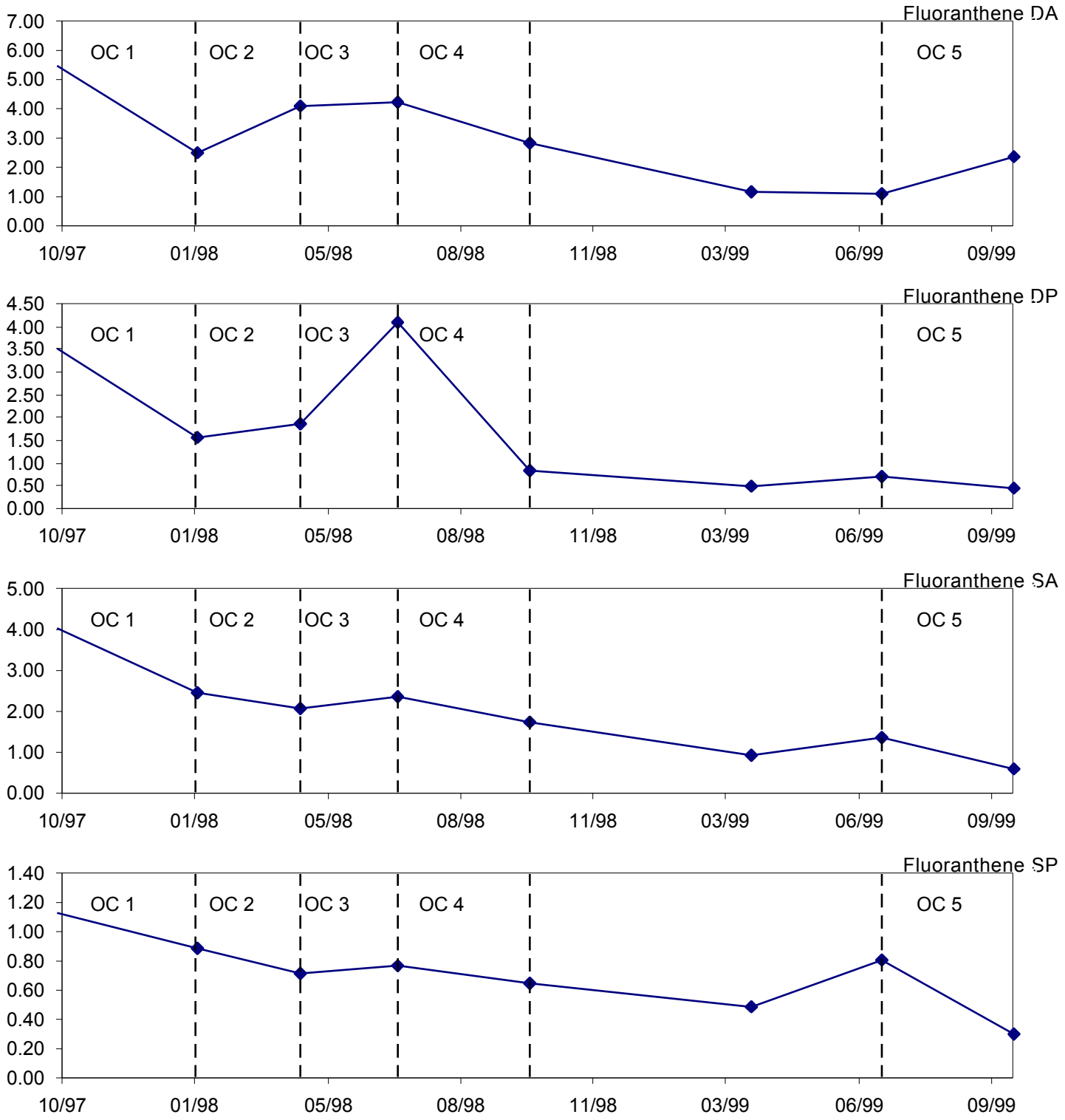


Figure 6.20 (A,B,C,D) Total PAH: Active Deep, Passive Deep, Active Shallow, Passive Shallow

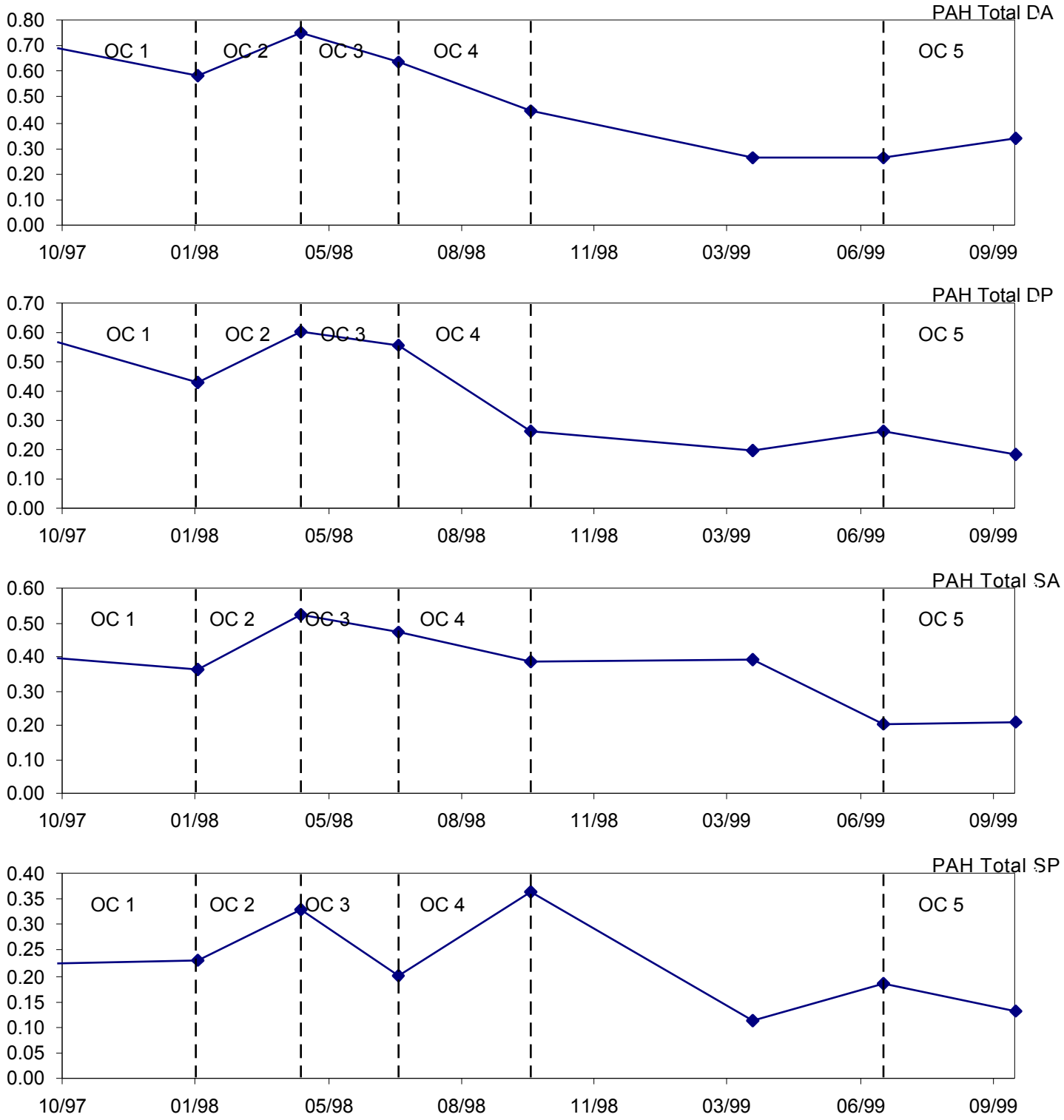


Figure 6.21 (A,B,C,D) PO4: Active Deep, Passive Deep, Active Shallow, Passive Shallow

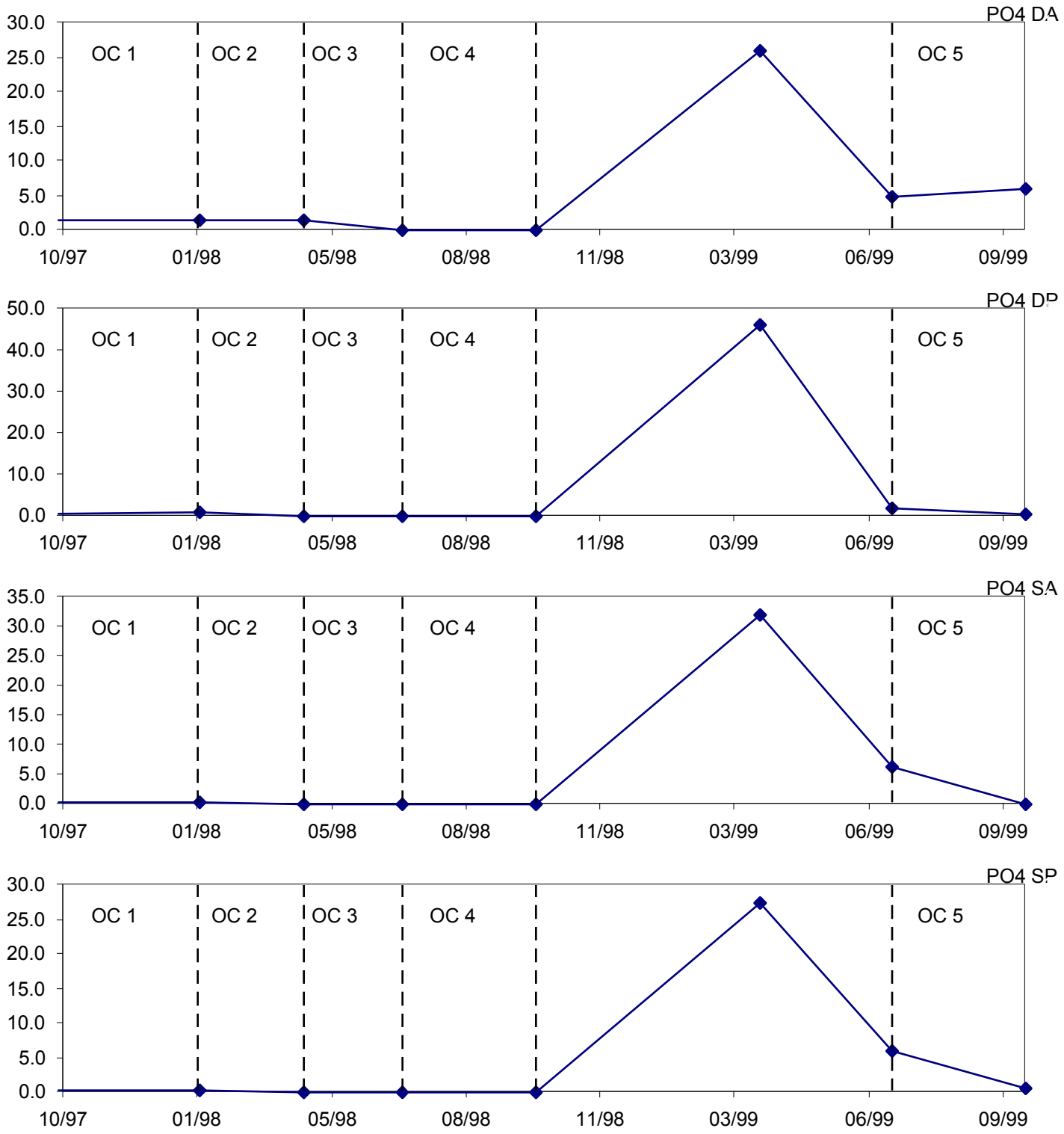


Figure 6.22 (A,B,C,D) Total Phosphorus: Active Deep, Passive Deep, Active Shallow, Passive Shallow

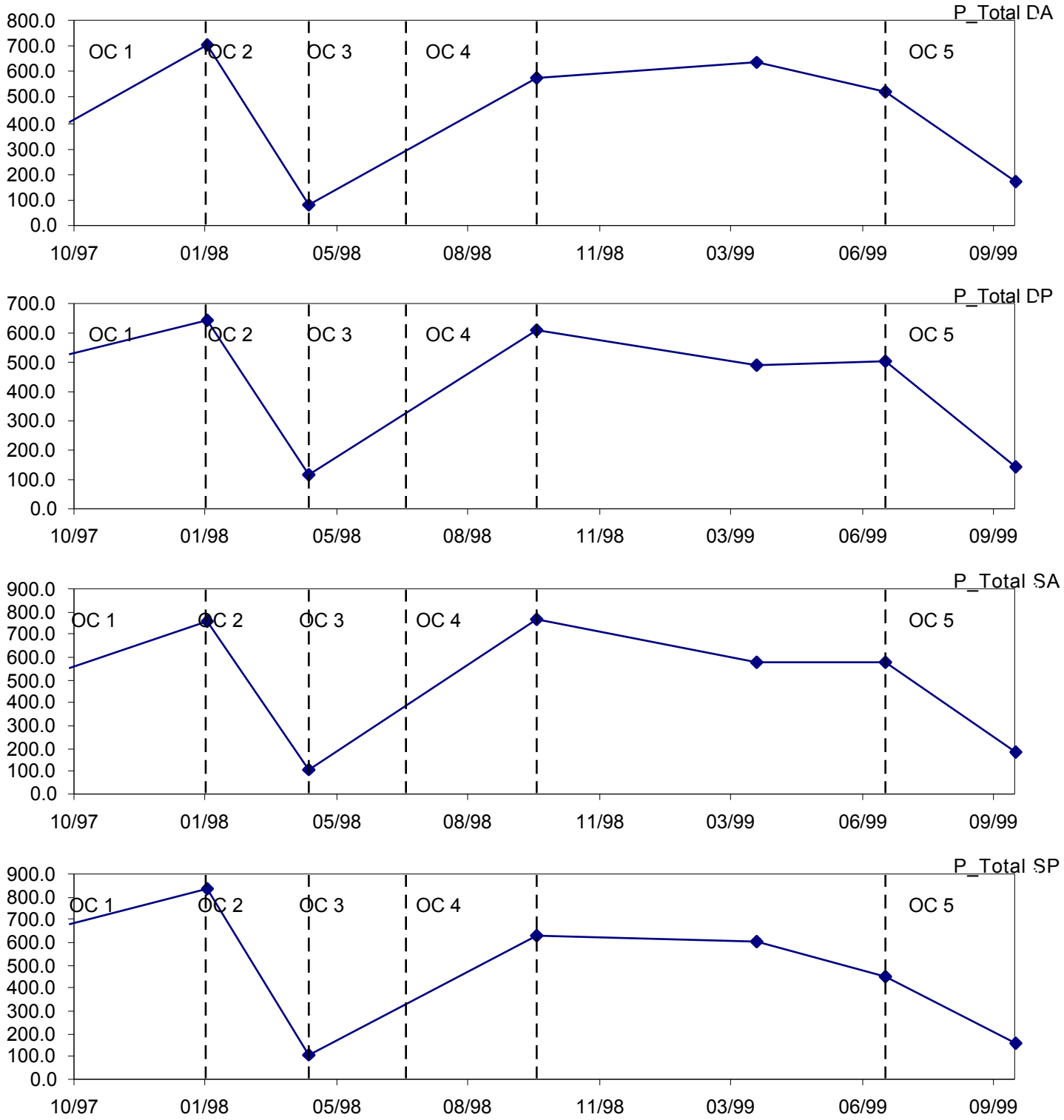


Figure 6.23 (A,B,C,D) NO2: Active Deep, Passive Deep, Active Shallow, Passive Shallow

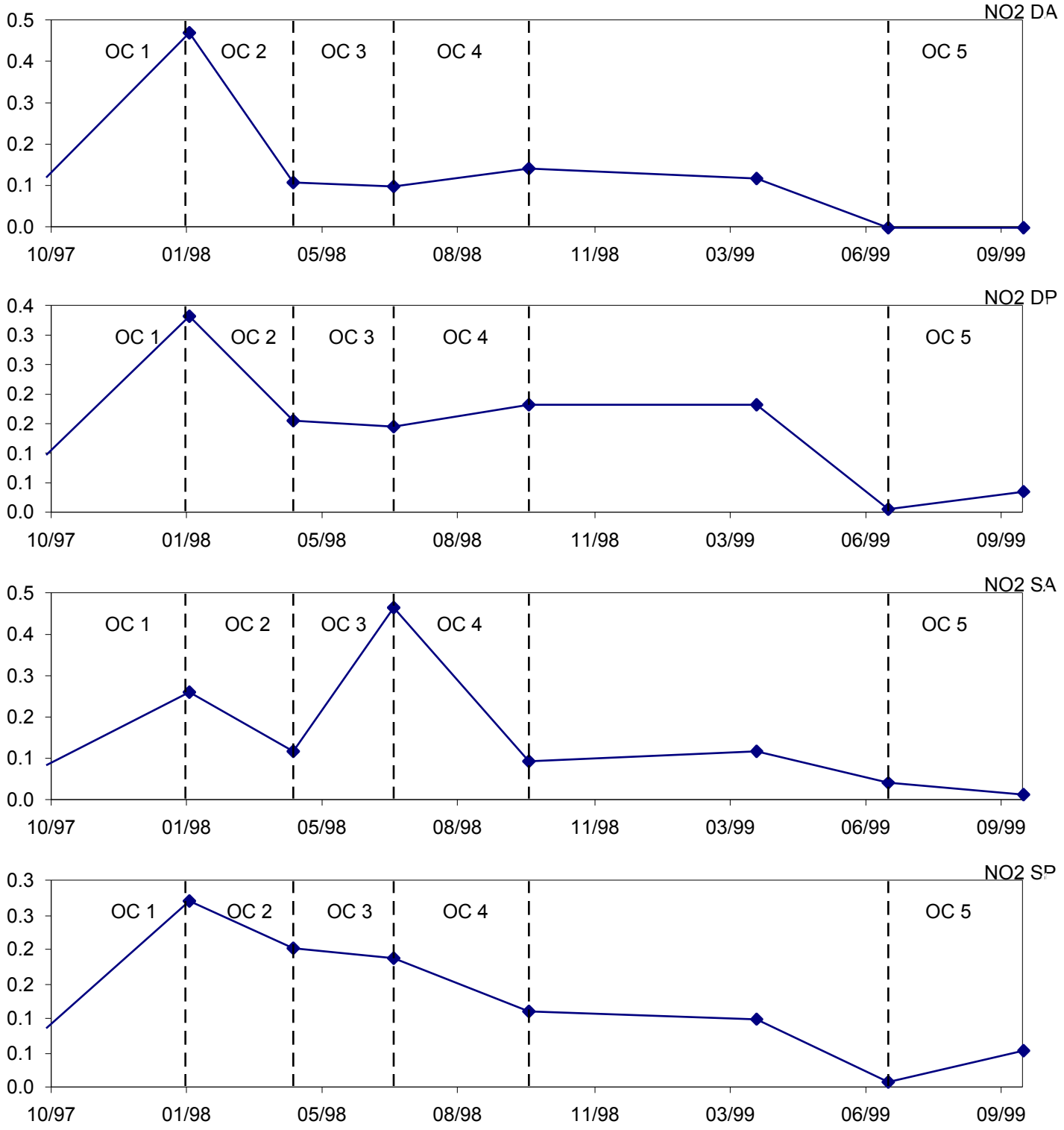


Figure 6.24 (A,B,C,D) NO3: Active Deep, Passive Deep, Active Shallow, Passive Shallow

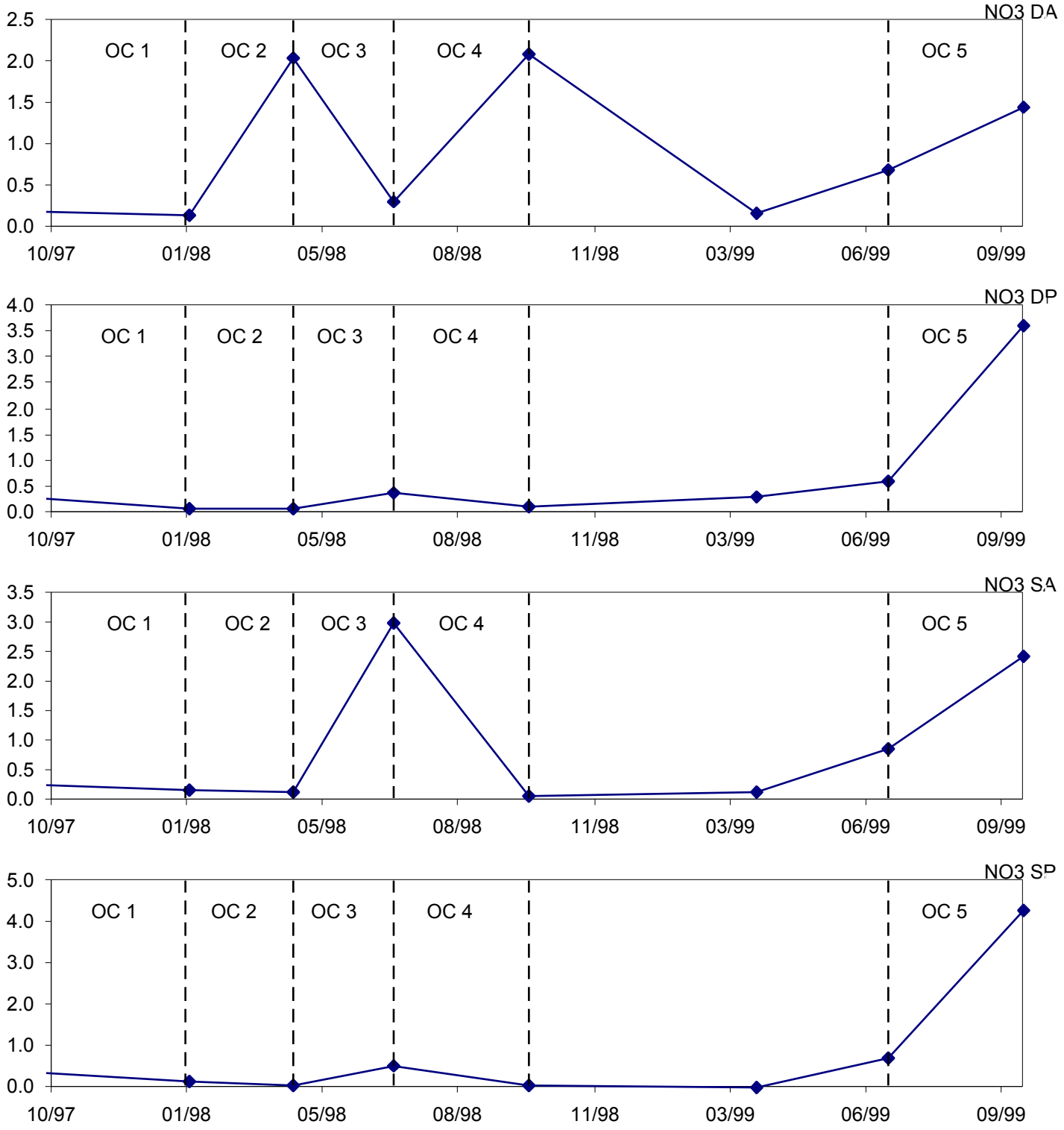


Figure 6.25 (A,B,C,D) NH4: Active Deep, Passive Deep, Active Shallow, Passive Shallow

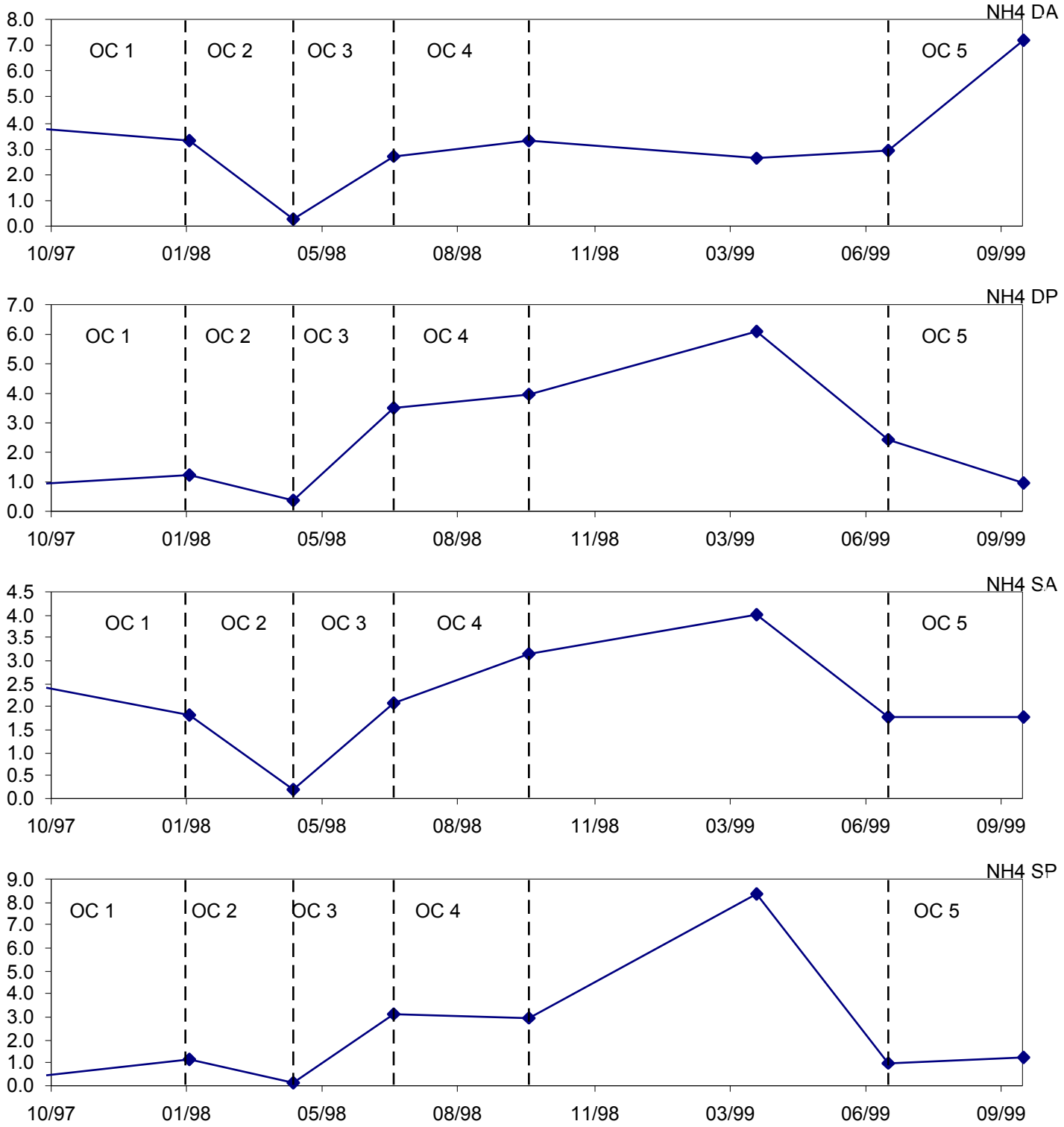


Figure 6.26 (A,B,C,D) TKN: Active Deep, Passive Deep, Active Shallow, Passive Shallow

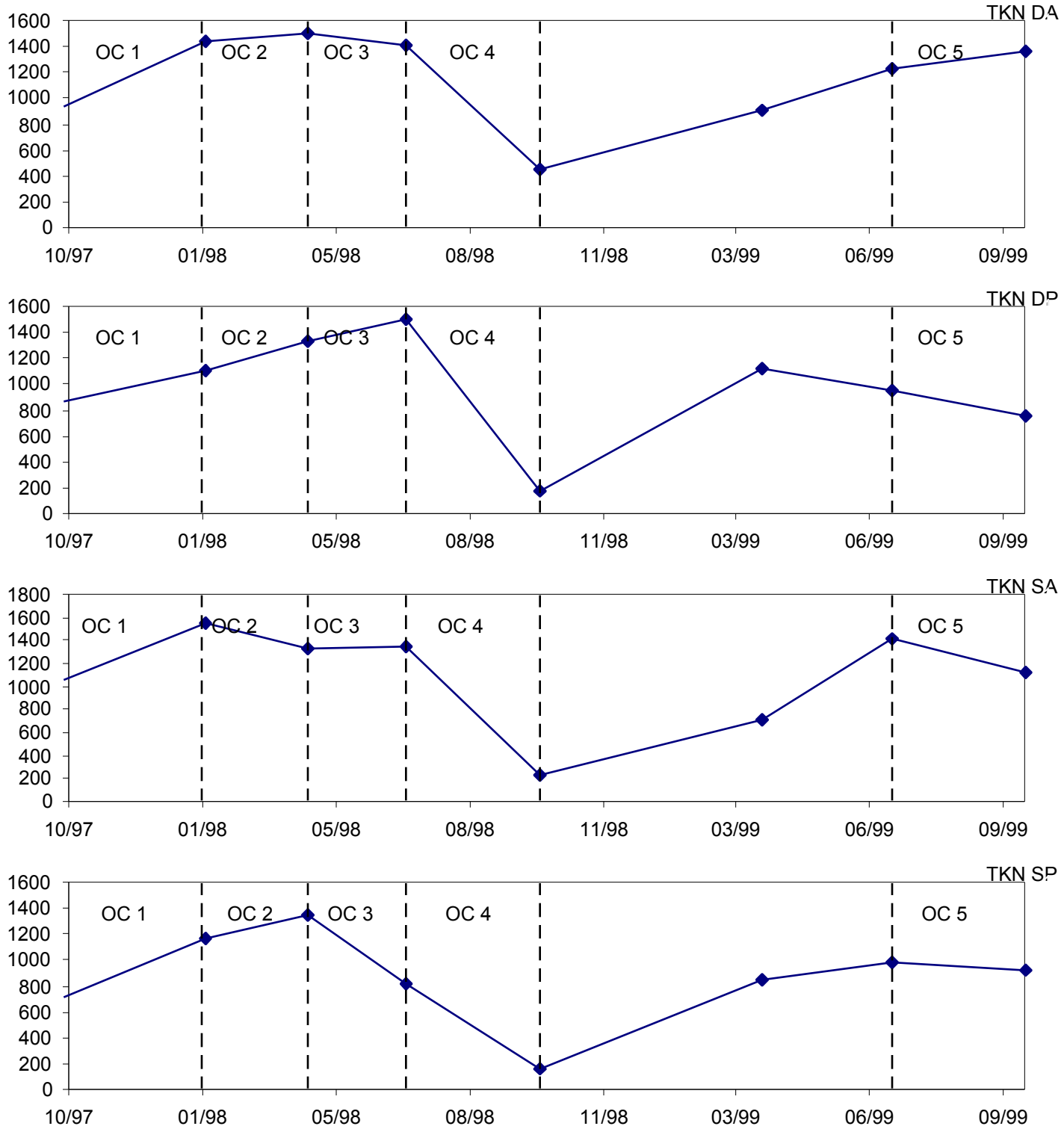


Figure 6.27 (A,B,C,D) TTC: Active Deep, Passive Deep, Active Shallow, Passive Shallow

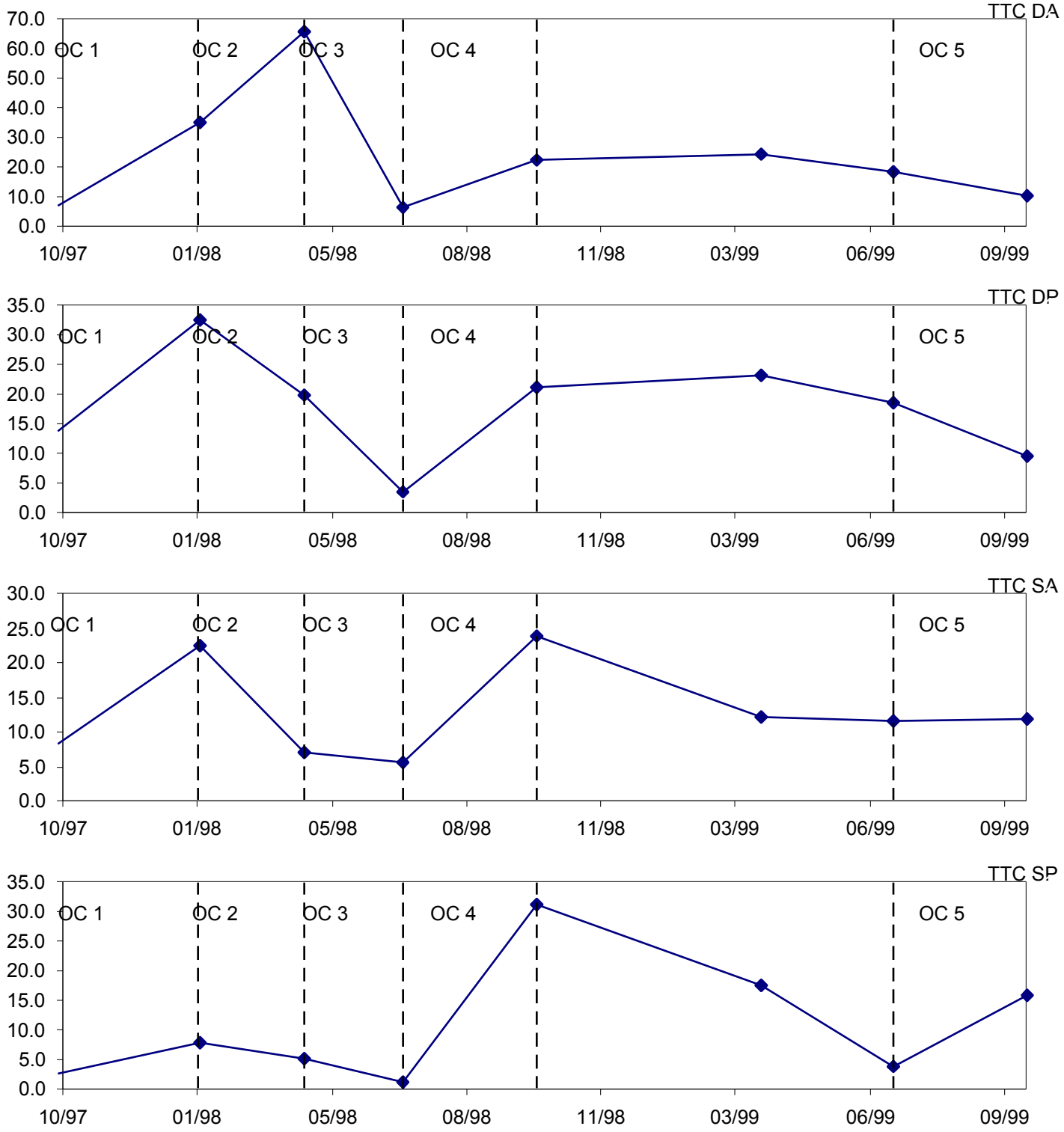


Figure 6.28 (A,B,C,D) Fungal CFW: Active Deep, Passive Deep, Active Shallow, Passive Shallow

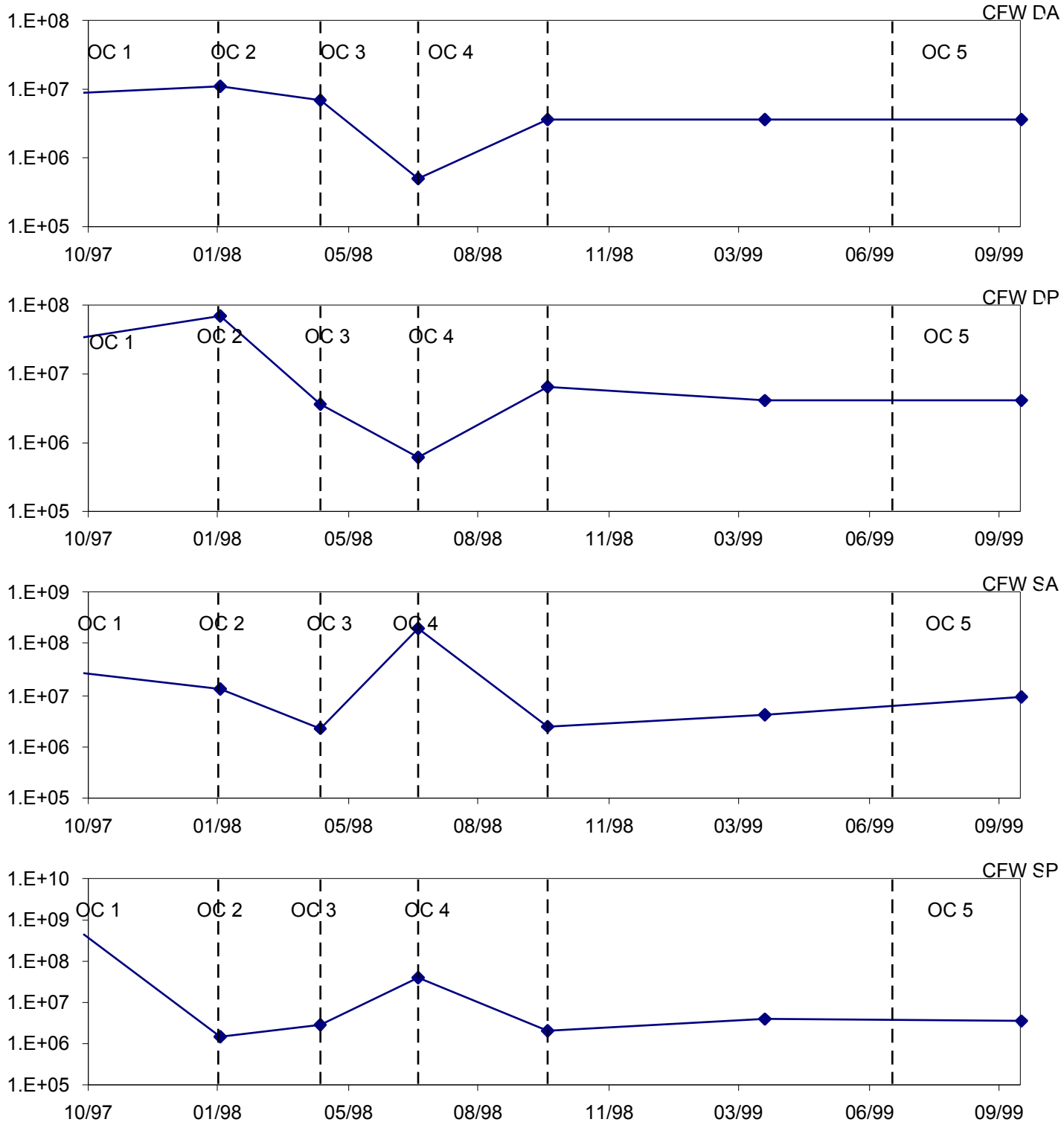


Figure 6.29 (A,B,C,D) DAPI: Active Deep, Passive Deep, Active Shallow, Passive Shallow

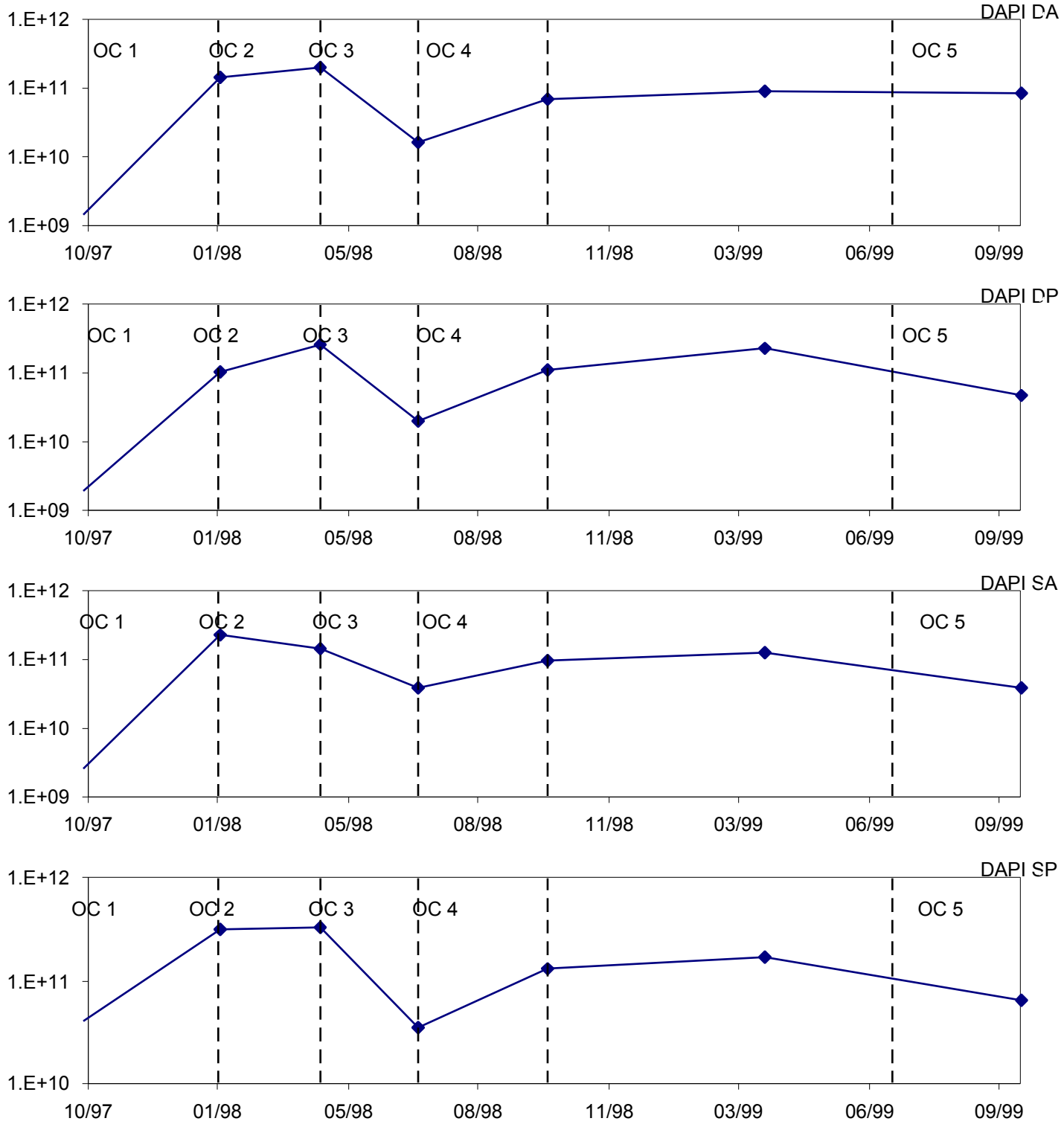


Figure 6.30 (A,B,C,D) MPN Petroleum 20: Active Deep, Passive Deep, Active Shallow, Passive Shallow

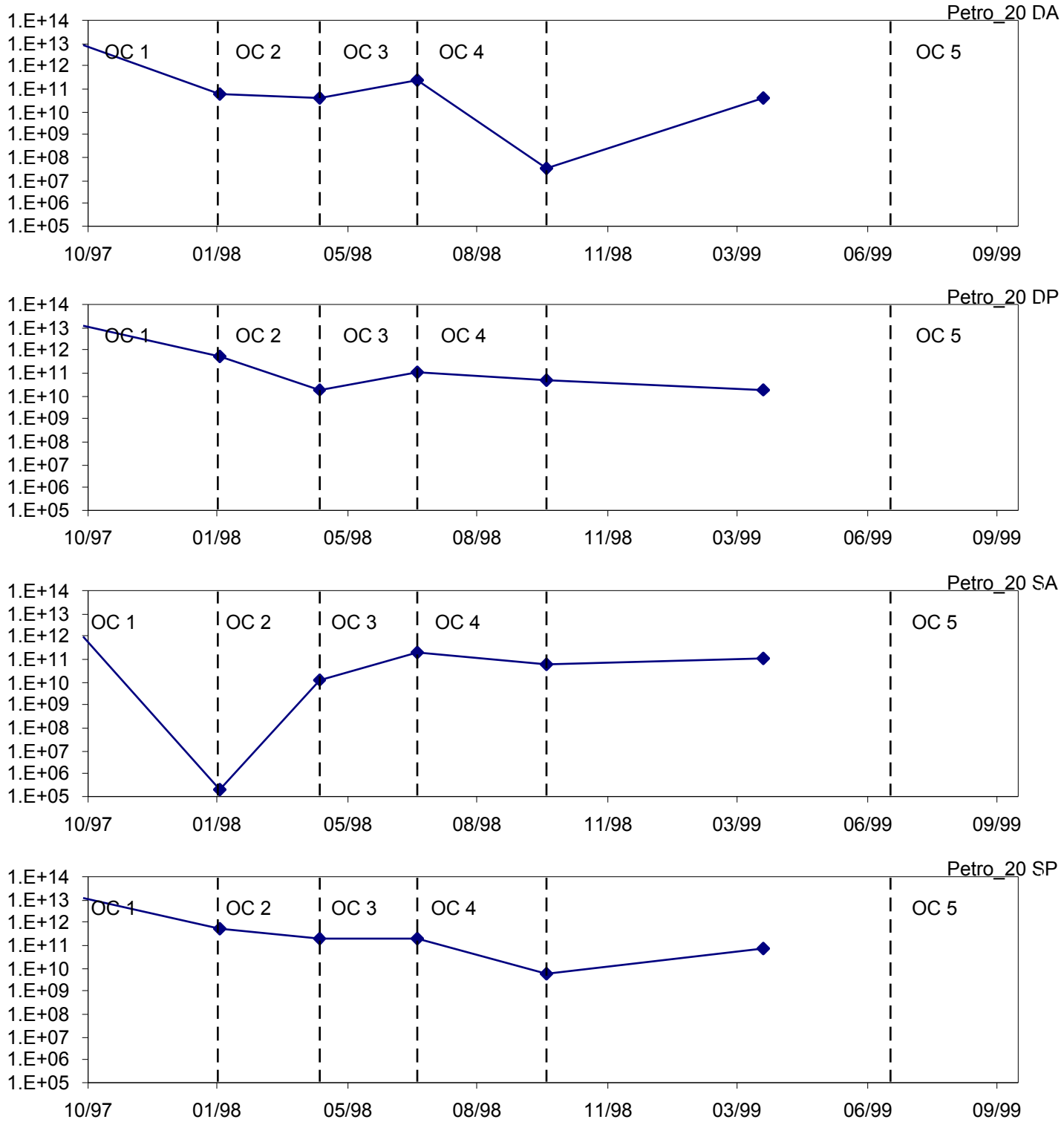


Figure 6.31 (A,B,C,D) MPN Petroleum 37: Active Deep, Passive Deep, Active Shallow, Passive Shallow

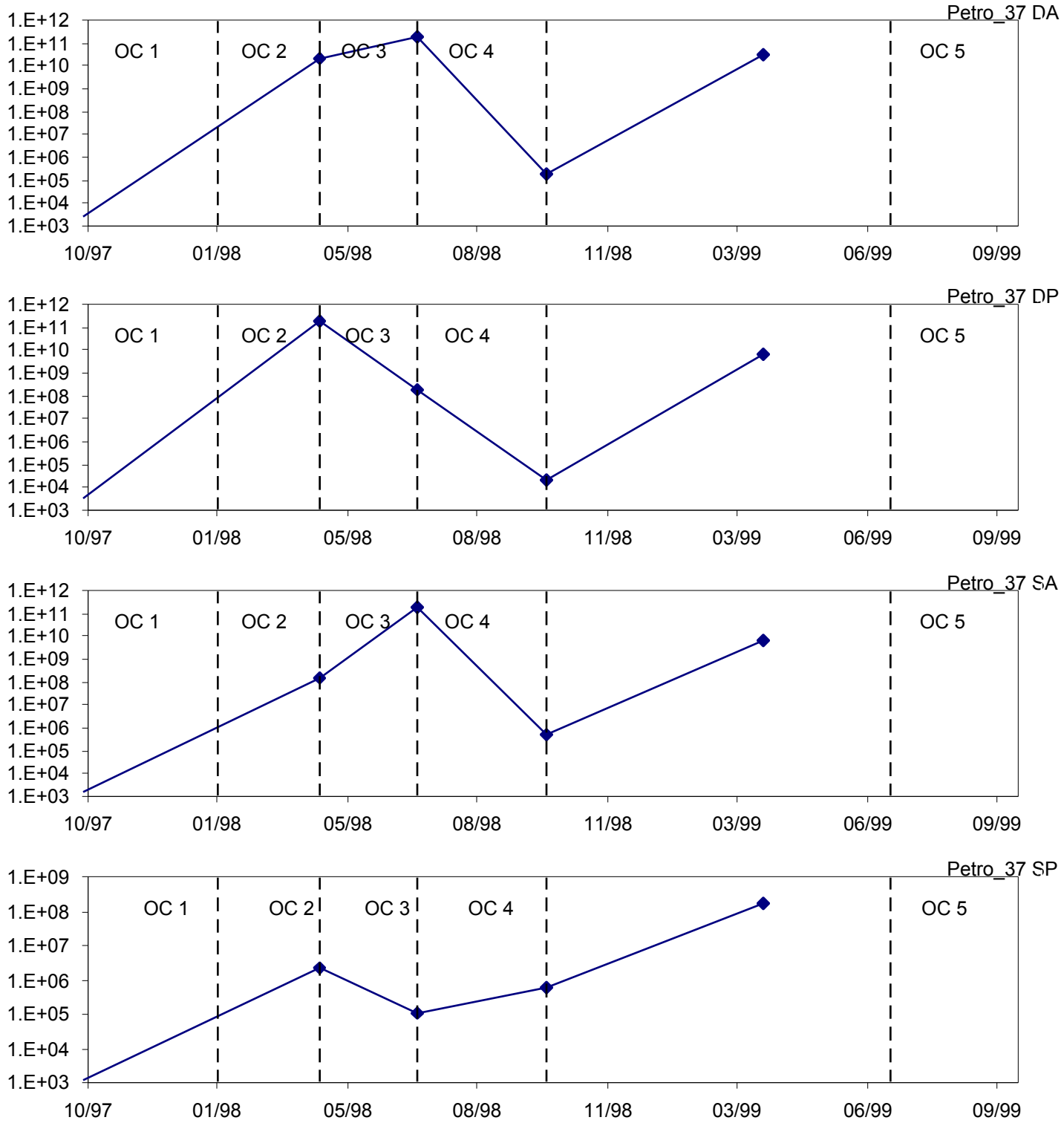


Figure 6.32 (A,B,C,D) MPN Napthalene 20: Active Deep, Passive Deep, Active Shallow, Passive Shallow

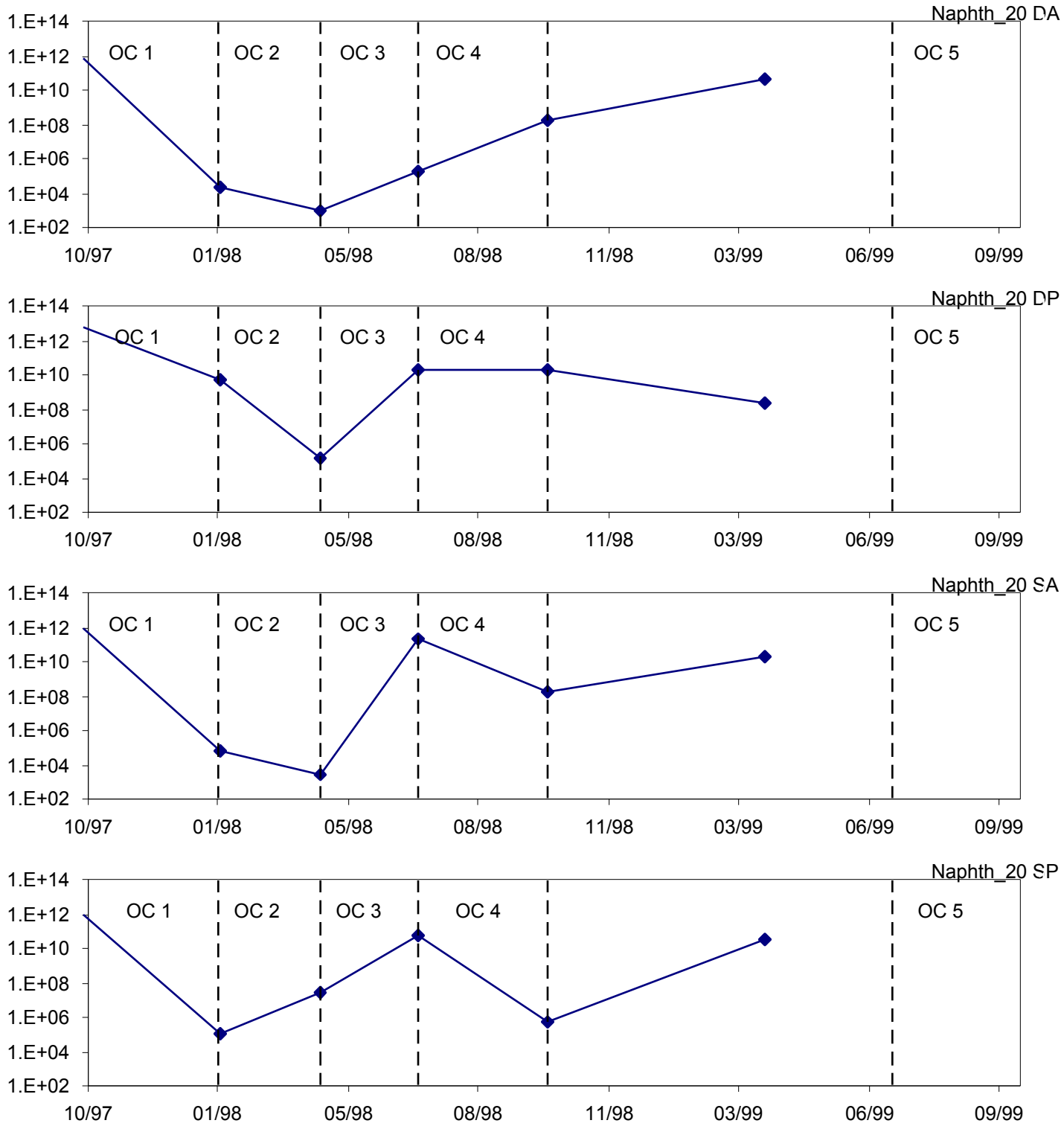


Figure 6.33 (A,B,C,D) MPN Napthalene 37: Active Deep, Passive Deep, Active Shallow, Passive Shallow

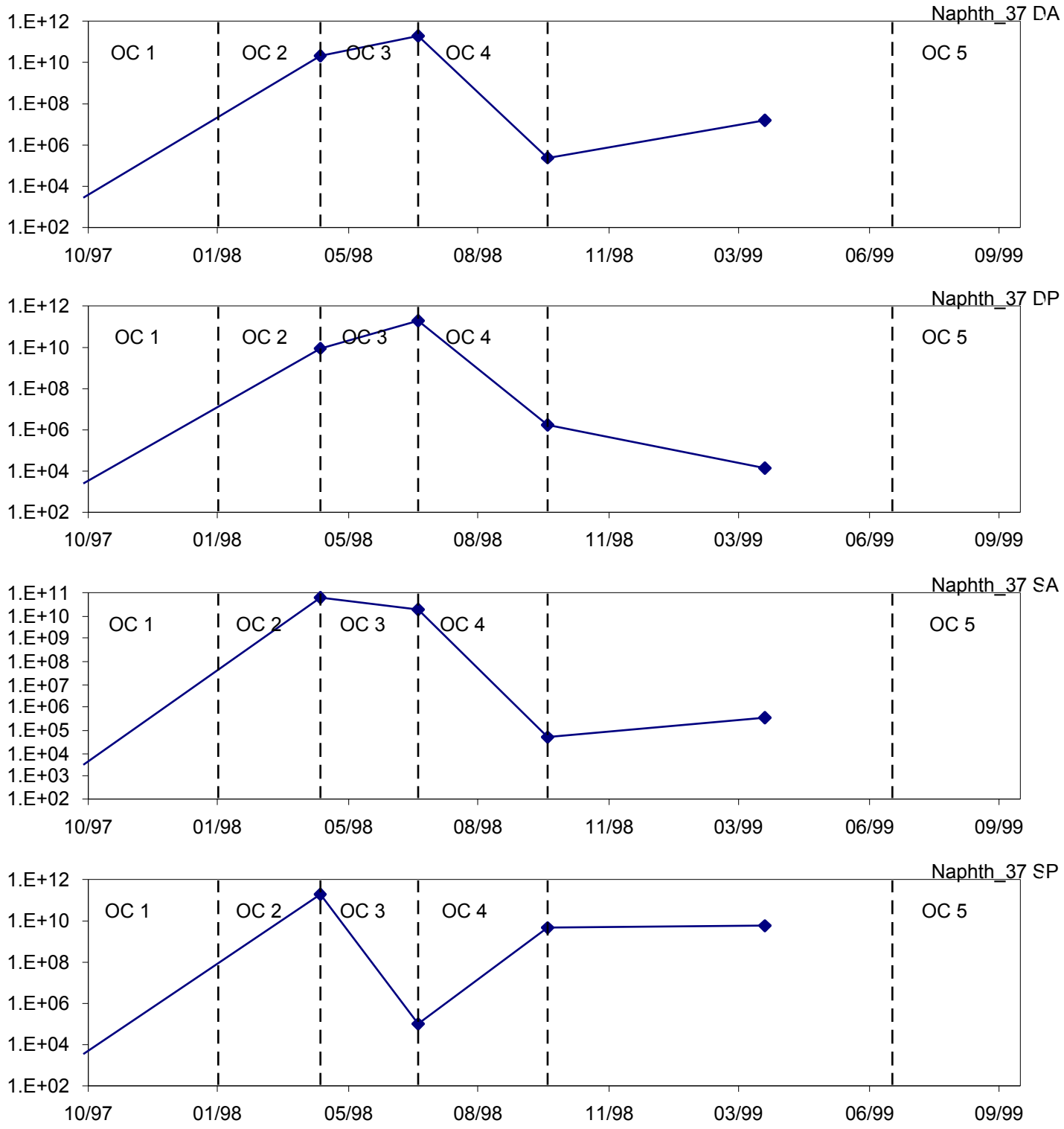


Figure 6.34 (A,B,C,D) CO2: Active Deep, Passive Deep, Active Shallow, Passive Shallow

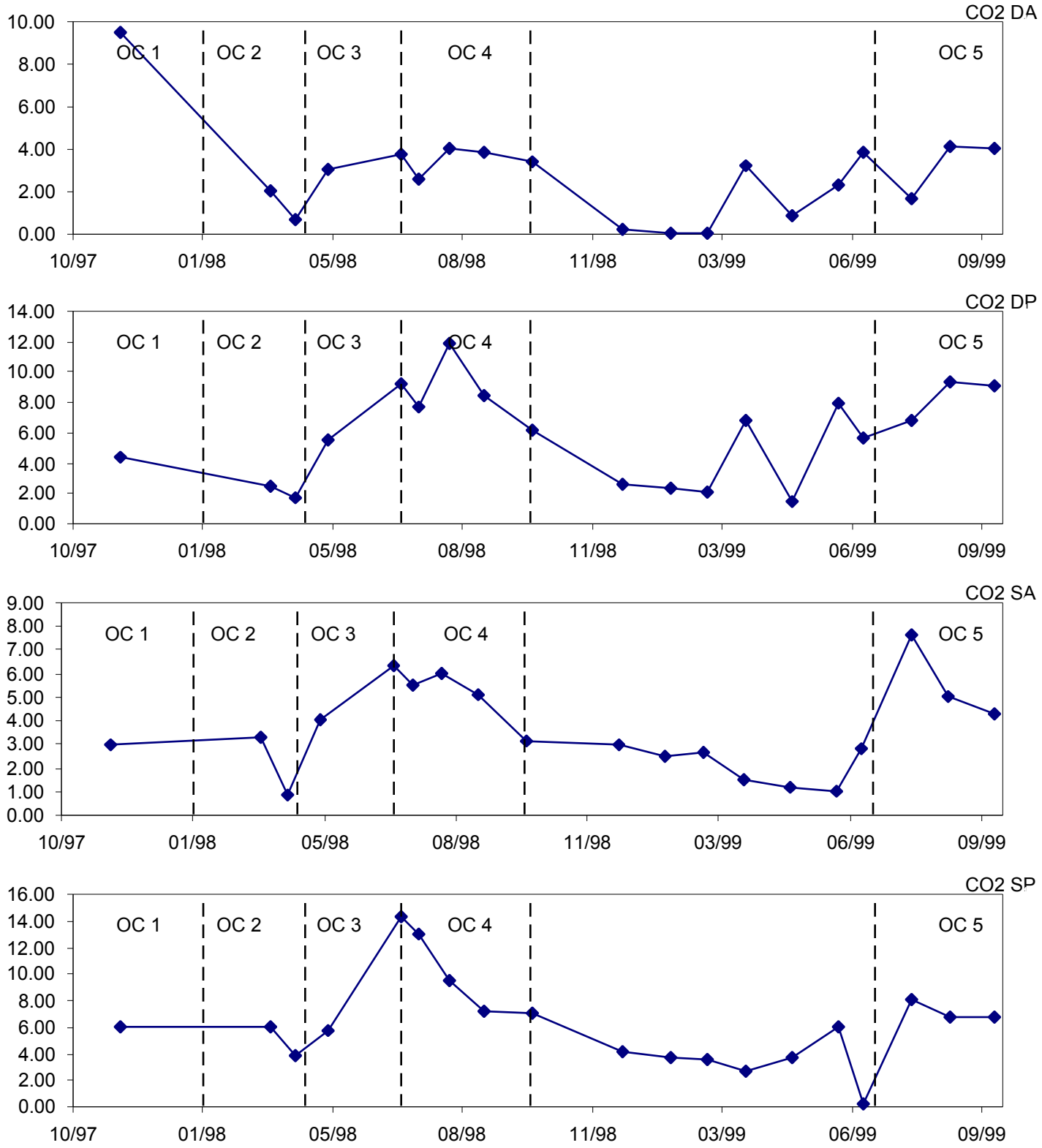


Figure 6.35 (A,B,C,D) CH4: Active Deep, Passive Deep, Active Shallow, Passive Shallow

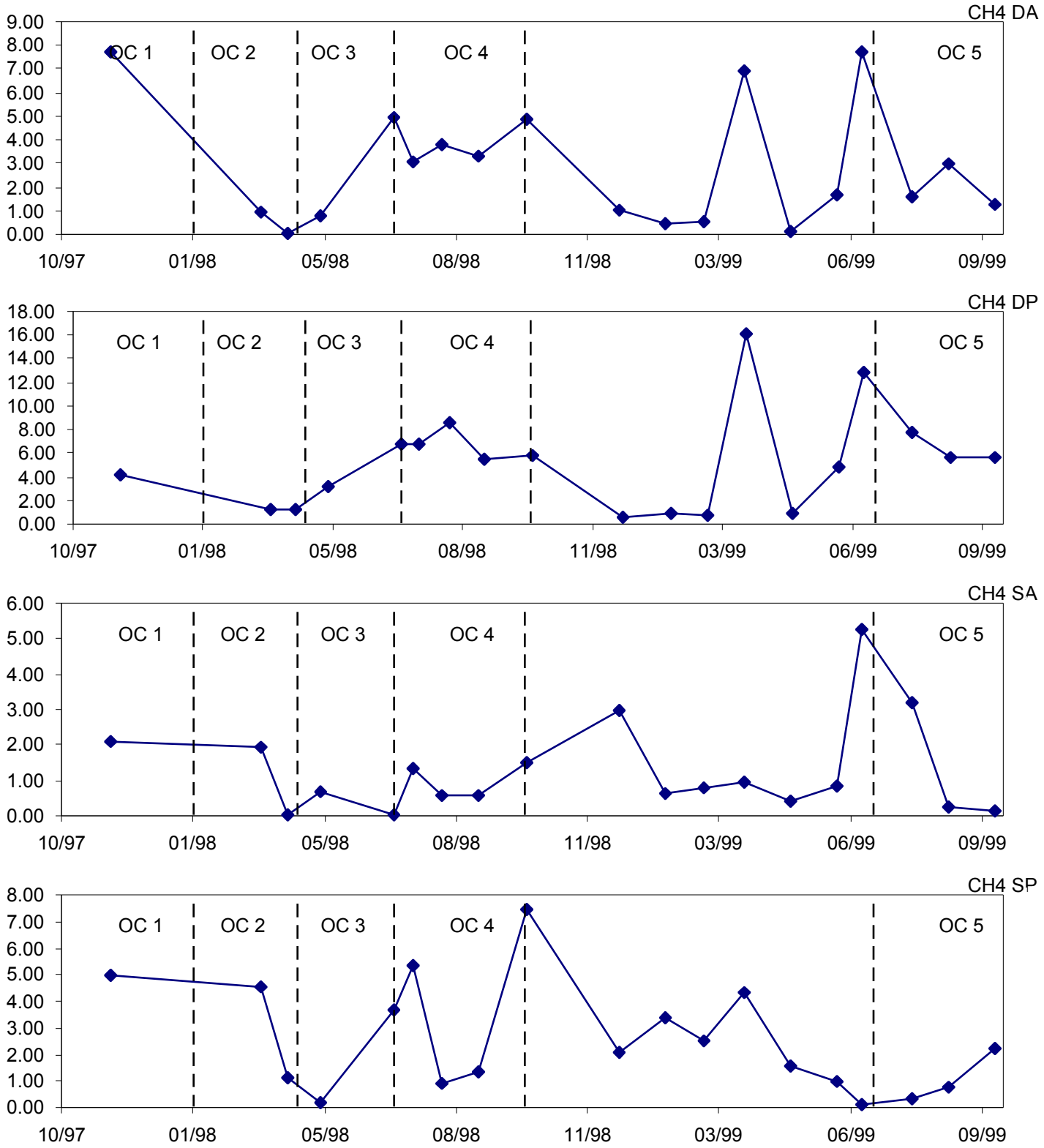


Figure 6.36 (A,B,C,D) O2: Active Deep, Passive Deep, Active Shallow, Passive Shallow

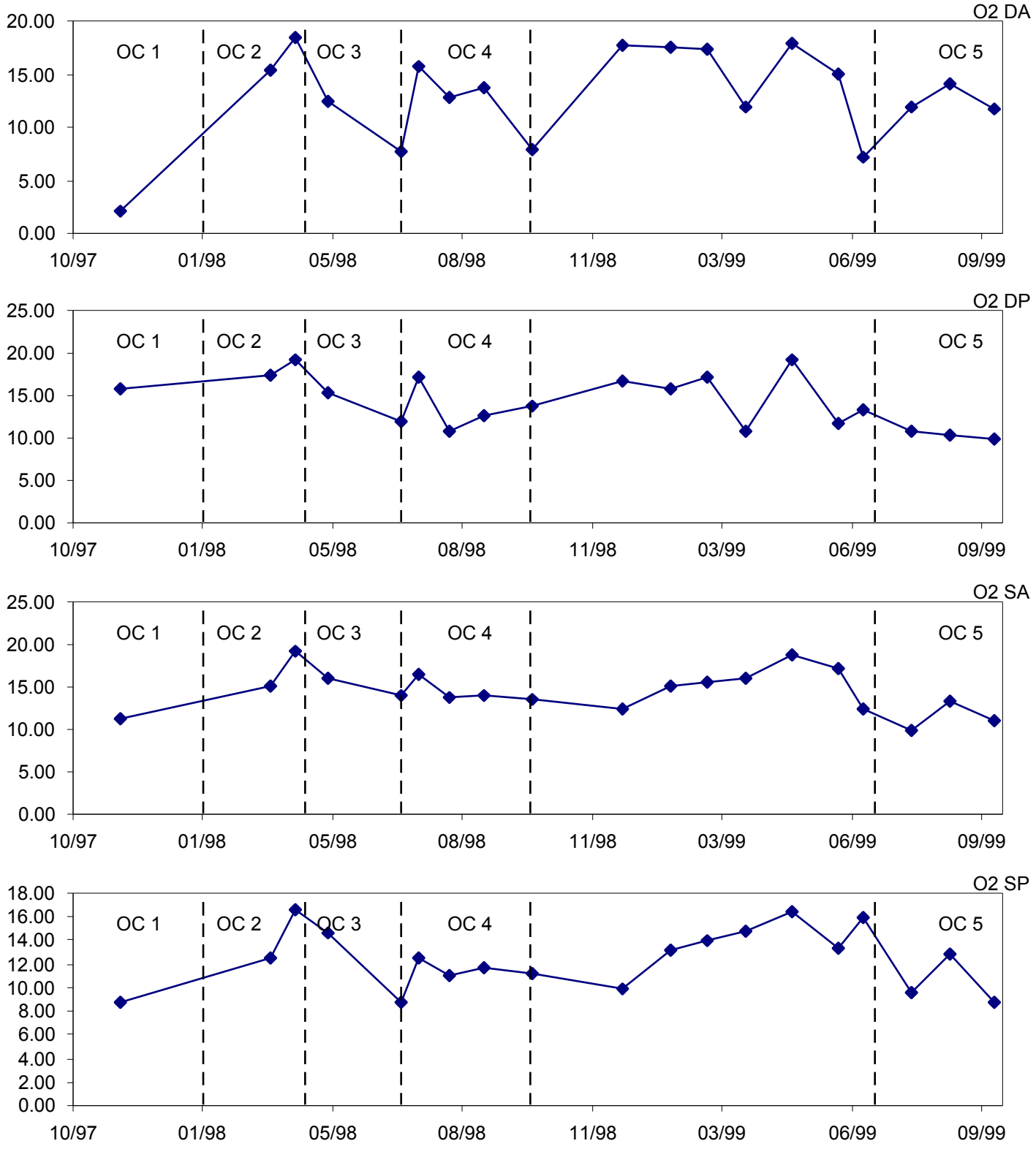
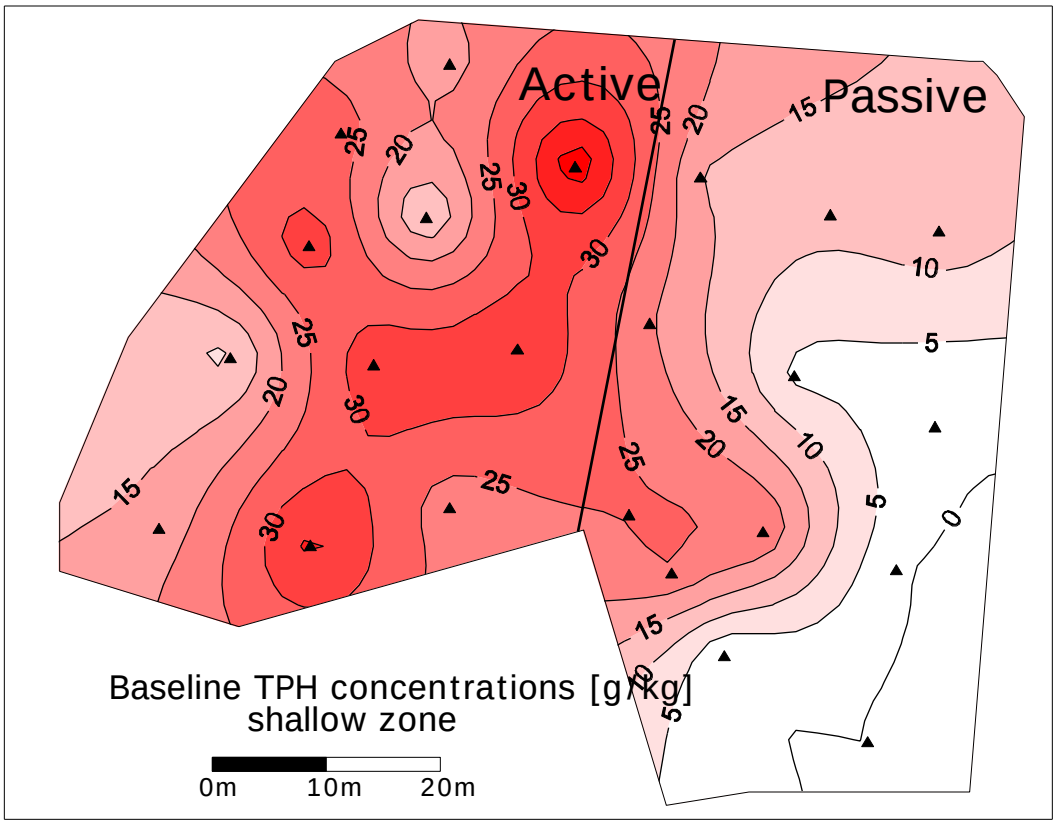


Figure 6.37 (A,B) Contour Plot of TPH Shallow: Baseline & Operating Campaign 2



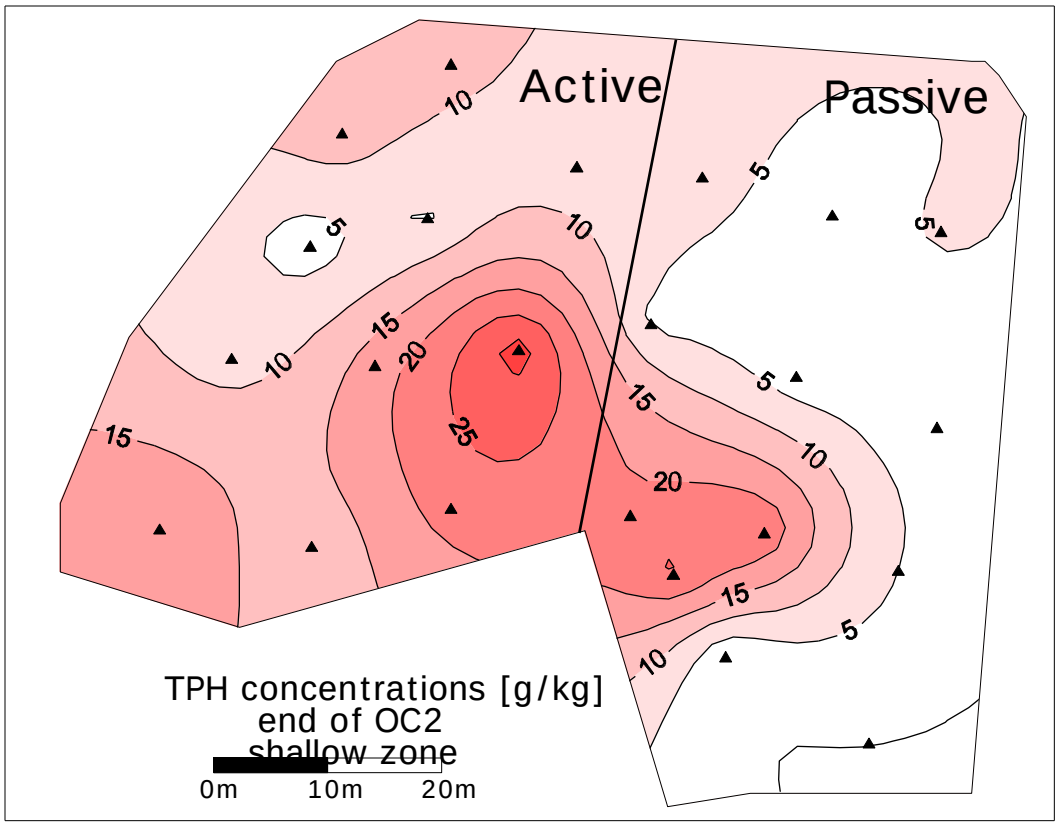
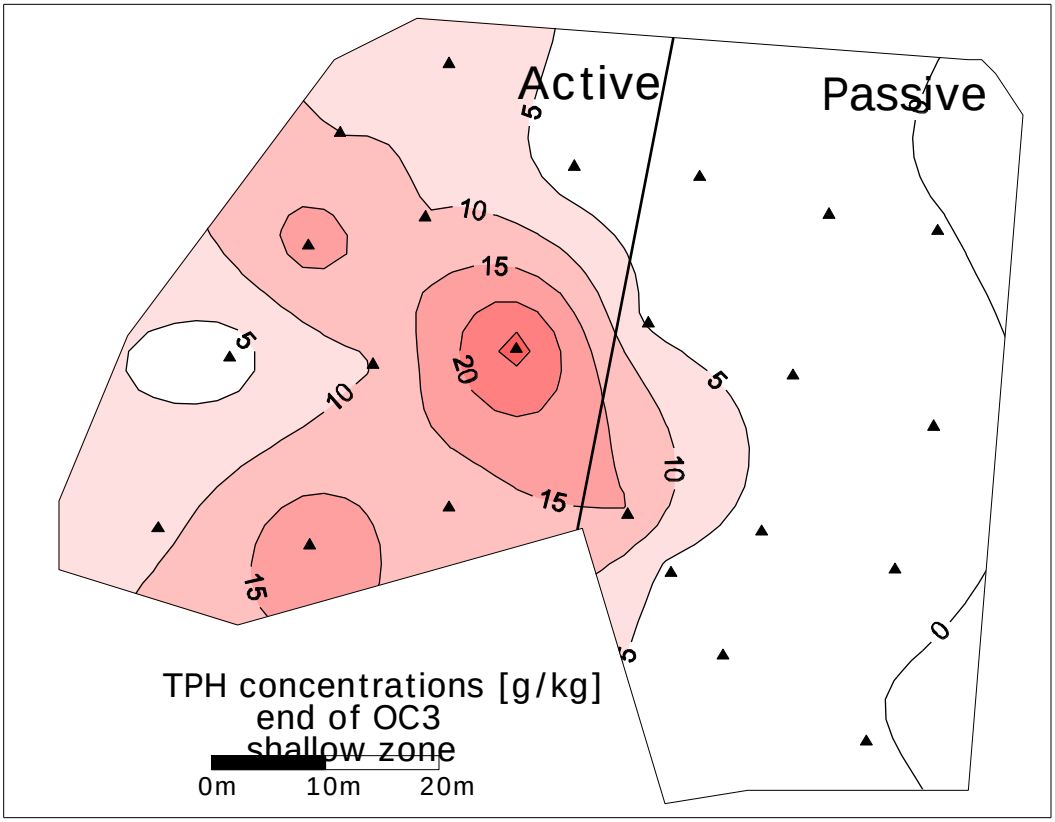


Figure 6.37 (C,D) Contour Plot of TPH Shallow: Operating Campaigns 3 & 4



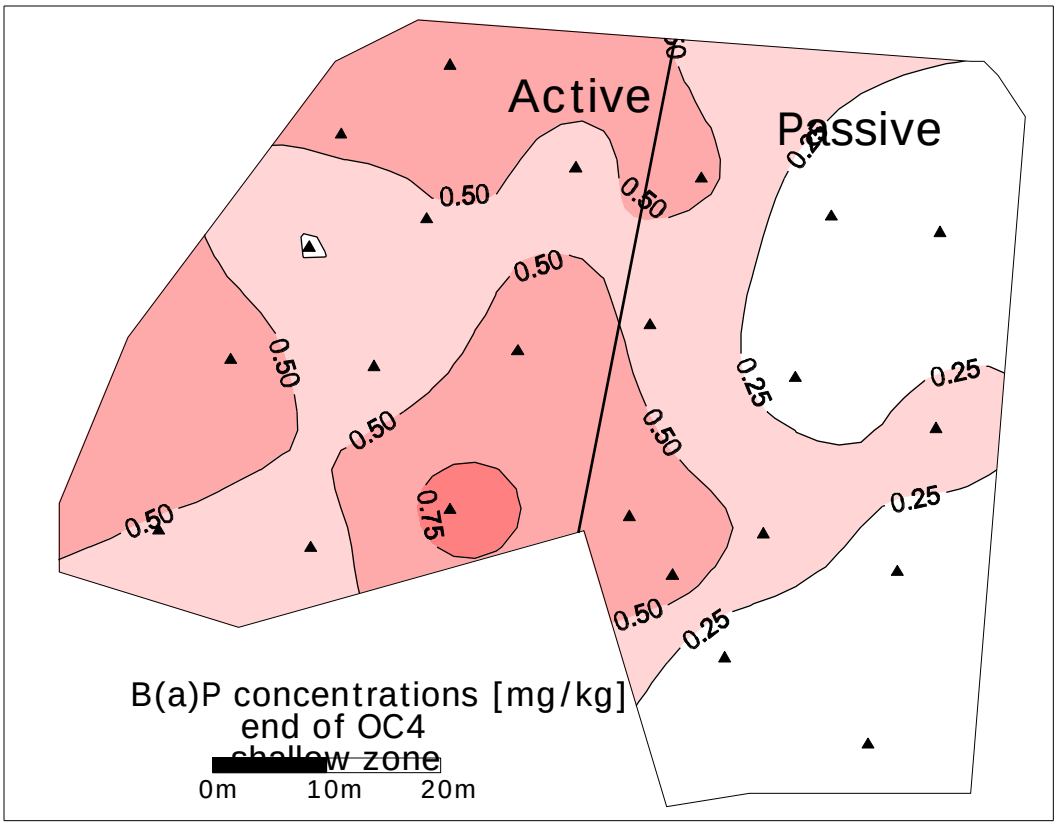


Figure 6.37 (E) Contour Plot of TPH Shallow: Operating Campaign 5

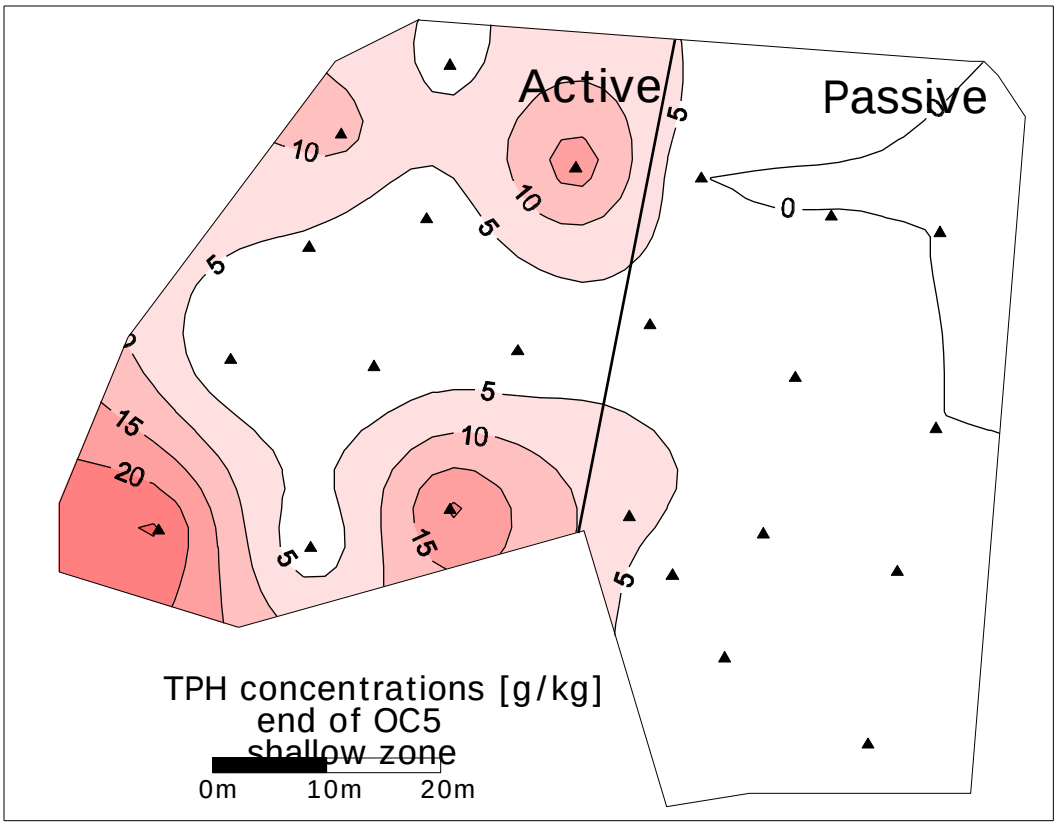


Figure 6.38 (A) Contour Plot of TPH Deep: Baseline

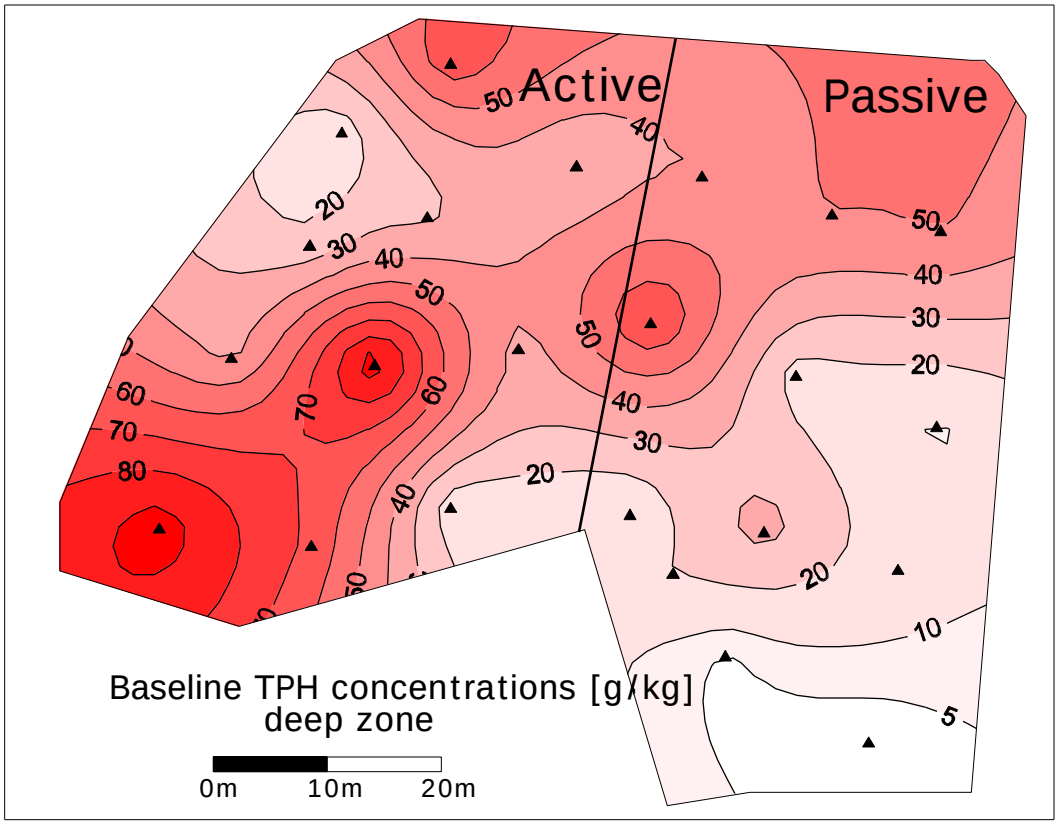
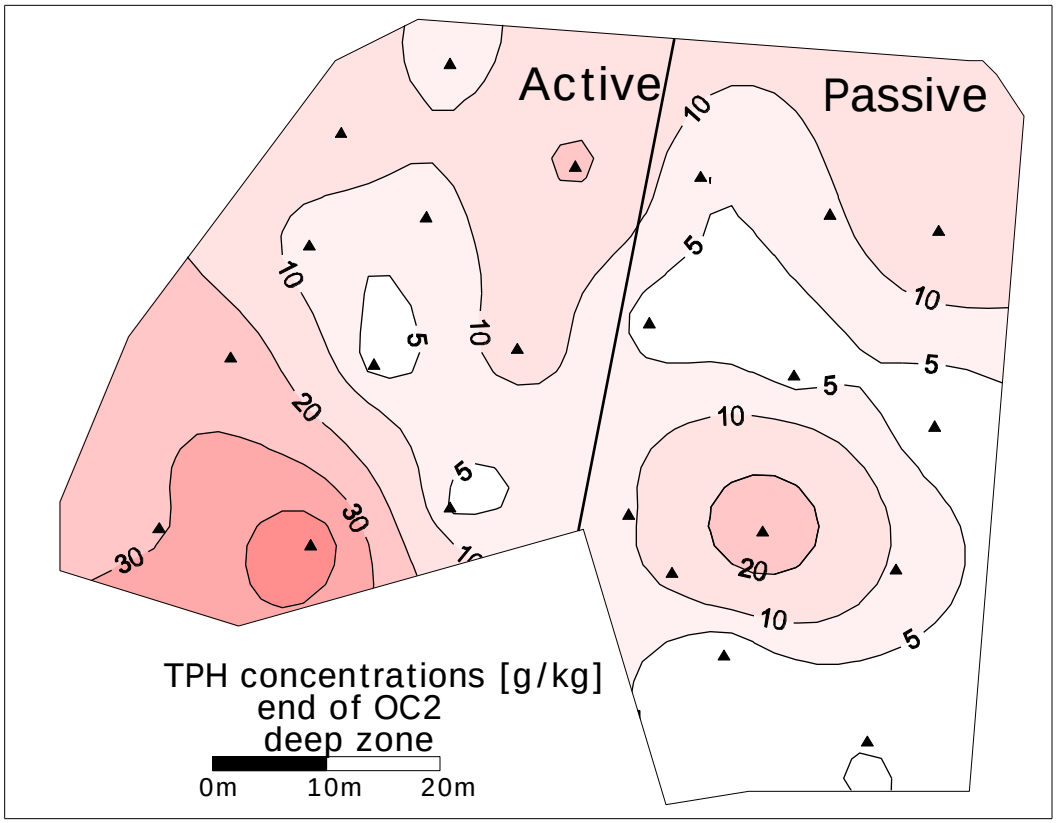


Figure 6.38 (B,C) Contour Plot of TPH Deep: Operating Campaigns 2 & 3



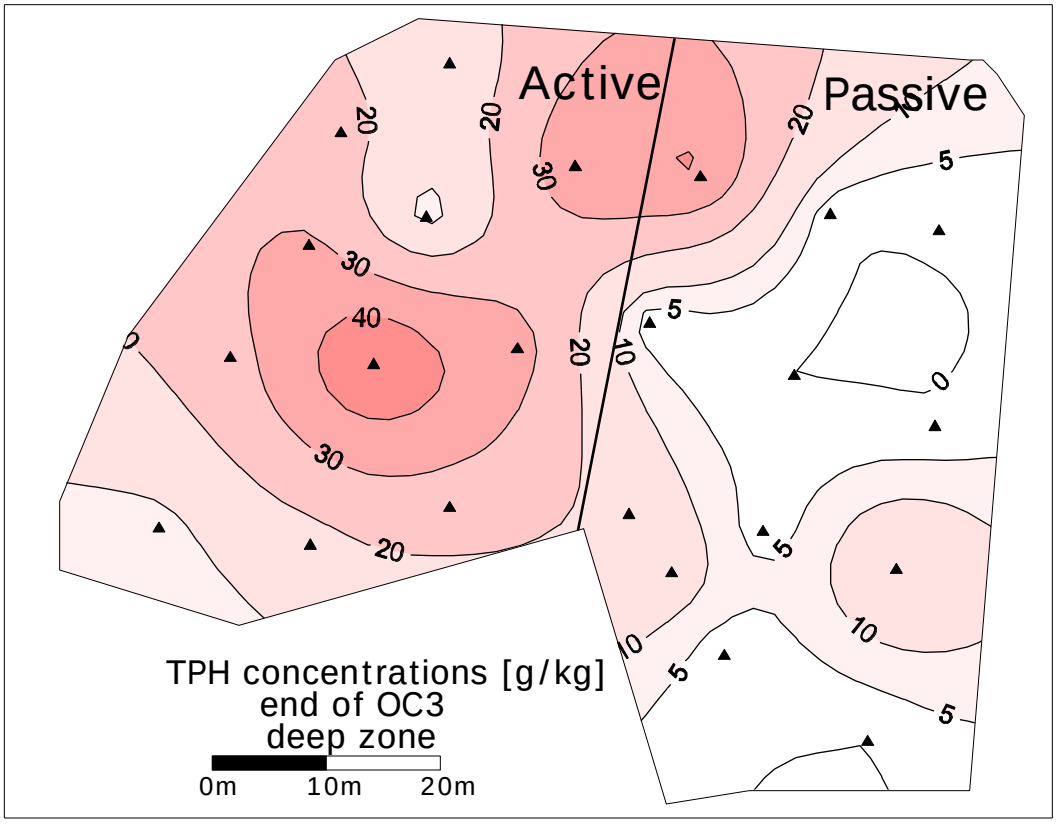
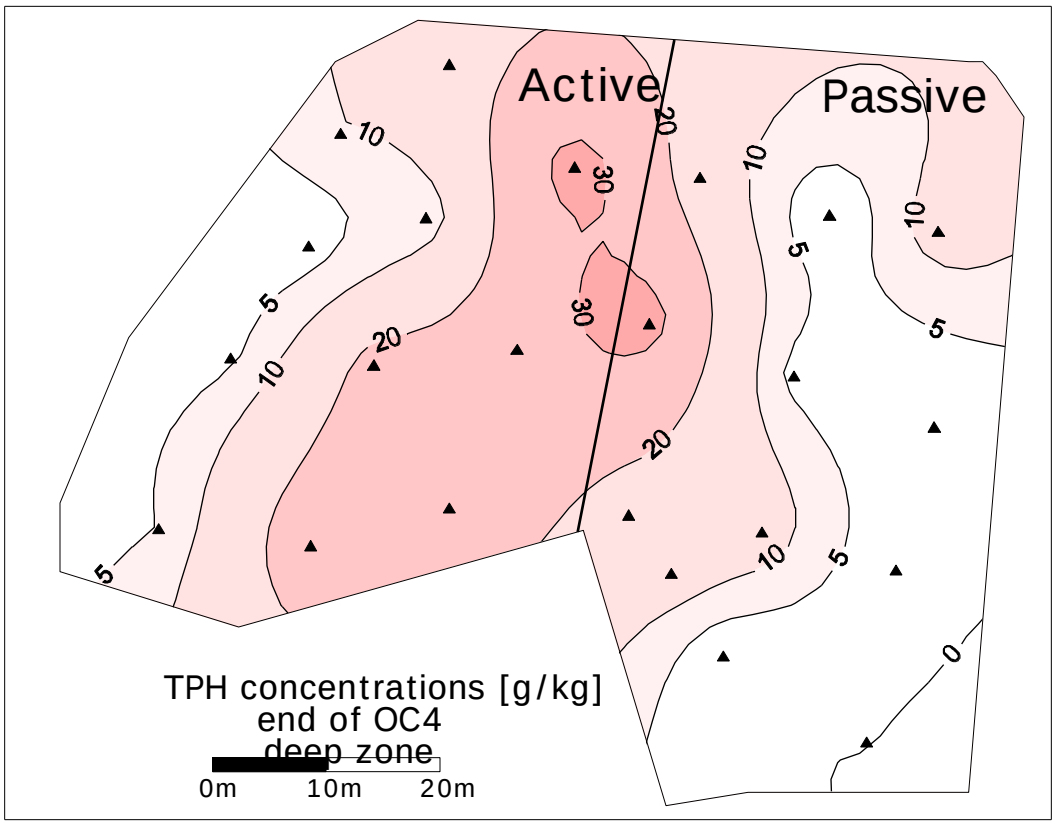


Figure 6.38 (D,E) Contour Plot of TPH Deep: Operating Campaigns 4 & 5



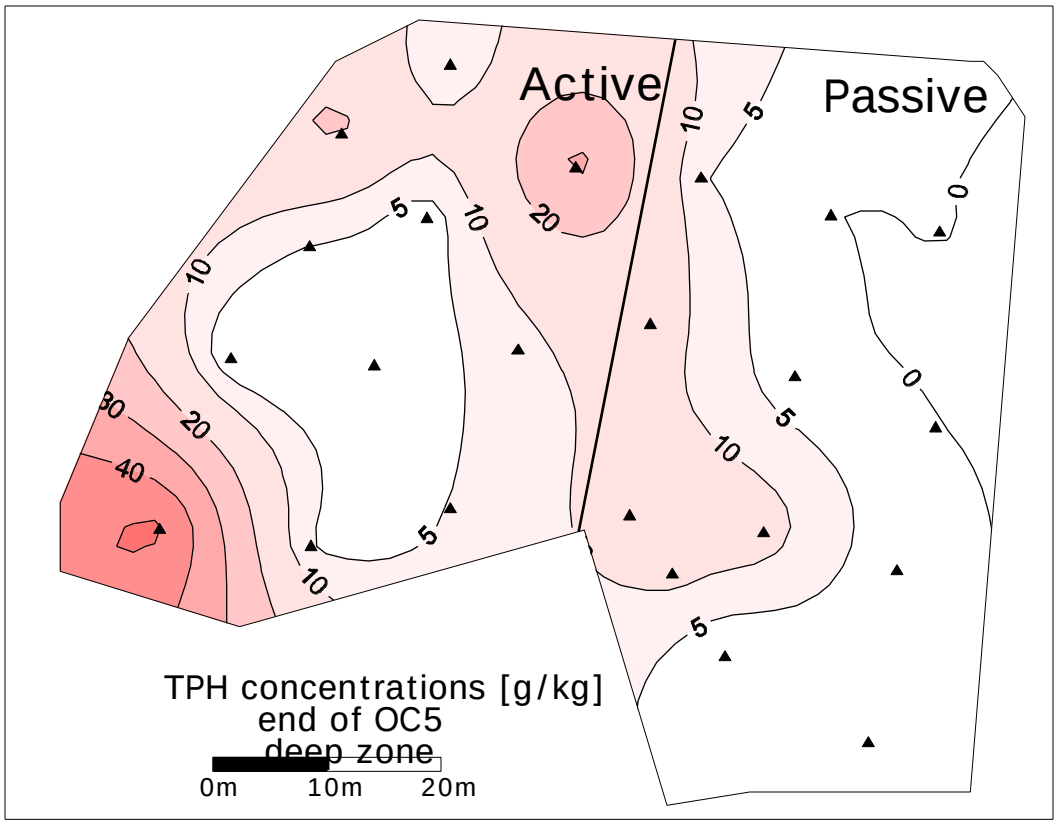
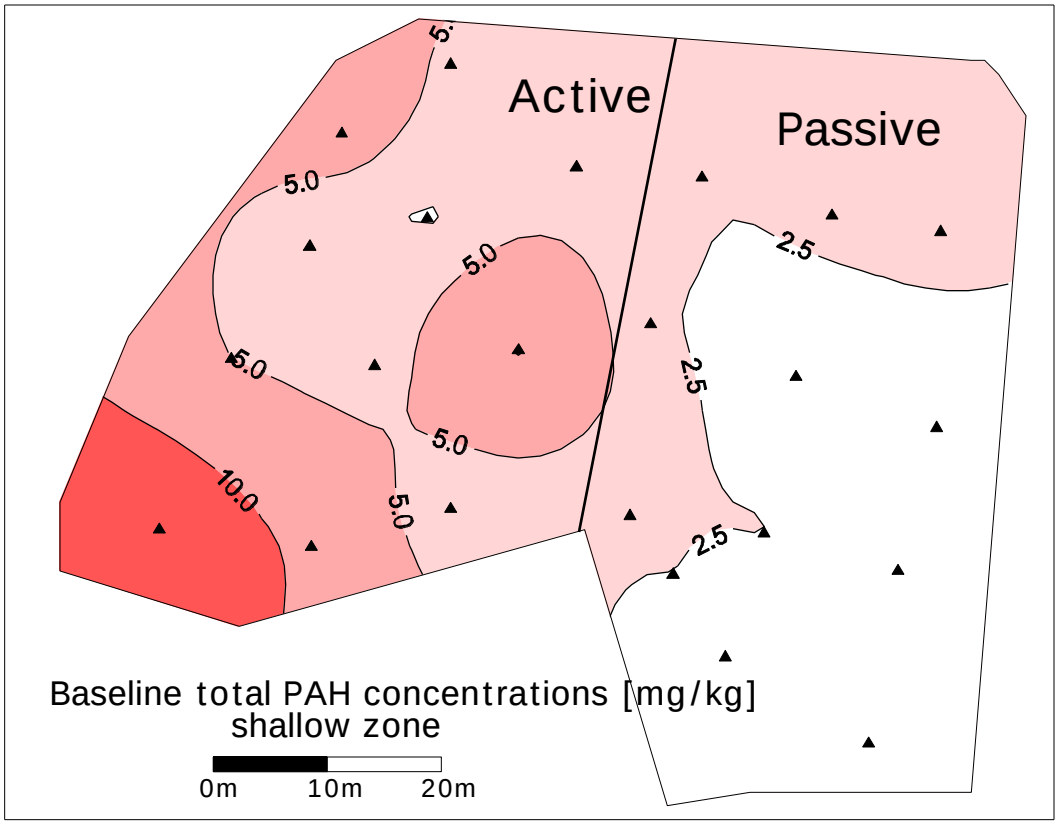


Figure 6.39 (A,B) Contour Plot of Total PAH Shallow: Baseline & Operating Campaign 2



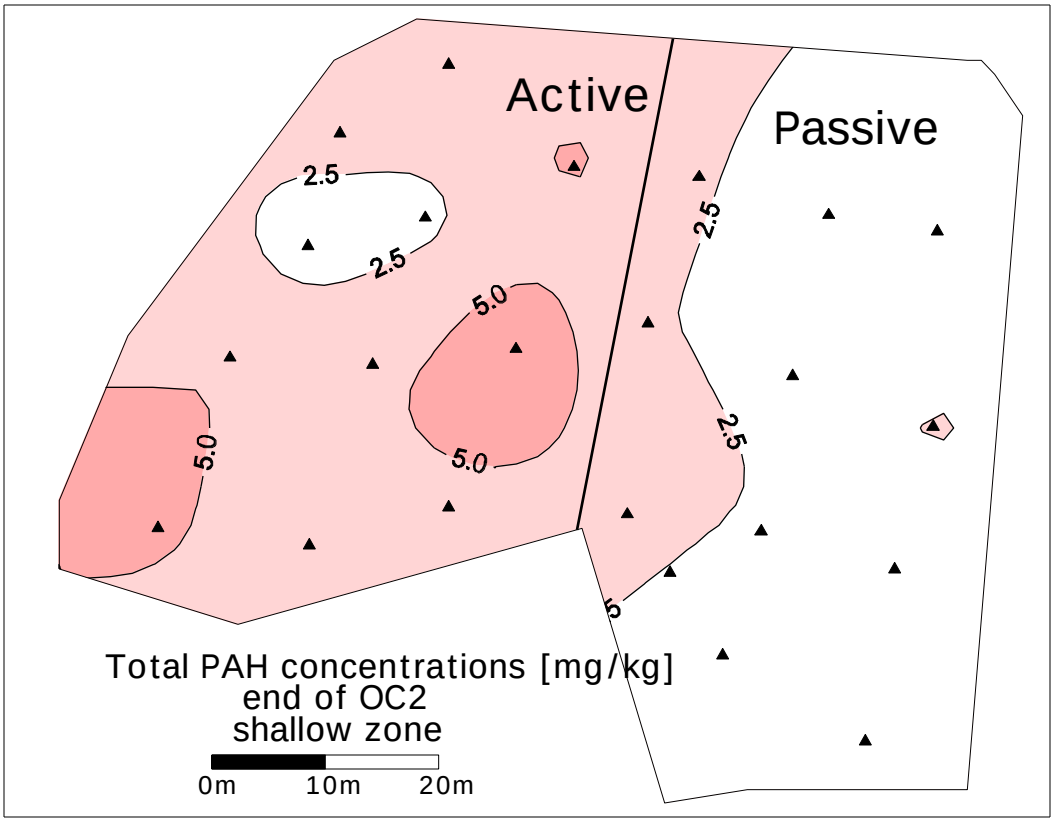
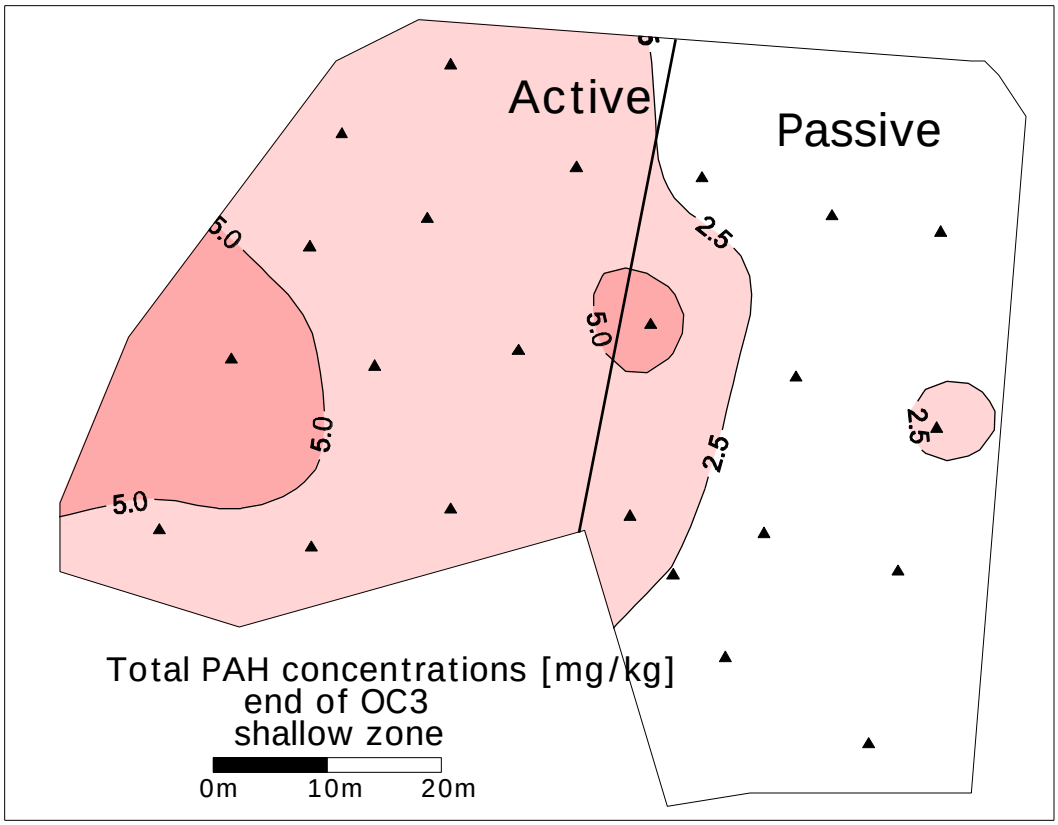


Figure 6.39 (C,D) Contour Plot of Total PAH Shallow: Operating Campaigns 3 & 4



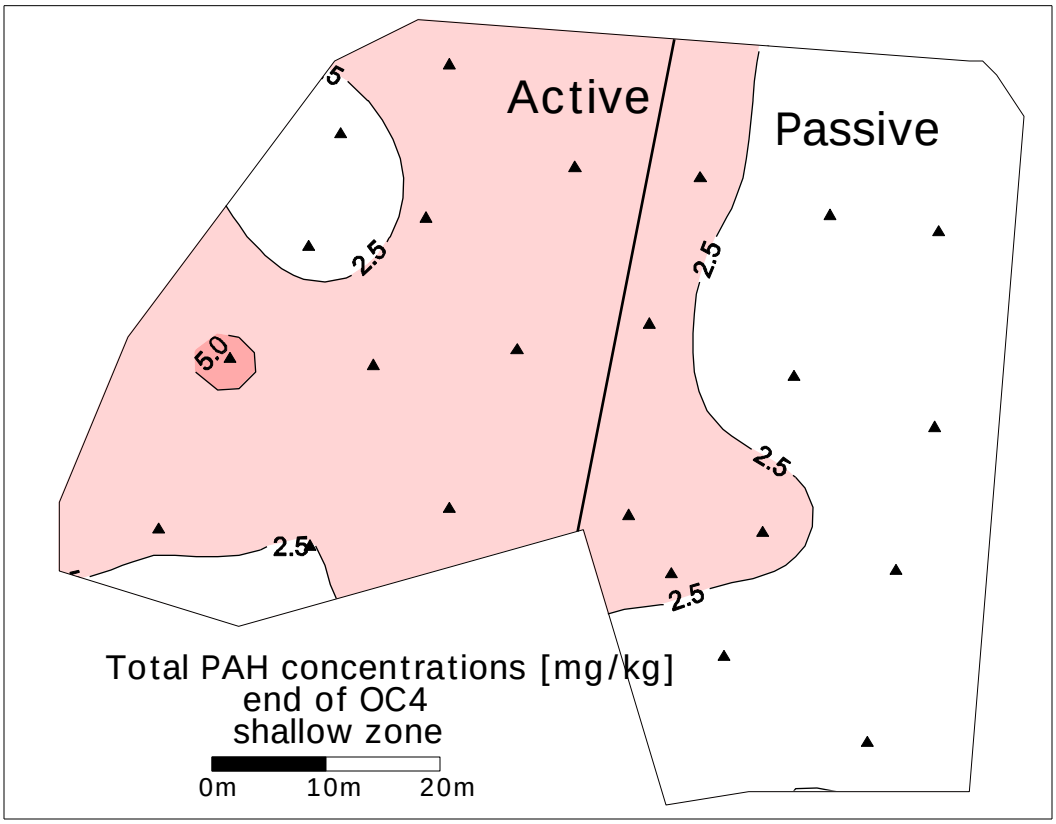


Figure 6.39 (E) Contour Plot of Total PAH Shallow: Operating Campaign 5

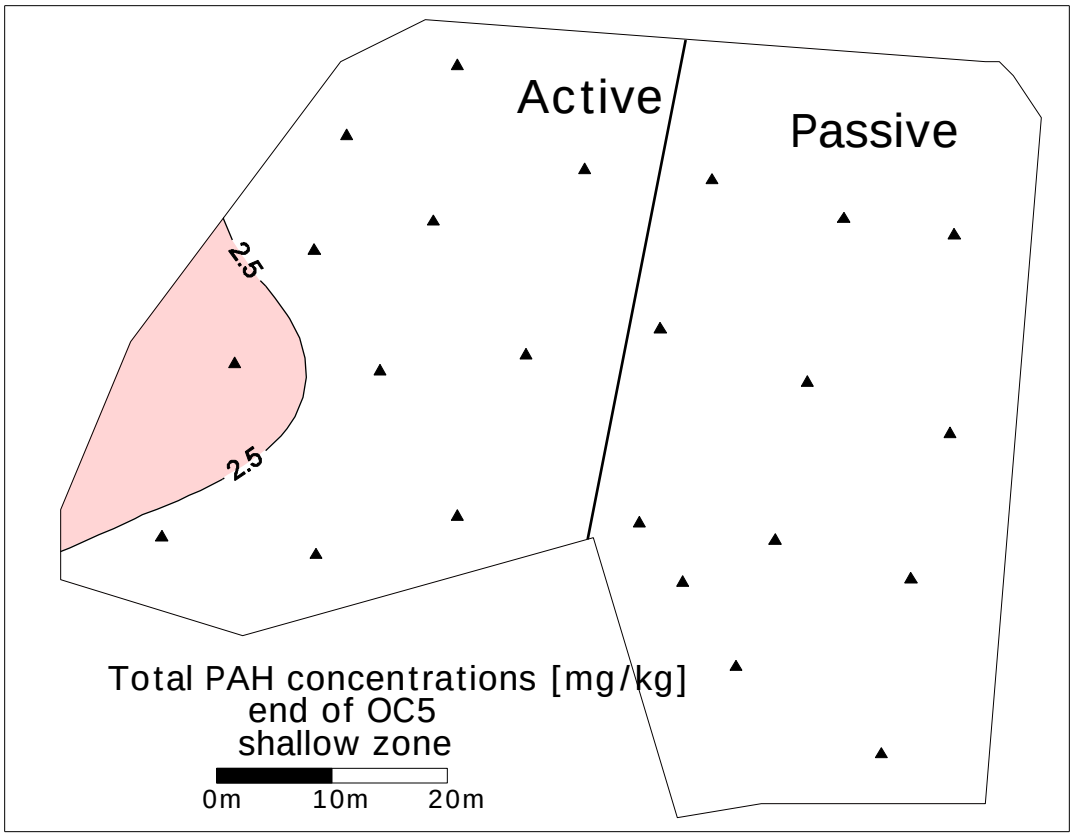


Figure 6.40 (A) Contour Plot of Total PAH Deep: Baseline

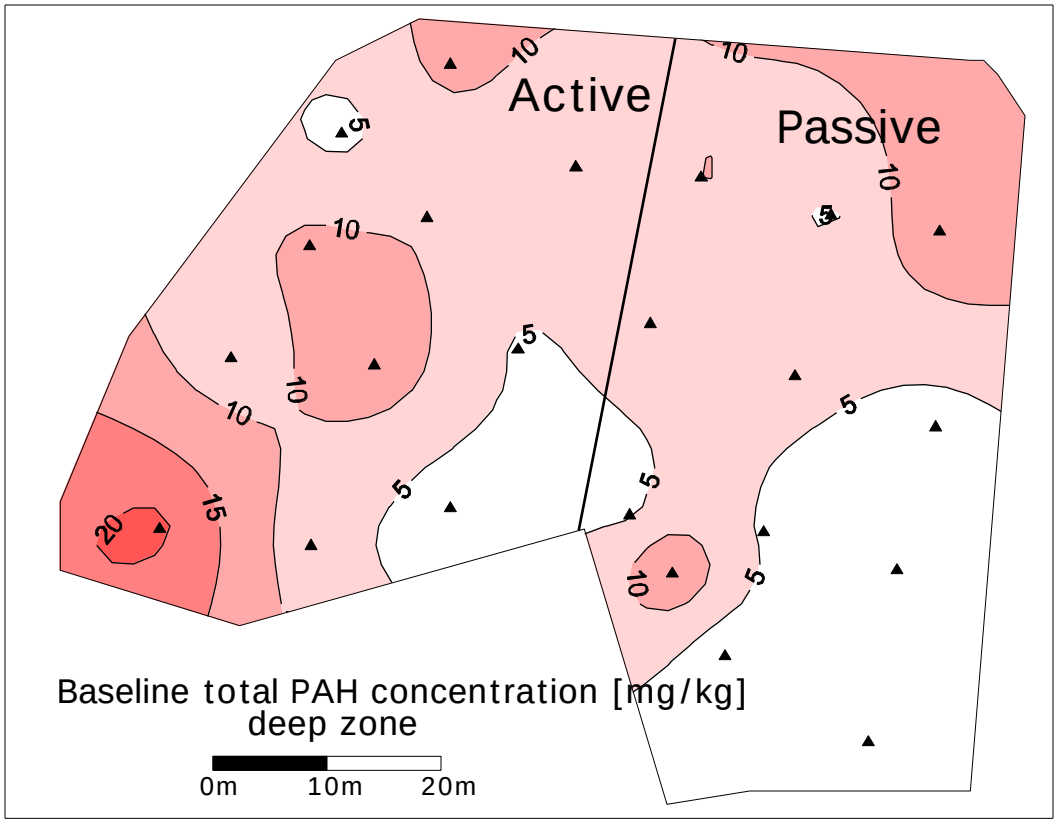


Figure 6.40 (B,C) Contour Plot of Total PAH Deep: Operating Campaigns 2 & 3

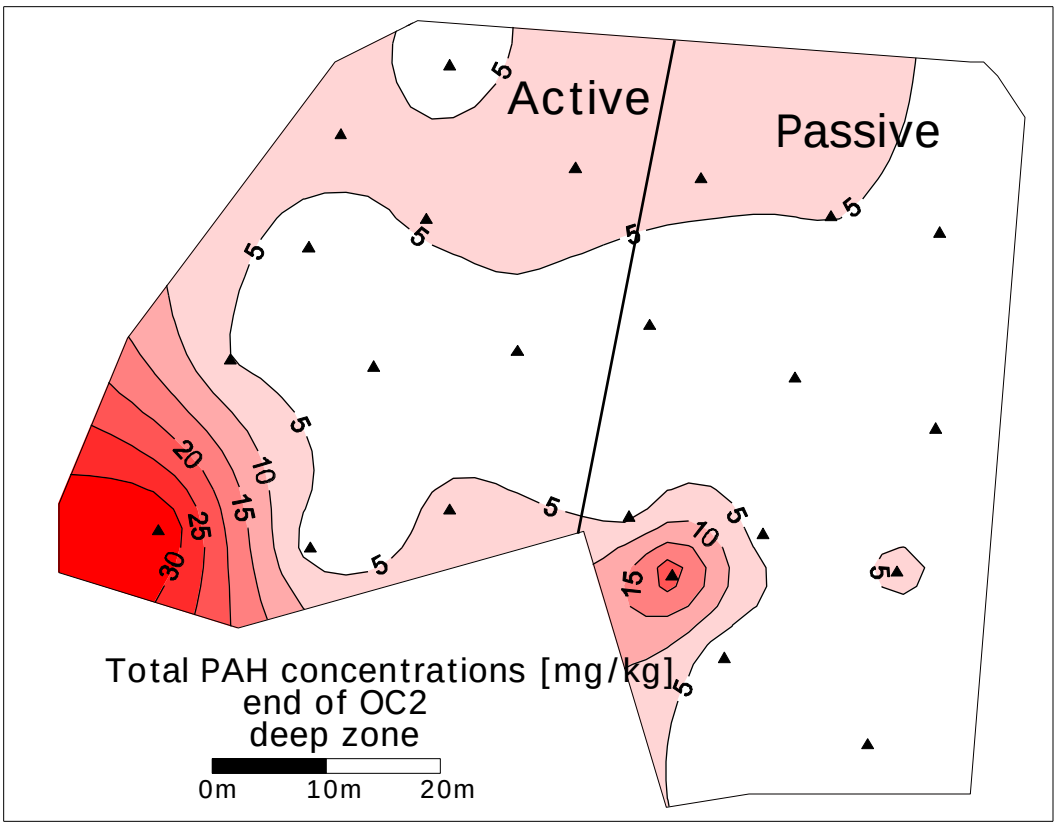
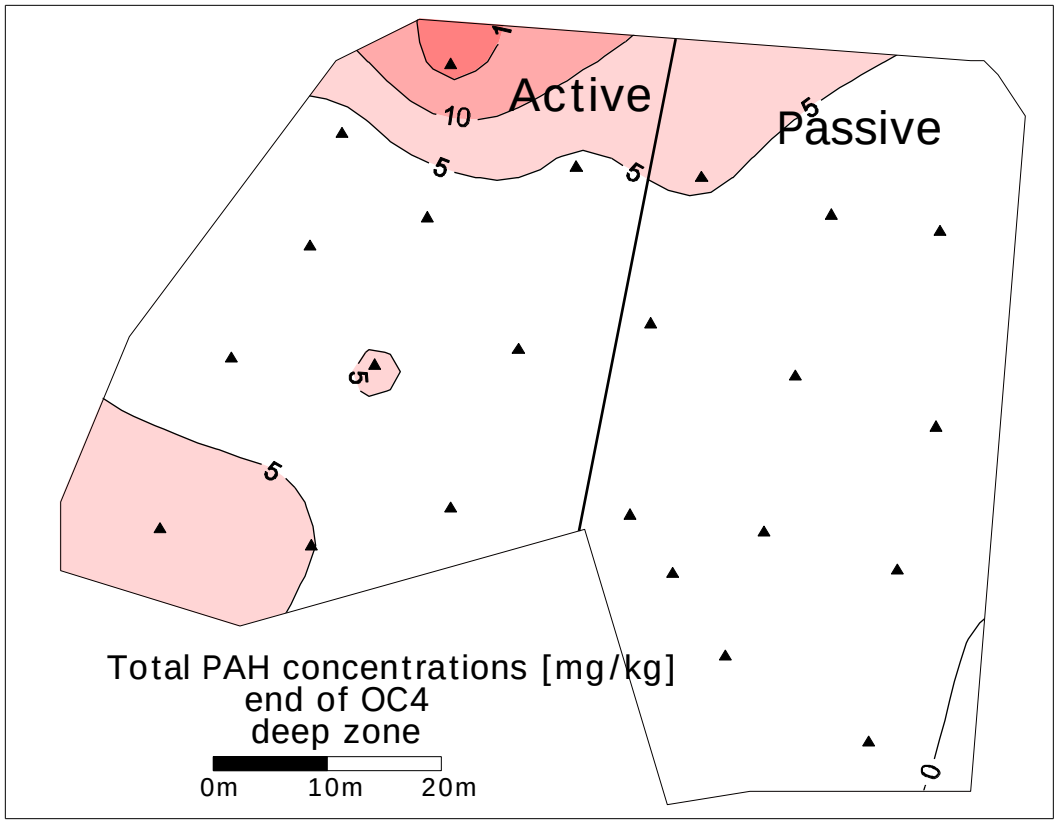


Figure 6.40 (D,E) Contour Plot of Total PAH Deep: Operating Campaigns 4 & 5



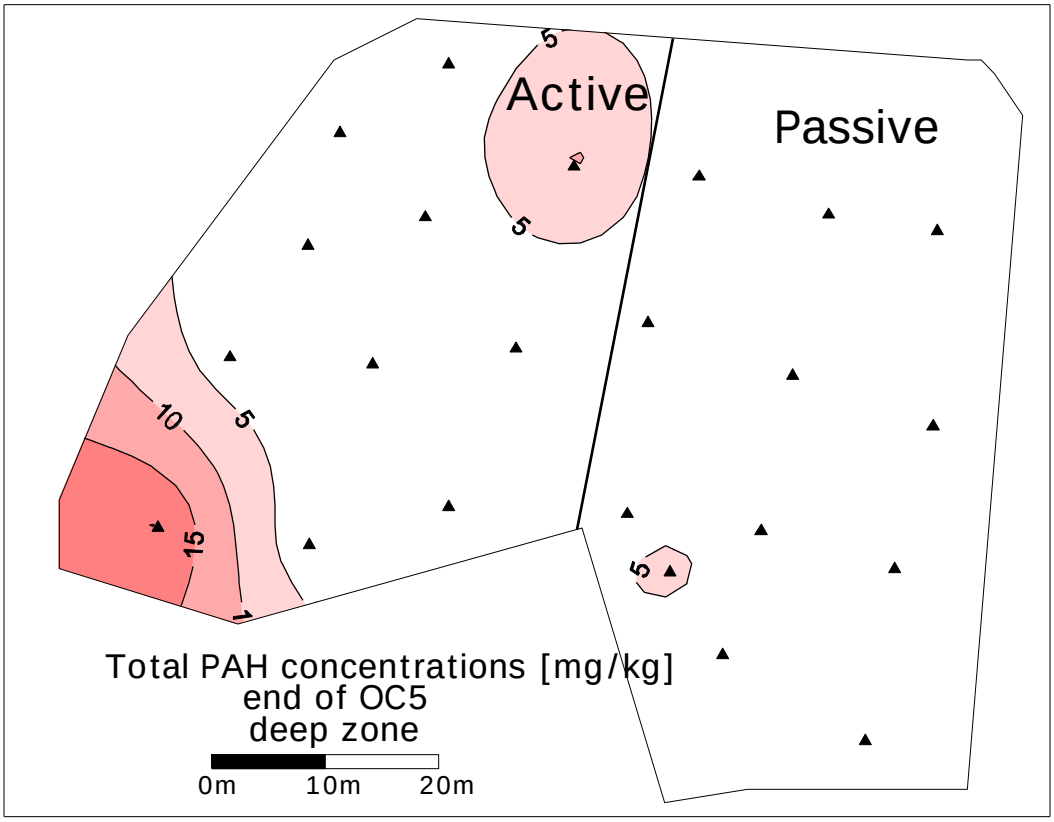
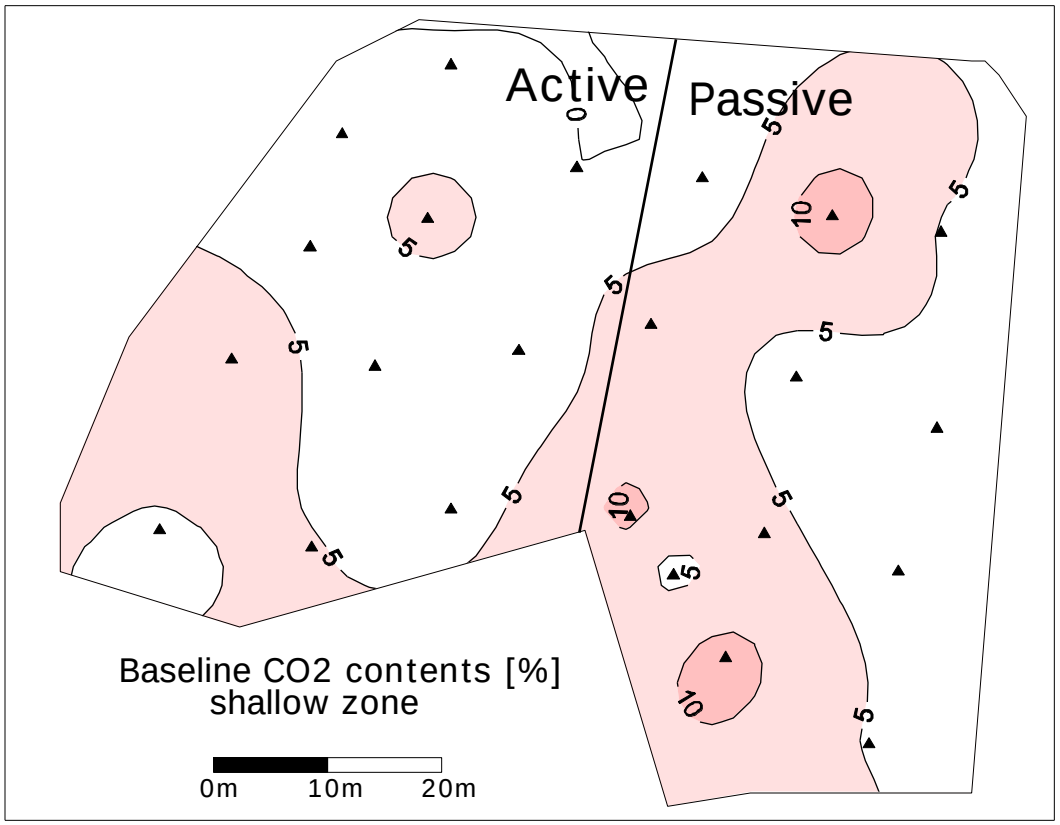


Figure 6.41 (A,B) Contour Plot of CO2 Shallow : Baseline & Operating Campaign 2



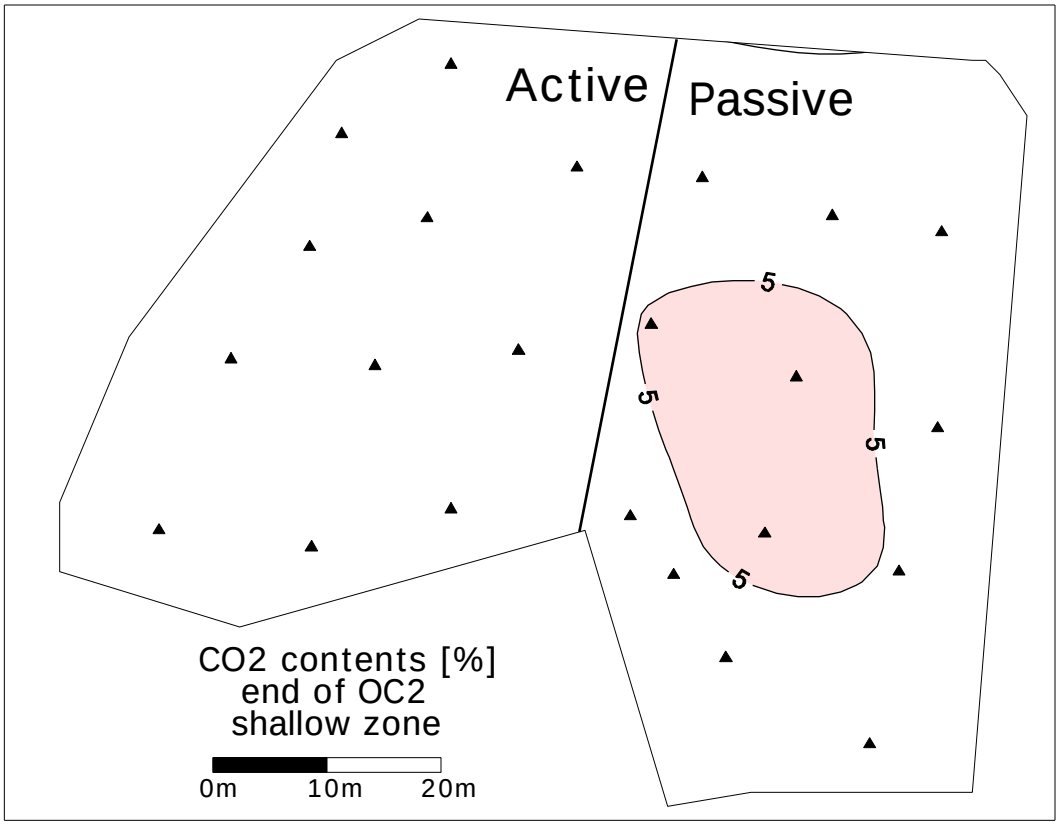
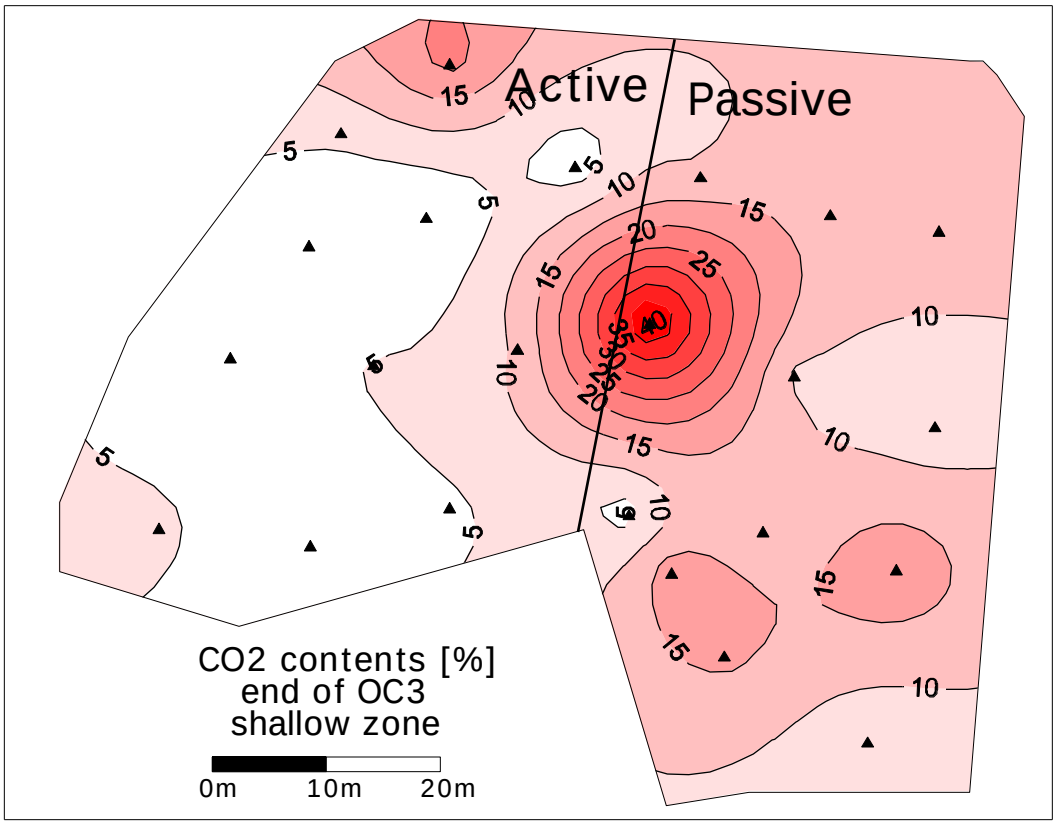


Figure 6.41 (C,D) Contour Plot of CO2 Shallow: Operating Campaigns 3 & 4



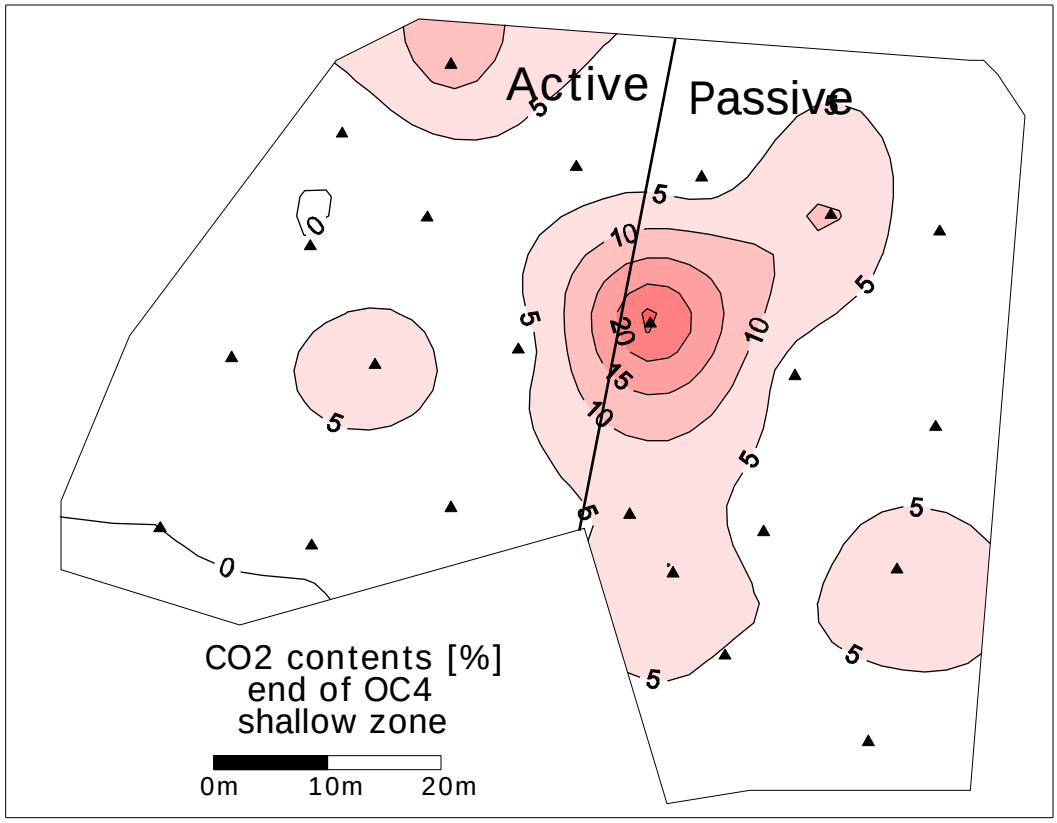


Figure 6.41 (E) Contour Plot of CO2 Shallow: Operating Campaign 5

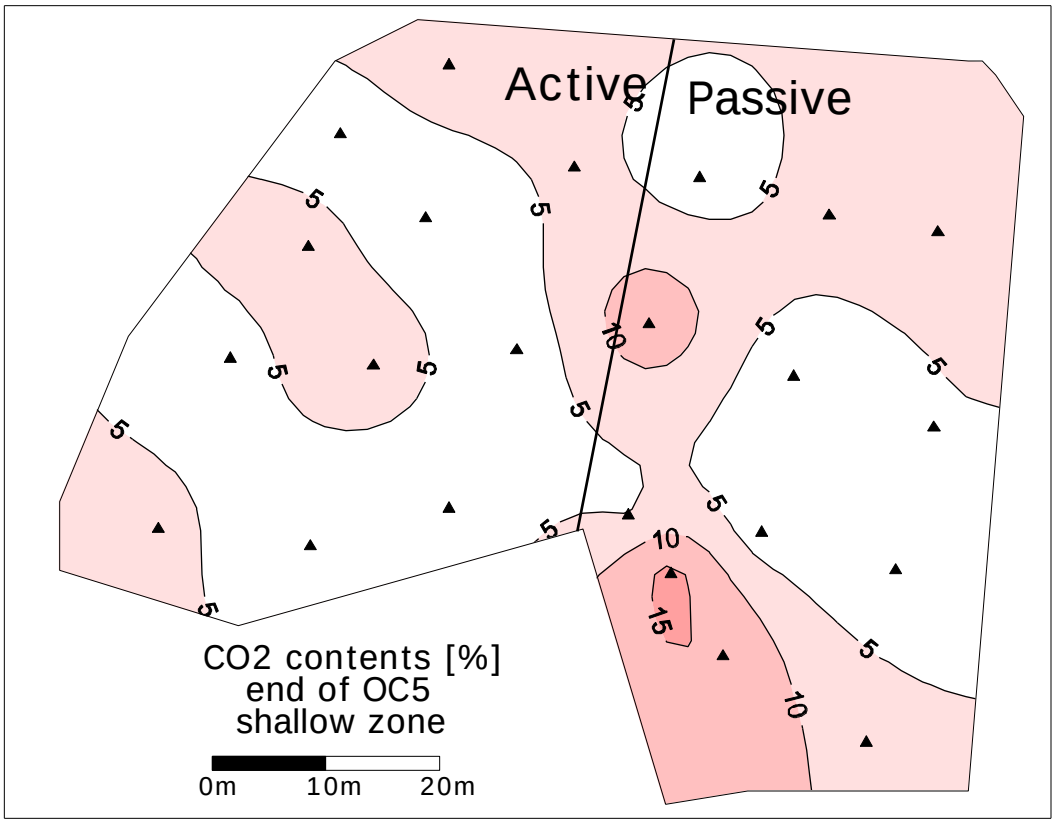


Figure 6.42 (A) Contour Plot of CO2 Deep:Baseline

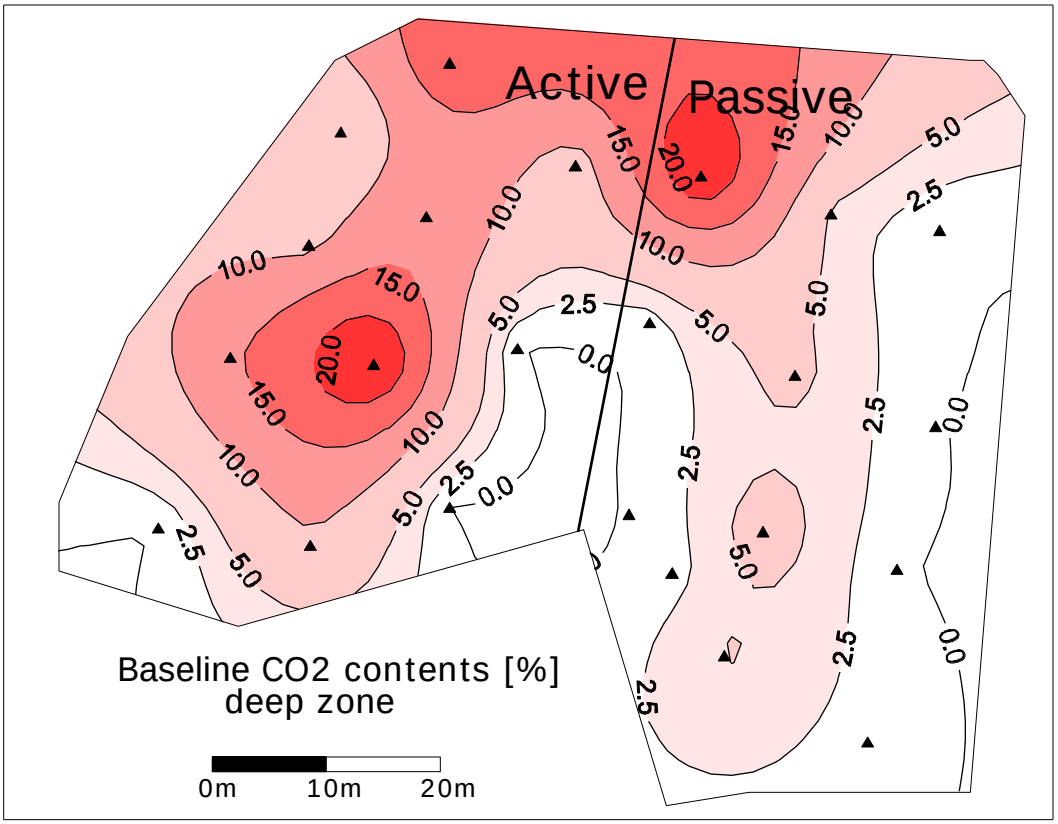
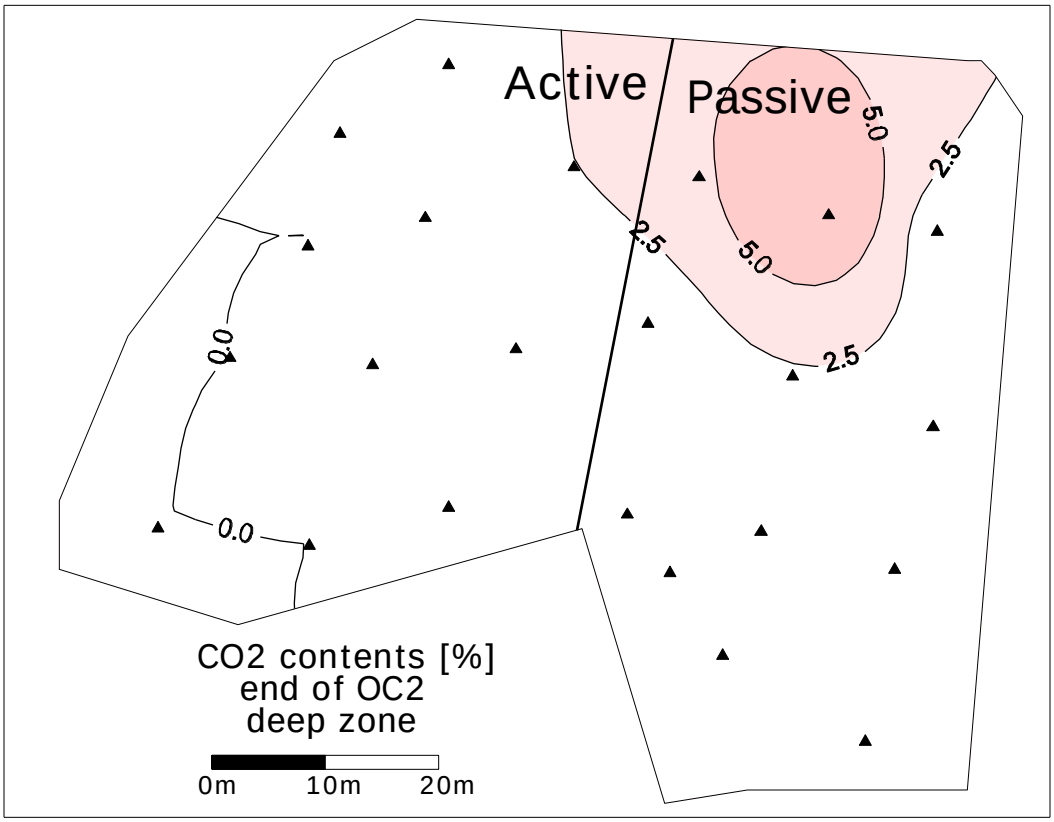


Figure 6.42 (B,C) Contour Plot of CO2 Deep: Operating Campaigns 2 & 3



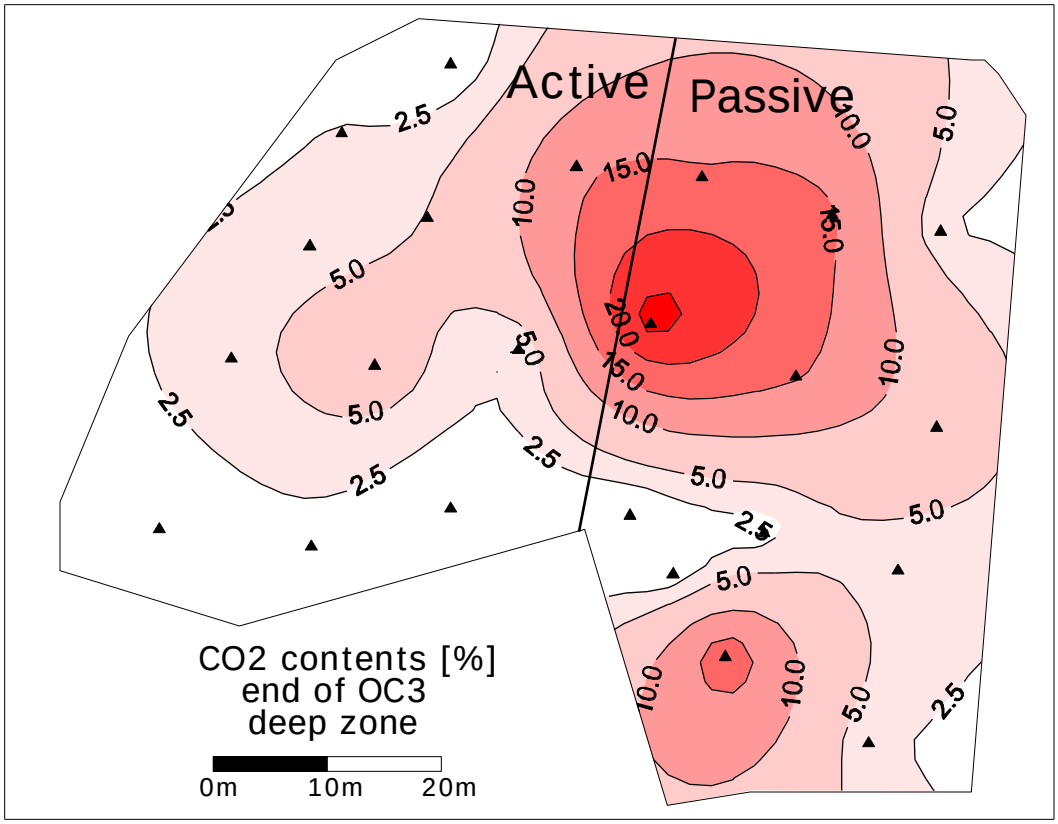
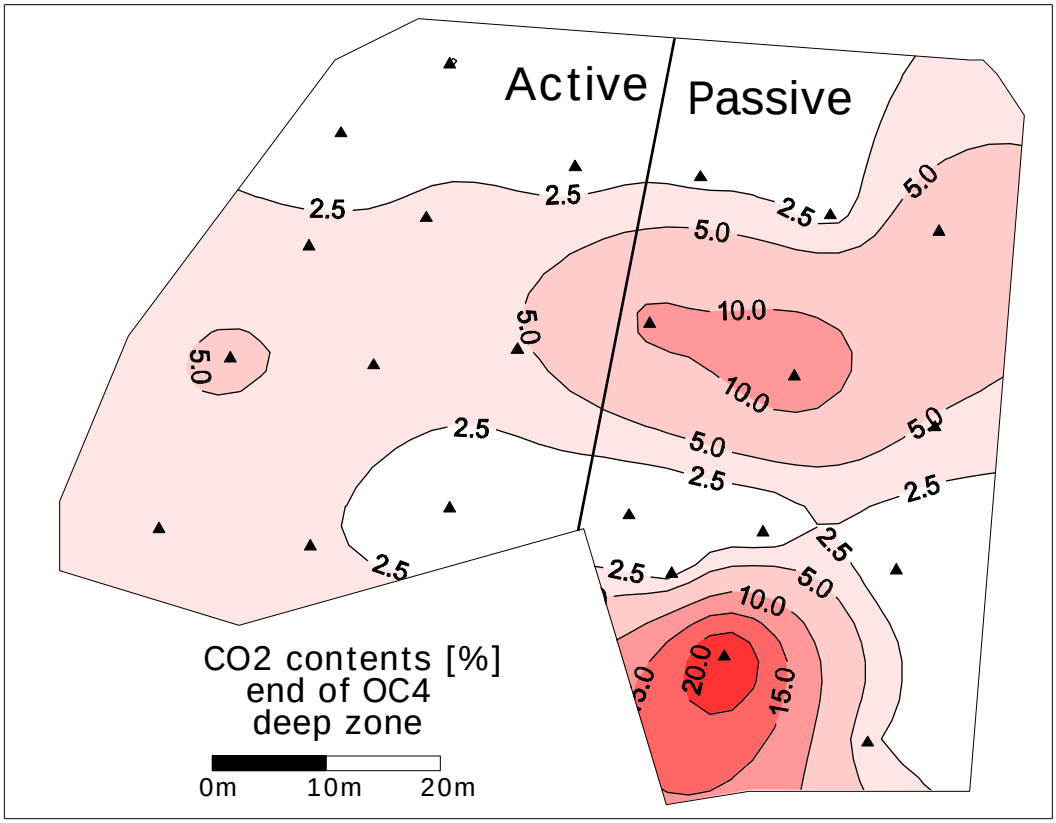


Figure 6.42 (D,E) Contour Plot of CO2 Deep: Operating Campaigns 4 & 5



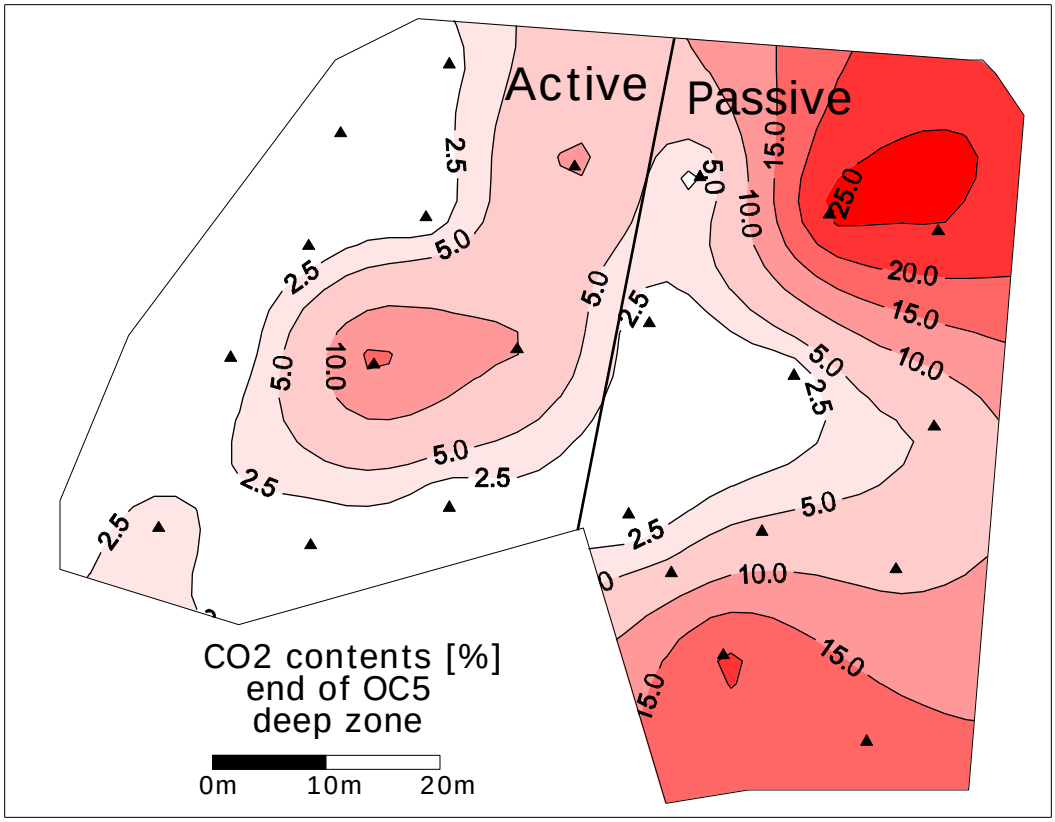
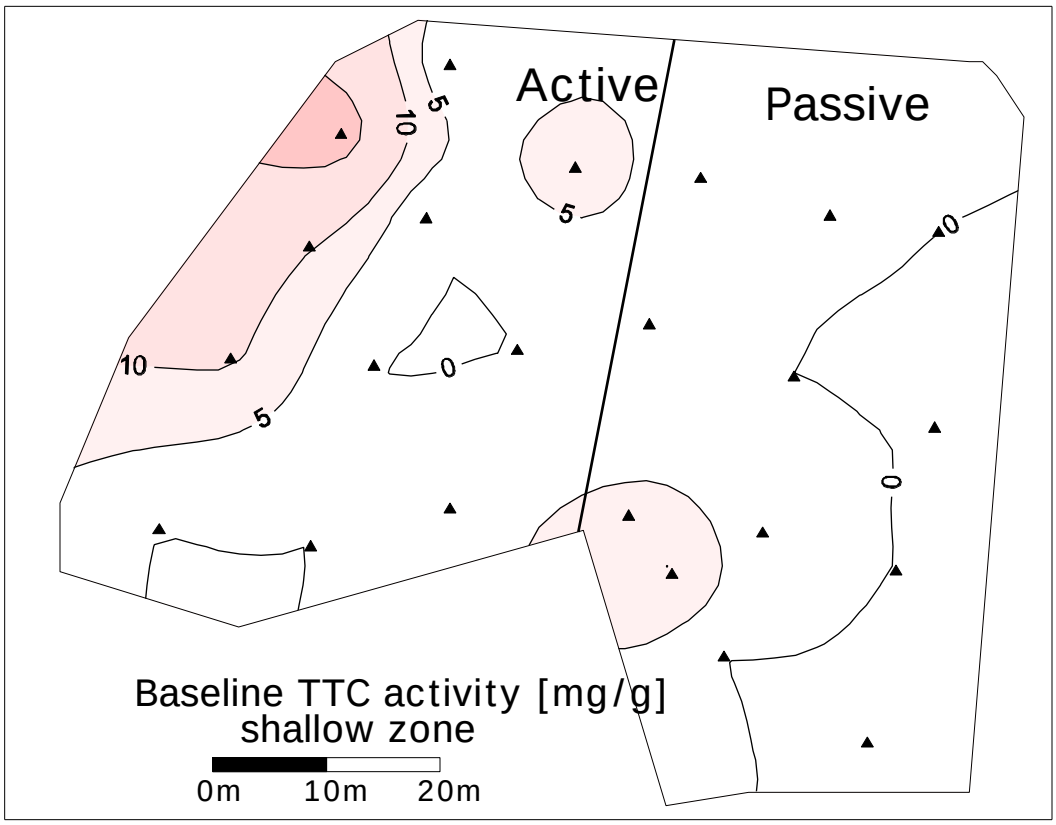


Figure 6.43 (A,B) Contour Plot of TTC Shallow: Baseline & Operating Campaign 2



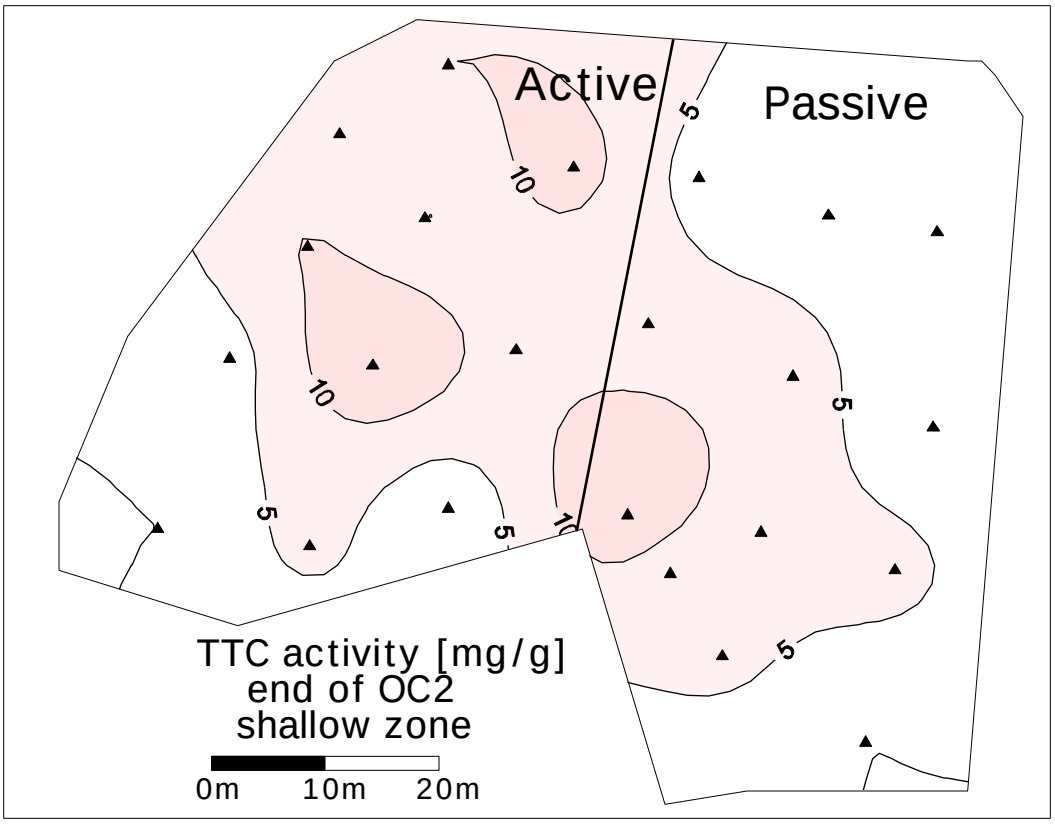
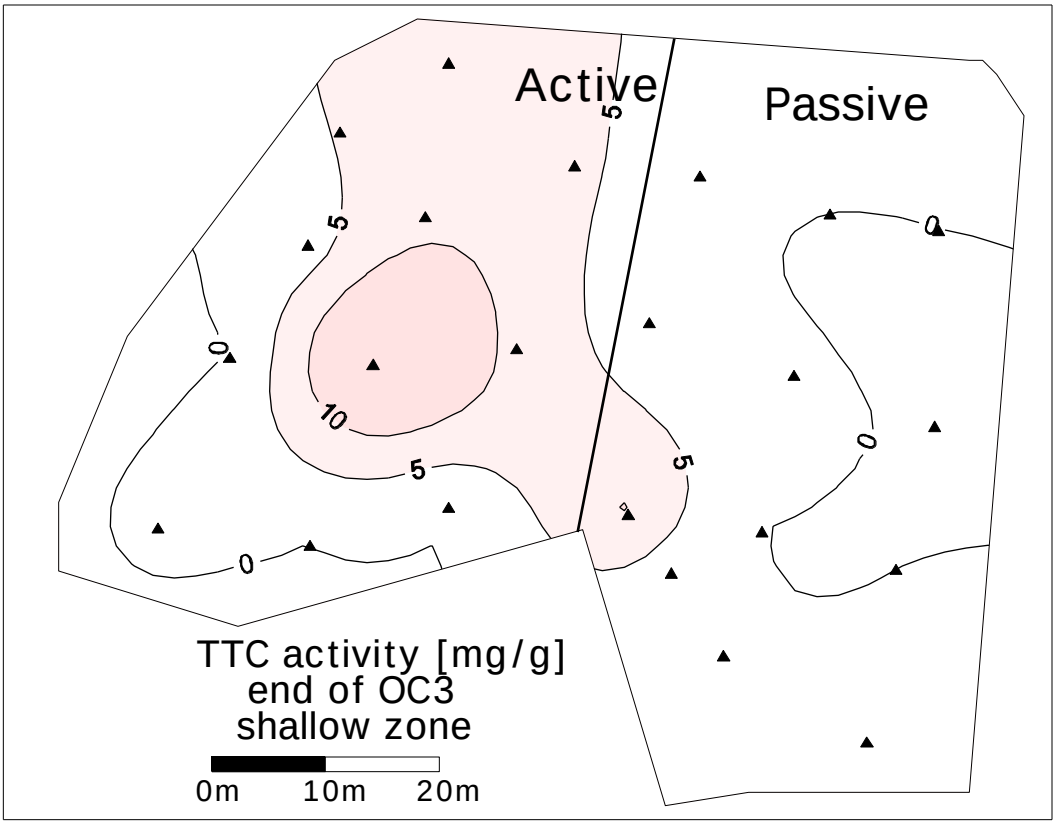


Figure 6.43 (C,D) Contour Plot of TTC Shallow: Operating Campaign 3 & 4



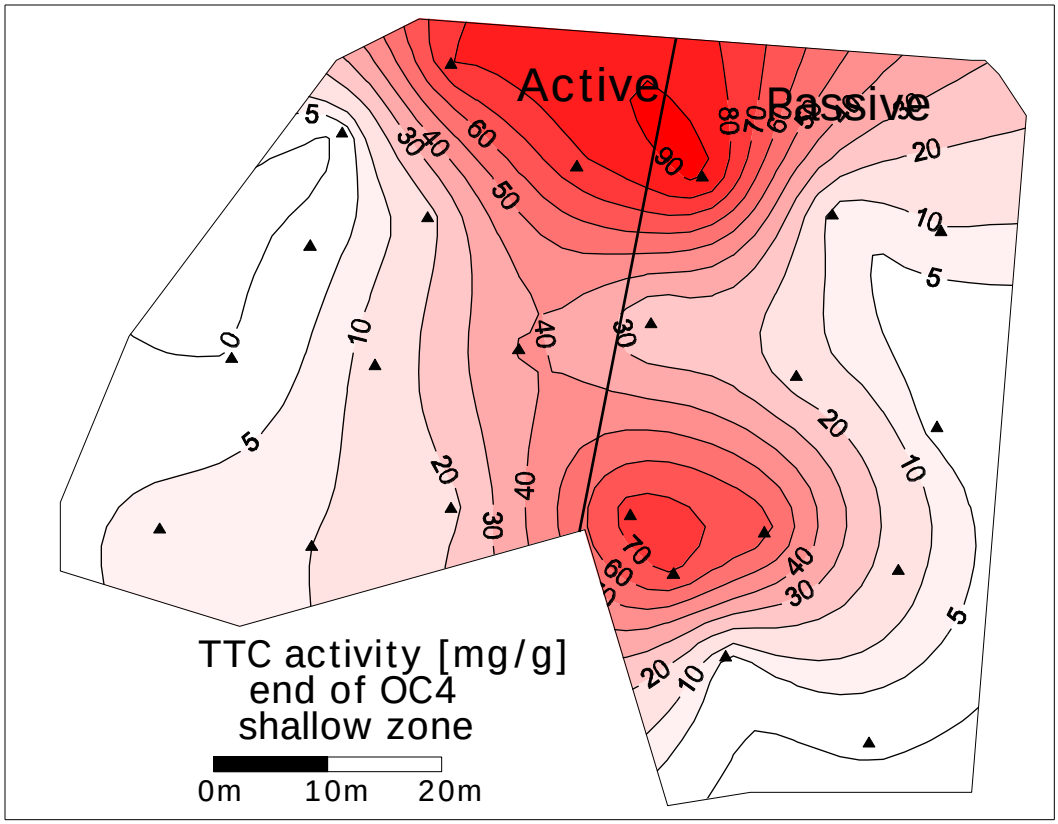


Figure 6.43 (E) Contour Plot of TTC Shallow: Operating Campaign 5

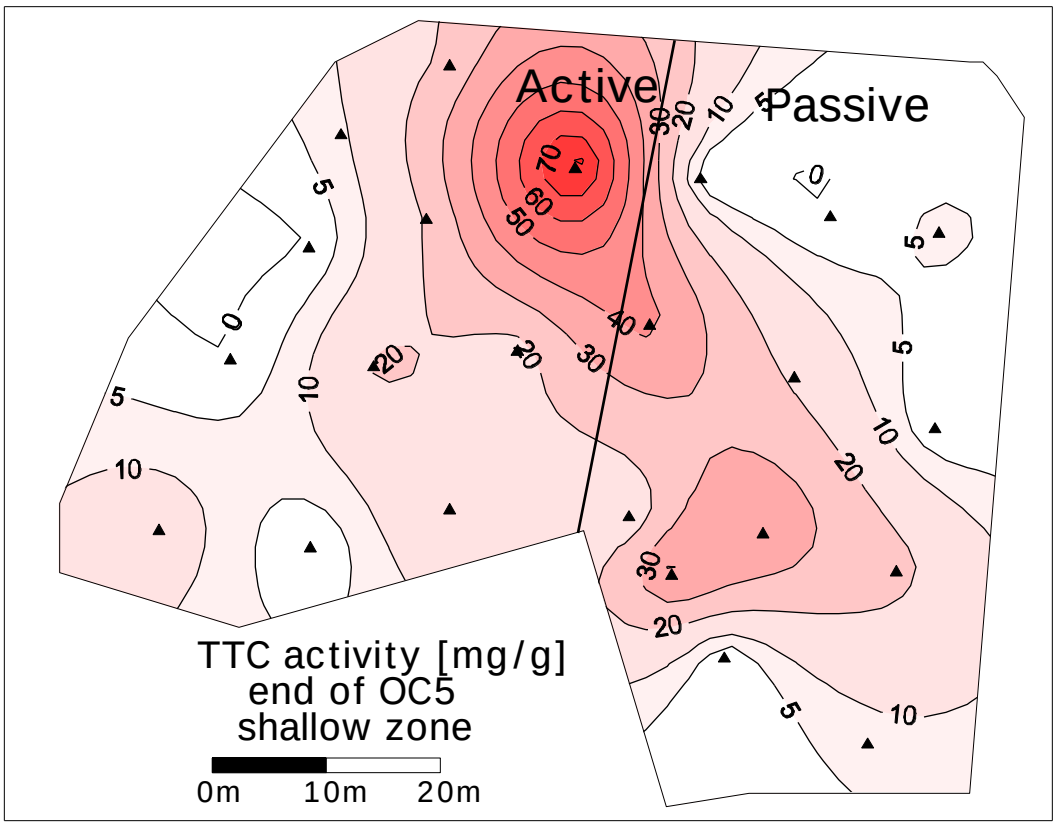


Figure 6.44 (A) Contour Plot of TTC Deep: Baseline

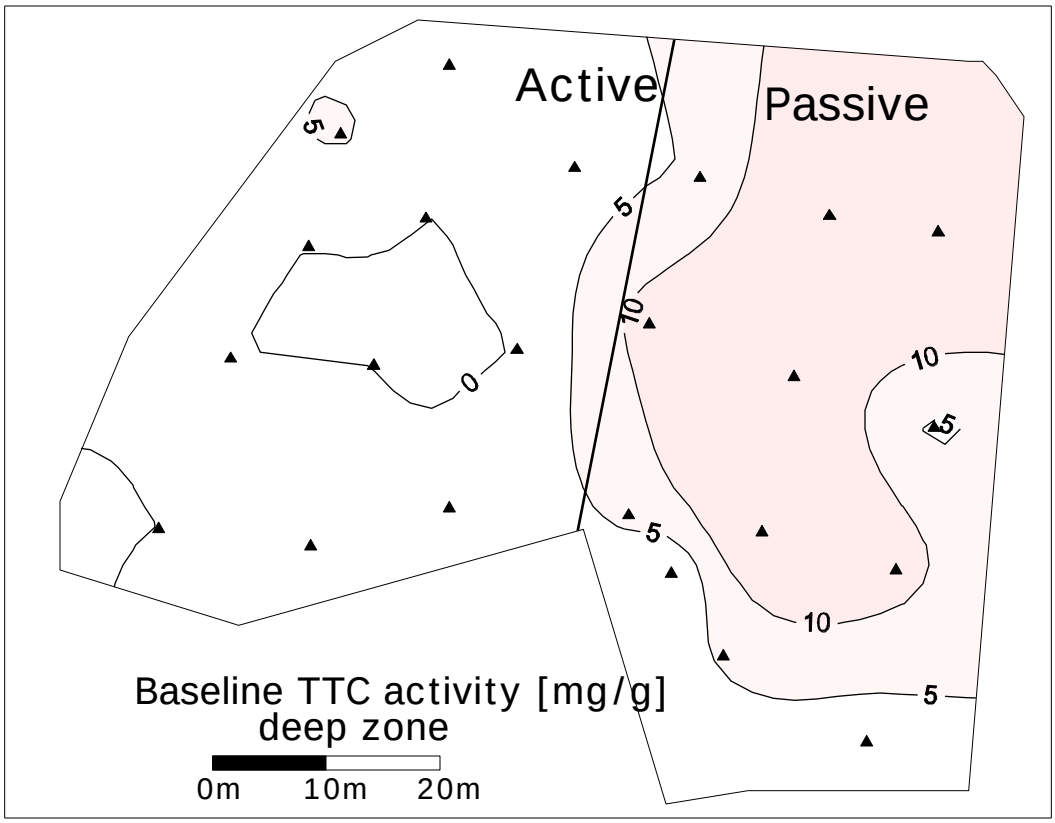
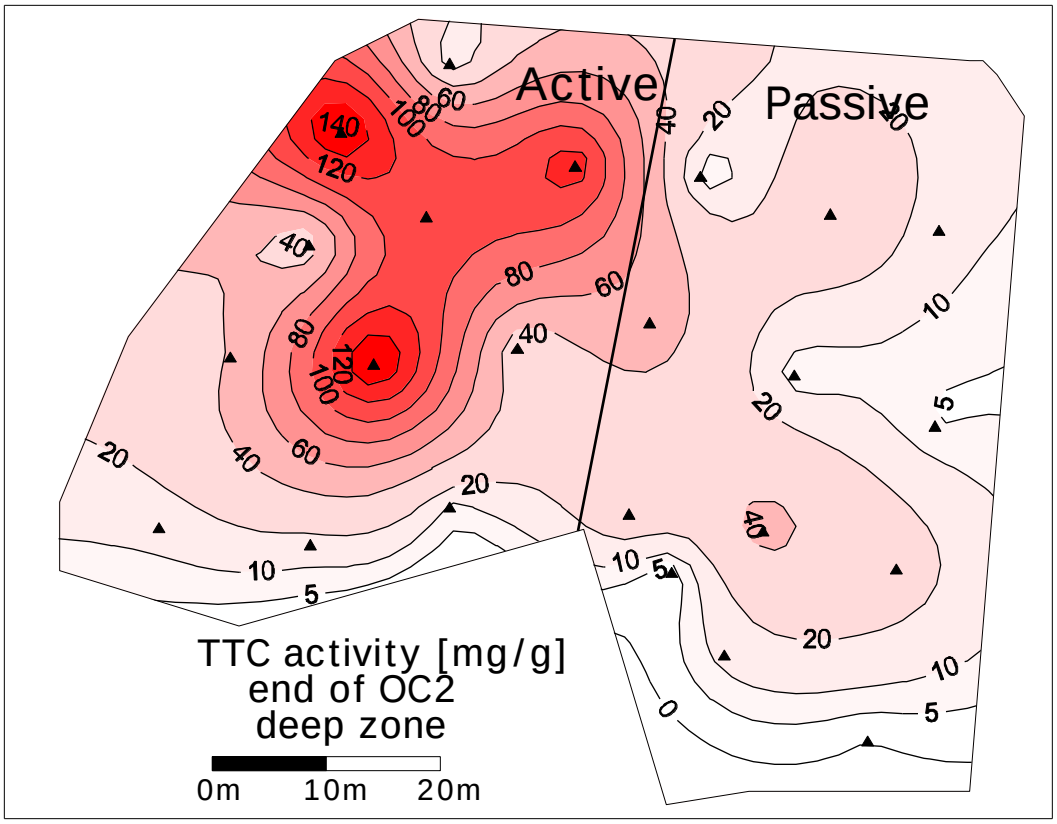


Figure 6.44 (B,C) Contour Plot of TTC Deep: Operating Campaigns 2 & 3



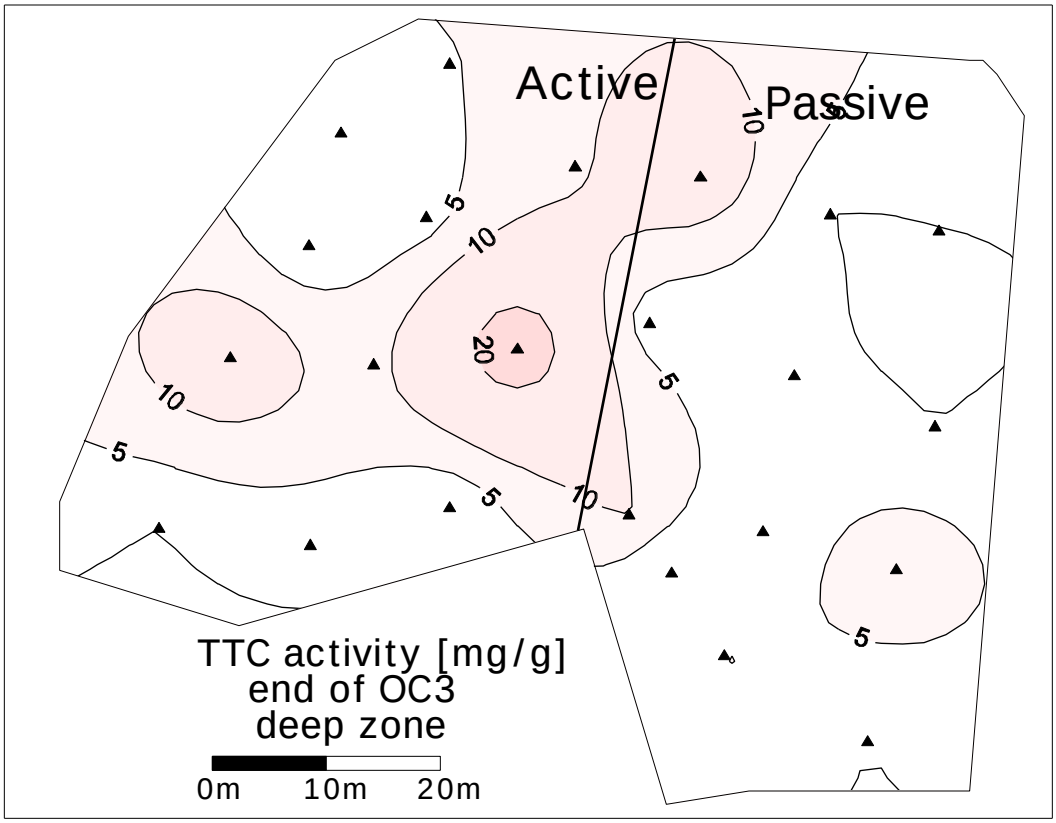
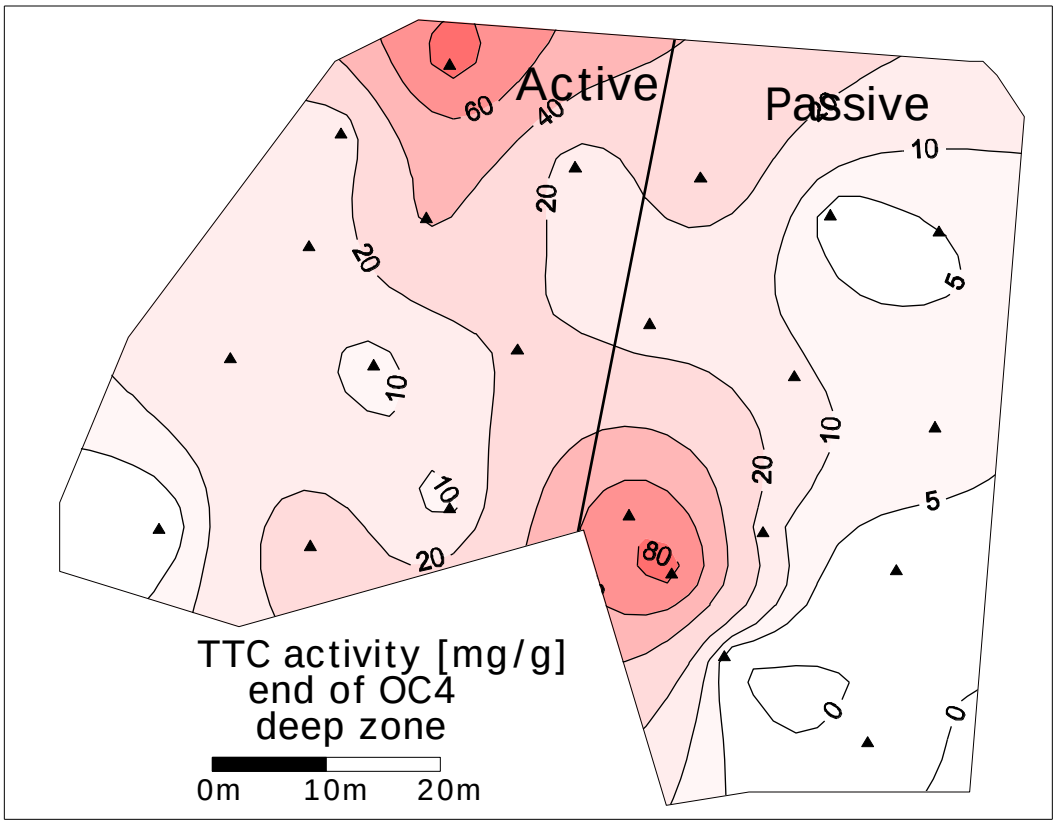


Figure 6.44 (D,E) Contour Plot of TTC Deep: Operating Campaigns 4 & 5



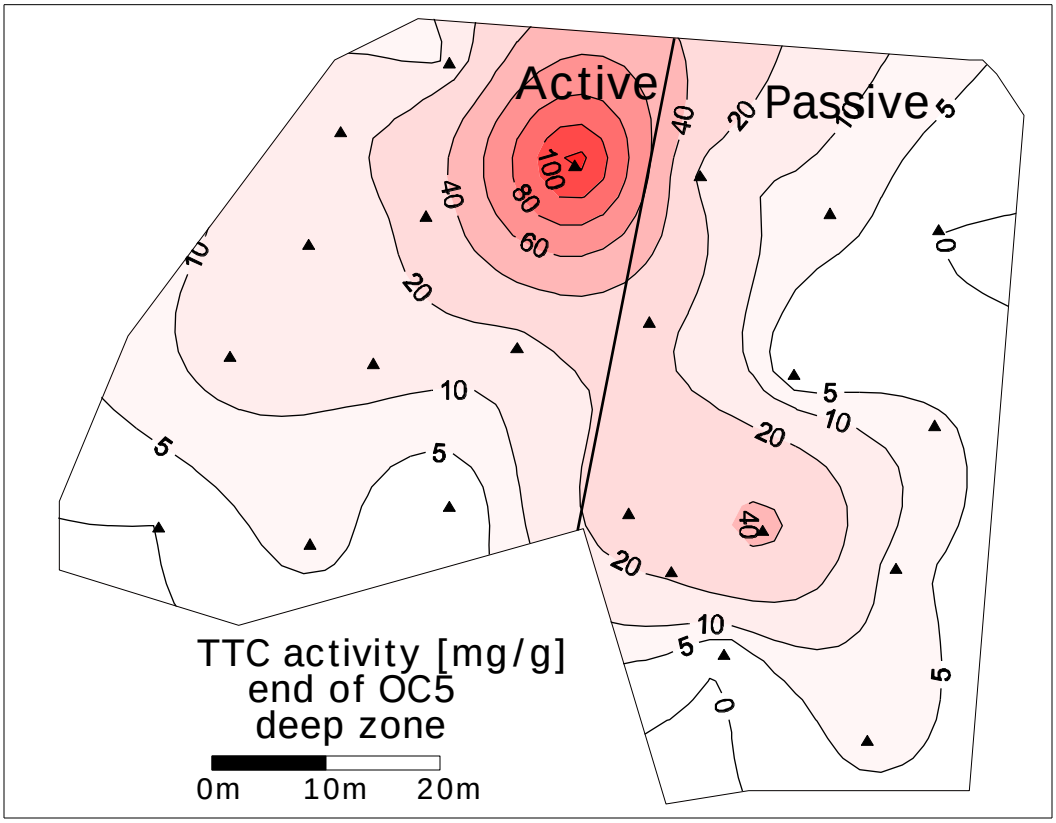
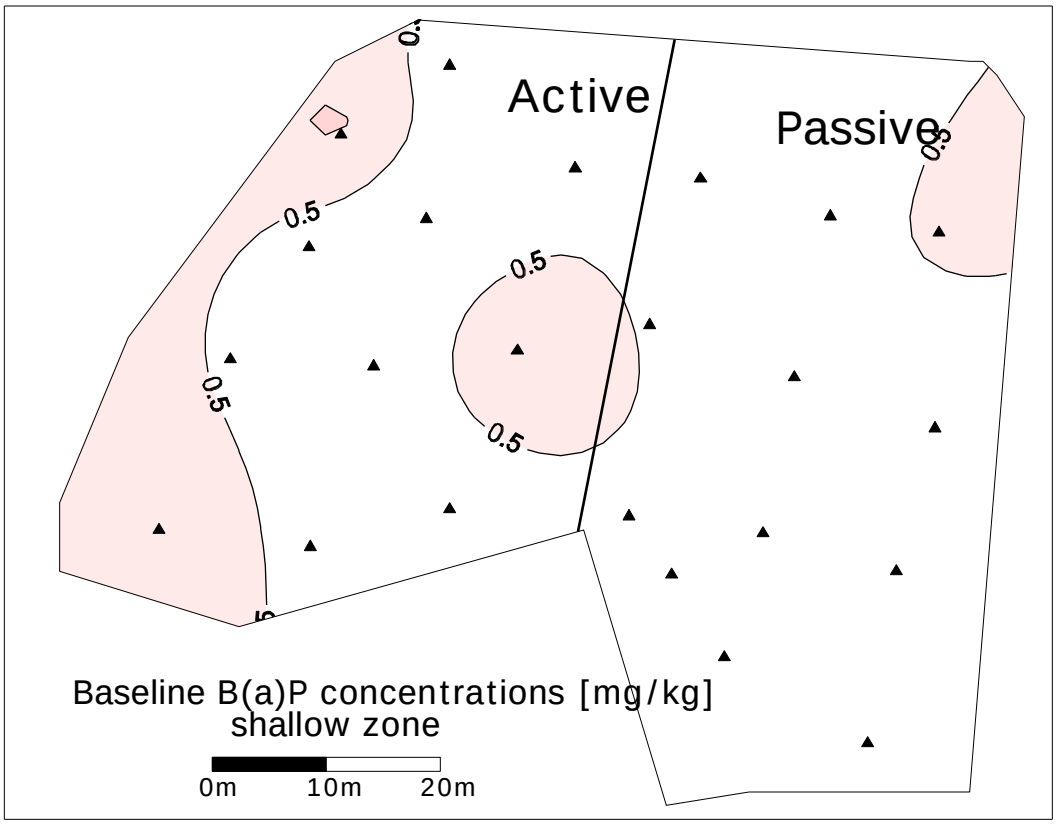


Figure 6/45 (A,B) Contour Plot of B (a)P Shallow: Operating Campaign 1 & 2



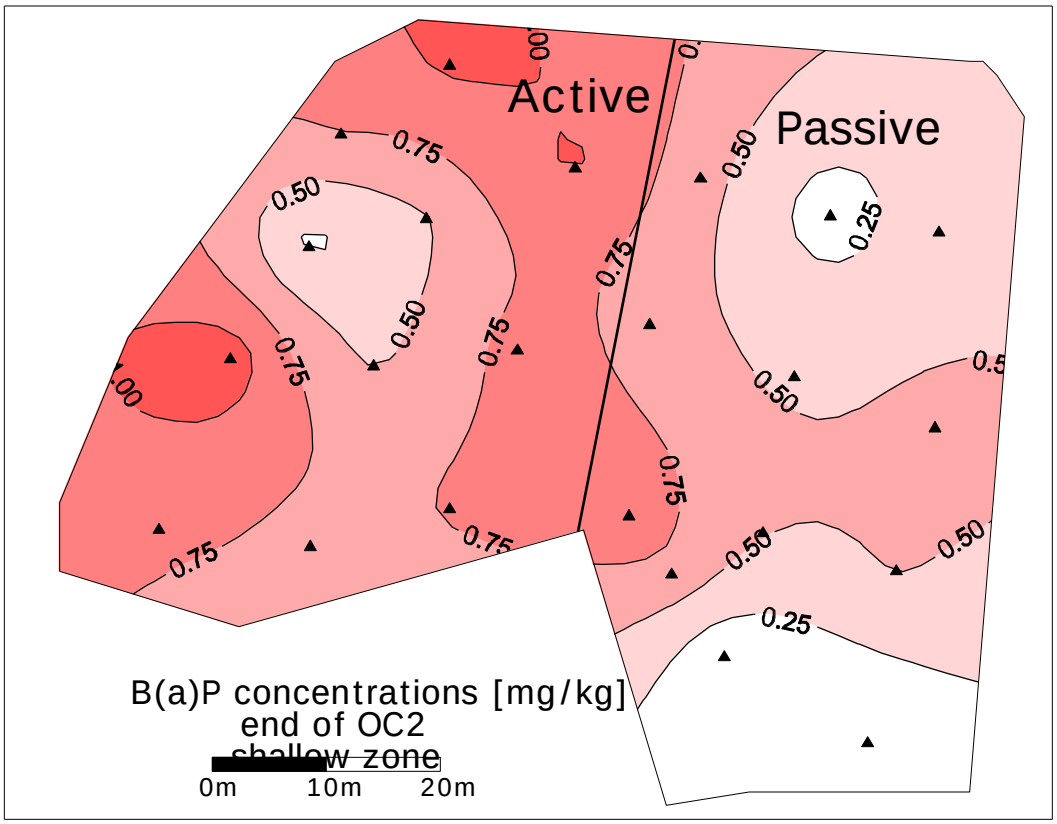
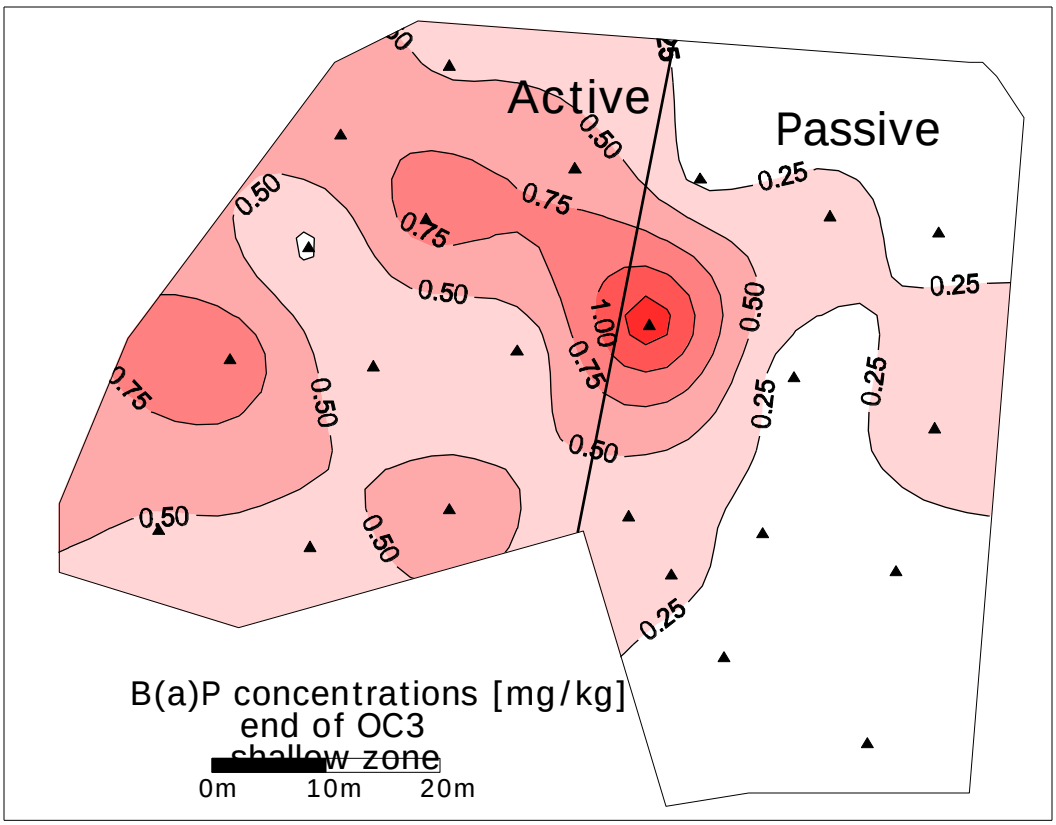


Figure 6.45 (C,D) Contour Plot of B(a)P Shallow: Operating Campaigns 3 & 4



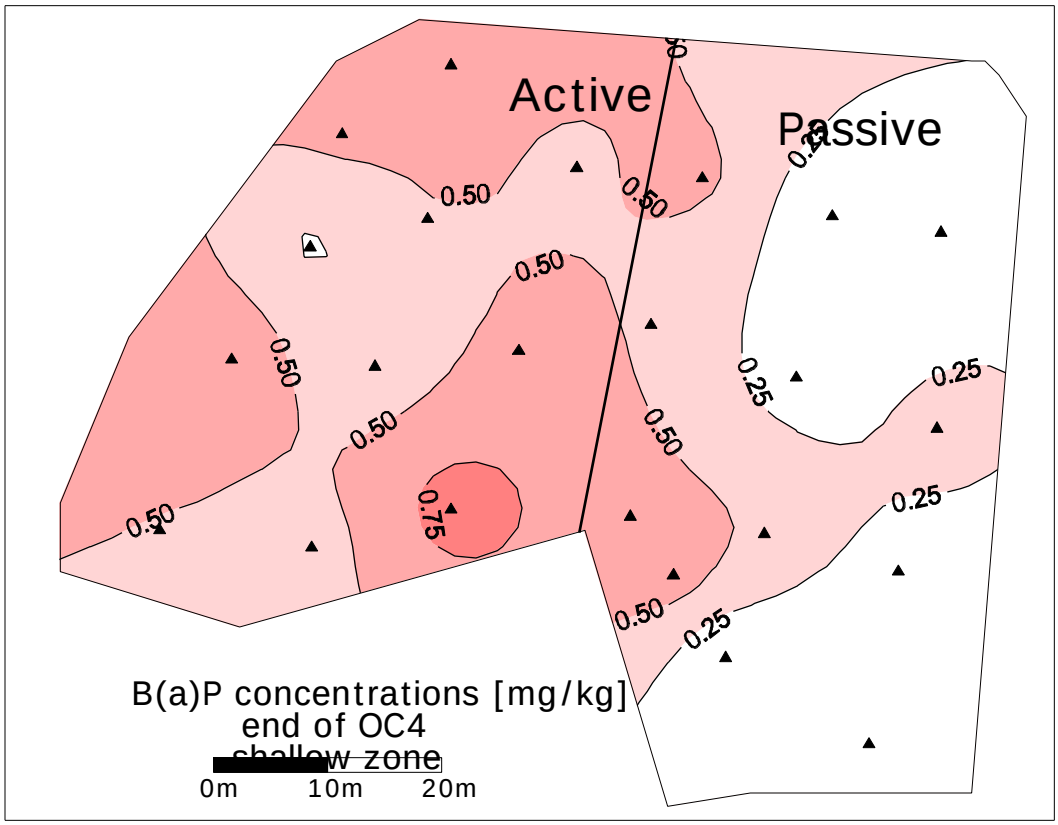


Figure 6.45 (E) Contour Plot of B(a)P Shallow: Operating Campaign 5

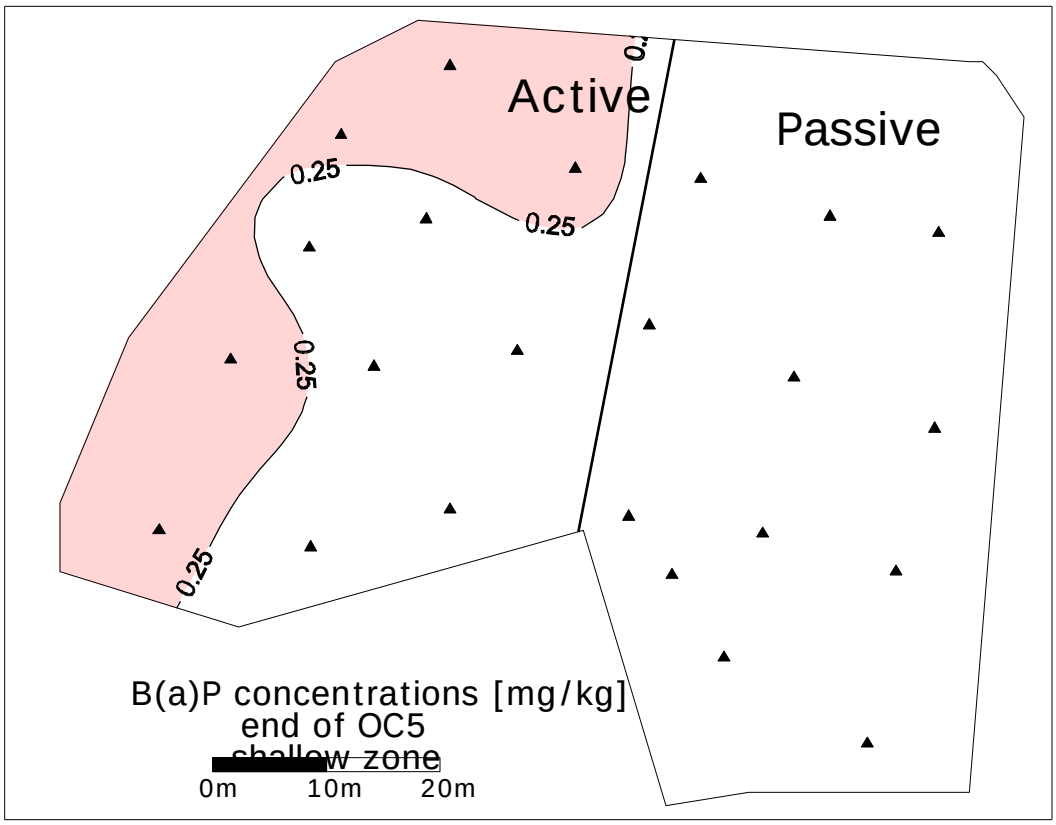


Figure 6.46 (A) Contour Plot of B(a)P Deep: Baseline

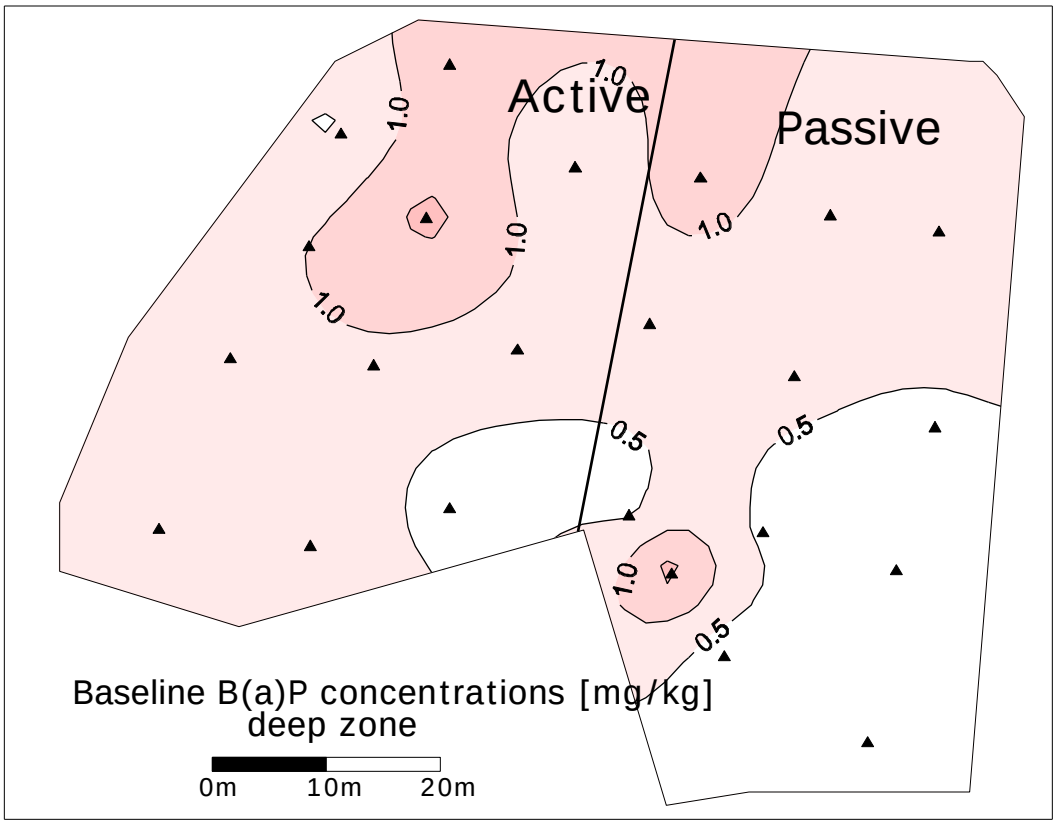
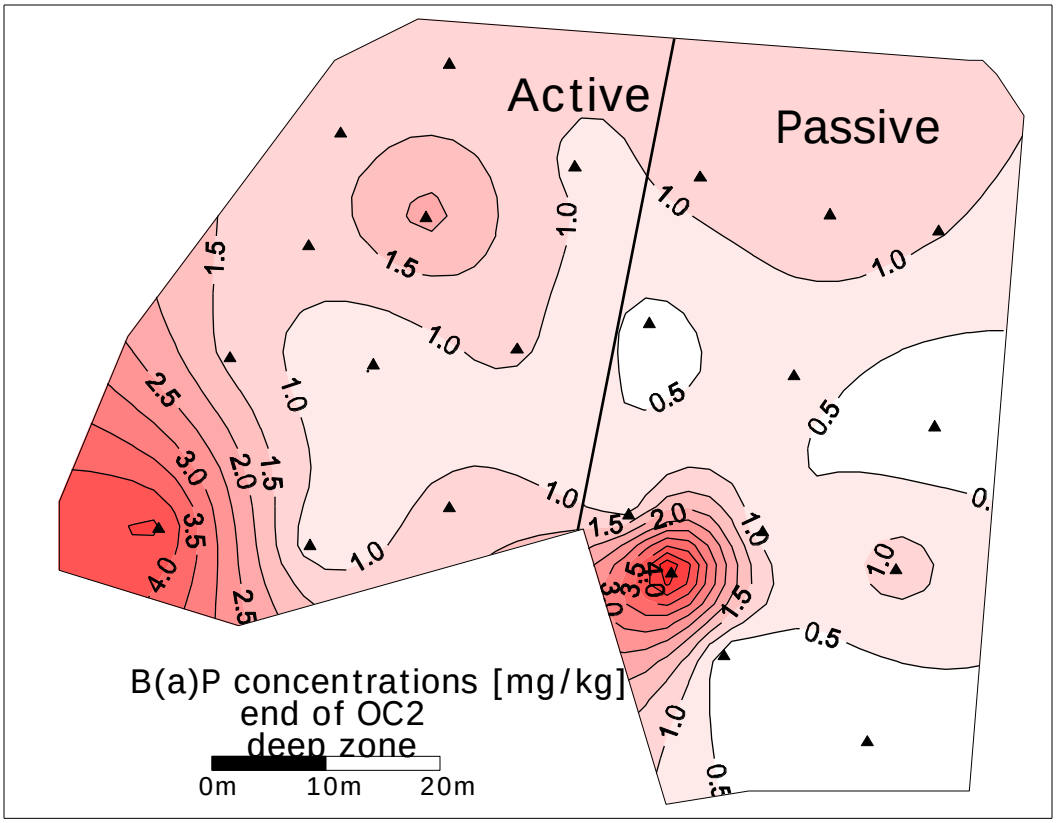


Figure 6.46 (B,C) Contour Plot of B(a)P Deep: Operating Campaigns 2 & 3



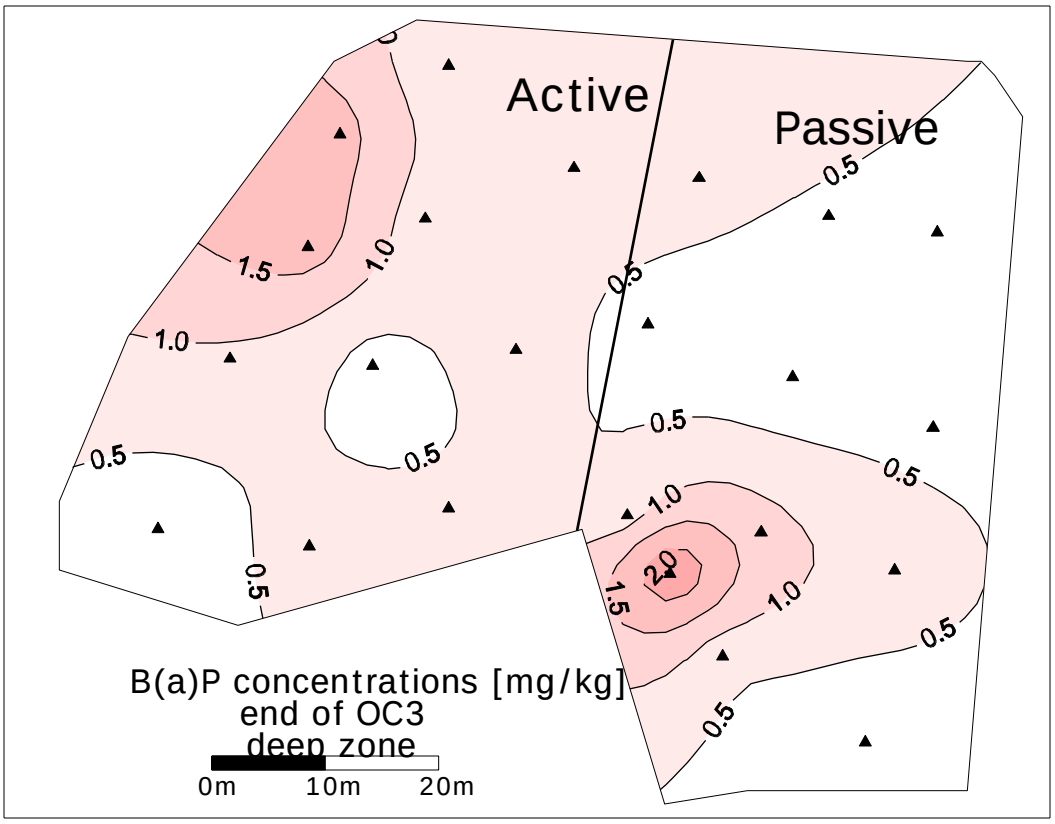
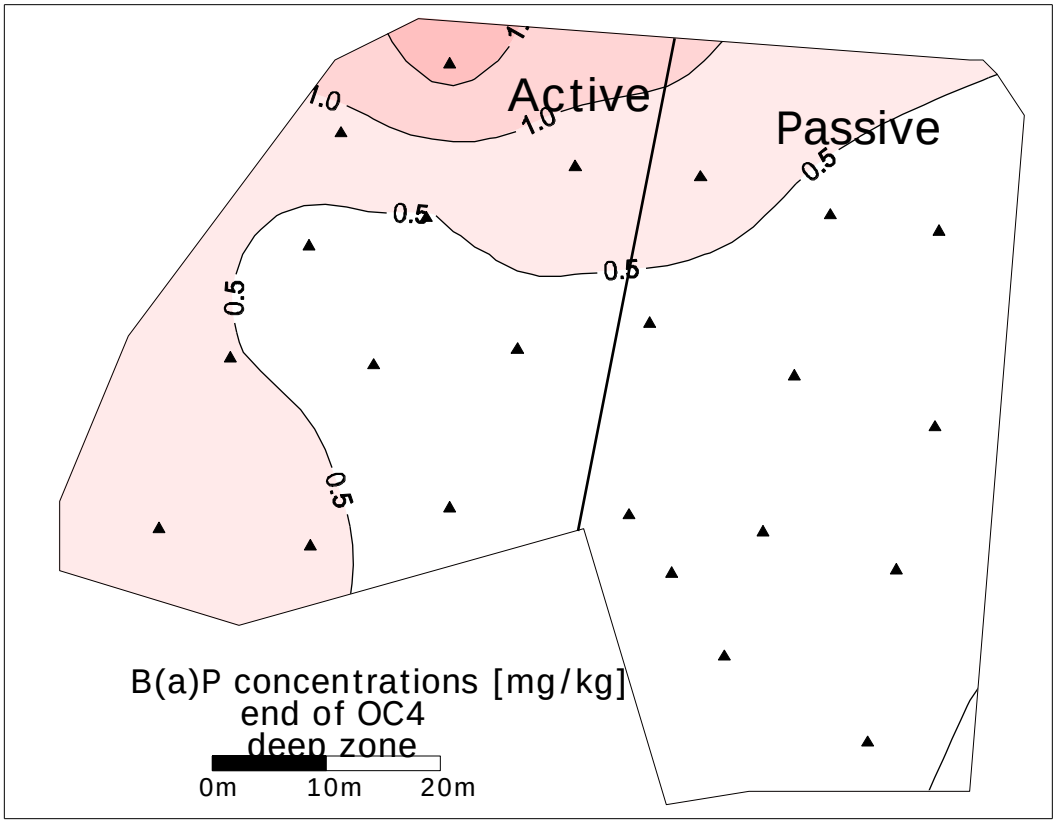


Figure 6.46 (D,E) Contour Plot of B(a)P Deep: Operating Campaigns 4 & 5



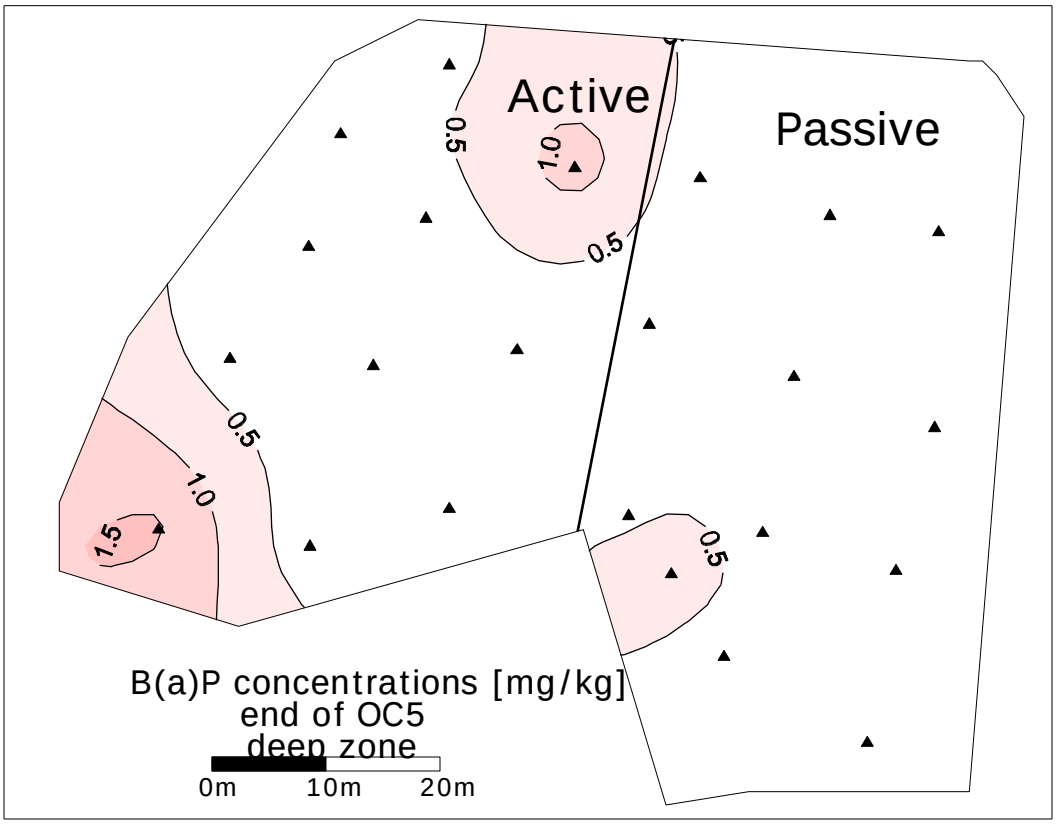
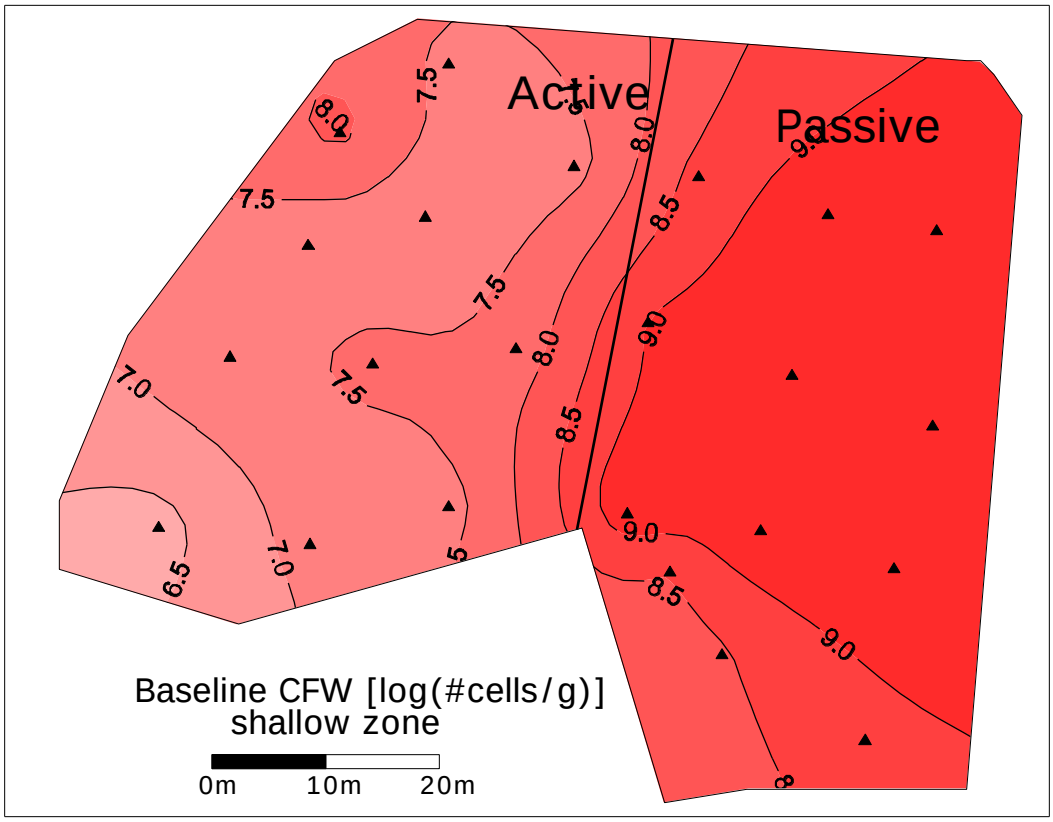


Figure 6.47 (A,B) Contour Plot of CFW Shallow: Baseline & Operating Campaign 2



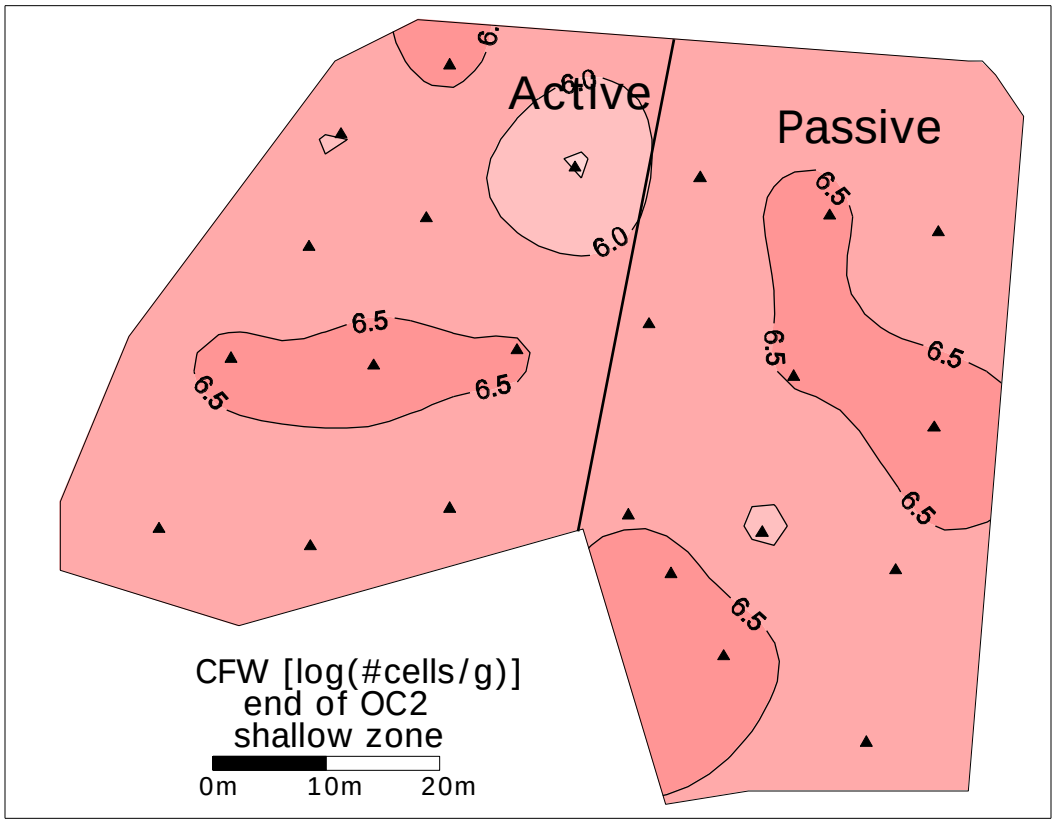
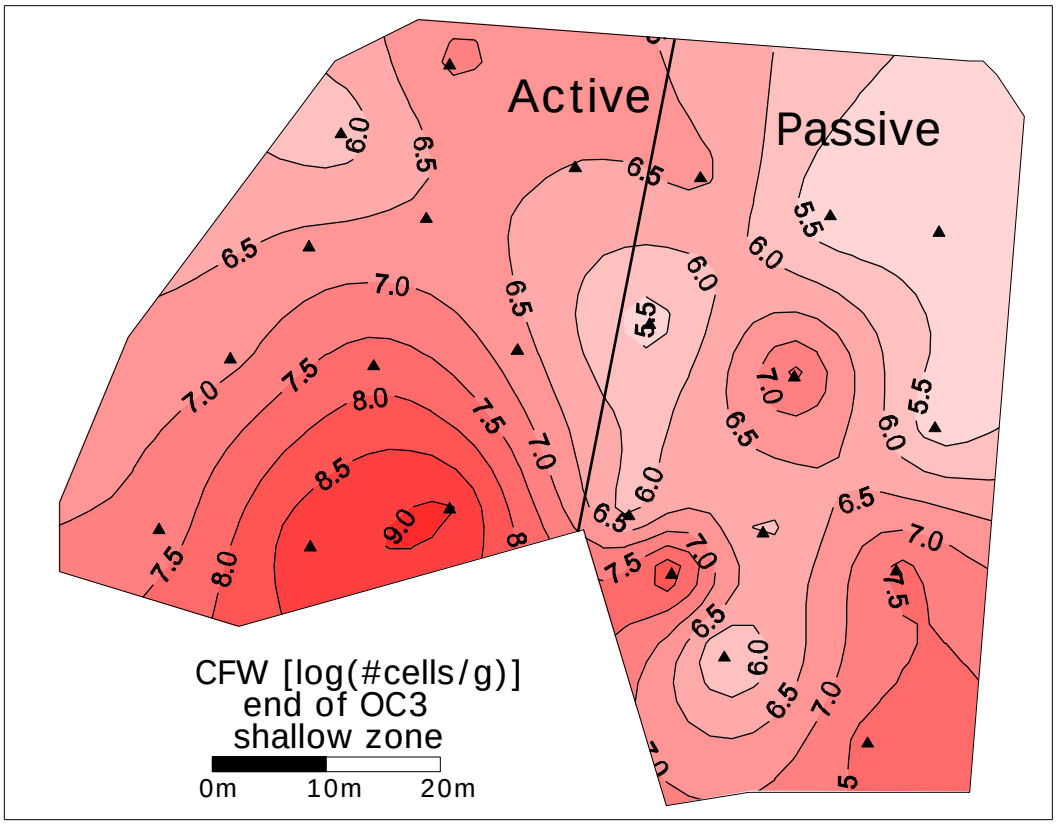


Figure 6.47 (C,D) Contour Plot of CFW Shallow: Operating Campaigns 3 & 4



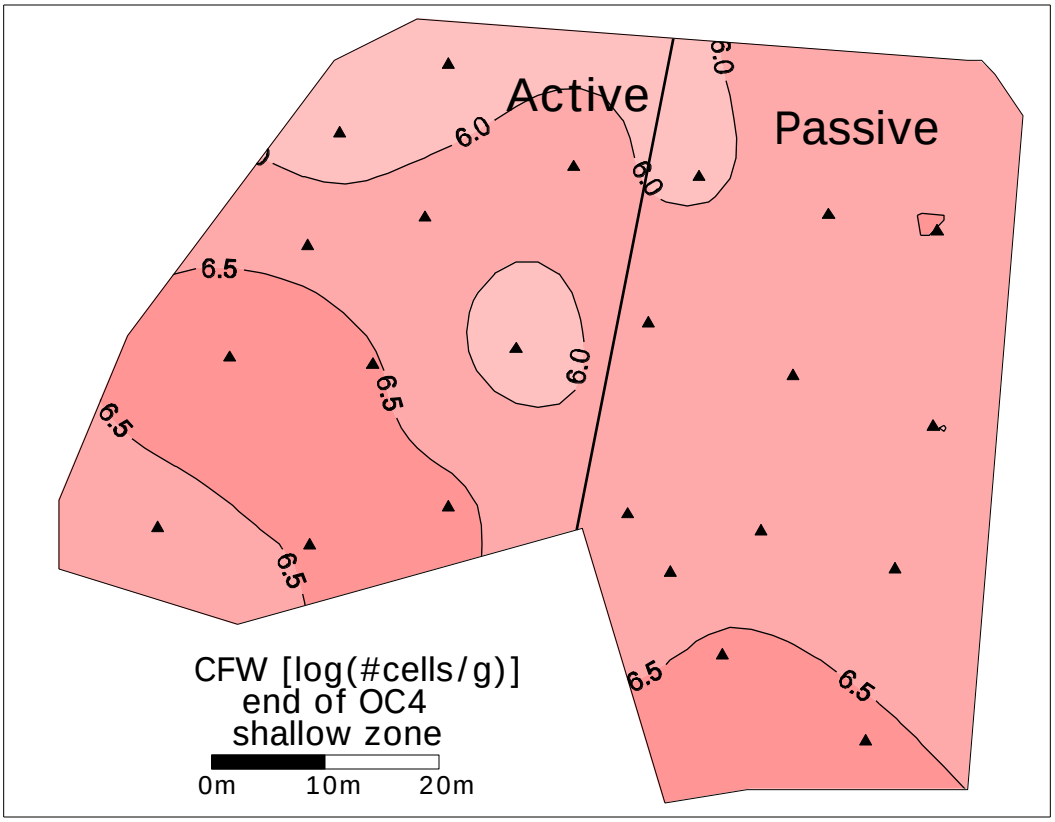


Figure 6.47 (E) Contour Plot of CFW Shallow: Operating Campaign 5

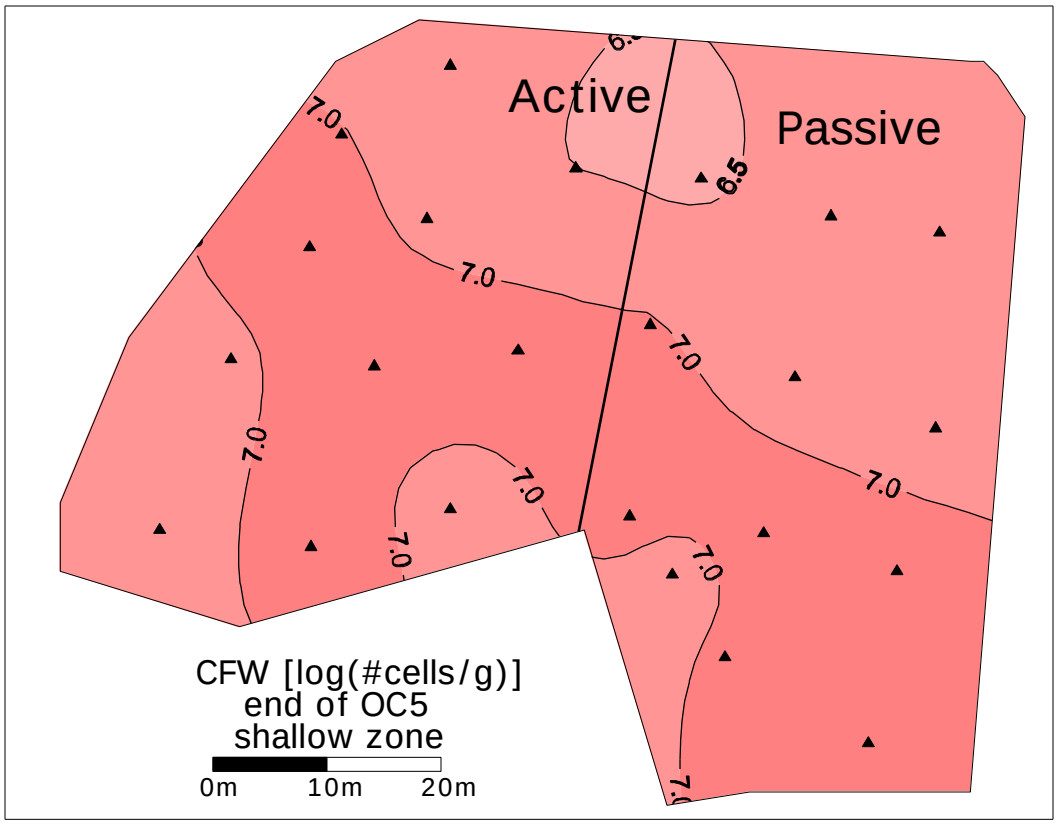


Figure 6.48 (A) Contour Plot of CFW Deep: Baseline

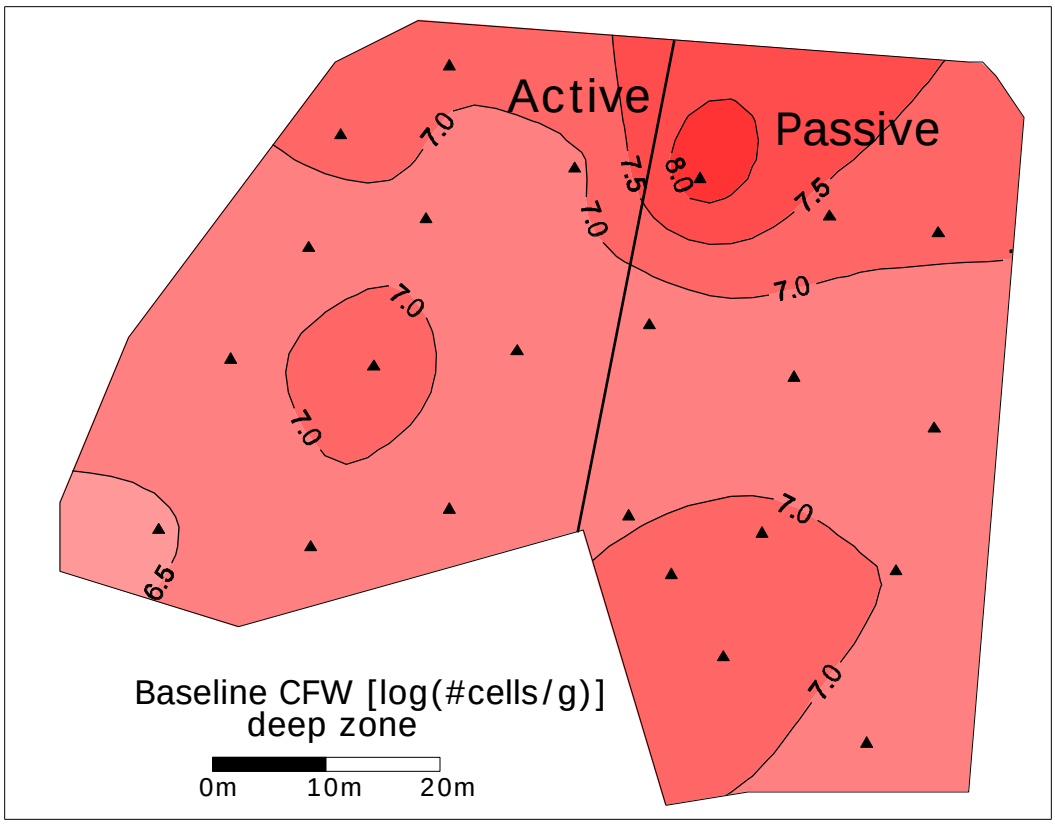
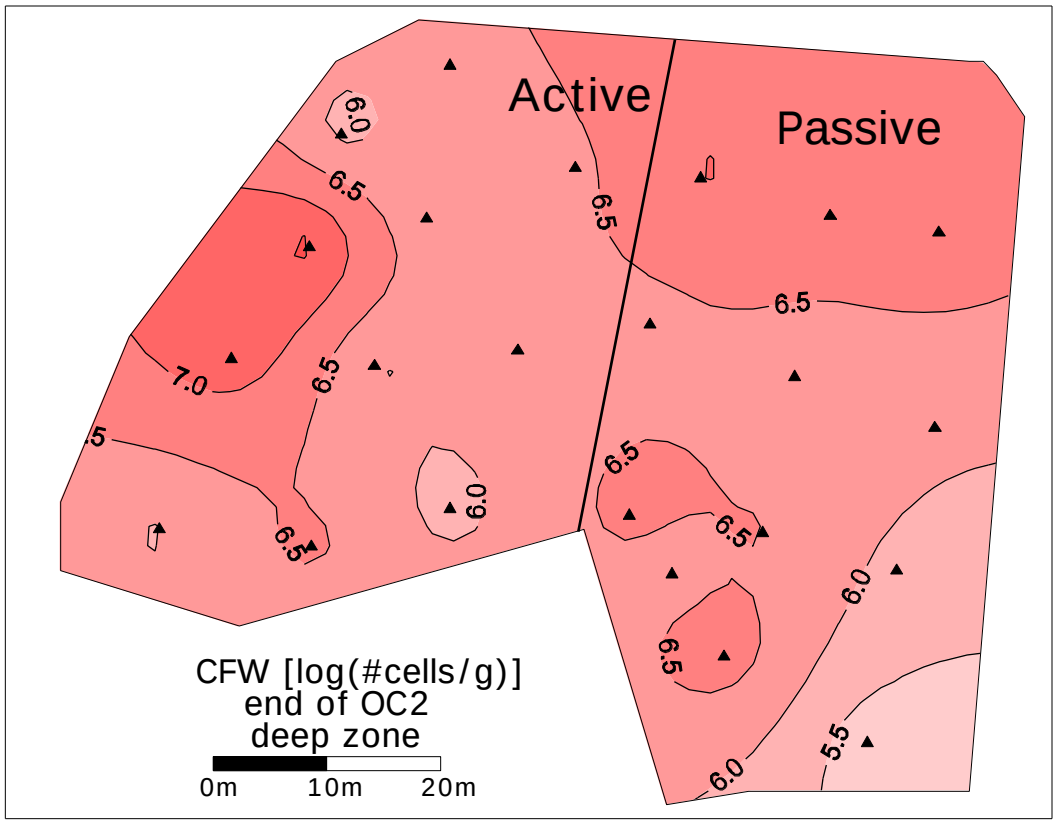


Figure 6.48 (B,C) Contour Plot of CFW Deep: Operating Campaigns 2 & 3



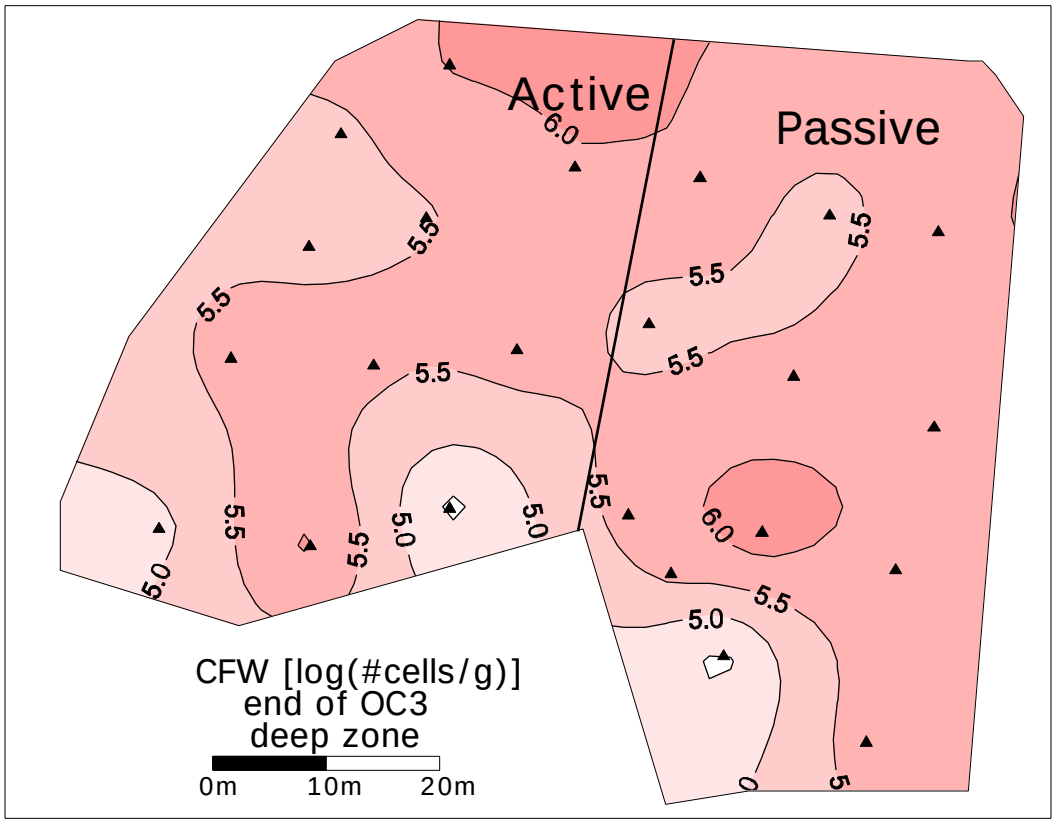
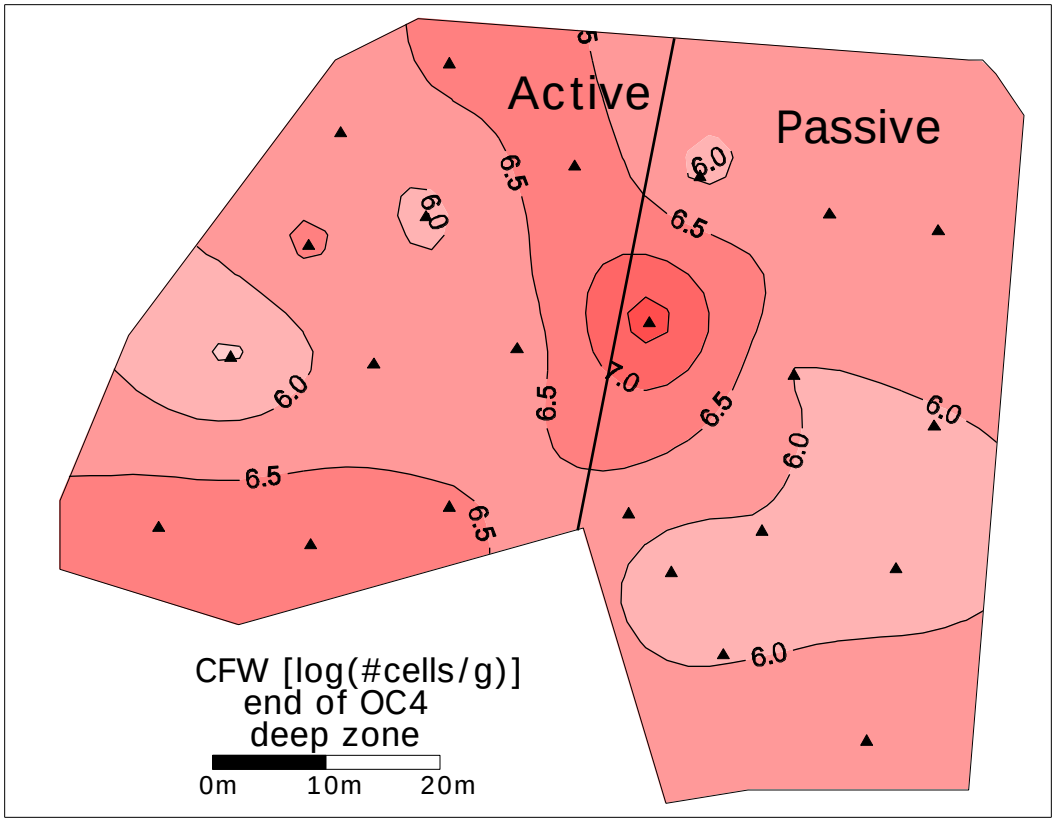
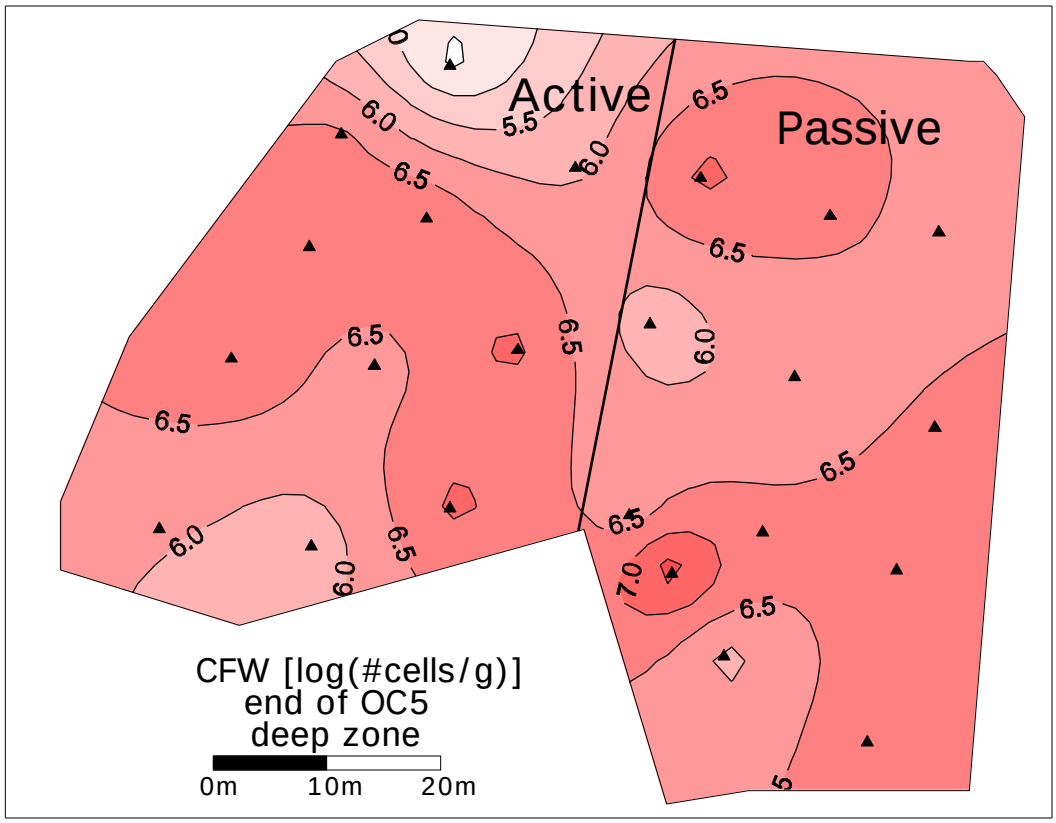
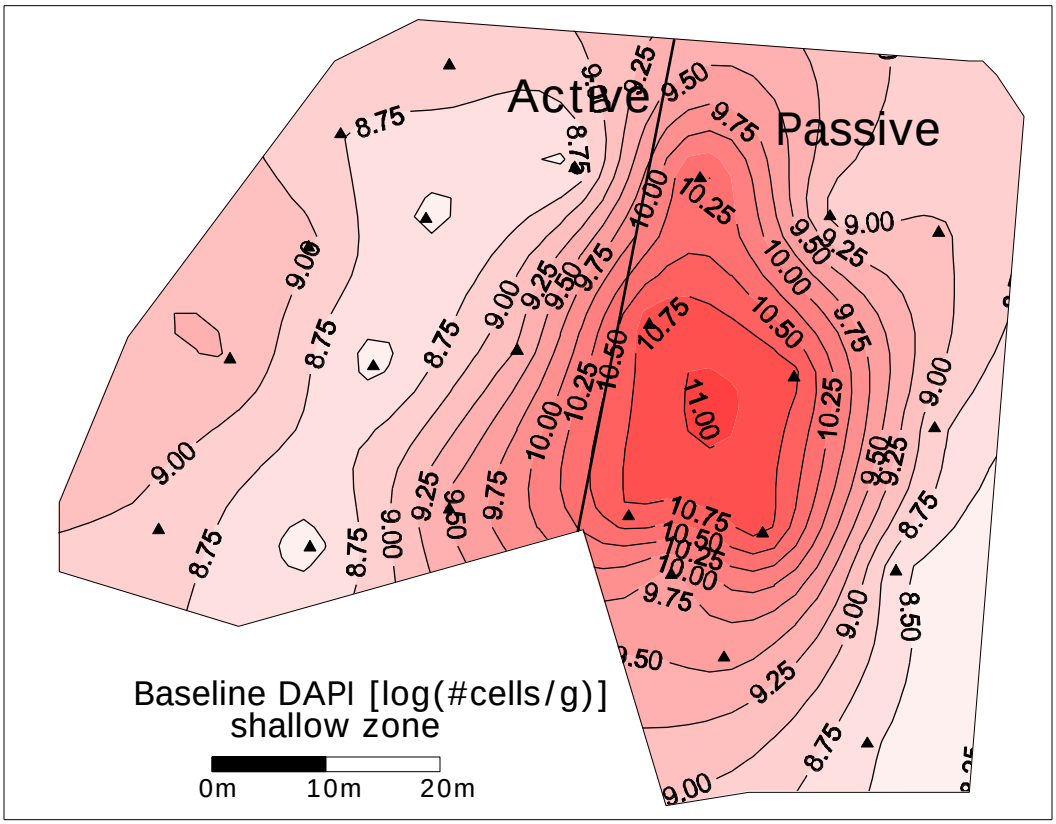


Figure 6.48 (D,E) Contour Plot of CFW Deep: Operating Campaigns 4 & 5





6.49 (A,B) Contour Plot of DAPI Shallow: Baseline & Operating Campaign 2



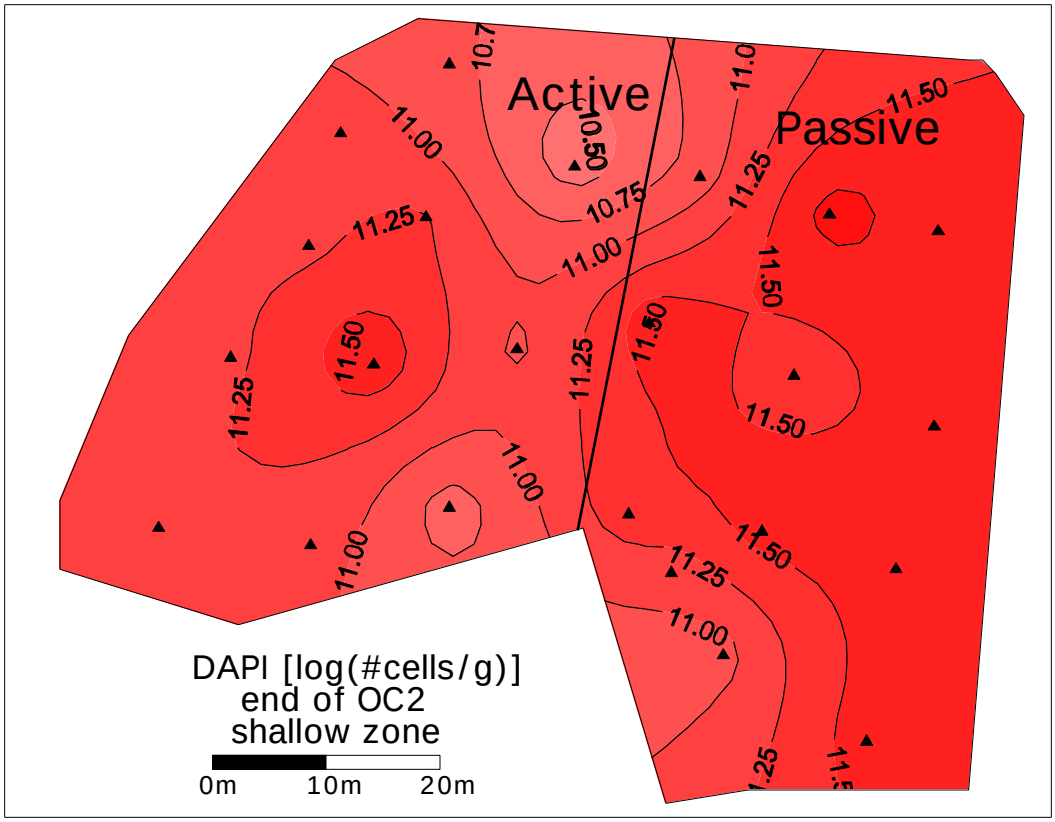
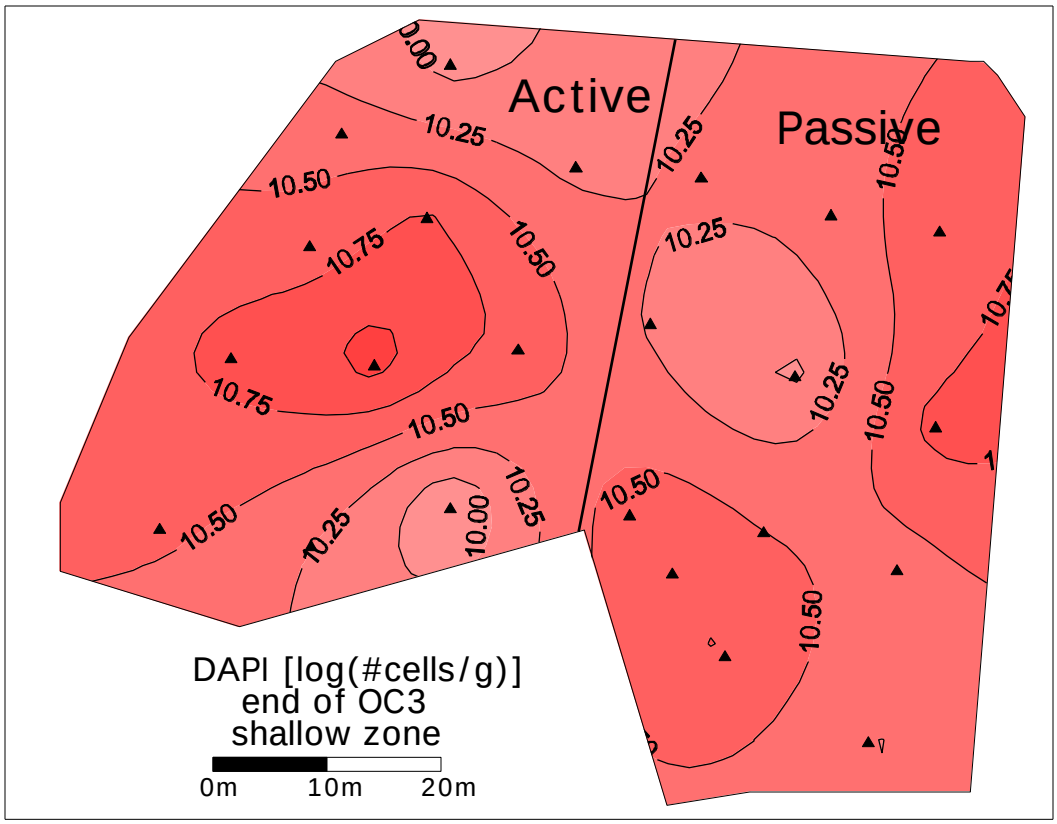


Figure 6.49 (C,D) Contour Plot of DAPI Shallow: Operating Campaigns 3 & 4



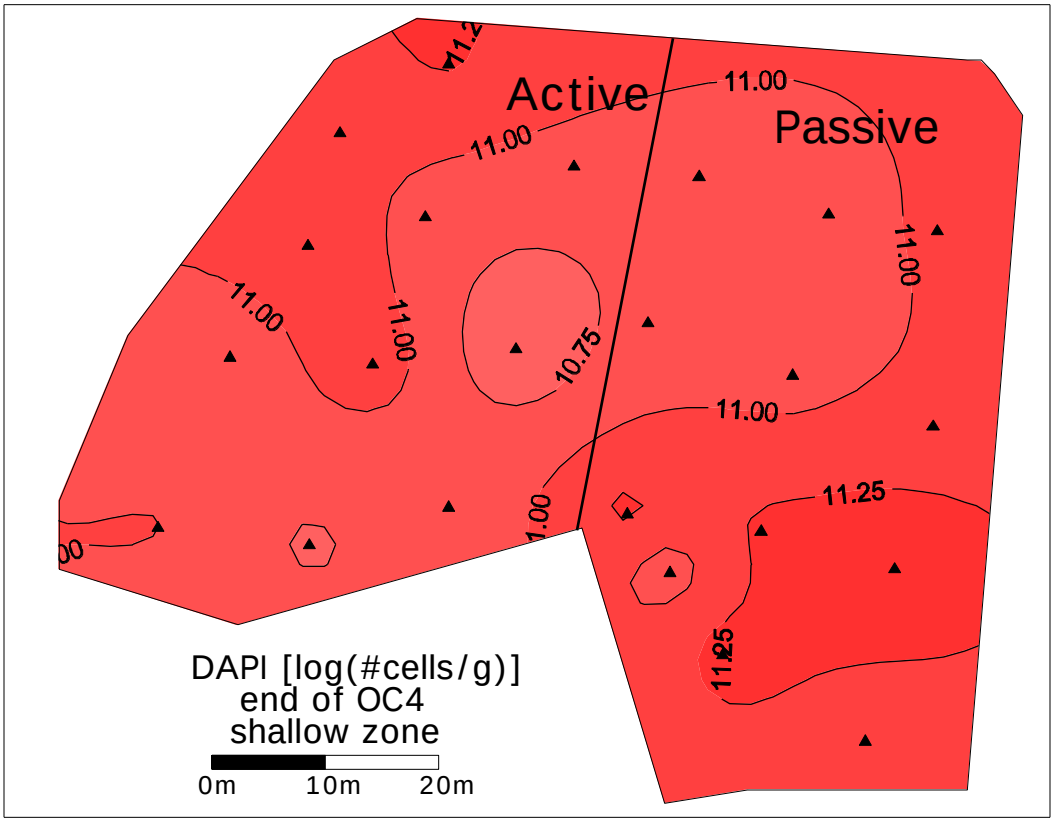


Figure 6.49 (E) Contour Plot of DAPI Shallow: Operating Campaign 5

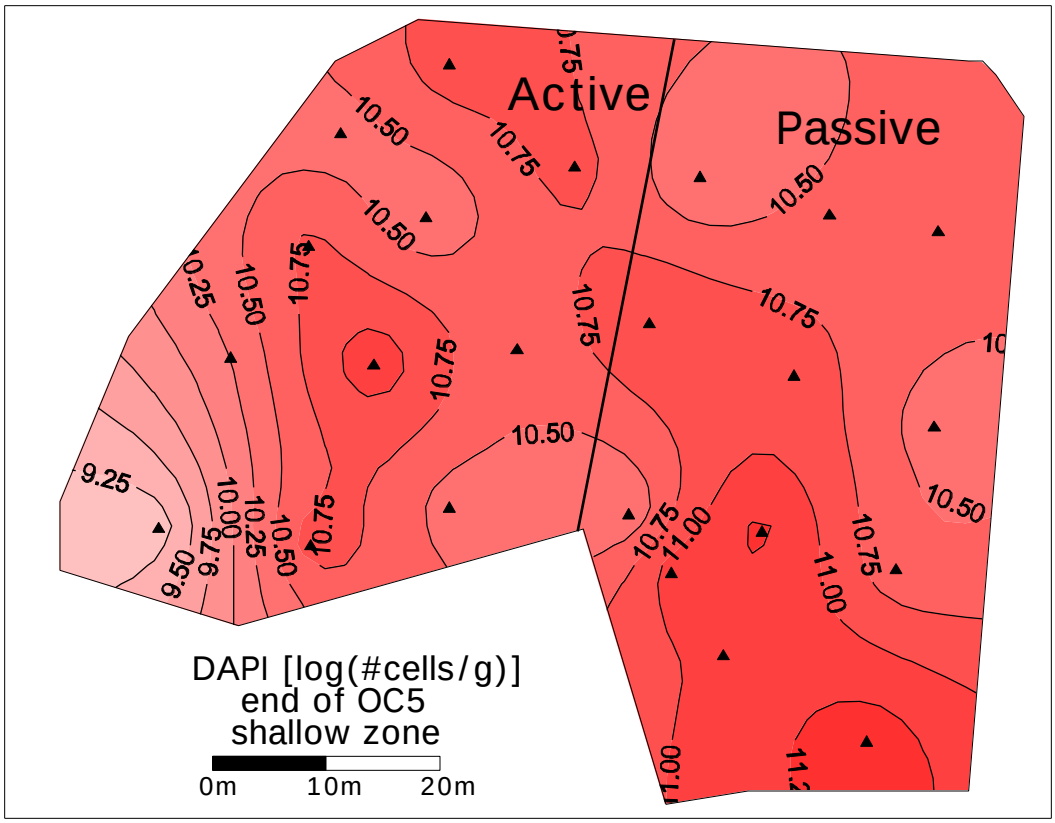


Figure 6.50 (A) Contour Plot of DAPI Deep: Baseline

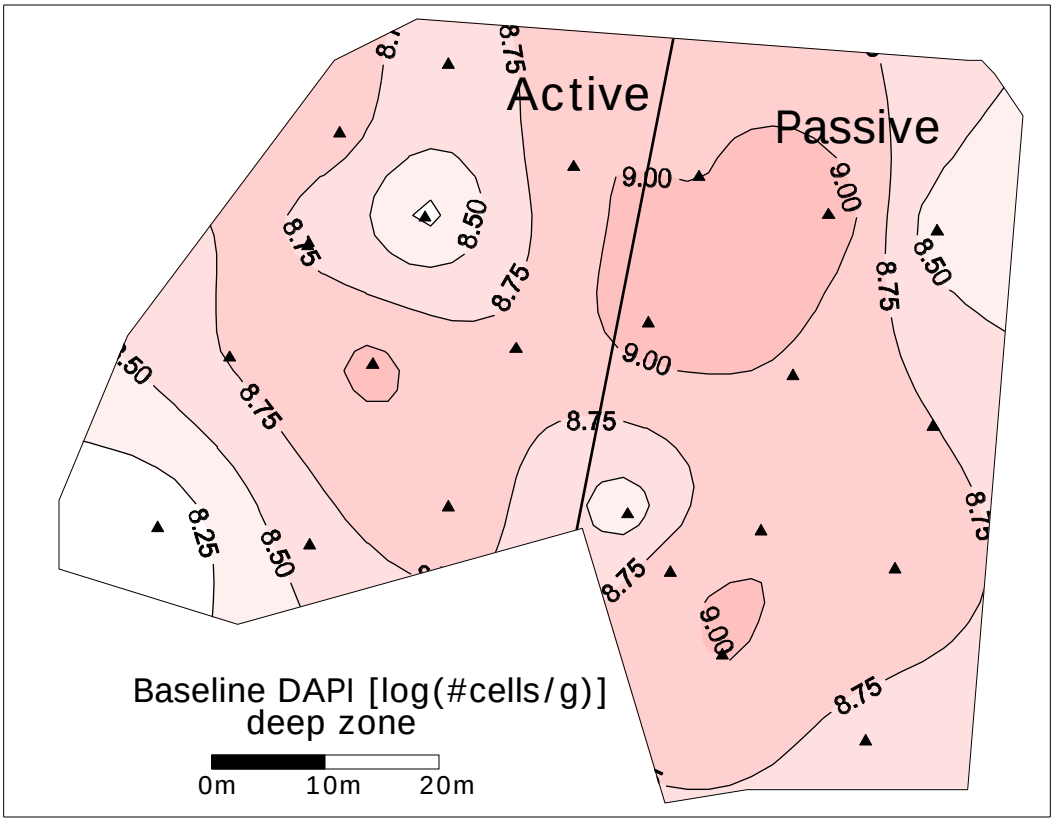
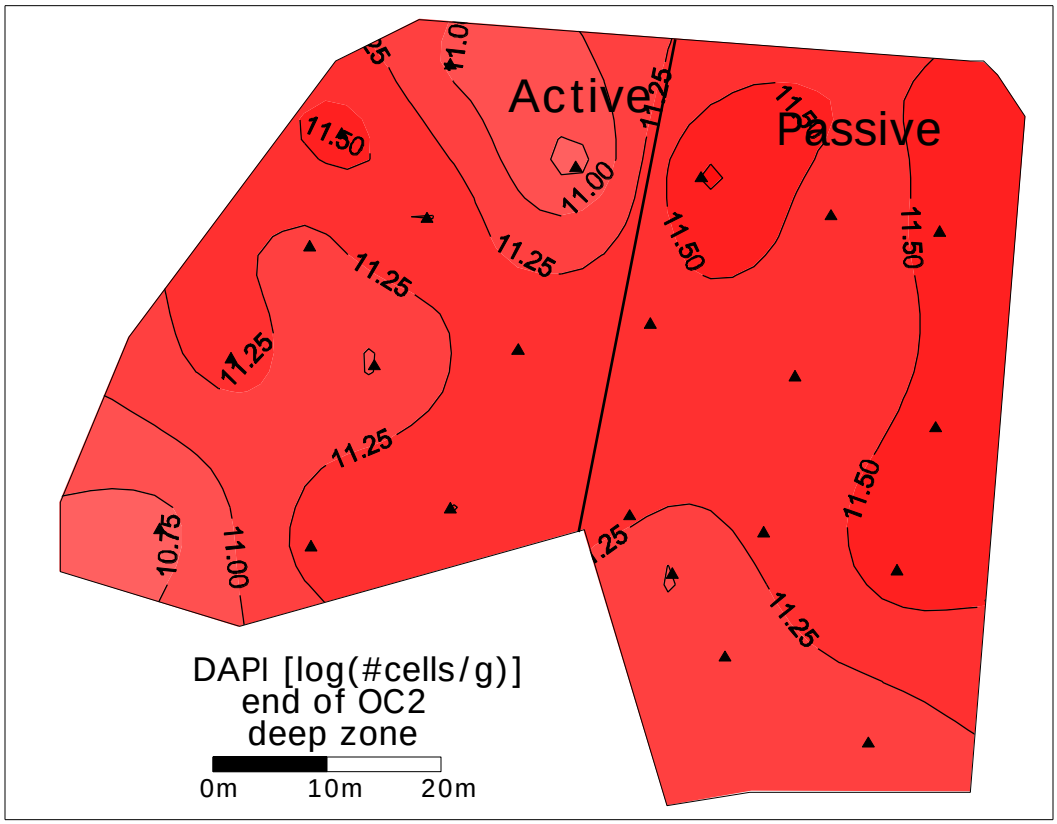


Figure 6.50 (B,C) Contour Plot of DAPI Deep: Operating Campaign 2 & 3



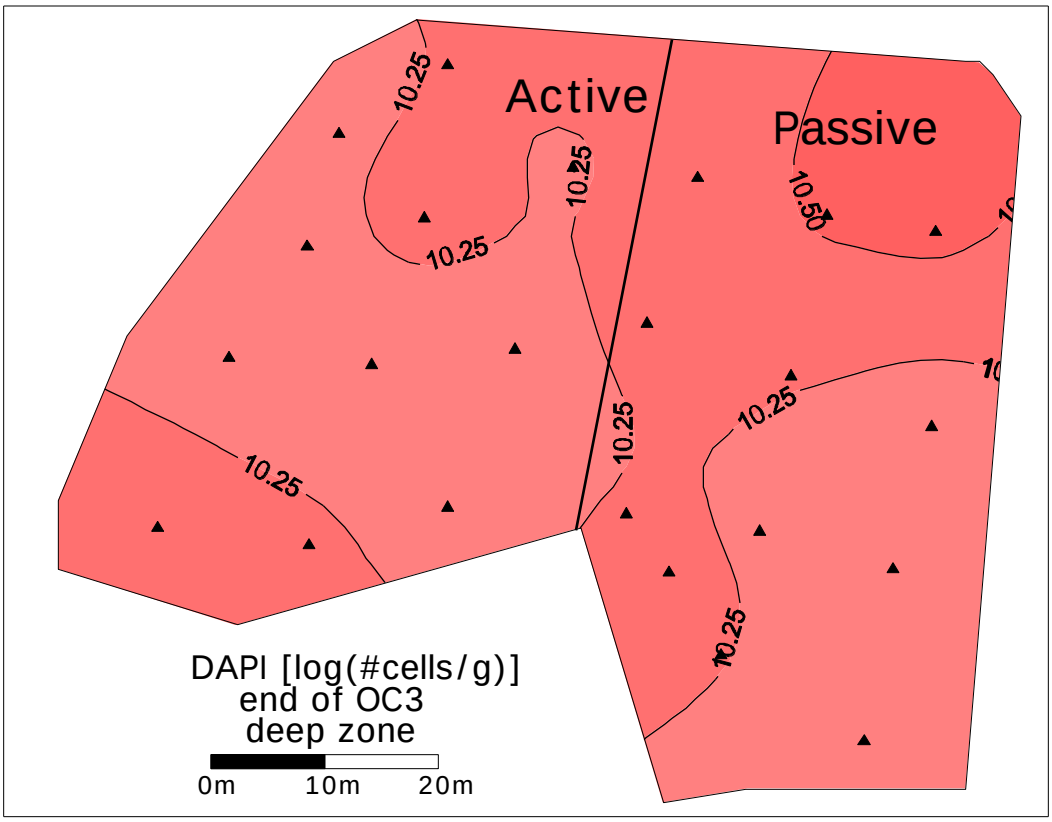
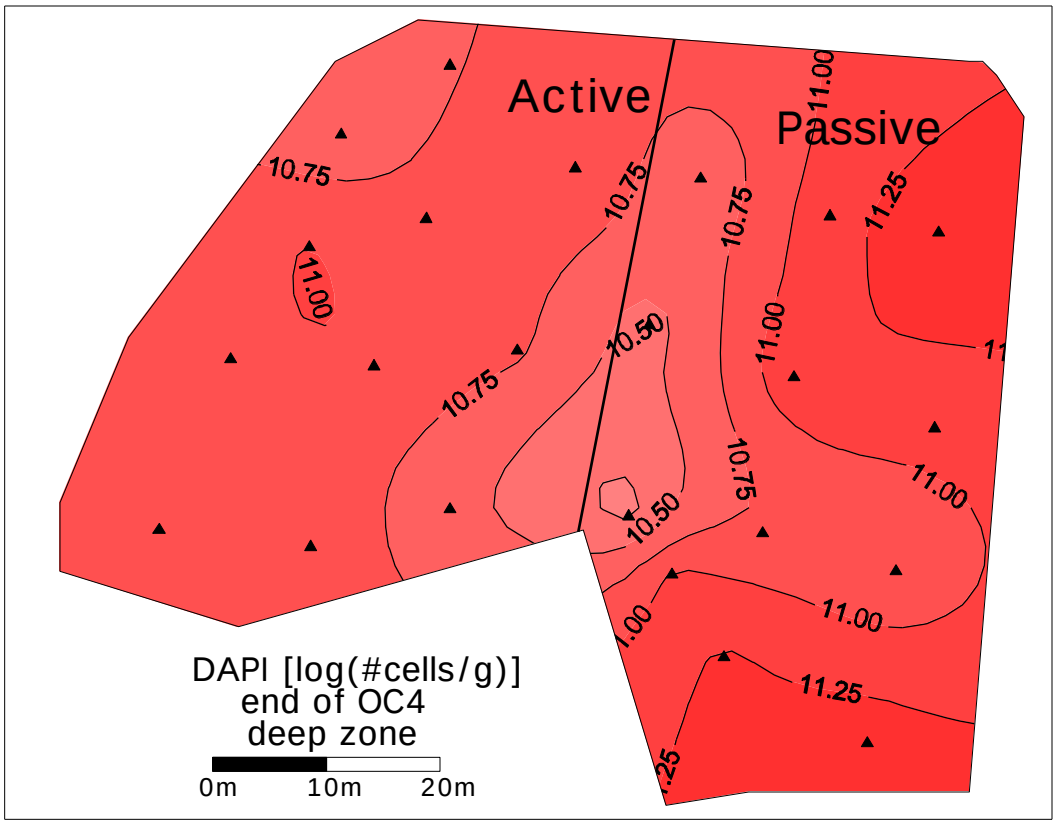


Figure 6.50 (D,E) Contour Plot of DAPI Deep: Operating Campaigns 4 & 5



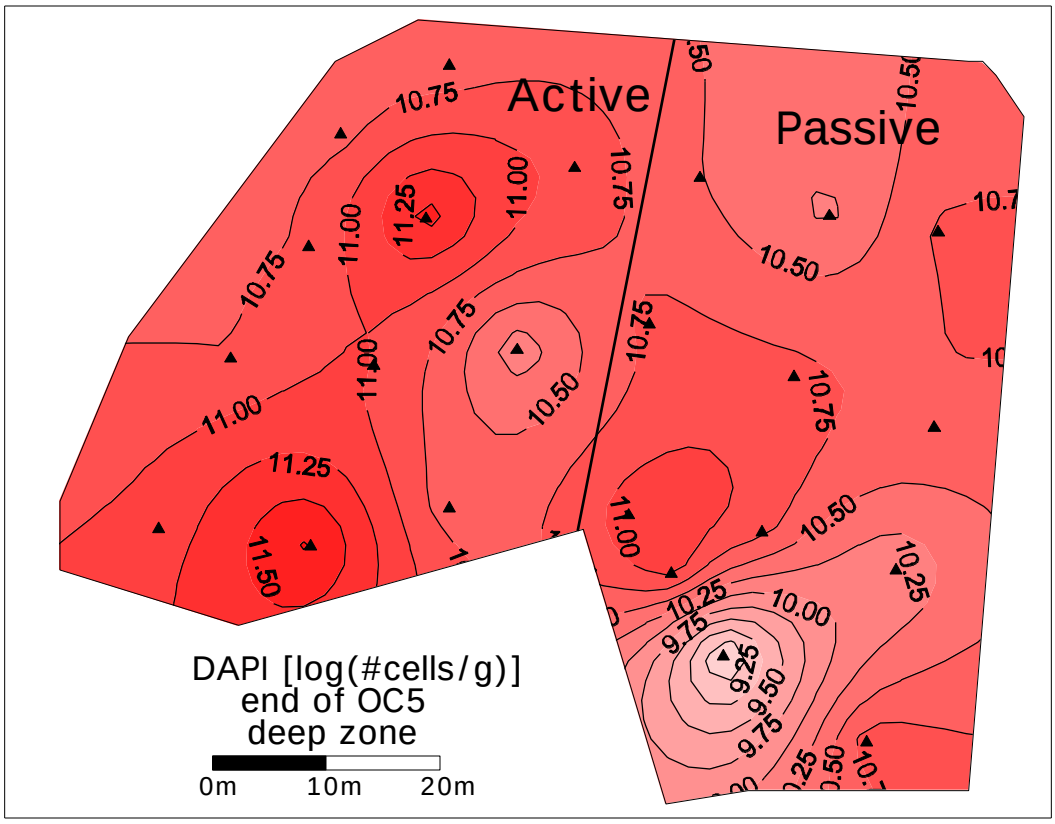
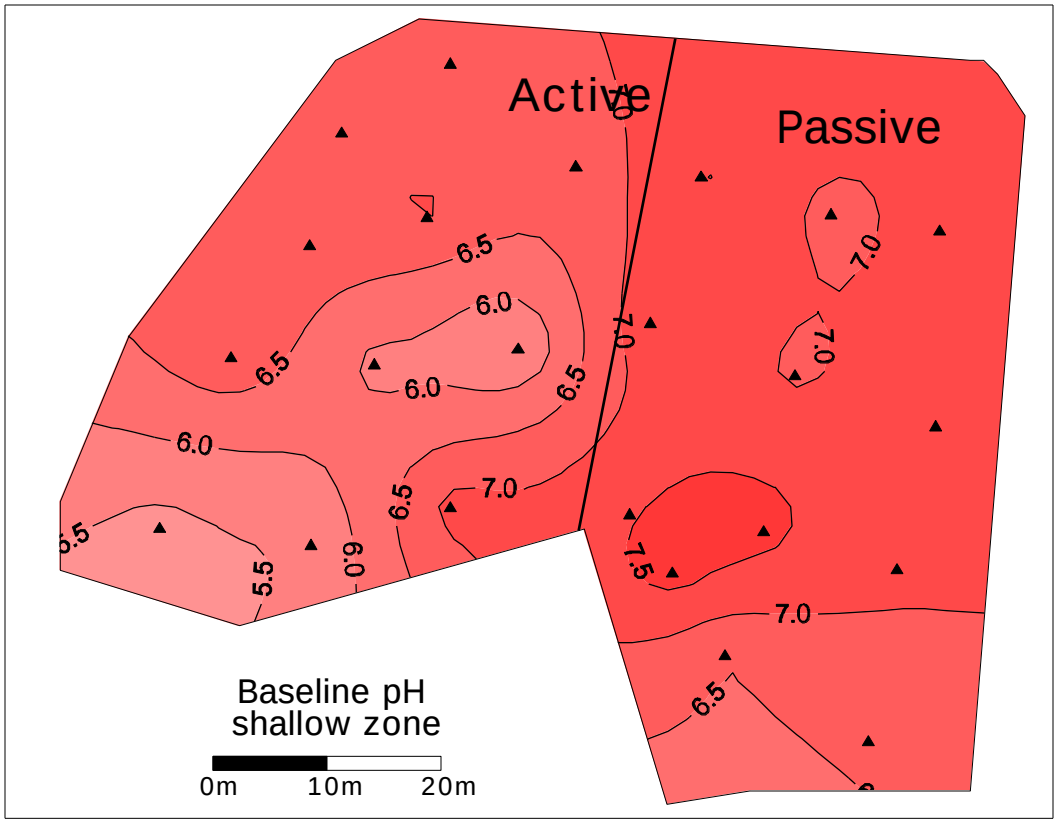


Figure 6.51 (A,B) Contour Plot of pH Shallow: Baseline & Operating Campaign 2



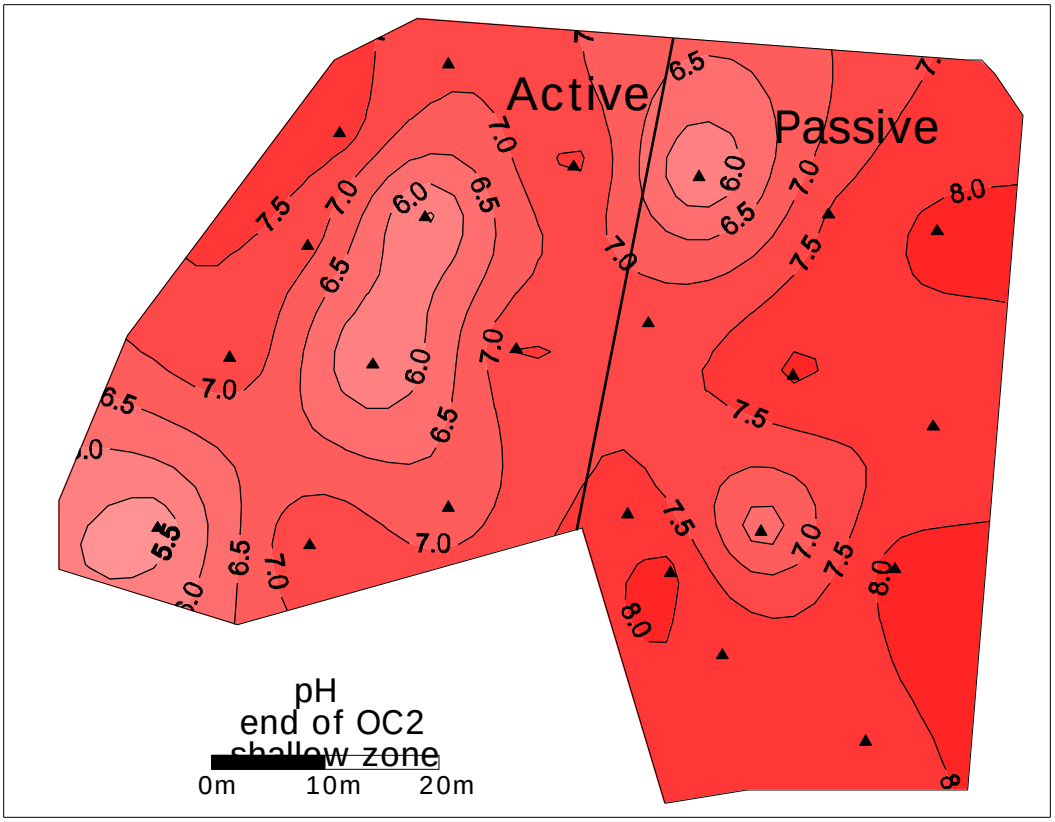
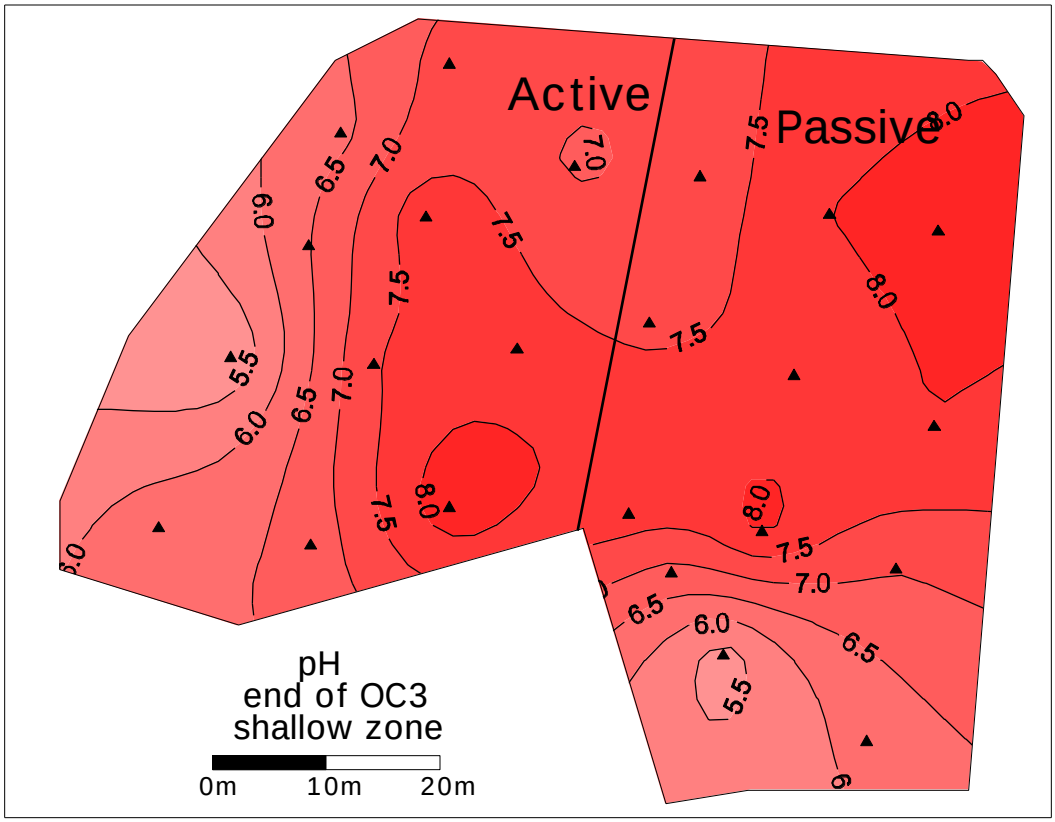


Figure 6.51 (C,D) Contour Plot of pH Shallow: Operating Campaigns 3 & 4



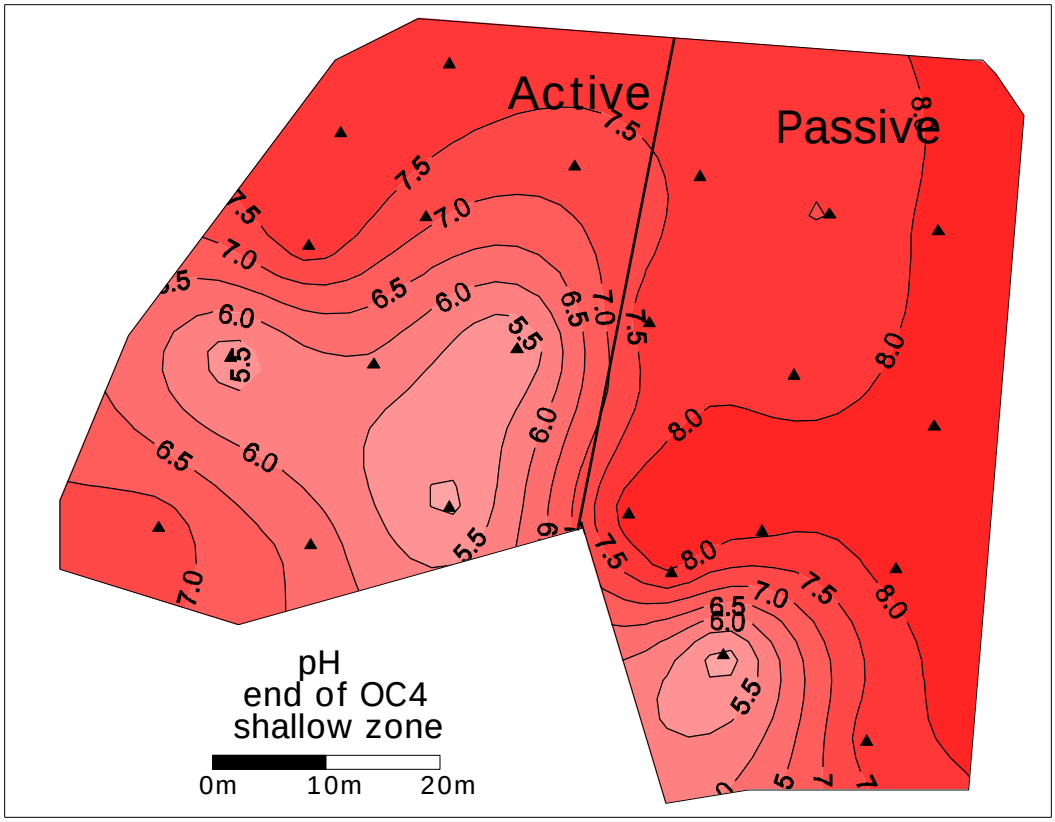


Figure 6.51 (E) Contour Plot of pH Shallow: Operating Campaign 5

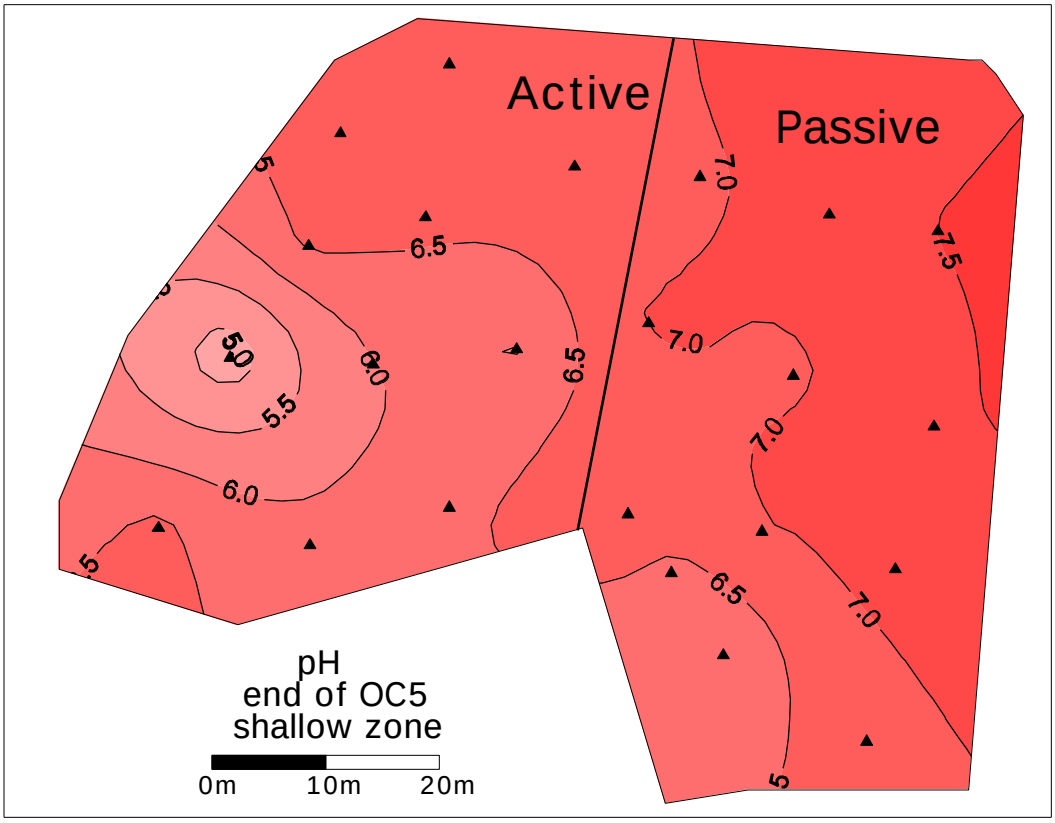


Figure 6.52 (A) Contour Plot fo pH Deep: Baseline

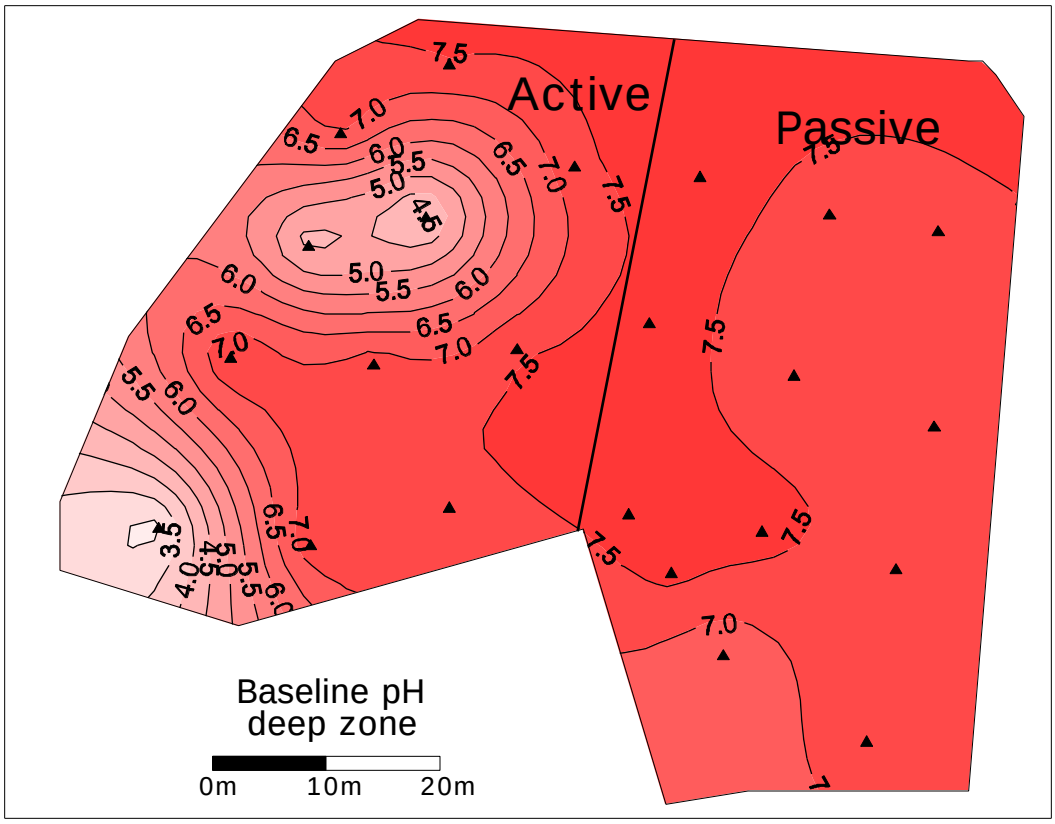
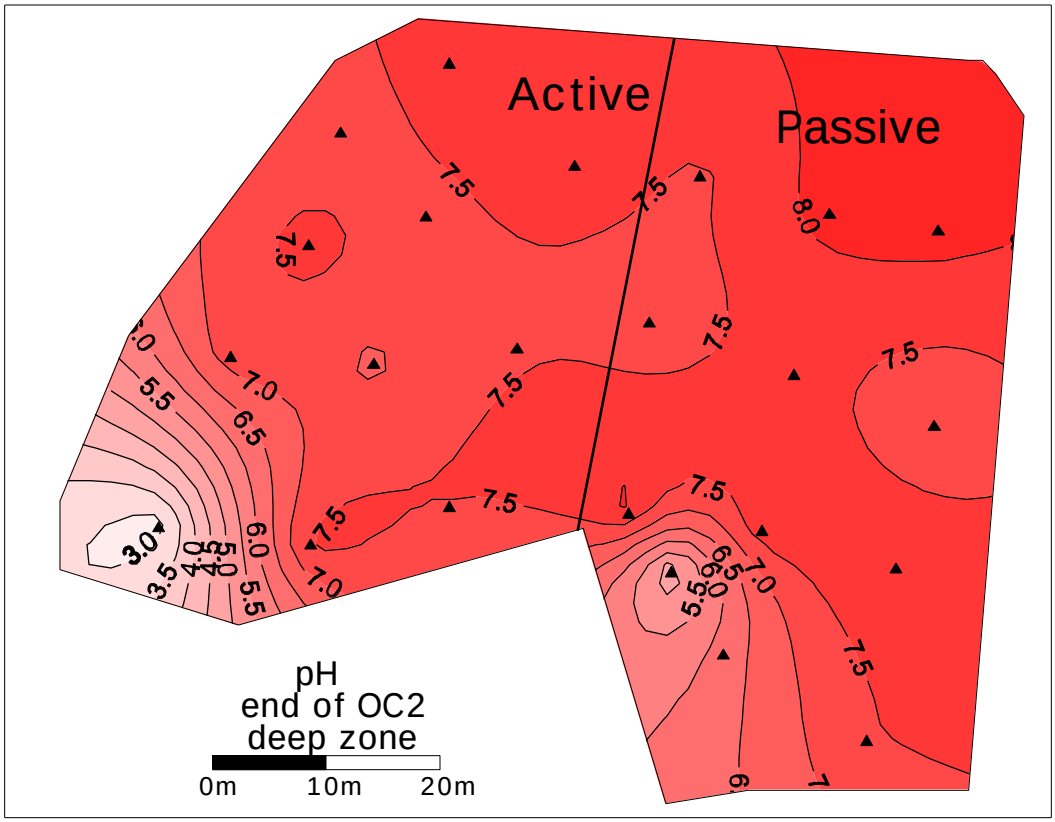


Figure 6.52 (B,C) Contour Plot of pH Deep: Operating Campaigns 2 & 3



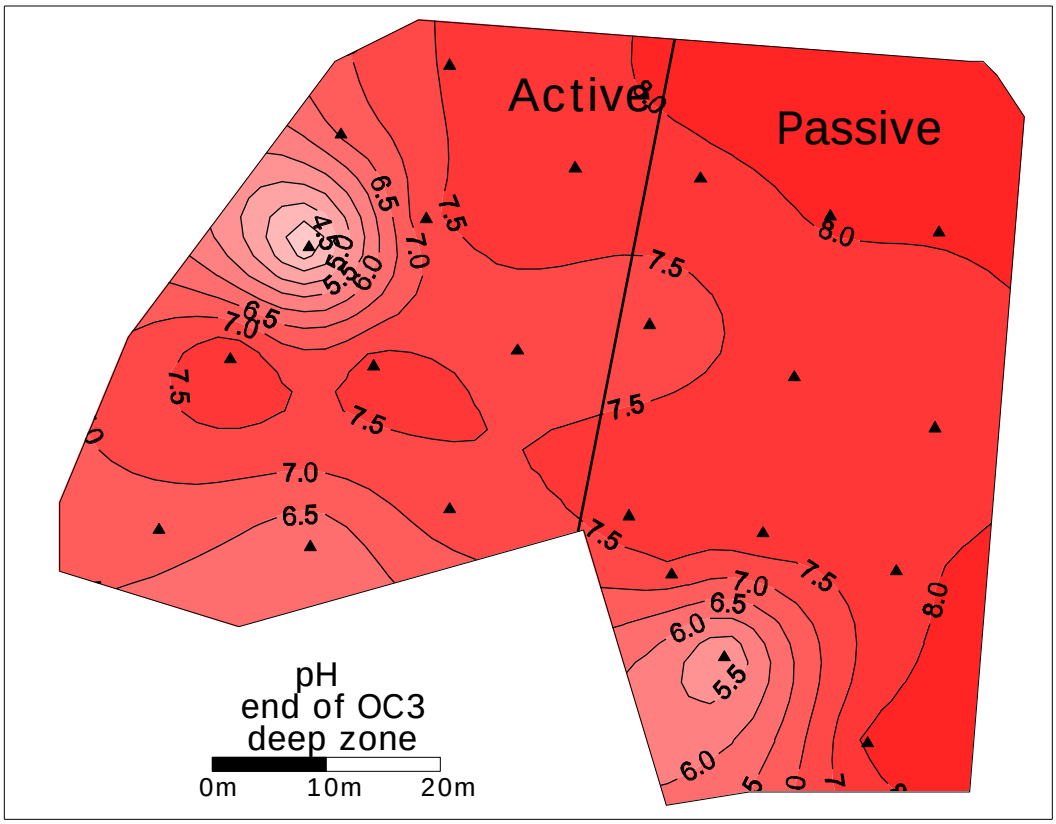
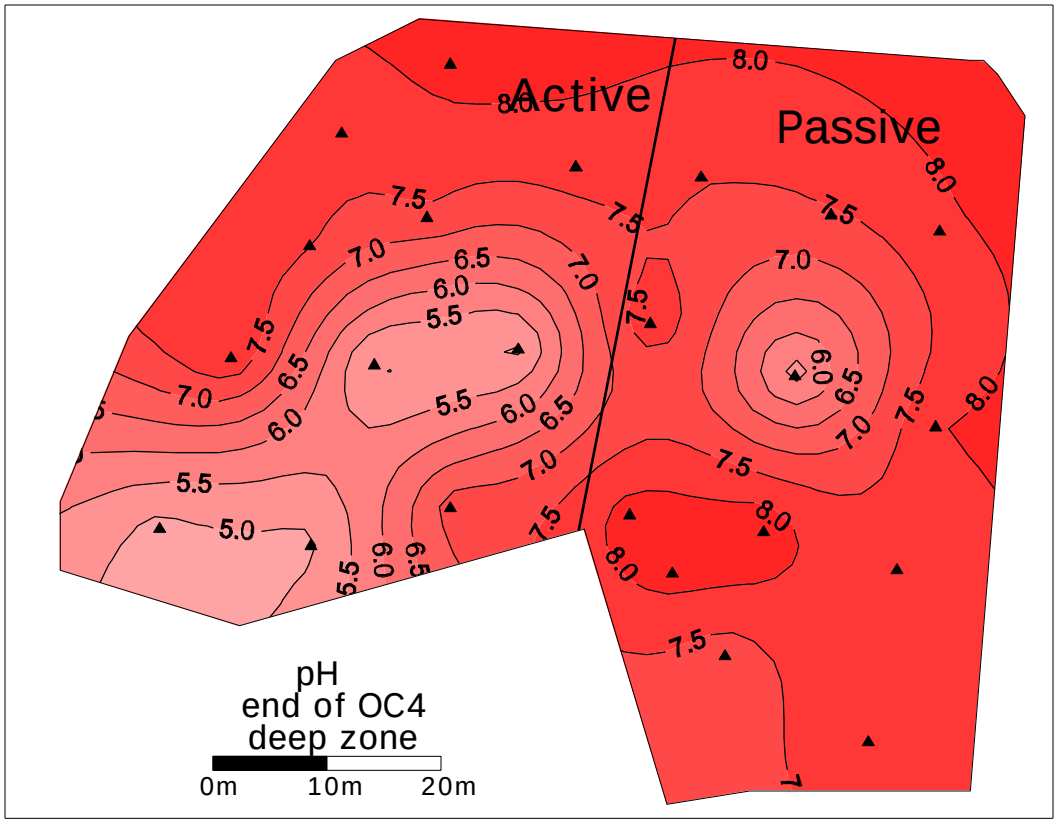


Figure 6.52 (D,E) Contour Plot of pH Deep: Operating Campaigns 4 & 5



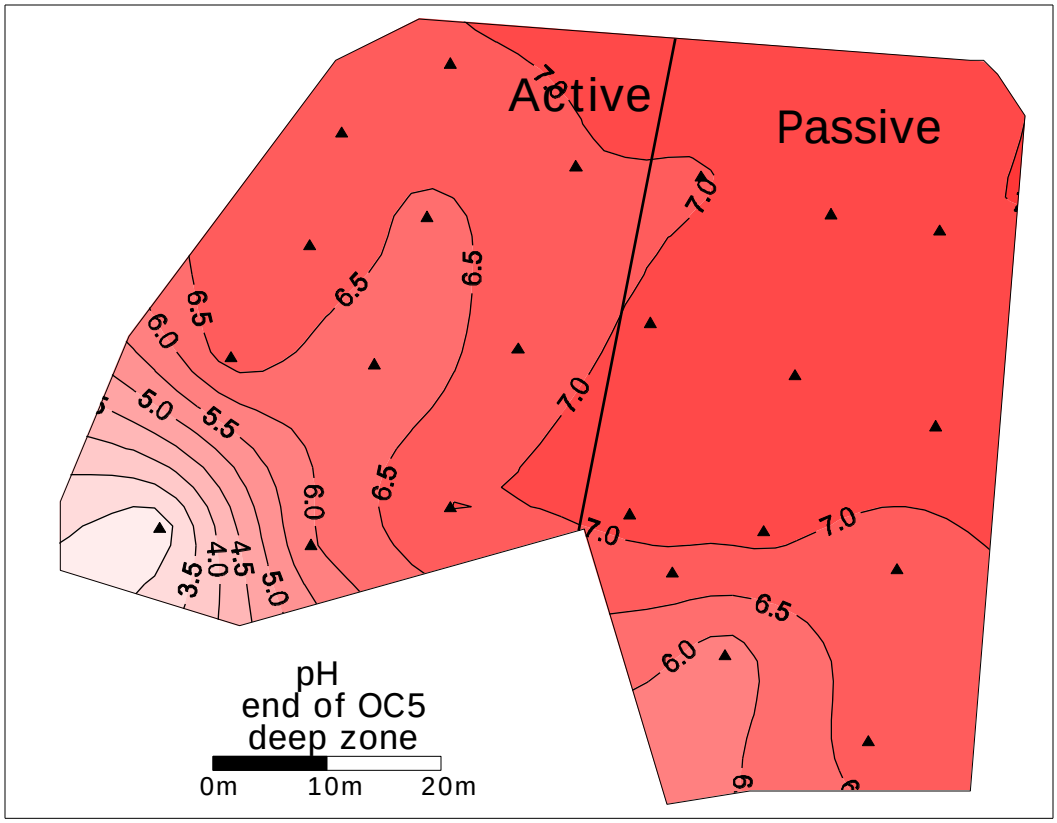
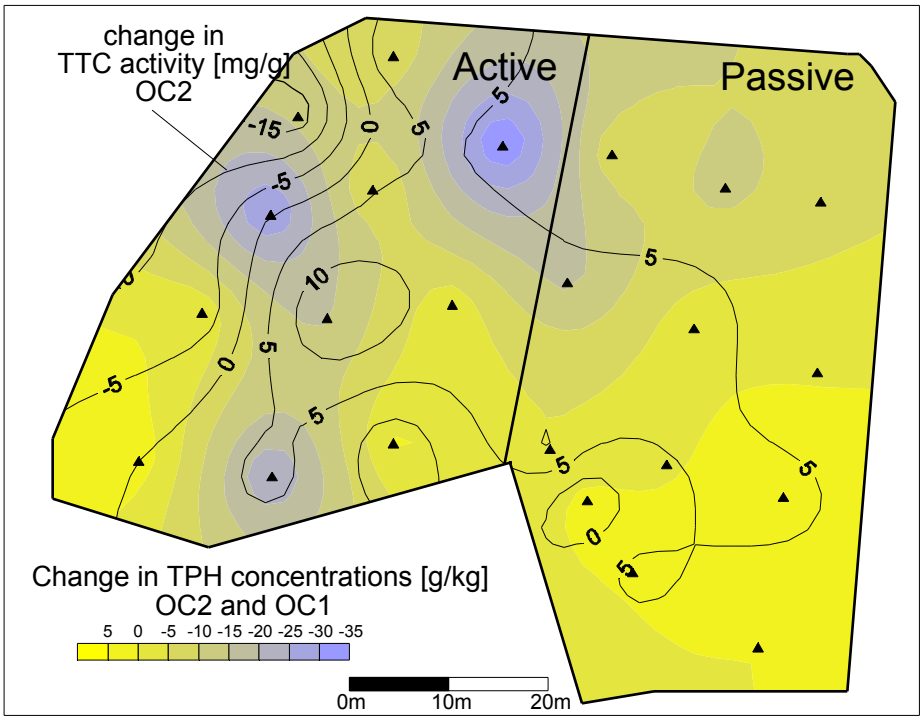


Figure 6.53 (A,B,C) Contour Plot of TPH Difference & TTC Difference Shallow: Baseline, Operating Campaigns 2 & 3



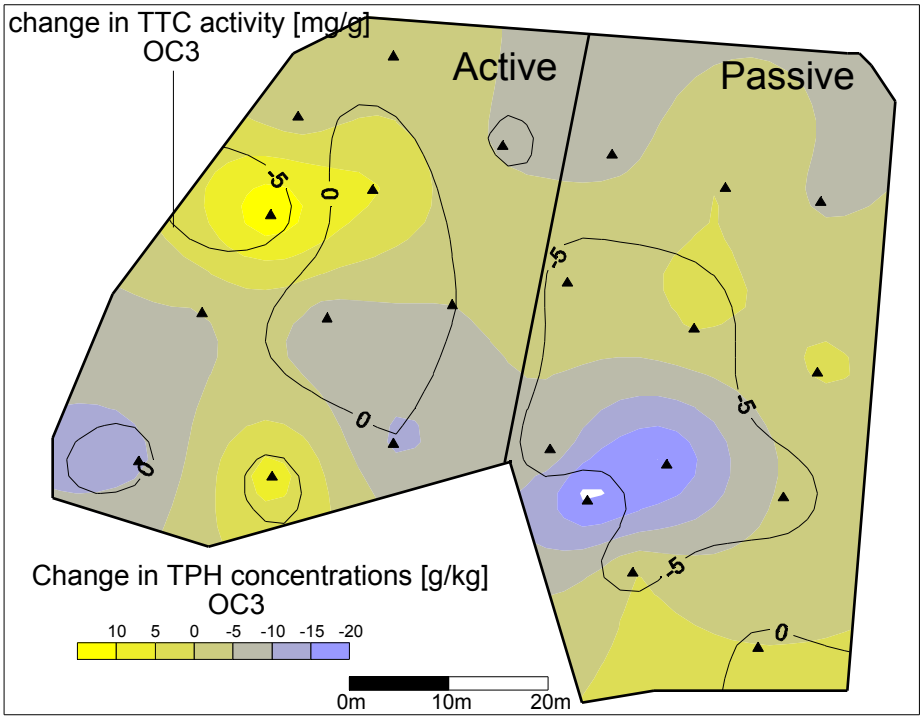
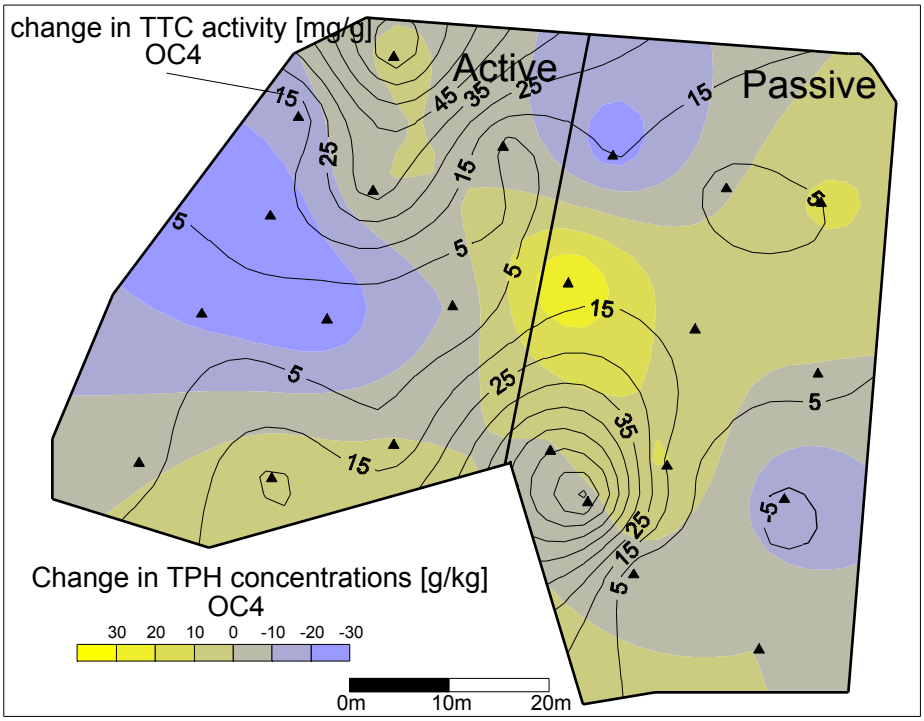


Figure 6.53 (D,E) Contour Plot of TPH Difference & TTC Difference Shallow: Operating Campaign 4 & Operating Campaign 5



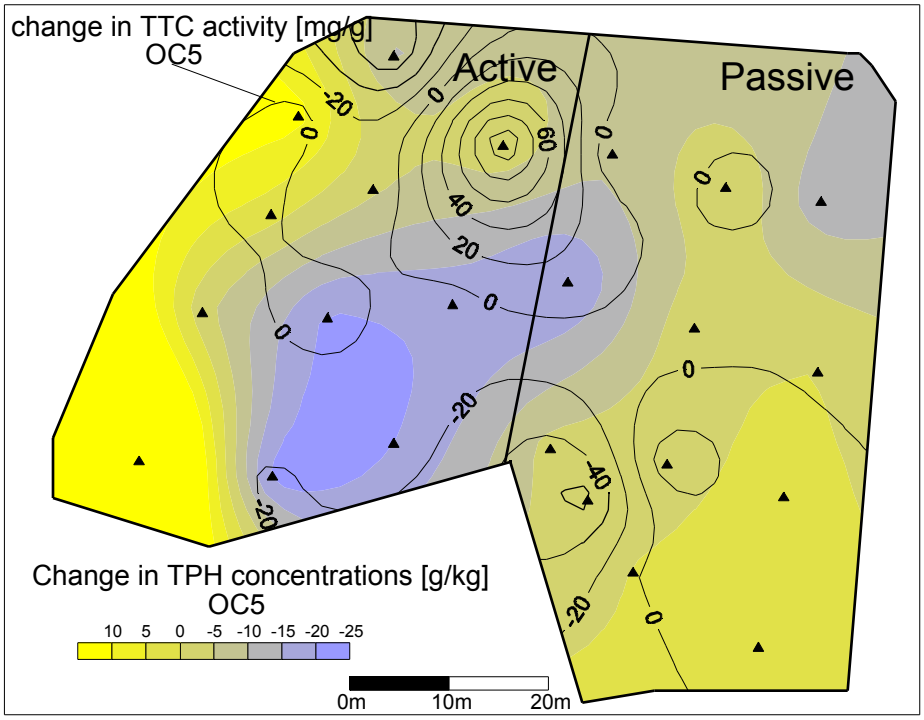
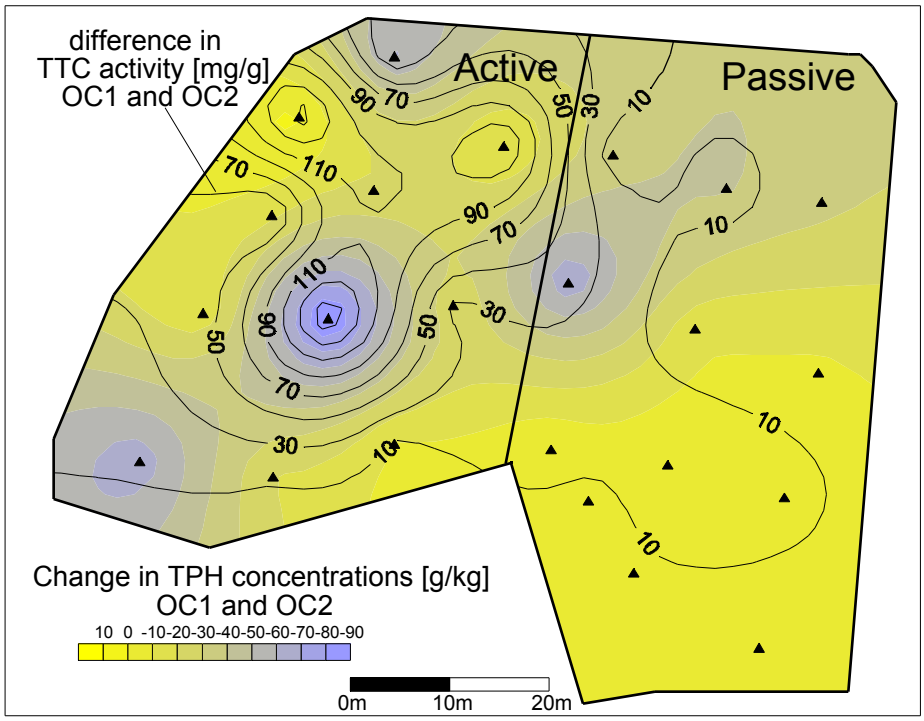


Figure 6.54 (A,B,C) Contour Plot of TPH Difference & TTC Difference Deep: Baseline, Operating Campaigns 2 & 3



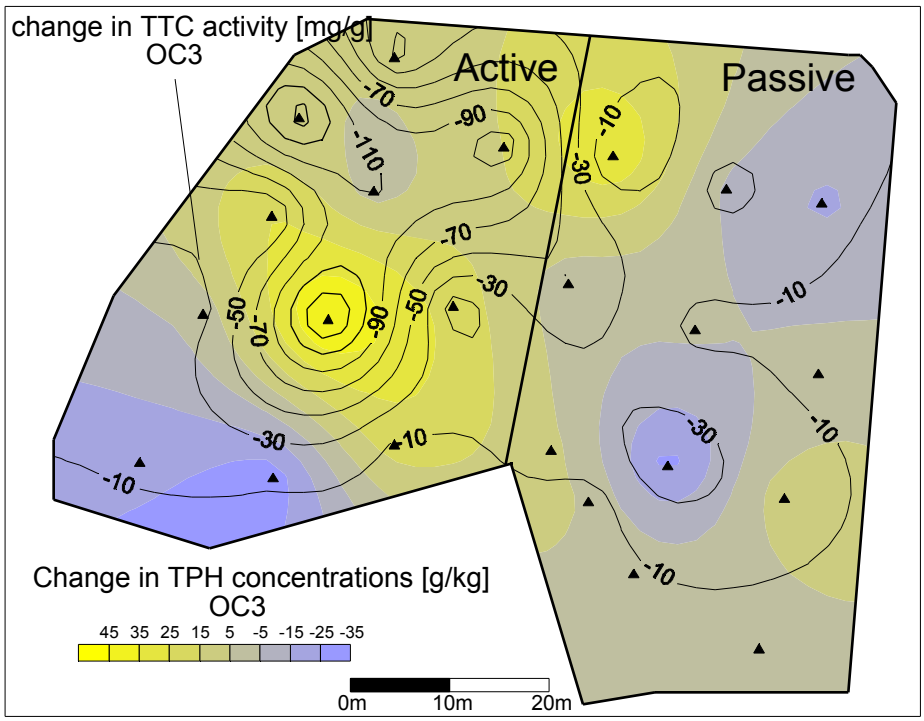
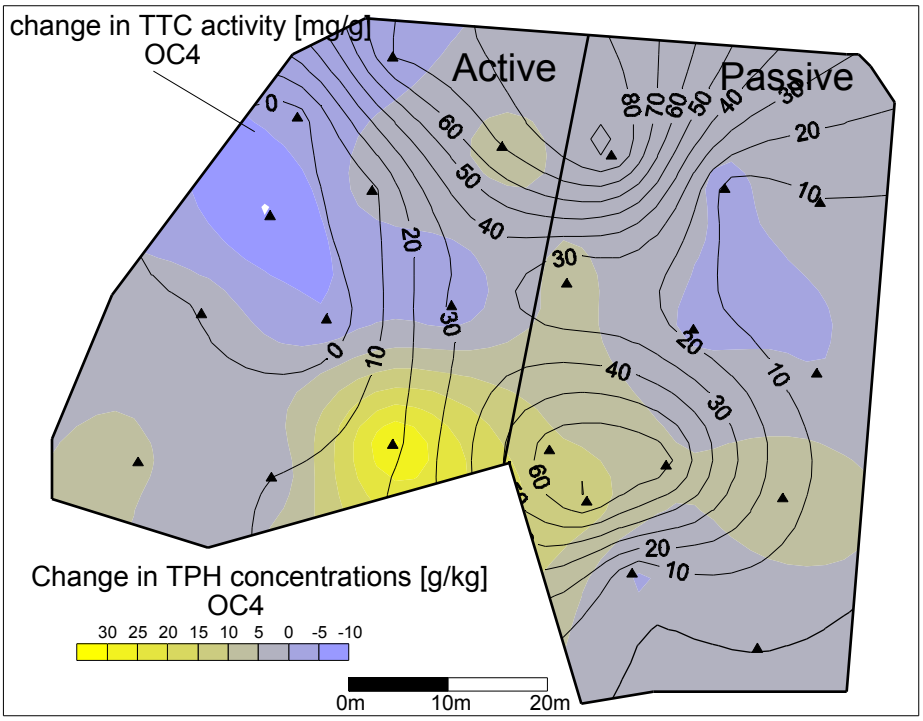


Figure 6.54 (D,E) Contour Plot of TPH Difference & TTC Difference Deep: Operating Campaigns 4 & 5



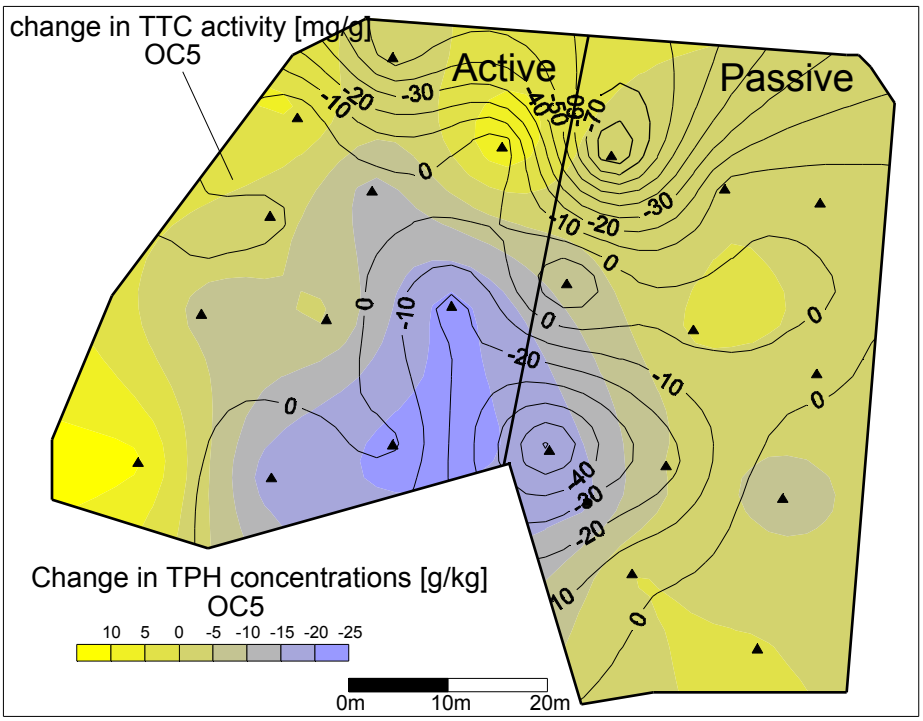


Table 6.1 Oxygen Requirements Based on Source

Oxygen Form	Oxygen Concentration in Water	Volume to Degrade 1 lb Hydrocarbon
Air-saturated Water	8 mg/L to 10 mg/L	180,000 L
Oxygen-saturated Water	40 mg/L to 50 mg/L	42,000 L
Hydrogen Peroxide	Up to 500 mg/L	6,100 L
Air	NA (21% vol./vol. in air	4,800 L

NA = not applicable

Table 6.2 Frequency and Parameters for Soil, Water and Soil Gas Samples and Monitoring

Required Parameters	Soil				Gas					Water/Liquid				Analysis Type	Analyst Ref.	Hold Time	Priority
	Base	Wk	Mn	Final	Base	Daily	Wk	Mn	Final	Base	Wk	Mn	Final				
DAPI	4 2		4	4						4 2		4	4	Micro	KU	3 wks Fixed & @ 4 °C	2
CFW (optional)	4 2		4	4						4 2		4	4	Micro	KU	24hr @ 4 °C	3
Naphtalene-degraders 7	4 2		4	4						4 2		4	4	Micro	KU	8hr @ 4 °C	1
Crude Oil-degraders 7	4 2		4	4						4 2		4	4	Micro	KU	8hr @ 4 °C	1
Respiraton Rates	4 1		4	4						4 1		4	4	Micro	KU	8hr @ 4 °C	2
TTC Activity	4 2		4	4						4 2		4	4	Micro	KU	8hr @ 4 °C	2
Metals 8	4			4										Lab	TM	6mn acidified w/ HNO_3, pH<2	2
BTEX 9	4		4														
VOC					4 2			4	4					Lab & Field	KZ+TM		2
TPH	4 2		4	4	4 2				4	4 2		4	4	Lab & Field	KZ+TM	ASAP, Max 14d @ 4 °C	1
TPH EXTRACT	4 2		4	4	4 2				4	4 2		4	4	Lab & Field	KZ+TM	Extract <14d & Anal <40d	1
PAH	4 2		4	4	4 2				4	4 2			4	Lab & Field	KZ+TM	Extract <14d & Anal <40d	1
% CO2					4 2		4 1,3							Field	KZ	N/A	1
% CH4					4 2		4 1,3							Field	KZ	N/A	2
% He					4 2		4 10	4						Field	KZ	N/A	2
Moisture	4 2	4												Field	KZ	N/A	1
NO2+3	4 2		4	4						4 2		4	4	Lab	TM	ASAP, Max 24hr @ 4 °C & acidified w/ H_2SO_4	2
NH4	4 2		4	4						4 2		4	4	Lab	TM	ASAP, Max 24hr @ 4 °C & acidified w/ H_2SO_4	2
TKN	4 2		4	4						4 2		4	4	Lab	TM	ASAP, Max 24hr @ 4 °C & acidified w/ H_2SO_4, 1.5<pH<2	2
% O2/Dissolved O2					4 2		4 1,3			4 2	4		4	Field	KZ	N/A	1
pH	4 2		4	4						4 2	4			Lab & field	KZ+TM	6mn w/ 1 thymol crystal/200ml	1
Redox Potential										4 2	4		4	Field	KZ	N/A	3
Conductivity										4 2	4		4	Field	KZ	N/A	3
$PO4^{-3}$	4 2		4	4						4 2		4	4	Lab	TM	ASAP or @ -10 °C	1
TOTAL P	4 2		4	4						4 2		4	4	Lab	TM	ASAP or @ -10 °C	2
BOD	4 2		4	4						4 2		4	4	Lab	TM	ASAP, Max 24hr @ 4 °C	2
COD	4 2		4	4						4 2		4	4	Lab	TM	ASAP, Max 24hr @ 4 °C unless acidified w/ H_2SO_4, pH<2	2
Pressure @ Piezometers					4 5		4 1,3		4					Field	KZ	N/A	1
Pressure @ Blower					4 5		4 1,3		4					Field		N/A	1
Temperature	4 2	4		4						4 2	4		4	Field	KZ	N/A	1
Air Flow/Usage						4								Field	KZ	N/A	1
Air Temp (Max/Min)					4 5		4 1,3		4					Field	KZ	N/A	2
Relative Humidity					4 5		4 1,3		4					Field	KZ	N/A	2
Rainfall					4 5		4 1,3		4					Field	KZ	N/A	2
Barometric Pressure					4 5		4 1,3		4					Field	KZ	N/A	2
He Flow/Usage					4 4	4 6								Field	KZ	N/A	2

1) Respiration Test
2) Baseline data taken before injection starts
3) Or after process change
4) Tracer test. Baseline data taken after injection starts and after any process change or nonuniformity
5) Baseline reading is taken after injection begins
6) If tracer test is one day or less, flow should be recorded/adjusted at least every two hours. If test lasts multiple days, flow should be recorded at least every four ho
7) Aerobic, anaerobic in passive zone only, 25°C, 45°C
8) Only 4 random samples from Active Section and 4 random samples from Passive Section
9) Baseline and monthly until <1 ppm
10) Weekly during Step Tests

Table 6.3 Dissolved Hydrocarbons and Corresponding Methods of Analysis

Analytical Group	Constituent	Analytical method
Gasoline	1,2-dichloroethane	EPA Method 8010
(all motor gasoline	benzene	EPA Method 8020
and Gasohol)	toluene	EPA Method 8020
	ethylbenzene	EPA Method 8020
	total xylenes	EPA Method 8020
	total volatile organic aromatics	EPA Method 8020
		EPA Method 5030
		GC-FID California
Middle distillates	naphthalene and	
(kerosene, diesel fuel	other semivolatiles	EPA method 8270
and light fuel oils)	BTEX	EPA method 8020
	n-propylbenzene	EPA method 8020
		EPA Method 3550
		GC-FID California[1]
Other or unknown	Priority pollutant	
metals		Toxicity
	Characteristic	Leaching Procedure
	Total Petroleum	EPA Method 9071
Hydrocarbons		with silica gel clean up
		EPA method 418.1[2] (screening only)

1. California Method: Leaking Underground Fuel Tanks Field Manual. Guidelines for Site Assessment, Clean-up and Underground Storage Tank Closure. State of California, May 1988.
2. Method 418.1 is no longer a recommended method by SCDHEC for final soil disposal determinations. However, this analytical method is acceptable for a preliminary screening process.

Table 6.4 Average Soil concentrations for Metals by Operating Campaign

Metal	OC-1	OC-2	OC-3	OC-4	OC-5	MCL (MU)	MCL (Ind)
As	7.00	8.00	8.00	6.00	7.00	20	60
Cd	5.74	2.02	5.06	0.62	0.48	3	15
Cr	36.4	27.6	22.5	31.0	24.7	50	500
Co	7.65	6.38	7.64	7.30	4.69	30	200
Cu	24.6	25.8	22.5	29.4	18.8	50	300
Pb	179	107	66	87	47	100	600
Hg	0.49	0.31	0.26	0.24	0.32	3	30
Ni	17.8	17.6	12.1	20.9	13.7	50	300
Zn	297	184	156	153	111	150	1000

All units in mg/kg, * Polish maximum contaminant level (MCL) guidelines (industrial use - Ind, 0-2 m, and multi-use - MU, 0.3-15 m)

Table 6.5 Leachate BOD and COD by Operating Campaign

Date/OC	COD (mg/L O2)	BOD (mg/L O2)
4/16/98 OC2	251	17.6
6/30/98 OC3	287	18.9
7/29/98 OC4	329	25.7
3/25/99 before OC5	229	13.6
10/6/99 after OC5	349	28.7

Table 6.6 Total Soil Parameter Correlation Matrix (Values in Bold indicate Significant Correlation

	Temp	DAPI	CFW	NA20	NA37	PE20	PE37
Temp	1						
DAPI	**-0.652**	1					
CFW	-0.2025	**-0.1249**	1				
NA20	**-0.3153**	**-0.3254**	**0.3995**	1			
NA37	-0.001	-0.0344	-0.0322	-0.0692	1		
PE20	**-0.3462**	**-0.3222**	**0.398**	**0.9971**	-0.0597	1	
PE37	**-0.2939**	0.1105	-0.0282	-0.0638	0.0157	-0.0551	1
TTC	**-0.4051**	**0.227**	**-0.1388**	**-0.2665**	0.0037	**-0.1306**	-0.057
pH	**0.3368**	0.0605	0.0159	-0.0961	0.0961	-0.0143	-0.0255
MOIS	**-0.2185**	0.0941	-0.1241	**-0.1513**	**0.1592**	-0.1087	0.0078
NO3	**0.2302**	-0.0361	0.0168	-0.0536	-0.0158	-0.0398	-0.0219
NO2	0.0728	**0.2026**	-0.1031	**-0.2451**	0.0286	**-0.2313**	-0.0496
PO4	**-0.5656**	**0.1594**	0.0306	0.0289	-0.0426	0.085	**0.3533**
NH4	**-0.3177**	-0.014	**-0.1214**	0.0918	-0.0583	-0.0937	-0.0403
PTOT	**-0.775**	-0.0733	0.1182	-0.018	-0.1356	-0.0169	-0.066
TKN	**0.2623**	0.0943	-0.0921	**-0.1252**	**0.147**	**-0.1224**	0.055
FLORAN	0.1409	**-0.1904**	-0.0431	**0.2171**	0.0254	**0.2172**	0.0011
BBFLUORA	**0.2162**	-0.1067	-0.0703	0.048	0.0472	0.0409	-0.0092
BKFLUORA	0.1372	-0.0279	-0.0831	-0.0606	0.0654	-0.0589	0.1105
BAPYRE	0.0854	-0.0425	-0.0744	0.0019	0.0361	0.0026	**-0.1535**
BOPERY	**0.2512**	**-0.3095**	-0.0636	**0.1776**	**0.1451**	0.0277	-0.0025
I123CDY	0.1632	**-0.141**	-0.0905	0.0814	0.1098	0.0848	0.1046
TPHTOT	**-0.1943**	**-0.3574**	-0.0304	**0.2532**	-0.1079	**0.2267**	**-0.2095**
TPHPOL	-0.1124	**-0.3187**	-0.053	**0.1932**	-0.0971	**0.1723**	**-0.2012**

	TTC	PH	MOIS	NO3	NO2	PO4	NH4
TTC	1						
pH	0.1017	1					
MOIS	**0.1801**	0.0212	1				
NO3	-0.0513	**-0.1046**	**-0.1711**	1			
NO2	0.0176	0.0651	**0.1762**	**0.2286**	1		
PO4	0.0272	**-0.1726**	-0.0386	-0.0466	0.0072	1	
NH4	0.0122	**-0.209**	-0.0105	-0.0113	-0.0064	**0.3421**	1
PTOT	-0.0633	-0.1085	**0.2366**	**-0.1619**	**0.1804**	**0.1139**	**0.138**
TKN	0.0376	-0.0663	**0.2268**	-0.0048	0.0253	-0.0509	**-0.1492**
FLORAN	0.013	**-0.3424**	**0.1103**	**0.1029**	-0.0331	-0.0434	**0.121**
BBFLUORA	**0.1619**	-0.0707	**0.1518**	-0.0461	-0.0071	-0.0374	**0.1408**
BKFLUORA	**0.1596**	**-0.1358**	**0.2128**	0.0464	-0.024	-0.0297	0.0589
BAPYRE	**0.1382**	**-0.1645**	**0.2229**	0.0636	-0.0113	-0.0514	-0.0085
BOPERY	0.0855	**-0.2128**	0.0466	0.0354	-0.0203	-0.0505	0.1003
I123CDY	**0.2188**	-0.0126	**0.2441**	-0.0243	0.0261	-0.0842	-0.0625
TPHTOT	**0.1627**	**-0.1526**	**0.2464**	-0.0916	-0.0044	-0.0038	0.084
TPHPOL	**0.1816**	**-0.1825**	**0.2367**	-0.0581	0.0015	-0.0126	0.0917

Table 6.6 Total Soil Parameter Correlation Matrix (Values in Bold indicate Significant Correlation (cont.)

	PTOT	TKN	FLORAN	BBFLUORA	BKFLUORA	BAPYRE	BOPERY
PTOT	1						
TKN	**-0.1969**	1					
FLORAN	-0.0699	**0.1781**	1				
BBFLUORA	-0.0975	**0.1959**	**0.6618**	1			
BKFLUORA	**-0.1697**	**0.2048**	**0.6462**	**0.7617**	1		
BAPYRE	**-0.2**	**0.2049**	**0.6739**	**0.69**	**0.9271**	1	
BOPERY	**-0.184**	**0.1586**	**0.7393**	**0.6606**	**0.688**	**0.6928**	1
I123CDY	**-0.133**	**0.2073**	**0.6002**	**0.7578**	**0.8061**	**0.8314**	**0.6905**
TPHTOT	0.0587	**0.1915**	**0.4611**	**0.408**	**0.315**	**0.3425**	**0.4599**
TPHPOL	0.0467	**0.2145**	**0.4952**	**0.4363**	**0.359**	**0.3875**	**0.5009**

	I123CDY	TPHTOT	TPHPOL
I123CDY	1		
TPHTOT	**0.4254**	1	
TPHPOL	**0.4654**	**0.9763**	1

Table 6.7 TPH Inventory by Operating Campaign

	Baseline	OC1	OC2	OC3	OC4	OC5
Metric Tons	148	100	68.6	68.6	66.8	28.1
% Remaining	100	68	46	46	45	19

Table 6.8 Biodegradation Rate by Operating Campaign and Treatment

Campaign	Average	Passive	Active
OC-1	80	44	119
OC-2	88	82	94
OC-3	<33	33	0
OC-4	<37	0	37
OC-5	91	60	121

All values in mg/kg soil/day

Chapter 7

Cost Analysis

Institute for Ecology of Industrial Areas
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Lawrence Berkeley National Laboratory
Terry Hazen

Savannah River Technology Center
Denis Altman, Albert Tien

Cost Analysis

The cost of using this technology to remediate the acidic and highly recalcitrant petroleum contaminated soil at the CZOR is estimated and compared to the actual costs for remediation of petroleum contaminated soil reported in the open literature. A conservative approach was taken in this comparison by using the actual costs of this demonstration. Since this was a demonstration, the analytical costs, and the specialized equipment costs were much higher than they would be in an actual deployment. The calculations use the average hourly rate for a Polish worker and a US worker (DOE site contractor, fully loaded). Equipment and materials costs were converted from $US to Polish Z (4.00 Z/$1.00). All equipment costs are actual purchase prices. The demonstration remediated 120 metric tons of TPH in 5000 metric tons of soil. These 4167 cubic yards of contaminated soil were remediated to cleanup standards. The cost per cubic yard was $96.33/Z142.76 (Table 7.1). If the specialized equipment was removed, the cost the was $86.98/Z105.37.

It must be emphasized that this was a demonstration. If the fully optimized system had been used from the beginning the remediation time would have been cut in half and the cost per cubic yard would have been reduced to $62.21/Z91.69.

If we compare these results to published costs for conventional treatment technologies, we see that even in the worst case scenario, this bioremediation application beats all costs except the soil washing costs reported by Davis et al. (1995). Thus the biopile remediation costs are lower than incineration, landfilling, stabilization, and asphalting. Considering the reduced time scenario this application even beats the cost of soil washing (Table 7.2). If we compare this demonstration to other biopile and bioremediation techniques we can see that it falls within the same range but is higher than the prepared bed bioreactor and biopile deployments reported by Kastner et al. (1997). Given that the material being remediated was extremely acidic, more than 100 years old and had heavy metal contamination also it compares well. The costs reported by Kastner et al. (1997) were for fresh diesel-contaminated soil, and inherently biodegradable PCS.

This demonstration showed that biopile type bioremediation for TPH and PAH contaminated soil can be a highly effective and cost effective solution for waste lagoon cleanup.

References

Davis, K. L., G. D. Reed, and L. Walter. 1995. A comparative cost analysis of petroleum remediation technologies. p. 73- 80. IN: Applied Bioremediation of Petroleum (ed.) R. E. Hinchee, J. A. Kittel, and H. J. Reisinger. Battelle Press, Columbus, OH.

Kastner, J. R., K. H. Lombard, J. A. Radway, J. Santo Domingo, G. L. Burbage, and T. C. Hazen. 1997. Characterization using laser induced fluorescence and nutrient injection via barometric pumping, p. 385-392. In Situ and On-Situ Bioremediation: Volume 1. Battelle Press.

Table 7.1 Bioremediation Treatment Costs

Bioremediation Treatment Costs	Cost/CY	Reference
Biopile costs at ISL (<100 ppm)	$30.75	Kastner et al. (1997)
Prepared Bed bioreactor (<100 ppm)	$46.07	Kastner et al. (1997)
Land treatment	$10-$100	EPRI (1988)
Biotreatment	$40-$100	Levin and Gealt (1993)
Bioremediation	$39-$111	Molnaa and Grubbs (1988)

Table 7.2 Conventional Treatment Costs

Conventional Treatment Costs	Cost/CY	Reference
Incinerate (Tennessee) (3 units)	$309.00	Davis et al (1995)
Incineration	>$100	EPRI (1988)
Incineration	$250-$800	Levin and Gealt (1993)
Incineration (mobile)	$195-$520	Molnaa and Grubbs (1988)
Soil Wash (Tennessee) (2 units)	$70.00	Davis et al (1995)
Landfill	$150-$250	Levin and Gealt (1993)
Landfill	>$100	EPRI (1988)
Landfill	$176-$202	Molnaa and Grubbs (1988)
Asphalt	$10-$100	EPRI (1988)
Stabilization/fixation	$130-$260	Molnaa and Grubbs (1988)

Chapter 8

Conclusions

Conclusions

Both the ESC and risk assessment represented firsts for the application of these procedures in Poland. These activities identified VOCs and BTEX as primary contributors to risks posed to present and future site workers at the refinery. Remedial goals for the cleanup of soils and sediments contaminated by lagoon sludge were established to guide the remedial activities. The innovative biopile design used a combination of passive and active aeration in conjunction with injection of nutrients and surfactants to increase biodegradation of the very acidic soil containing high concentrations of polynuclear aromatic hydrocarbons (PAHs). Simultaneous lab studies using soil columns were used to optimize treatment techniques and verify field observations under more controlled conditions. This full-scale demonstration showed that, with minimal cost, the total mass of petroleum hydrocarbons could be reduced by more than 81% (120 metric tons) over the 20 month project. During this time the most toxic compounds were reduced to levels acceptable for multi-use resource activities. Though a variety of biodegradation monitoring methods were used, measures of microbial number and activity (i.e., direct fluorochrome counts and dehydrogenase activity) were found to be best correlated with rates of biodegradation in the biopile. In addition, our data indicate that passive aeration could reach the same end point as active aeration, it would just take longer. Rates of biodegradation were comparable to other prepared bed studies of petroleum contaminated soil, i.e., 121 mg/kg soil/day (82 mg/kg soil/day in the passive side). However, given that this material was highly weathered and very acidic these rates are much higher than expected. Much of this increase can probably be attributed to the vegetative material added as a bulking agent, surfactant addition and to the aeration process.

The finding that microbial counts and dehydrogenase measurements accurately reflect biodegradation rates suggests that these direct measurements can be used to provide real time control of biopile operation to maximize biodegradation rates under a variety of conditions. The cost savings from passive aeration may provide an advantage over active aeration when clean-up time is not a primary consideration. This demonstration also emphasized that biodegradation is initially quite rapid, but in less than 12 months requires additional stimulation via nutrient or surfactant addition. The remediation strategies that have been applied at the CZOR waste lagoon were designed, managed and implemented under the direction of the Savannah River Technology Center/IETU team in cooperation with the CZOR and Florida State University, for the United States Department of Energy. This collaboration between DOE, IETU and its partners, provides the basis for international technology transfer of new and innovative remediation technologies which can be applied to DOE sites, in Poland and at other locations worldwide.

Appendices

Appendix A

List of Acronyms and Abbreviations

APR	Air Purifying Respirator
B&K	Brüel & Kjær
BETX	Benzene, Ethyl Benzene, Toluene and Xylene
bgs	below ground surface
bp	Boiling Point
CFU	Colony Forming Units
CH	Fat clay or very fine high plasticity clay
CL	Fine grained clay of low to medium plasticity
COC	Contaminants Of Concern
COR	Czechowice Oil Refinery
DAPI	4, 6 Diamindino 2 phenylindole
DOE	United States Department of Energy
ESC	Expedited Site Characterization
FID	Flame Ionization Detector
FSU	Florida State University
GC	Gas Chromatography
GPR	Ground Penetrating Radar
GW	Coarse grained gravel sand mixture
HASP	Health and Safety Plan
IETU	Institute for Ecology of Industrial Areas
ISCST	Industrial Source Complex /Screening Techniques
LEL	Lower Explosive Limit
LUST	Leaking Underground Storage Tank
NIOSH	National Institute of Occupational Health and Safety (USA)
OSHA	Occupational Safety and Health Act (USA)
ORP	Oxidation-Reduction Potential
PAH	Polycyclic Aromatic Hydrocarbon
RACE	Risk Abatement Center for Central and astern Europe
SCDHEC	South Carolina Department of Health and Environmental Control
SPM	Single Point Monitor

SRS	Savannah River Site
SRTC	Savannah River Technology Center
SSO	Site Safety Officer
TCD	Thermal Conductivity Detector
TOC	Total Organic Carbon
TPH	Total Petroleum Hydrocarbons
USEPA	U.S. Environmental Protection Agency
VOC	Volatile Organic Hydrocarbon
sVOC	Semi-Volatile Organic Hydrocarbon
WSRC	Westinghouse Savannah River Company

Appendix B Training and Outreach Activities

Courses

Tien, A. J. Guest lecturer, Biodegradation and Bioremediation Technologies, Technical University Gliwice, Prof. Mitsch

Tien, A.J., Guest Lecturer, Environmental Engineering Case Studies, Geosystems, Georgia Tech University, Dr. Grubb

Tien, A. J. Tien, Guest Lecturer, Lehrstuhl fuer Biology Seminars, University of Konstance, Prof. A. M. Cook and Prof. B. Shink

Exchange Activities

University of Charleston, Geohydrology Class, Presentation of Poland Project, SRTC, Spring 1999.

Technical University Czestochowa, Environmental Sciences Class, Czechowice Oil Refinery, Czechowice, Poland 1998

Institute for Soil Protection and Amelioration, St. Petersburg. Tour of Czechowice Oil Refinery, Czechowice, Poland 1998

Institute of Ecology for Industrial Areas, Tour of SRS, Aiken, SC 1996 and 1999

Czechowice Oil Refinery, Tour of SRS, Aiken SC 1996

Tours and presentations of bioremediation at the Poland demonstration site. May, 1996, Katowice, Poland. Polish Institute for Ecology of Industrial Areas.

Tour and presentation of the Poland Demonstration Site, Visitors Day 1998, Czechowice Oil Refinery, Czechowice, Poland

U.S. Department of Energy, Tour and presentation of the Poland Demonstration Site, 1998, Czechowice Oil Refinery, Czechowice, Poland

Symposia

Altman, D. J.. Invited Session Chair, Site Remediation Methods, Fourth International Symposium and Exhibition on Environmental Contamination in Central and Eastern Europe. Warsaw, Poland 15-17th Sept 1998

Tien, A. J. Invited Session Chair, Sampling and Monitoring Methods, Fourth International Symposium and Exhibition on Environmental Contamination in Central and Eastern Europe. Warsaw, Poland 15-17th Sept 1998

Tien, A. J. Invited Panelist, International Technology Development, Sigma Xi Forum on International Cooperation in Science and Technology. Vancouver, B. C. 12-13 November 1998.

Hazen, T. C. Invited Symposium Co-Chair. In Situ Bioremediation: Natural vs. Accelerated.March, 1998, Notre Dame, IN. Bioremediation for Industry. Society for Industrial Microbiology.

Hazen, T. C. Invited Session Chair. In situ bioremediation in the subsurface. August, 1999, Aspen, CO. Fourth International Symposium on Subsurface Microbiology.

Hazen, T. C. Invited Session Chair. Remediation. November 1999, San Francisco, CA. Fourth USA/CIS Joint Conference on Environmental Hydrology and Hydrogeology.

Students

K-12

Kevin Rouse	STW/ Barnwell High School

Undergraduate

Denita Williams	SCAMP/SCSU-Orangeburg
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Daniel Tedrick	Davidson University
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Wes Roberts	Florida State University
Nancy Roberts	Florida State University
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Reyn Anderson	New York University

Post-Doctoral

Geralyne Lopez de Victoria	SRTC/ORISE
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Albert Tien	SRTC/ORISE

Appendix C Project Staff

Institute for Ecology of Industrial Areas

Ewa Marchwinska	Project Management
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Stefan Godzik	Project Management
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Jacek Wypych	Chemical Laboratory Staff
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Alan Davis	Project Administration
Loreen Kollar	Administration, Logistic Support
Candice Allbaugh	Administration, Logistic Support
Laymon Gray	Field Management
Wes Roberts	Computer Support
Steven Hodge	Computer Support
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David Barge	Computer Support

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Albert Tien	On-Site Technical Lead and Project Coordinator, Post-Doctoral Fellow, PI (1996-present)
Denis Altman	Engineer, Design Authority, PI (1998-1999)
Terry C. Hazen	Manager and PI (1995-1998)
Ken Lombard	On-Site Technical Lead, Training and Technical Support (1995-1997)
Carl B. Fliermans	Microbiology Consultation and Training

Marilyn Franck	Technical Assistance
Deborah Holiday	Clerical Assistance
MaryAnn Johnson	Technical Assistance
Pam McKinsey	Technical Assistance
James Napier	Technical Assistance
Jorge Santo Domingo	Post-doctoral Fellow
Fatina Washburn	Engineering and Project Management Assistance

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Al Bevlo	PI, ESC Project Manager
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Connie Bailey	Communications

Lawrence Berkeley National Laboratory

Terry C. Hazen	Technical Consultant to FSU 1998-1999

Czechowice Oil Refinery

Piotr Dudek	Refinery Staff
Ryszard Chrapek	Refinery Staff
Aleksander Martyniczyn	Refinery Staff
Bogdan Jagosz	Refinery Staff
Jerzy Mol	Refinery Staff

Appendix D Presentations and Publications

Presentations

Dziewiecka, B., K. Lukasik. Assessment of Cancer Risk as a Result of Consumption of Vegetables Produced in the Vicinity of PAHs Emission Sources. May/June, 1999, Miedzyzdroje, Poland. VII Meeting of the Polish Toxicological Association.

Hazen, T. C, Invited Seminar. Recent Innovations is Bioremediation. June 1999, Charleston, SC. ER-TEC'99 Environmental Restoration Technology End User Conference sponsored by DOE/DOD/EPA.

Hazen, T. C. Invited Seminar. Bioremediation of Contaminated Subsurface Environments. May, 1999, Chicago, IL. American Society for Microbiology Annual Meeting.

Hazen, T. C. Invited Seminar. Innovative Bioremediation Demonstrations of Petroleum Contaminated Sites in Poland and US. March 1999, Berkeley, CA. Petroleum Environmental Research Forum hosted by Chevron.

Hazen, T. C., A. J. Tien, A. Worsztynowicz, K. Ulfig, and D. J. Altman. Invited Seminar. Bioremediation Field Demonstration of a Sludge Lagoon at a Polish Petroleum Refinery. November 1999, San Francisco, CA. Fourth USA/CIS Joint Conference on Environmental Hydrology and Hydrogeology.

Tien, A. J. and D. Altman. 1999. Robust Technologies for Environmental Restoration-Joint US-Polish Experiences. Proceedings of the Southeastern Environmental Management Association. 4 Novemeber , Martinez, GA.

Hazen, T. C. Bioremediation Overview. U.S. Department of Energy-Supported Research and Development in Central and Eastern Europe and Russia. September, 1998, Warsaw, Poland. Fourth International Symposium and Exhibition on Environmental Contamination in Central and Eastern Europe (Warsaw'98).

Hazen, T. C. Bioremediation: State-of-the-Science. Special Workshop on DOE projects in Poland. September, 1998, Warsaw, Poland. Fourth International Symposium and Exhibition on Environmental Contamination in Central and Eastern Europe (Warsaw'98).

Hazen, T. C. Invited Symposium. "How do I know if in situ bioremediation is feasible?" March, 1998, Notre Dame, IN. Bioremediation for Industry. Society for Industrial Microbiology.

Tien, A. J. 1998. Carbon-Limited Growth-From the laboratory to the field. Invited lecture sponsored by the Environmental Biotechnology Department, Silesian Technical University, Gliwice, Poland.

Tien, A. J. 1998. Poland Today-An Environmental Overview. Invited lecture sponsered by the Dept. of Environmental Engineering, Georgia Institute of Technology, Atlanta GA.

Tien, A. J. 1998. An Environmental Overview of Poland. Invited lecture sponsored by Sigma Xi and the Office for International Education. Las Vegas, NM. 18 November 1998.

Tien, A. J. 1998. Project Review of the Czechowice Oil Refinery Project . Invited talk. Savannah River Technology Center, Aiken SC.

Tien, A. J., A Worsztynowicz, K. Zacharz, D J. Altman, T C. Hazen. 1998. Technology Development and Transfer for Environmental Remediation: Joint American and Polish Cooperation International Technology Development, Sigma Xi Forum on International Cooperation in Science and Technology. Vancouver, B. C. 12-13 November 1998.

Tien, A. J., A. Worsztynowicz, K. Ulfig, D. Altman, and T. C. Hazen. 1998 Comparison of Aeration and Nutrient Ammendment Strategies During Bioremediation of Petroleum Sludge Contaminated Soils From A Polish Refinery- Batch and Soil Column Studies. 98th Annual Meeting of the American Society for Microbiology, Atlanta GA.

Tien, A. J., A. Worsztynowicz, K. Ulfig, D. Altman, and T. C. Hazen. Comparison of Aeration and Nutrient Amendment Strategies During Bioremediation of Petroleum Sludge Contaminated Soils From A Polish Refinery- Batch and Soil Column Studies. May, 1998, Atlanta, GA. American Society for Microbiology Annual Meeting.

Tien, A. J., D.Altman, A Worsztynowicz and K. Zacharz. 1998. DoE's First Demonstration Project in Poland- Bioremediation of a Process Waste Lagoon at the Czechowice Oil Refinery. Fourth International Symposium and Exhibition on Environmental Contamination in Central and Eastern Europe. Warsaw, Poland.

Ulfig, K., A. Tien, G. Plaza, A. Worsztynowicz, and T. C. Hazen. Microbiological changes in petroleum-contaminated soil during bioremediation at a Polish petroleum refinery. September, 1998, Warsaw, Poland. Fourth International Symposium and Exhibition on Environmental Contamination in Central and Eastern Europe (Warsaw'98).

Worsztynowicz, A., A. J. Tien, D. Rzychon, K. Ulfig. 1998. Contaminated Land remediation in the "Czechowice Refinery". Contaminated Land Management in Central and Eastern Europe. Katowice, Poland.

Worsztynowicz, A., A. J. Tien, D. Rzychon, K. Ulfig. 1998. Environmentally Friendly Soil Clean-up Methods in the "Czechowice Refinery". Fourth Annual EcoFair, Katowice, Poland.

Worsztynowicz, A., A. Tien, K. Ulfig, K. Zacharz, M. Adamski, and D. Rzychon, and T. C. Hazen. Soil Cleaning at the Czechowice Refinery. September, 1998, Warsaw, Poland. Fourth International Symposium and Exhibition on Environmental Contamination in Central and Eastern Europe (Warsaw'98).

Worsztynowicz, A., A. Tien, K. Ulfig, K. Zacharz, M. Adamski, D. Rzychon, T. Hazen 1998. Soil cleaning at Czechowice Refinery. Training Course. Remediation Technologies: New Trends and Tools for Soil Decontamination. IETU, Katowice, 30.11.-5.12.1998.

Dziewiecka, B, K. Lukasik. Determination of PAHs in Soil and Waste Contaminated with Petrochemicals. September, 1997, Torun, Poland. IV National Chromatographic Seminar on Chromatography and Other Separation Techniques in Eco-Analytics.

Hazen, T. C. Invited Moderator. July, 1997, Boston, MA. Roundtable: Passive vs. Accelerated Remediation. Second Annual Novel Remediation Technology Symposium: Innovative Remedial Technologies for Cost Effective Site Solution.

Hazen, T. C. Invited Seminar. Aerobic bioremediation in situ. August, 1997, Reno, NV. Bioremediation Symposium Society for Industrial Microbiology.

Hazen, T. C. Invited Seminar. Aerobic bioremediation. November, 1997, Orlando, FL. 3rd Annual Florida Remediation Conference.

Hazen, T. C. Invited Seminar. Bioremediation Technologies. March, 1997, Columbia, SC. University of South Carolina, School of the Environment.

Hazen, T. C. Invited Seminar. Field Bioremediation strategies. November, 1997, Germantown, MD. DOE Natural and Accelerated Bioremediation Research Program.

Hazen, T. C. Invited Seminar. Full-Scale field remediation Demonstrations: Lessons Learned. September, 1997, Berkeley, CA. Lawrence Berkeley National Laboratory.

Hazen, T. C. Invited Seminar. July, 1997, Boston, MA. In Situ Bioremediation using nutrient injection. Second Annual Novel Remediation Technology Symposium: Innovative Remedial Technologies for Cost Effective Site Solution.

Hazen, T. C. Invited Workshop. Bioremediation. September, 1997, Katowice, Poland. Risk Abatement Center of Central and Eastern Europe.

Lombard, K. H., A. Worsztynowicz, T. C. Hazen, and B. Jagosz. Bioremediation techniques for the clean-up of a petroleum waste lagoon. April, 1997, New Orleans, LA. In Situ and On-Site Bioreclamation, The Fourth International Symposium.

Lukasik, K., B. Dziewiecka, J. Wypych. Determination of petrochemicals in environmental samples. September, 1997, Torun, Poland. IV National Chromatographic Seminar on Chromatography and Other Separation Techniques in Eco-Analytics.

Tien, A. J., D. J. Altman, and T. C. Hazen. 1997. Bioremediation demonstration of a process waste lagoon. DOE EM-50 Polish Initiative Program Review. Katowice, Poland.

Tien, A.J., K. Ulfig, and A. Worsztynowicz. 1997. Soil column biotreatability studies. Environmentally Friendly Soil Bioremediation Workshop, Katowice, Poland.

Ulfig, K, G. Plaza, A.J. Tien, T. Manko, and A. Worsztynowicz. 1997. Changes in number and activity of microorganisms during remediation of petroleum contaminated soils in column studies. Polish National Environmental Biotechnology Symposium. Ustron, Poland.

Ulfig, K., G. Plaza, T. C. Hazen, C. B. Fliermans, M. M. Franck, and K. H. Lombard. Bioremediation treatability and feasibility studies at a polish petroleum refinery. April, 1997, New Orleans, LA. In Situ and On-Site Bioreclamation, The Fourth International Symposium.

Worsztynowicz, A., A. J. Tien, D. Rzychon, K. Ulfig. 1997. Biopile. Polish National Environmental Biotechnology Symposium. Ustron, Poland.

Altman, D. J., T. C. Hazen, R. Legrand, R. Hickey, K. H. Lombard, F. A. Washburn, and C. J. Berry. Methanotrophic treatment of contaminated well water using bioreactors. September, 1996, Warsaw, Poland. Third International Symposium and Exhibition on Environmental Contamination in Central and Eastern Europe.

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