GROUNDWATER MODELLING OF A PHYTOREMEDIATION AREA IN SOUTH EASTERN BRAZIL

BY

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1. INTRODUCTION

Phytoremediation can be defined by the set of technologies used for soil, surface water or groundwater clean-up through the use of plants. This technology has been in development for the last twenty years and has received considerable interest from the environmental agencies, consultants and researchers.

The interest in phytoremediation relies essentially on the fact that there are low costs involved compared to other remediation technologies. Phytoremediation is relatively well accepted by regulatory agencies and most of the time avoids waste disposal and/or use of more aggressive remediation techniques.

Although much research has been done in order to explore the potential of phytoremediation, there are still some difficulties to overcome regarding the evaluation of effectiveness, especially when phytoremediation is used as a hydraulic barrier and, thus, changes in the hydrogeologic regime play a major role.

The lack of tools to assess the effectiveness of phytoremediation systems has led to the need for research and development of new methods and procedures to evaluate and quantify the processes occurring in these systems.

1.1. Aims

The general objective of this work is to evaluate the potential of groundwater modelling as a tool to quantify effectiveness and major hydrodynamic processes that occur in phytoremediation systems.

To evaluate the potential of groundwater modelling, a groundwater model of a phytoremediation system was built. The phytoremediation system is located in an industrial site in South Eastern Brazil.

In order to achieve the general objectives, specific objectives were delineated based on technical requirements and data availability, namely:

- Review of the processes involved in phytoremediation;
- Development of a hydrogeological / hydrogeochemical model for the studied site where phytoremediation was implemented; and

- Use of groundwater modelling tools to assess the effectiveness of phytoremediation using plants as hydraulic control barriers.

1.2. Motivation for the project

Although several phytoremediation studies have been conducted and monitored in field and benchmark scales, only a few of these studies have used numerical groundwater models to evaluate phytoremediation effectiveness. The use of groundwater models in this project contributes to the evaluation of these models as tools to support phytoremediation design, implementation and monitoring.

2. METHODOLOGY

In order to achieve the proposed objectives, several methods and procedures were used throughout the various stages of this study. It is important to emphasize that one of the objectives of this study is the evaluation of groundwater modelling as a method to quantify the effectiveness of phytoremediation systems in terms of hydrodynamic processes.

The methods and procedures can be divided according to the order in which these methods were used during the different stages of study:

- Literature report review;
- Data collation methods;
- Data analysis methods;
- Groundwater modelling methods; and
- Methods used during the analysis of modelling results.

Although a chronological order was used to subdivide the applied methods, several methods were conducted simultaneously, and many of them were reapplied or reviewed throughout the development of the study. A detailed description of the methods used during the different stages is provided below.

2.1. Literature and report review

A brief literature review was conducted prior to the study, in order to provide background information about the phytoremediation state of art. Several articles, scientific papers and presentations were analysed, and a compilation of the findings of these studies was prepared and is presented in Section 3.

2.2. Data collation

Most of the data used in this study was acquired previously, during the phytoremediation implementation and monitoring. A careful review and collation of all the available data was then prepared. Available data was essentially found in monitoring reports, implementation reports, and data obtained in spreadsheets, tables and figures.

All the collated data was stored in an Excel spreadsheet in order to provide a single source of information for the study, which allowed for quicker data analysis.

Several plans in AutoCAD data exchange data (DXF) were acquired, including site facilities, topographic contours, boreholes and surface water body locations. All the plans were merged into one single DXF file, in order to store all the graphical information in one source.

2.3. Data analysis

Once the data was collated and merged in the spreadsheets and DXF files, all the available data was analysed in order to create hydrogeological and hydrogeochemical conceptual models, as well as to convert the available data into the input and calibration format required by the groundwater modelling software.

From the data analysis, several graphs and tables were generated, as well as several grids containing interpolated monitoring results, in order to create proper contours. The data grids and contours were built using the software Surfer 8, released by Golden Software Inc., and Tripol, developed by the Institute for Groundwater Studies.

Furthermore, in order to facilitate the development of the conceptual model, three-dimensional representations of features such as borehole log data, location and site facilities were prepared using the software Rockworks 2006, developed by Rockware.

2.4. Groundwater modelling

Several methods were used during the groundwater modelling set-up and calibration. The whole modelling exercise consisted essentially of using the saturated groundwater modelling software MODFLOW, to create steady-state and transient calibrated models for the site and, once the calibrated models were built, estimated drawdown and evapotranspiration rates imposed by the phytoremediation system.

Most of the methods and guidelines used were based on procedures and software created by the United States Geological Survey (USGS) and are detailed in Section 6.

2.5. Analysis of modelling results

The results obtained from groundwater modelling are represented in an XY grid data format, such as hydraulic heads, drawdown and evapotranspiration rates. Based on the grid results, several contour maps were created using the software Surfer 8 released by Golden Software, Inc. The generated contours were overlaid with further information plans such as site plans and borehole locations.

Water balance results are provided as ASCII text files and were then exported to Excel spreadsheets in order to allow the creation of time series graphics and tables. The tables and graphics generated from these results allowed a conceptual analysis and interpretation of these results in terms of the phytoremediation framework.

3. PHYTOREMEDIATION TECHNOLOGY REVIEW

3.1. Introduction

The term phytoremediation was coined in the early 1990’s and is related to the set of technologies that uses plants for clean-up, or remediation, of soil, surface water and groundwater due to degradation, extraction or containment mechanisms. Since its inception, this technology has been of great interest to relevant stakeholders due to its relatively low costs, if compared to other conventional techniques used to date.

Field and laboratory tests have shown that phytoremediation, through its different processes, can be successfully applied to a wide range of contaminants, such as organic compounds (TPH, BTEX, PAHs), chlorinated compounds (trichloroethylene, tetrachloroethylene, chloroform), metals (lead, cadmium, zinc, arsenic, chromium, selenium), pesticides (atrazine, cyanazine, alachlor), radionuclides (cesium-137, strontium-90 and uranium), nutrient wastes (ammonia, nitrate and phosphate) and ammunition wastes (TNT and RDX).

3.2. Phytoremediation mechanisms

Phytoremediation acts on contamination in three different ways, namely containment, extraction and destruction. Containment of contaminants acts on its migration, reducing the migration rates or even stopping migration. Extraction processes include plant uptake and further volatilization, degradation or storage within the plant. Destruction of contaminants includes all biodegradation processes occurring within the plant, rhizosphere, soil, and water or aquifer media. Figure 3.1 shows the most relevant phytoremediation mechanisms.

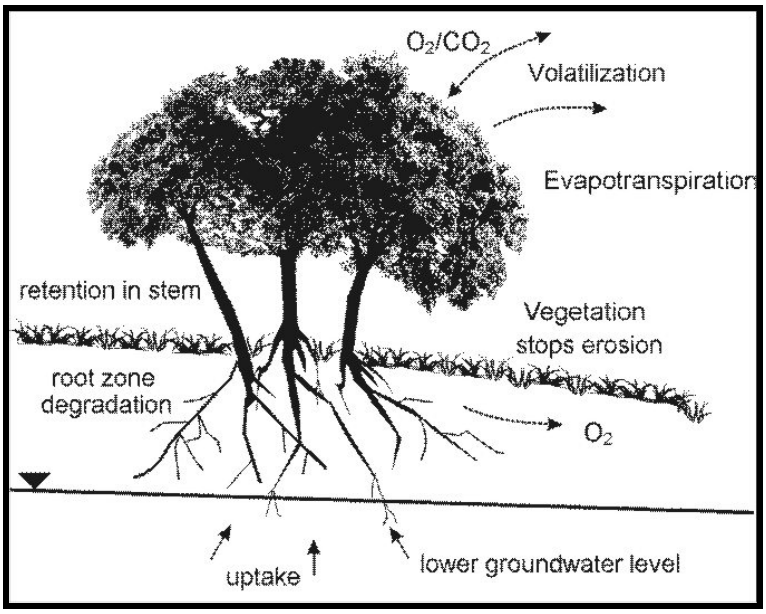

Figure 3.1 - Main phytoremediation processes (modified from Black, 1999).

According to USEPA (2000), the phytoremediation techniques can be grouped, based on their various mechanisms, as summarized in Table 3.1.

Table 3.1 - Phytoremediation mechanisms summary (modified from EPA, 2000).

Mechanism	Process Goal	Media
Phytoextraction	Contaminant extraction and capture	Soil, sediment and sludge
Rhizofiltration	Contaminant extraction and capture	Groundwater and surface water
Phytostabilization	Contaminant containment	Soil, sediment and sludge
Rhizodegradation	Contaminant destruction	Soil, sediment, sludge and groundwater
Phytodegradation	Contaminant destruction	Soil, sediment, sludge, surface water and groundwater
Phytovolatilization	Contamination extraction from media and released into the air	Groundwater, soil, sediment and sludge
Hydraulic control	Contaminant degradation or containment	Groundwater and surface water
Vegetative cover systems	Contaminant containment, erosion control	Soil, sludge and sediments
Riparian Corridors	Contaminant destruction	Groundwater and surface water

Each mechanism can be used for specific media and contaminants and will be described in detail in the following sections.

3.2.1. Phytoextraction

Phytoextraction can be defined as the translocation of contaminants from soil and/or water to the plant, by root uptake. The remediation is based on contaminant removal by harvesting the plants. According to USEPA (2000) the phytoextraction technique results in a much smaller mass to be disposed of, if compared with excavation methods.

Phytoextraction processes are primarily used in soil, sediments and sludge, although these processes can also be used, to a lesser extent, for treatment of surface and groundwater (USEPA, 2000). Most studies regarding phytoextraction mechanisms were conducted in sites and laboratories with metal contamination, as organic contaminants are more efficiently removed by phytovolatilization processes. However, phytoextraction can act as a secondary mechanism.

Regarding the uptake of organic contaminants, according to Pilon-Smits (2004), these compounds must not be too hydrophilic (log $K_{ow} < 0.5$) nor too hydrophobic (i.e. log $K_{ow} > 3$). When the organics are too hydrophilic they cannot pass through the plant membranes and, when the organics are too hydrophobic, they get stuck in the plant membranes and cannot enter the cell fluids.

Plants used in phytoextraction include Indian mustard (*Brassica juncea*) and sunflowers (*Helianthus sp.*) due to their fast growth, high biomass and high tolerance and accumulation of metals. Nanda Kumar et al. (1995), Salt et al. (1995) and Raskin et al. (1994) have reported that Indian mustard can accumulate lead, chrome (VI), cadmium, copper, zinc, strontium, boron and selenium. Adler (1996) has reported accumulation of cesium and strontium in sunflowers.

A special category of plants called hyperaccumulators have been researched due to their high performance in the phytoextraction processes. Brooks (1998) defines hyperaccumulators as plants that accumulate one or more inorganic elements to levels 100-fold higher than common species grown in the same conditions.

Although the hyperaccumulators can accumulate large concentrations of metal, these plants are usually slow-growing, have a small biomass and shallow root systems. In these cases, the use of metal accumulators, like corn, sorghum and alfalfa may be more effective (USEPA, 2000).

Site considerations regarding phytoextraction implementation include soil conditions, groundwater, surface water, contaminant concentrations and climatic conditions.

The selected plants will grow faster and be more effective in soils with favourable conditions and in soils with small or no leaching of contaminants. Depending on the selected plant, soil conditions, such as pH, may need to be adjusted. The addition of chelators can increase the bioavailability of the contaminants, improving the effectiveness of phytoextraction.

The phytoextraction is basically performed by plant uptake through its roots; and the clean up zone is restricted to the root system depth. Groundwater phytoextraction is, thus, restricted to unconfined aquifers with shallow water levels.

Contaminant concentrations are critical for the effectiveness of phytoextraction. High concentrations can have phytotoxic effects on the plants, decreasing the effectiveness or even causing the death of the whole system. Kumar et al. (1995) reported concentrations for cadmium, chrome (III and VI), copper, nickel, lead and zinc which are not phytotoxic to Indian mustard (*Brassica juncea*).

Climatic conditions must also be addressed, as most hyperaccumulators grow only under specific climatic conditions.

3.2.2. Rhizofiltration

Rhizofiltration mechanisms consist of contaminant adsorption and/or precipitation onto the plant roots. The sorbed/precipitated contaminant can be further uptaken, concentrated and translocated. Root exudation can cause or increase contaminant precipitation.

Unlike the phytoextraction techniques, the rhizofiltration mechanisms are not effective in soil remediation. Rhizofiltration mechanisms are more effective in high-water content conditions, such as ponds or tank systems (USEPA, 2000).

According to Young (1996), wetlands have been used successfully for many years in the treatment of nutrients, metals and organic contaminants. Wieder (1993) and Walski (1993) reported that the long-term wetlands use in treatment of acid mine drainage result in an increase in pH and a decrease in toxic metal concentrations. The use of wetlands can promote rhizofiltration processes, as well as other processes such as rhizodegradation, phytovolatilization and phytoextraction. Figure 3.2 shows a schematic representation of the main phytoremediation processes that occur in wetlands.

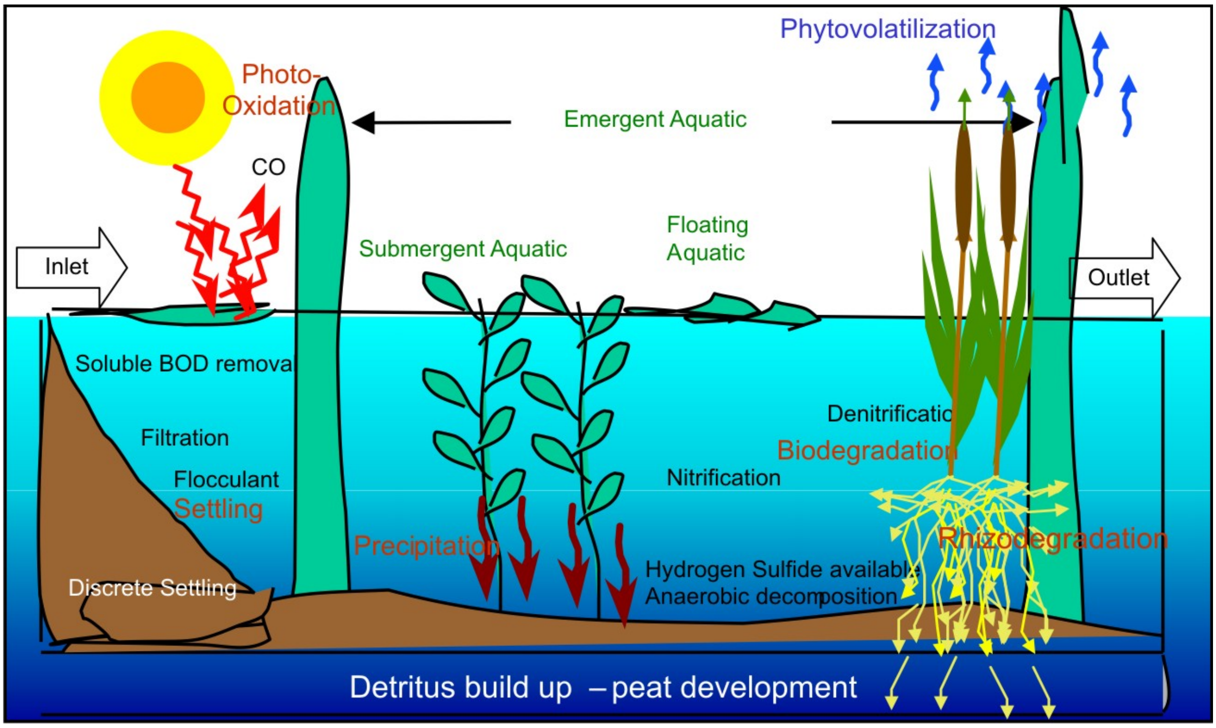

Figure 3.2 - Phytoremediation processes occurring in Wetlands (modified from ITRC, 2003).

Rhizofiltration has been researched and applied to metal and radionuclide contamination. Dushenkov *et al*. (1995) and Salt *et al*. (1997) reported effective rhizofiltration of lead, cadmium, copper, nickel, zinc and chromium using Indian Mustard (*Brassica juncea*) and Milfoil (*Myriophyllum spicatum*).

Radionuclide rhizofiltration has been applied in the United States Department of Energy pilot projects with uranium wastes and in water from a pond near the Chernobyl nuclear plant in Ukraine (Schnoor, 1997). Dushenkov *et al*. (1997) and Salt *et al*. (1997) have reported rhizofiltration of cesium and strontium in a bench-scale using sunflowers (*Helianthus sp.*) and Indian mustard (*Brassica juncea*).

Site considerations for rhizofiltration include root depth, soil conditions, groundwater and surface water conditions. Rhizofiltration is not sensitive to climatic conditions as the plants are in most cases grown in water and often inside greenhouses (USEPA, 2000).

Soil is basically used for cultivating plants prior to installation, as this technology mostly involves hydroponics or aquatic use of plants. According to USEPA (2000), the volumes of groundwater and/or surface water to be remediated must be estimated, as the ex-situ engineered rhizofiltration system needs to accommodate the predicted volume and discharge rates. Water chemistry must also be taken into consideration, and often requires a pre-treatment such as pH adjustment, filtration or other modifications in the water chemistry to improve the rhizofiltration effectiveness.

3.2.3. Phytostabilization

Berti (2000) defined phytostabilization as the use of plants to stabilize pollutants in soil, either by simply preventing erosion, leaching and runoff, or by converting pollutants to less bioavailable forms (e.g. via precipitation in the rhizosphere). Cunningham *et al*. (1995b) used the term phytolignification to refer to a specific form of phytostabilization where organic compounds are incorporated into plant lignin.

Phytostabilization is caused by rhizosphere microbiology and chemistry and/or alteration in the soil environment and contaminant chemistry. Soil pH can be modified by the plant due to the root exudates or production of carbon dioxide (USEPA, 2000). Soil affected by the plant can convert metals from a soluble to an insoluble oxidation state (Salt *et al*., 1995).

According to USEPA (1997a), phytostabilization can occur due to the chemical processes such as sorption, precipitation, complexation or metal valence reduction.

Phytostabilization is essentially applied in the treatment of soil, sediments and sludge and, according to USEPA (2000), has the great advantage of avoiding soil removal and disposal as well as enhancing ecosystem restoration. On the other hand, phytostabilization systems may require long-term monitoring and maintenance to prevent leaching, as the contaminant remains in place.

This technique is recommended in most cases only as an interim measure or where removal or treatment is not practically possible. It can also be used as a polishing technique when contaminant levels are below the target levels (Schnoor, 1997).

Contaminants for which phytostabilization can be used include arsenic, cadmium, chromium, copper, mercury, lead and zinc. Salt *et al*. (1995) reported the effective phytostabilization of copper, zinc and lead in mine wastes using Indian mustard (*Brassica juncea*) and grasses. Phytostabilization of cadmium through the use of poplars (*Populus sp.*) at mine wastes has been reported by Pierzynski et al. (1994).

Plants used in metal phytostabilization vary according to the contaminant concentration and site conditions. Plants termed metal-tolerant are used in sites with heavy metal-contaminated soils. The term metal-tolerant is assigned to plants which can live in soils with high metal concentrations.

Raskin *et al*. (1994) reported that Indian mustard (*Brassica juncea*) can reduce the leaching of metals in soil by over 98%. Salt *et al*. (1995) reported the use of Colonial bentgrass (*Agrostis tenuis* cv Coginan, and *Agrostis tenuis* cv Parys) and Red fescue (*Festuca rubra* cv Merlin) at mine wastes. Hybrid poplars were studied by Pierzynski *et al*. (1994) at a Superfund site to determine their metal tolerance.

Site consideration must be addressed for soil and climatic conditions. According to Cunningham *et al*. (1995a), phytostabilization is most appropriate and, thus more efficient, in heavy textured soils and soils with high organic matter content. Depending on soil conditions, amendments to the soil, such as the use of fertilizers, might be applied to increase the vegetation growth. These amendments can also help to phytostabilize the soil (Berti and Cunningham, 1997).Climatic conditions must be addressed, as the plants and thus the whole phytoremediation system can be impacted by weather conditions. Irrigation during dry seasons may be required according to precipitation rates.

3.2.4. Rhizodegradation

Rhizodegradation is also known as rhizosphere remediation, phytostimulation or plant-assisted bioremediation. It consists of creating favourable conditions for biodegradation through the increasing of bacteria, mycorhizal fungi and other factors that increase degradation of organic compounds in soil.

According to Jordahl *et al*. (1997), the number of beneficial bacteria increased in the root zone of hybrid poplar trees relative to an unplanted reference site. The number of denitrifiers, BTEX degrading organisms and general heterotrophs were also increased. Schnoor (1997) also reported that some plants may release exudates into the soil, which can promote or stimulate degradation of organic compounds. Stimulation occurs through the induction of enzyme systems in existing bacterial population, increasing the growth of new species that are able to degrade contamination, or increasing soluble substrate concentrations for all micro-organisms. Foth (1990) showed that the leakage of sugar, alcohols and acids can be between 10 to 20% of plant photosynthesis on an annual basis.

Anderson *et al*. (1993) have demonstrated that the plants help the microbial transformations metabolizing the organic pollutants through the Mycorrhizae fungi associated with plant roots, stimulating bacterial transformation through the plant exudates (enzyme induction), substrate enhancement through the build-up of organic carbon, and oxygen pumping to the roots, ensuring aerobic reactions.

Rhizodegradation techniques can be applied to soil, sediments, sludge and groundwater. Rhizodegradation in groundwater is however restricted to sites with shallow groundwater levels.

Contaminants that can be remediated by rhizodegradation include TPH (Total Petroleum Hydrocarbons), PAH (Polycyclic Aromatic Hydrocarbons), BTEX (Benzene, toluene, ethylbenzene and xylenes), pesticides, chlorinated solvents and Pentachlorophenol (USEPA, 2000).

Schwab (1998) studied several sites contaminated with TPH and demonstrated that rhizodegradation and humification were the most important mechanisms of contaminant disappearance, with little uptake occurring. Degradation of PAH (Chrysene, benzo(a)anthracene, benzo(a)pyrene, and dibenzo(a,h)anthracene) has been demonstrated to be much higher in vegetated soils than in non-vegetated soils (April and Sims, 1990).

Jordahl *et al*. (1997) reported that soil from the rhizosphere of poplar trees (*Populus sp.*) had higher populations of benzene, toluene and o-xylene degrading bacteria than non-rhizosphere soils. Experiments conducted by Anderson *et al*. (1994) showed that pesticides, such as atrazine, metolachlor and trifluralin herbicides have increased degradation rates in rhizosphere soils compared to non-rhizosphere soil.

Anderson and Walton (1995) reported greater mineralization of TCE in vegetated soil compared to non-vegetated soils. Ferro *et al*. (1994b.) reported that PCP (Pentachlorophenol) was mineralized at a greater rate in a planted system than in an unplanted system.

Site considerations for rhizodegradation include soil conditions, climatic conditions, groundwater and surface water. Soil's physical and chemical characteristics must allow for significant root penetration and growth (USEPA, 2000). Groundwater and surface water (through the unsaturated zone) movement can be induced by the transpiration of plants, moving contaminants to the root zone.

3.2.5. Phytodegradation

Also known as phytotransformation, phytodegradation is the set of processes including contaminant uptake and breakdown through metabolic processes within the plant, or breakdown of external contaminants through the reactions with compounds produced by plants.

Several groups of enzymes that are released (exudates) by plants can mineralise organic compounds, degrade organic compounds to stable forms that are stored in the plant and increase solubility. Enzyme groups involved in rhizodegradation include dehalogenases, mono- and di-oxygenases, peroxidises, peroxygenases, carboxylesterases, laccases, nitrilases, phosphatases and nitroreductases (Wolfe and Hoehamer, 2003).

Phytodegradation techniques can be used in soils, sediments, sludge and groundwater remediation. Surface water can also be remediated using phytodegradation through the irrigation of plants with the contaminated water or use of aquatic plants.

Contaminants that have been researched in phytodegradation studies include chlorinated solvents, herbicides, insecticides, munitions, phenols and nutrients.

Newman *et al*. (1997a) reported that TCE was metabolized to trichloroethanol, trichloro acetic acid through the use of poplar trees (*Populus sp.*). McCutcheon (1996) found the plant-formed enzyme dehalogenase in sediments. This enzyme can dechlorinate chlorinated compounds. Furthermore, Dec and Bollag (1994), reported that minced horseradish roots successfully treated wastewater containing up to 850 ppm of 2,4-dichlorophenol in the presence of oxireductase enzymes.

Carreira (1996) discovered a plant-formed enzyme nitrilase in sediments, which can promote herbicides degradation. Burken and Schnoor (1997) reported that atrazine in soil was taken up by trees and then hydrolyzed and dealkylated to less toxic metabolites within the roots, stems and leaves of the trees.

Applicability in phytodegradation of several plants has been investigated. McCutcheon (1996) reported that the aquatic plant Parrot Feather (*Myriophyllum aquaticum*) and the algae Stonewort (*Nitella*) have been used for degradation of TNT through the nitroreductase enzyme. This enzyme has also been identified in other plants, such as algae, ferns, monocots, dicots and trees.

Hybrid poplars have been reported to promote TCE and atrazine degradation by Gordon *et al*. (1997), Newman *et al*. (1997a) and Burken and Schnoor (1997). Poplars (*Populus sp.*) have also been used to remove nutrients from groundwater (Licht and Schnoor, 1993).

Conger and Portier (1997) demonstrated that Black Willow (*Salix nigra*), Yellow Poplar (*Liriodendron tulipifera*), Bald Cypress (*Taxodium distichum*), River Birch (*Betula nigra*), Cherry Bark Oak (*Quercus falcata*) and Live Oak (*Quercus viginiana*) were able to support some degradation of the herbicide bentazon.

Soil conditions, groundwater and climatic conditions are the main site considerations that must be addressed. According to USEPA (2000), phytodegradation is most appropriate for large areas of soil having shallow contamination. Groundwater in the saturated zone cannot be remediated by phytodegradation unless the water levels are shallower than the root system depth of the plants. However, groundwater, as well as surface water, can be pumped and use to irrigate the plants and, thus, promote phytodegradation. Regarding climatic conditions, research and pilot scale studies have been developed in a wide variety of climatic conditions and so far climate is not seen to be a critical factor.

3.2.6. Phytovolatilization

USEPA (2000) defines phytovolatilization as the uptake and transpiration of contaminant through the use of plants. The contaminants can be released in their original form or as metabolites. Processes involved in phytovolatilization include contaminant uptake, plant metabolism and plant transpiration. Phytodegradation mechanisms can occur simultaneously with phytovolatilization.

Phytovolatilization can be used in the remediation of soils, sediments, sludge and groundwater. It has, however, mostly been applied in groundwater remediation.

Contaminant metabolites can be more or less toxic than their original forms, depending on their composition. Less-toxic metabolites include elemental mercury and dimethyl selenite gas (originated from methyl mercury and selenium), while more toxic metabolites include vinyl chloride (originated from TCE).

Most of the use and research of phytovolatilization have been applied to TCE, selenium and mercury. TCE, and TCA (1,1,1-trichloroethane) and carbon tetrachloride phytoremediation have been reported by Newman *et al*. (1997a & b) and Narayanan *et al*. (1995).

According to Pyerzinski *et al*. (1994), selenium mercury and arsenic can form volatile methylated species and, thus, be phytovolatilized. Bañuelos *et al*. (1997 a & b) demonstrated that selenium has been taken up and then transpired from soil and groundwater. Meagher and Rugh (1996) showed that engineered plants were able to volatilize mercury and defined levels of phytotoxicity to unaltered plants.

Most studied plants in phytovolatilization systems include poplars (*Populus sp.*), Indian mustard (*Brassica juncea*) and Canola (*Brassica napus*). Newman *et al*. (1997a) demonstrated the phytovolatilization of TCE due to transformation to volatile forms within the trees. The use of Indian mustard and Canola used in phytovolatilization of selenium (as selenate) was reported by Adler (1996). In this study, selenate was converted to the less toxic form, dimethyl selenite gas, and then released into the atmosphere. A genetically modified weed from the Mustard Family was used to convert mercuric salts to metallic mercury and released it into the atmosphere (Meagher and Rugh, 1996). The weed was modified to include a gene for mercuric reductase, which is able to convert mercuric salts to less toxic forms. Figure 3.3 shows a hybrid poplar used on a site contaminated by TCE.

Figure 3.3 - Hybrid poplar used on a site contaminated by TCE (extracted from Chappell, 1997).

Phytovolatilization systems are sensitive to soil and weather conditions, thus, site consideration of implementation of these techniques include soil and climatic conditions. Soil must be able to transmit enough water to the plants in order to promote effective uptake and further volatilization. Climatic factors such as temperature, precipitation, humidity, insulation and wind velocity can affect transpiration rates (Tucci, 1993).

3.2.7. Hydraulic control

Phytoremediation through hydraulic control is the use of plants to change the groundwater flow direction in order to control the migration of contaminants. This technique is also known as phytohydraulics or hydraulic plume control. Specific types of plants can take up and transpire significant volumes of water and, thus, decrease the water levels. Depending on the volume extracted, the drawdown cones can create flow barriers and contain the contaminant migration.

Most effective hydraulic control occurs when the root depth is below the saturated zone and water uptake is made straight from the unsaturated zone. However, plants with root systems above the groundwater levels can influence contaminants in groundwater through interfacing with the capillary fringe, as demonstrated by Sheppard and Evenden (1985).

The hydraulic control can be used basically for groundwater and, to a lesser degree, for surface water remediation. According to USEPA (2000), contaminants that can be remediated through hydraulic control include all water-soluble organics and inorganic compounds, since their concentrations do not exceed phytotoxic levels.

Plants that are able to promote hydraulic control include phreatophytes, cottonwoods (*Populus deltoids spp.*) and hybrid poplar trees. Gatliff (1994) reported the use of cottonwood and hybrid poplar trees in seven sites to remediate shallow groundwater contaminated with heavy metals, nutrients or pesticides. Nelson (1996) reported the use of poplar trees (*Populus sp.*) to create a barrier to groundwater flow in a site contaminated by hydrocarbons.

Site considerations that must be addressed include hydrogeologic and climatic conditions. The amount of water that needs to be taken up in order to create the barrier will vary according to the aquifer parameters, such as thickness, hydraulic conductivity and specific yield. Climatic conditions such as precipitation, temperature and wind speed can influence the transpiration rates of the plants. Furthermore, transpiration rates are unlikely to be constant throughout the year due to seasonal changes.

3.2.8. Riparian Corridors

Riparian Corridors, also known as buffer strips, have been used for many years in the containment of erosion near rivers and surrounding areas. In the last fifteen years, studies have shown that the riparian corridors can also be used to contain migration of contaminants through the rivers. These corridors consist of buffer strips of plants and the remediation and/or containment occurs by the plant water uptake, contaminant uptake and plant metabolism (USEPA, 2000). In addition, the fauna and flora habitat can be greatly improved using of these techniques. Figure 3.4 shows a schematic cross-section of a typical riparian corridor.

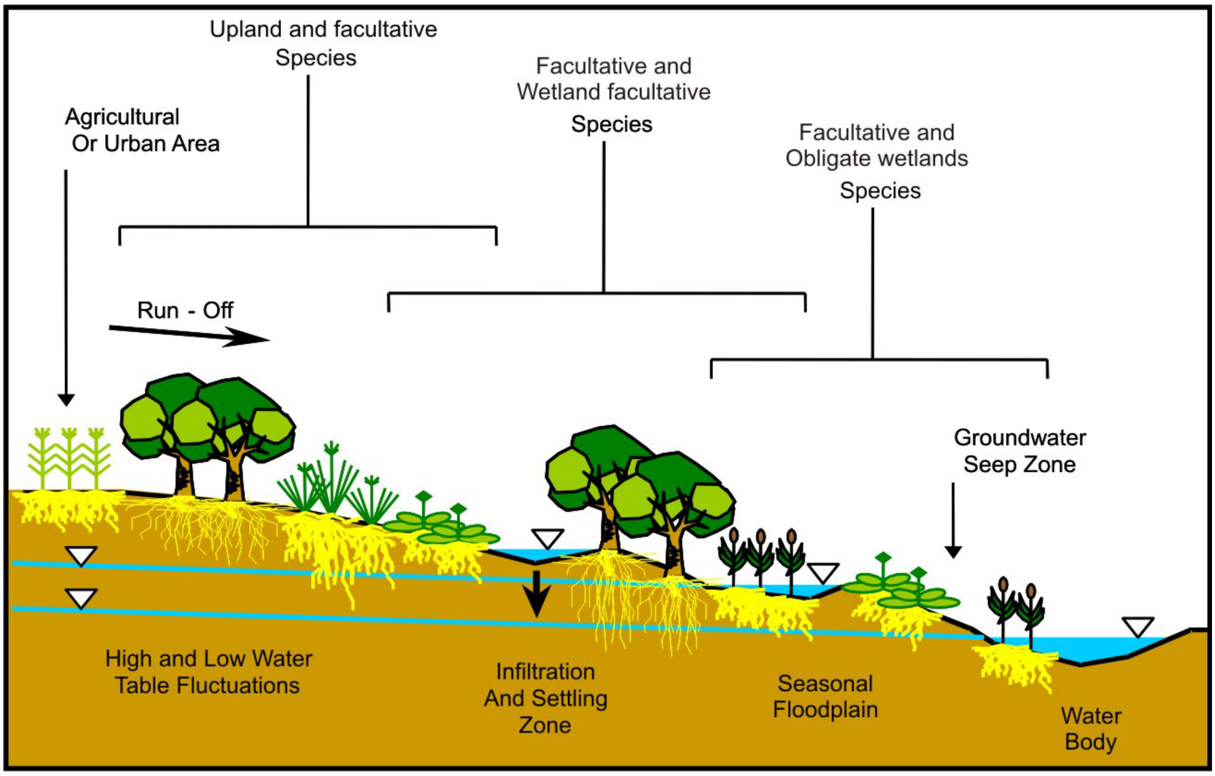

Figure 3.4 - Riparian corridor schematic cross-section (modified from ITRC, 2003).

Research on riparian corridors has focused on nitrate remediation in surface and groundwater media. Licht (1990) reported the use of poplar trees (*Populus sp.*) to control nitrate-nitrogen contamination in agricultural sites. Licht and Schnoor (1993) reported the use of riparian corridors to remediate nitrate in the field, and to promote mineralization of atrazine by poplar trees in the laboratory.

Site considerations regarding the use of riparian corridors include soil, weather and hydrogeologic conditions. Soil texture and the degree of saturation are critical factors in plant growth, although planting techniques can mitigate unfavourable conditions. Riparian corridors must have their root systems in contact with the contaminated media (groundwater and/or surface water) otherwise remediation will not be effective. The amount of water taken up by the plants is directly related to climatic conditions such as precipitation, temperature and wind speed.

4. DESCRIPTION OF THE STUDIED PHYTOREMEDIATION SITE

In order to evaluate the value of groundwater modelling as a tool to assess the effectiveness of phytoremediation systems, data from a phytoremediation system implemented in an area impacted by chlorinated compounds in South Eastern Brazil was used. This data was compiled and used to build site-specific steady-state and transient models to estimate drawdown and evapotranspiration rates. A summary of all obtained data is presented in the sections below.

4.1. Site overview

The site operational activities started in 1975 and included chemical and pharmaceutical manufacturing. All the industrial facilities and land was then sold to another pharmaceutical company, which continued the operational activities until December 1998, when the land was again sold to a chemical manufacturing company.

Most of the historical information of contamination events was provided by local workers who were employed during the operational period of the site. Several contamination events were reported on the site during its operational activities.

Local workers reported that during the years of 1985 and 1986 a major effluent leakage occurred in the building 1000 and 2000 areas. The leakage occurred in a pipeline that transported the effluents from the building to the neutralization tanks, causing it to collapse onto the floor of these buildings. The effluent reached the underground sewage systems and a local water course, causing the death of the fish population in the nearby drainages. In 1989, another effluent leak occurred close to the building 2000, also causing the collapse of the floor.

The first neutralization tanks were built directly over the ground and operated during the periods of 1975 to 1992. These neutralization tanks likely suffered some leakage and, thus, posed a potential contamination source. These tanks were deactivated in 1992, when new neutralization tanks were built. During the building of these tanks, a sewage pit was found. According to local workers, this pit was used to receive the laboratories and sanitary sewage between 1975 and 1985. The new neutralization tanks were used until 1994, when the industrial facility ended its operations.

Potential contaminants existing in pharmaceutical effluent include chlorinated compounds (such as chloroform and acetone), BTEX and inorganic compounds (such as sulphate and chloride).

Old solvent storage facilities included raw material storage tanks that were potential sources of contamination, which might have occurred during discharge and storage events. Compounds of the raw material include 1,2-dichloroethane, chloroform, methanol, isopropanol, acetone, toluene and ethylic alcohol.

An environmental study including borehole drilling, soil and groundwater sampling was performed in the industrial area in 1997. The results of the study indicated the presence of acetone in the soil and chloroform, benzene and acetone in the groundwater. Table 4.1 shows the highest concentrations of these compounds found during the environmental study.

Table 4.1 - Maximum concentrations found in the environmental study (1997).

Compound	Soil (mg/kg)	Groundwater (mg/l)
Acetone	13	120
Chloroform	ND	220
Benzene	ND	0,93

In addition, other contaminant events due to the operation of infiltration ponds occurred between 1975 and 1992, the periods during which the ponds remained active. These events will not be described and are not included in this study, as the infiltration ponds were located on the other side of the water divide and, thus, do not have any hydrogeological relation with the leakage events that occurred from the industrial facilities.

4.2. Phytoremediation system

In order to mitigate the impacts caused by the contamination events that occurred between 1985 and 1989, a remediation plan was designed. *In-situ* oxidation and phytoremediation were applied in different site areas, according to the contaminant concentrations.

In-situ oxidation was performed using the Fenton peroxide reagent in the source areas where chloroform concentrations exceeded 200 mg/l. The first injection events were performed in January of 2000 in the injection boreholes PI-01 and PI-02. The injected volumes varied from 0.3 to 25 cubic metres with peroxide concentrations between 5 and 12.5%. Additional injection events were performed in May and June of 2003 to eliminate remnant concentration from the residual phase. Figure 4.1 shows an injection event performed in the injection borehole PI-01 in May 2003.

Figure 4.1 - Peroxide injection in the injection borehole PI-01, May 2003.

Down-gradient of the source area is an artificial lake (dam), which was a potential receptor of the contamination plumes. A phytoremediation system was therefore implemented between the contamination source (industrial area) and the lake to act as a final last barrier to eventual contamination. Figure 4.2 shows the phytoremediation system and Figure 4.3 shows the phytoremediation plan view. Several techniques could have been used to address the area between the source and the lake, but the original intention was to provide an additional low-cost safety measure to protect the lake. Thus, phytoremediation was considered to be the best option at the remediation design stage.

Figure 4.2 - Phytoremediation system and down-gradient lake, April 2002.

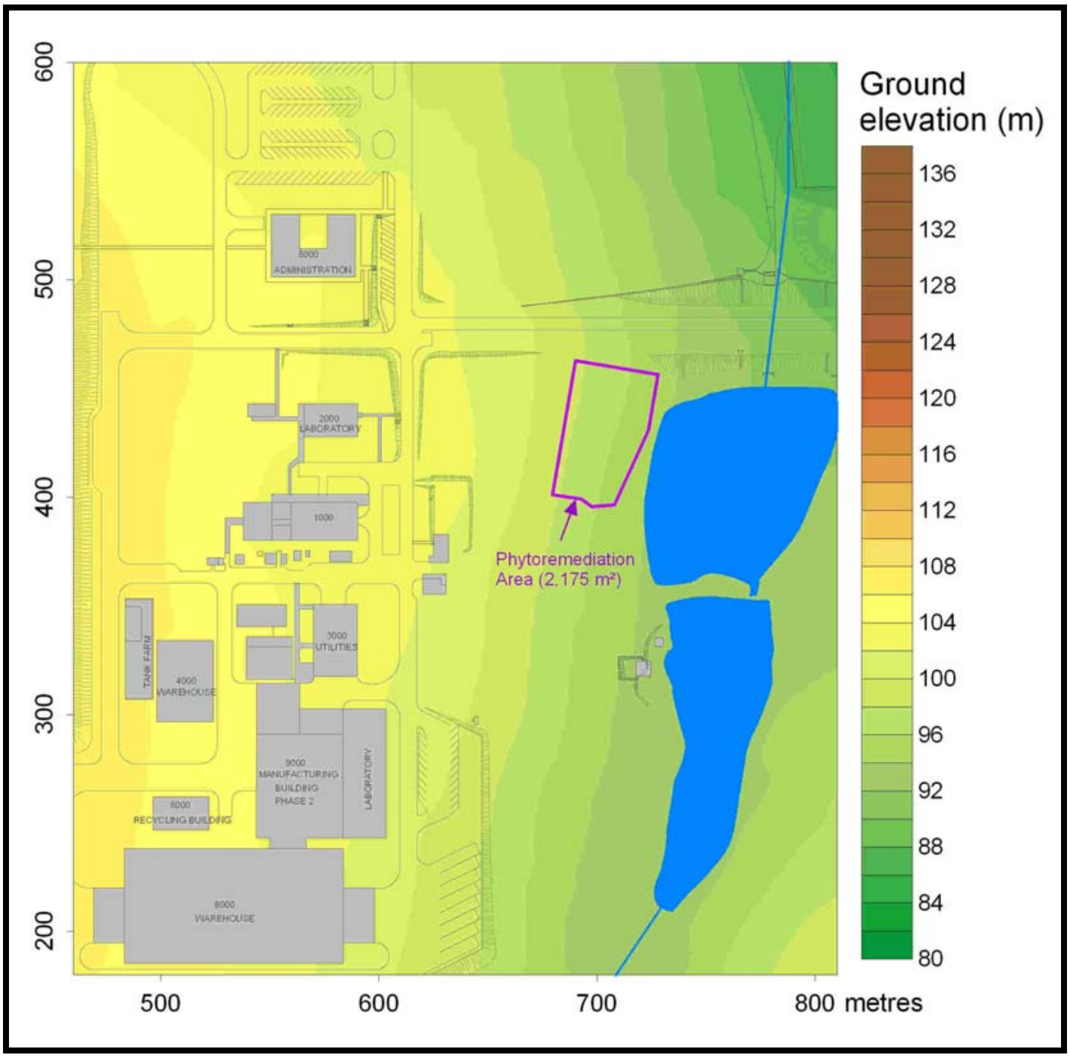

Figure 4.3 - Phytoremediation plan.

The main objectives of the phytoremediation on the site were to promote a hydraulic barrier to remnant contamination from the source areas and increase the biodegradation in the area.

Plants from mesophytic tropical wet forests and from the Cerrado[1] were selected and 179 trees were planted in an area of 2,175 square metres. Plants with broad leaves, which were non-deciduous and fast growing with wind-dispersed seeds (i.e. fruits not consumed by birds or mammals) were prioritized. Plants from wet forests were planted close to the lake due to the fact that the water levels are shallower in those areas, while Cerrado plants were planted in areas further from the lake, where the groundwater levels are slightly deeper. The phytoremediation layout of the plants is shown in Figure 4.4 and Table 4.2 summarizes the plant species used in the phytoremediation system.

[1] Cerrado is the African savanna equivalent climate.

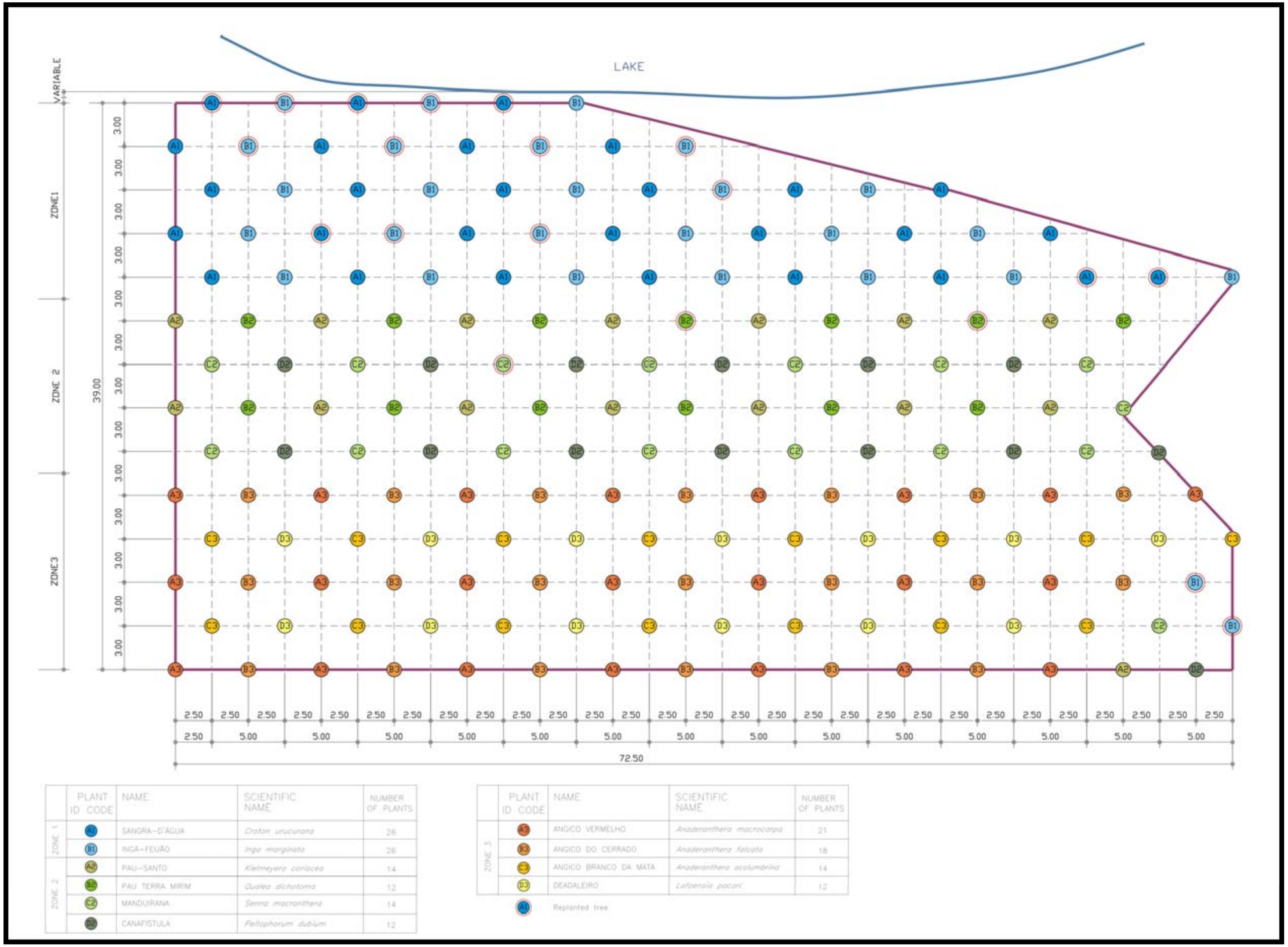

Figure 4.4 - Phytoremediation plant layout.

Table 4.2 - Plant species used in the phytoremediation system.

Plant ID Code	Local Name	Scientific Name	Typical Climate	Adult Size
A1	Sangra d'água	*Croton urucurana*	Wet areas	7-14m
B1	Ingá-feijão	*Inga marginata*	Wet areas	5-15m
A2	Pau-santo	*Kielmeyera coriacea*	Cerrado	3-8m
B2	Pau-terra-mirim	*Qualea dichotoma*	Cerrado	10-18m
C2	Manduirana	*Senna Macranthera*	Wet areas	6-8m
D2	Canafístula	*Peltophorum dubium*	Wet areas	15-25m
A3	Angico-vermelho	*Anadaranthera macrocarpa*	Cerrado	13-20m
B3	Angico-do-cerrado	*Anaderanthera falcate*	Cerrado	8-16m
C3	Angico-branco-da- mata	*Anaderanthera columbrina*	Cerrado	12-15m
D3	Deadaleiro	*Lafoensia pacari*	Cerrado	10-18m

After eighteen months, fifteen percent of the plants had died and were replaced by new plants. The cause of the deaths remains unknown. It is unlikely that the plants died due to phytotoxicity as the root systems probably had not reached the saturated zone.

In order to evaluate the efficiency of the phytoremediation, a monitoring program was undertaken. Seven monitoring boreholes (PZF-1, PZF-2, PZF-3, PZF-4, PZF-5, PZF-6 and PZF-7) were installed before planting in order to obtain baseline data. Figure 4.5 shows the location of these boreholes.

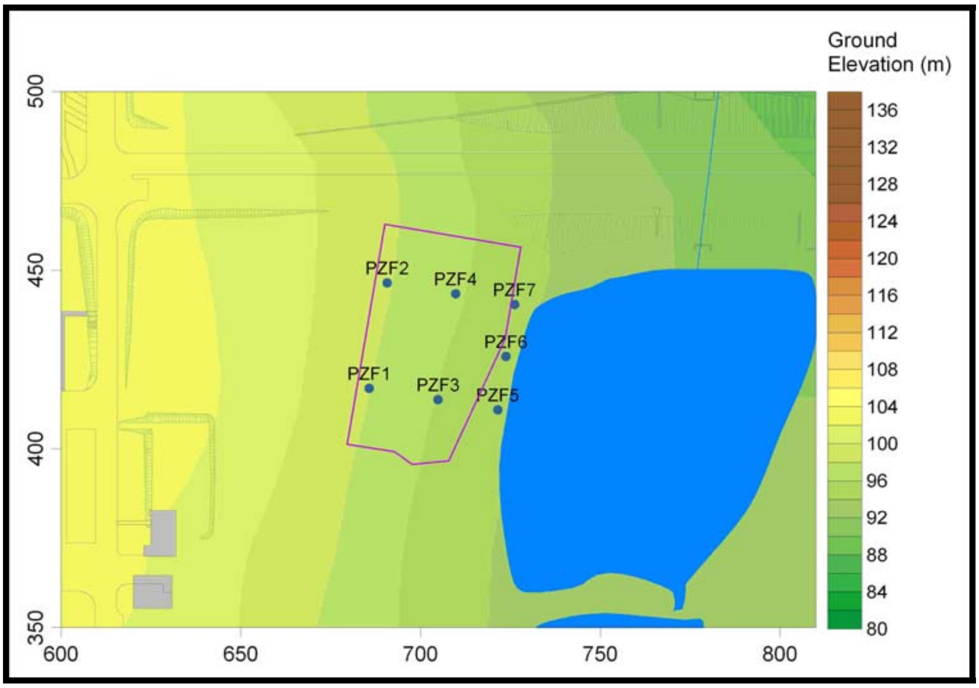

Figure 4.5 - Phytoremediation monitoring borehole positions.

Parameters that were monitored included soil, groundwater and plant characteristics. These parameters are summarized in the table below.

Table 4.3 - Parameters monitored throughout the phytoremediation process.

Parameter	Frequency			
	Baseline	Monthly	Quarterly	Annual
Groundwater parameters				
VOC (Volatile Organic Compounds)	X		X	
Chloride	X		X	
TDS (Total Dissolved Solids)	X		X	
TOC (Total Organic Carbon)	X		X	
In-situ parameters[2]	X		X	
Background parameters[3]	X		X	
Soil parameters				
Macronutrients[4]	X			X
Cation/ Anion[5]	X			X
Moisture	X			X
TOC (Total Organic Carbon)	X			
Sieve analysis	X		X	
Plant parameters				
Plant height	X		X	
Growth rates		X		
Survival rates		X		
Pest / diseases examination	X	X		
Hydrological parameters[6]				
Rainfall rates	X	X		
Potential evapotranspiration rates		X		
Temperature rates		X		

[2] *In-situ* parameters include groundwater levels, Eh, pH, dissolved oxygen and temperature.

[3] Background parameters include sulphate, sulphide, nitrate, iron (Fe^{2+} and Fe^{3+}), magnesium, sodium and alkalinity.

[4] Macronutrients include nitrogen, phosphorus and sulphur.

[5] Cation/Anion scan includes sodium, calcium, magnesium, iron, potassium, manganese, chloride, sulphate, nitrate, carbonate and bicarbonate.

[6] All the hydrological parameters were acquired from nearby meteorological stations.

4.3. Geology

The outcropping geology in the study area is constituted by the sedimentary rocks of the Itararé sub-group. The Itararé sub-group is the geologic record of a glacial sedimentation that occurred in the Permo-carboniferous Period and, together with the post-glacial sedimentary rocks of the Furnas Formation, constitutes the Tubarão Group. Figure 4.6 shows a geologic sketch of the region.

The Itararé sub-group overlies, through an erosive contact, the Tatuí Formation or the granitic/metamorphic basement. The average thickness is approximately 370 metres.

This stratigraphic unit is characterised by its high heterogeneity and absence of layers or lenses with large lateral extension. According to Chang (1984), the high heterogeneity observed in this sub-group is related to the variety of sedimentary environments, modified by glaciation and deglaciation periods; and the extreme heterogeneity of the detritic supply, dominantly of glacial origin.

DAEE (1981) subdivided the sub-group into three sub-units (lower, intermediate and upper units), based on the sandstone percentages. The study area is classified as the lower unit and consists mainly of by reddish mudstones and greenish grey diamectites. Shales of marine origin can be found within these lithologies.

Logs of deep water-supply boreholes drilled near the site indicated an interlayering of highly compacted greyish clayey lenses, fine to medium sandstones and mudstones.

Volcanic rocks belonging to the Serra Geral Formation are found outcropping to the north of the site and as sills in the study area. These volcanic rocks are mainly basalts of the lower cretaceous age.

The weathered horizons show a relatively higher homogeneity, probably as result of weathering processes. These horizons are composed of silty and sandy clay layers with thicknesses ranging between 15 and 20 metres. The weathered horizons in the basalt sill areas show a higher clay percentage.

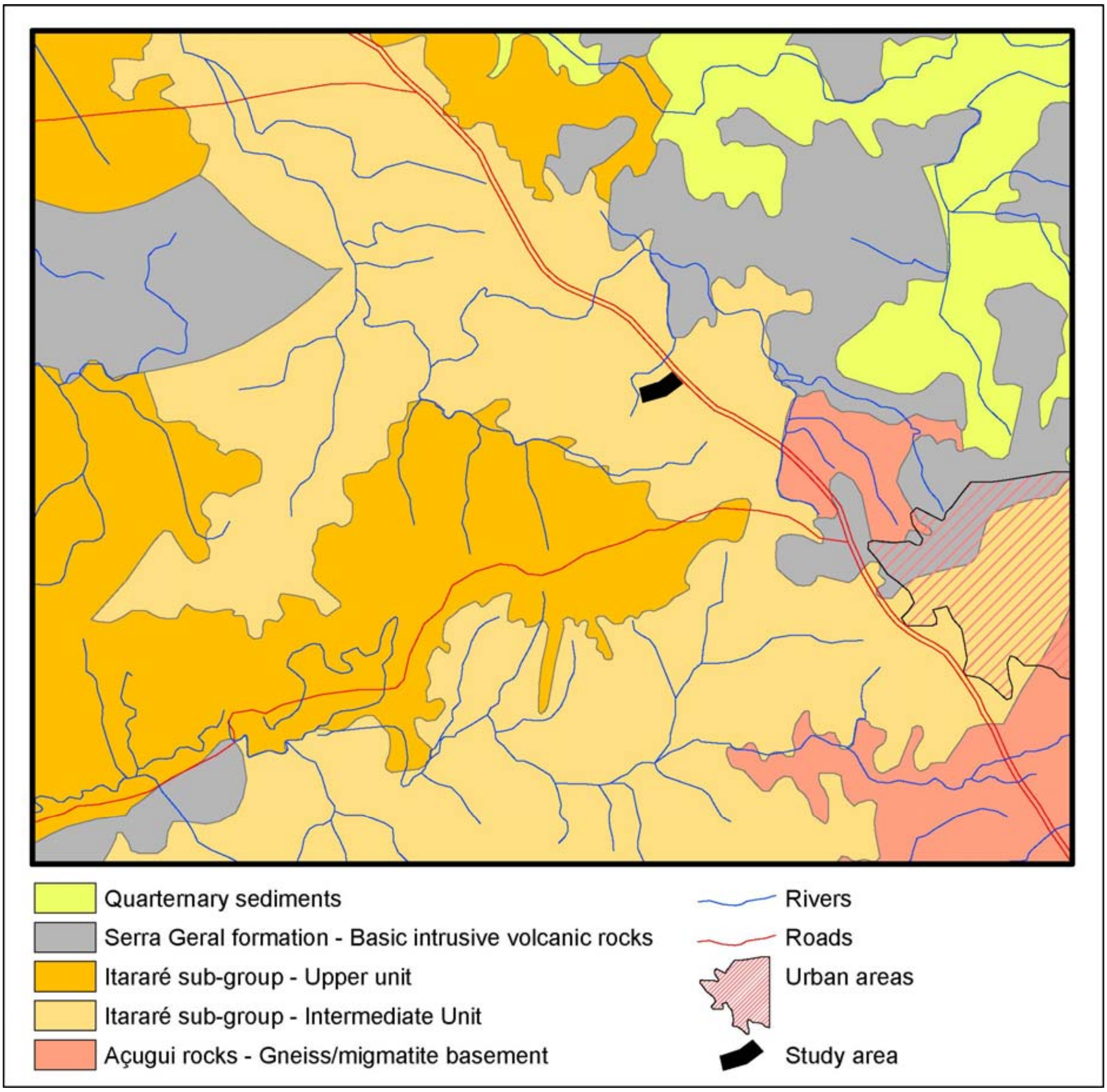

Figure 4.6 - Geology sketch of the study area (adapted from DAEE, 1981).

The rocks from the Açugui and Serra Geral Formations have the porous media groundwater occurrence restricted to the weathered horizons, due to the crystalline character of the metamorphic and volcanic rocks. Fractured flow in these rocks may occur in the unweathered horizons through faults and secondary fractures.

Sedimentary rocks from the Itararé sub-group show A primary porous media occurrence in both weathered and unweathered horizons, where the major occurrence is located in the weathered zone. Fractured flow also occurs in the sedimentary rocks, mainly along fault planes and minor fractures. In addition, groundwater occurrence in the quaternary sediments is predominantly porous, without the presence of faults or secondary fractures.

The weathered horizon in the area constitutes an aquifer with unconfined behaviour. Depending on the permeability values of the overlying weathered horizon, the unweathered zone might have a semi-confined to confined behaviour.

4.4. Hydrology and climate

Hydrological data was obtained from a variety of sources. Daily rainfall data from 1988 to 1999 and 2001 to 2004 was obtained on the ANA (Agência Nacional de Águas) Hidroweb homepage. The Hidroweb homepage is a free service provided by ANA where most of the Brazilian hydrological data is stored and available for download.

Monthly rainfall, temperature and potential evapotranspiration data was obtained from CIIAGRO (Centro Integrado de Informações Agrometeorológicas). All the data was gathered at a weather station located approximately eight kilometres from the site.

The study area is characterized by its sub-tropical climate, with average temperatures of 17 degrees Celsius in the winter months (May-July) to 27 degrees Celsius in the summer months (December-February).

Potential evaporation rates range from 25 to 150 mm/month. The hotter months have the higher potential evapotranspiration rates, while the smaller rates are found in the colder months.

Average monthly rainfall rates vary from 20 mm/month in the dry season to 280 mm/month in the wet season. However, rainfall peaks up to 350 mm/month can be found throughout the historical series. Figure 4.7 illustrates the average monthly rainfall dates, based on data from 1988 to 2004. Figure 4.8 summarizes the time series data of the monitored hydrologic parameters.

The hot seasons (spring and summer) act as catalysers in the hydrological cycle, in the sense that the increase in temperature accelerates evapotranspiration rates and, consequently, accelerates rainfall rates. Thus, exchange rates between groundwater, surface water and atmosphere are increased in these seasons.

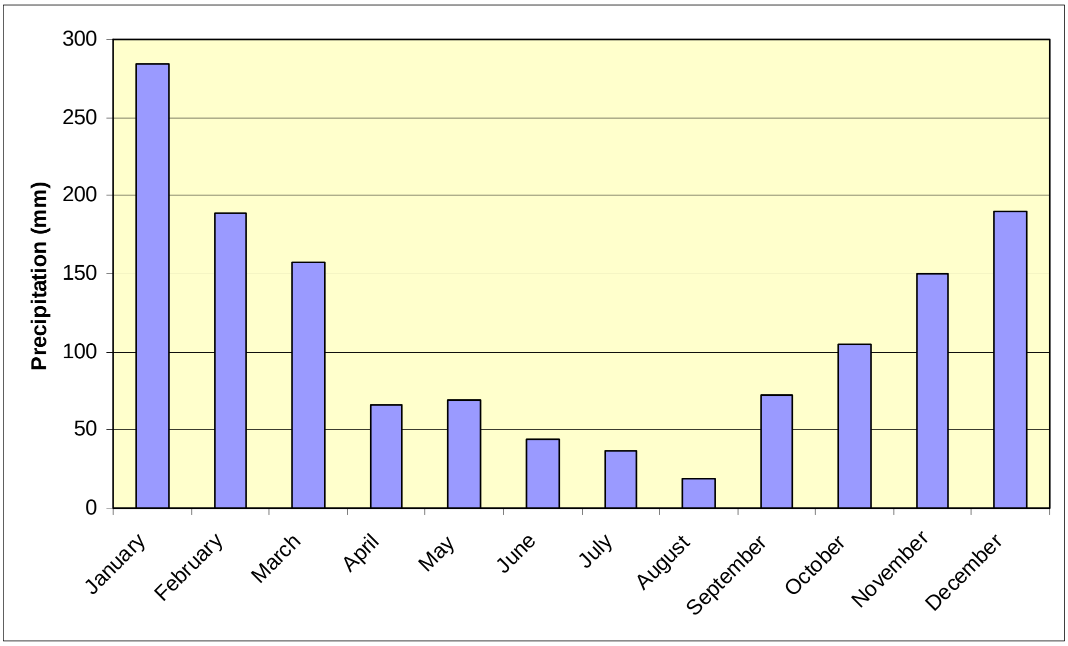

Figure 4.7 - Average monthly rainfall rates.

Run-off estimations were conducted using the SCS method (SCS, 1957) in order to obtain the rainfall fraction that infiltrates the soil. The SCS method makes use of the assumption that the ratio between the total rainfall and rainfall that flows on the ground surface as run-off (effective rainfall) is similar to the ratio of infiltrated volume and maximum soil capacity, using the following equation :

$$Q = \frac{(P - 0.2\ S)^2}{P + 0.8\ S}$$

Where Q is the effective rainfall, P is the total rainfall and S is the maximum soil capacity. S values can be determined by the expression:

$$S = \frac{25400}{CN} - 254$$

Where CN is an empirical value that reflects the conditions of soil and soil cover and can be found in the table presented by SCS (1957).

Run-off ratios show significant variation throughout wet and dry seasons. During the wet seasons, 35 to 55% of rainfall flows through drainages and streams, while only 1 to 15% of rainfall flows as run-off in the dry seasons. Considering an effective recharge between 5 and

10%, approximately 35 to 60 % of rainfall water returns to the atmosphere by evapotranspiration in wet seasons and 30 to 75% returns to the atmosphere during the dry seasons.

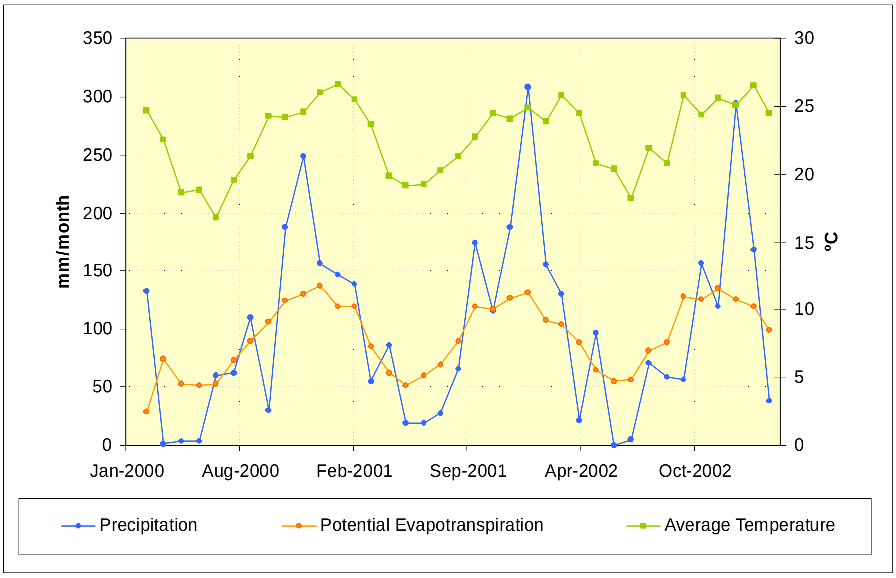

Figure 4.8 - Time series of the monitored hydrological parameters.

4.5. Hydrogeology

4.5.1. Aquifer description

The aquifer impacted by the contamination events on the site is basically restricted to the weathered zone of sedimentary rocks from the Tubarão Group and basic intrusive rocks from the Serra Geral Formation. This weathered zone constitutes an unconfined aquifer composed of sandy to clayey soils with some small gravel lenses, according to the original lithologies.

The thickness of this weathered zone is about 20 metres, overlying an unweathered basalt sill. It is likely that the contaminants did not flow through the basalt unweathered zone, which acts as a flow barrier to the lower lithologies. In addition, it is unlikely that there was fractured flow in the weathered zone, due to the absence of faults and image lineaments in the area.

The weathered zone can be divided in two zones, or layers, according to its soil texture. The upper layer is composed of a sandy-clay soil with thickness ranging from 4 to 8 metres. The lower layer is composed of a silty-clay or clayey soil with thickness ranging from 4 to 16 metres.

Inflow into the aquifer is primarily composed by direct recharge from rainfall. Recharge/rainfall rates are dependent on soil use and ground slope. Areas with pavement, such as buildings and roads, may have lower recharge and higher runoff rates. However, horizontal flow occurring in the unsaturated zone may attenuate this effect.

Outflow includes natural drainages and the artificial lake, which is situated next to the phytoremediation area. In dry seasons the lake can promote some inflow depending on the groundwater levels.

4.5.2. Aquifer parameters

Pumping test data from the site only includes slug tests performed in the monitoring and pumping boreholes located near to the deactivated infiltration ponds and, thus, there is no available data near the phytoremediation area. The hydraulic conductivities obtained from these boreholes were used as guides, as the lithologies in the deactivated ponds and phytoremediation areas are similar.

Table 4.4 summarizes the results obtained from the slug tests performed in the deactivated ponds area. The histogram of the hydraulic conductivities obtained by the slug tests is shown in Figure 4.9.

The hydraulic conductivities range from 0.0181 to 9.42 m/day. Higher conductivity values are related to the sandy weathered horizons while the lower conductivity values are related to horizons composed predominantly of silt and clay.

The geometric mean of 0.61 m/day seems to be more representative than the average for the area, due to the large range of the hydraulic conductivities. Furthermore, conductivity values on the industrial buildings and phytoremediation areas are expected to be slightly lower, due to the clayey soil composition.

Storage parameters such as porosity and specific yield were not calculated for the area, as the slug test data is in most cases not adequate to estimate such parameters.

Considering the following parameters constant throughout the remediation area:

- Groundwater gradient: 1.5 %
- Hydraulic conductivity: 0.61 m/day
- Specific yield: 0.04

A value of 0.22875 m/day is expected for the groundwater flow velocity. Using the phytoremediation width of 60 metres and the average aquifer thickness of 20 metres, a flow rate of 10.98 m^3/day is expected through the phytoremediation area. The estimated volume stored in the phytoremediation area is approximately 1740 cubic metres.

These estimations are very limited considering the assumptions and inherent uncertainties regarding the aquifer parameters and, therefore, were only intended to be used for conceptual purposes. A detailed calculation of overall flow rates and estimated storage is shown in Section 6.5.4.

Table 4.4 - Results from the slug tests performed in the infiltration ponds area.

Borehole	Hydraulic Conductivity (m/day)	Borehole	Hydraulic Conductivity (m/day)
PB-1	1.53	PB-12	3.41
PB-2	1.04	PB-13	9.42
PB-3	2.24	PZ-A	0.03
PB-4	4.29	PZ-B	0.03
PB-5	8.24	PZ-C	0.50
PB-6	1.27	PZ-D	1.30
PB-7	0.18	PZ-E	0.10
PB-8	0.36	PZ-F	0.04
PB-9	4.44	PZ-I	0.35
PB-10	0.83	PZ-O	0.02
PB-11	2.31	PZP	0.05
		Average	1.93
		Geometric Mean	0.61

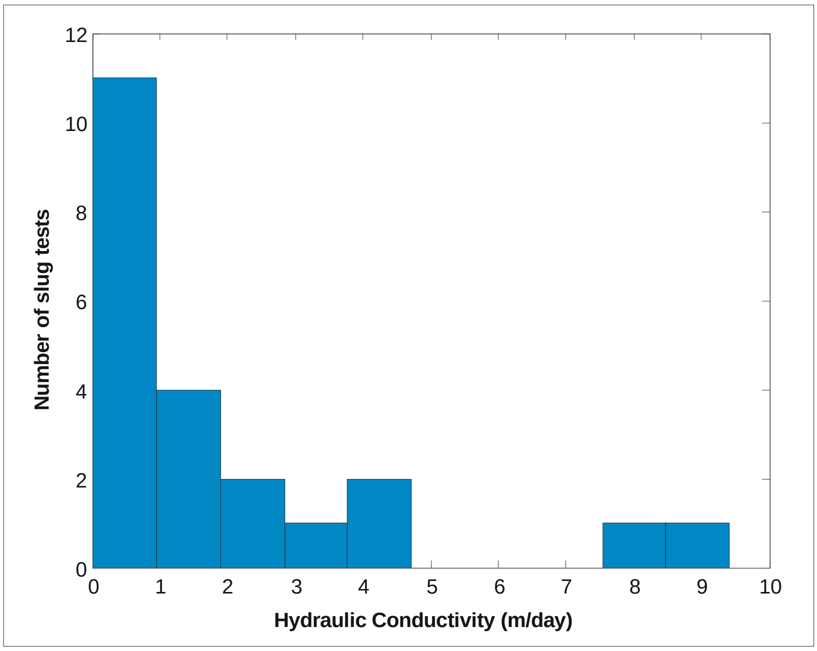

Figure 4.9 - Histogram of the results obtained from the slug tests.

4.5.3. Groundwater levels

Groundwater level measurements were undertaken in the phytoremediation monitoring boreholes (PZF-1 to PZF-7) on average, on a three-monthly basis. In addition, measurements were undertaken in the monitoring boreholes drilled near the source area (i.e. the industrial buildings) during the source area monitoring events. The water levels from the phytoremediation monitoring boreholes are shown in Table 4.5.

Table 4.5 - Water levels measured in the phytoremediation boreholes.

Borehole	Ground elevation (metres)	Water levels							
		August 2000	March 2001	June 2001	August 2001	December 2001	May 2002	October 2002	January 2003
PZF-01	98.03	92.87	93.82	93.14	92.66	92.54	93.14	92.45	92.84
PZF-02	98.15	92.53	93.39	92.9	92.38	92.15	92.78	92.14	92.56
PZF-03	96.14	92.55	92.9	92.7	92.47	92.36	92.71	92.33	92.61
PZF-04	96.91	92.41	93.04	92.66	92.3	92.16	92.60	92.11	92.45
PZF-05	94.16	92.60	92.46	92.41	92.43	92.28	92.43	92.38	92.47
PZF-06	94.13	92.41	92.5	92.43	-	92.27	92.43	92.37	92.45
PZF-07	94.6	92.9	92.4	92.42	92.4	92.24	92.41	92.35	92.44

The average groundwater levels range from 92.9 to 92.44 metres, using the data obtained from August 2000 to January 2003. The groundwater level oscillation is mostly related to rainfall. It is also noted that the higher oscillations were observed in the boreholes further from the lake (PZF-1, PZF-2, PZF-3 and PZF-4), while the boreholes close to the lake show very small oscillations as observed in Figure 4.10 and Figure 4.11. This fact indicates the strong influence of the lake on the nearby water levels.

Comparing the rainfall rates oscillation and groundwater levels oscillation, a time delay is noted between rainfall and recharge in the unsaturated zone. The relationship between rainfall and recharge will be discussed in detail in Sections 4.5.2, 5.1 and 6.5.4.

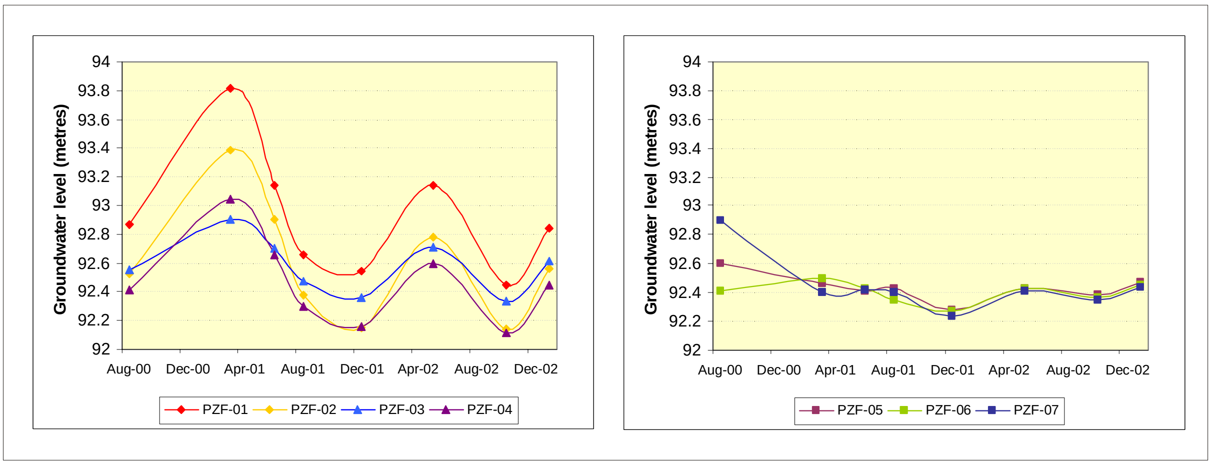

Figure 4.10 - Groundwater level oscillation in the monitoring boreholes.

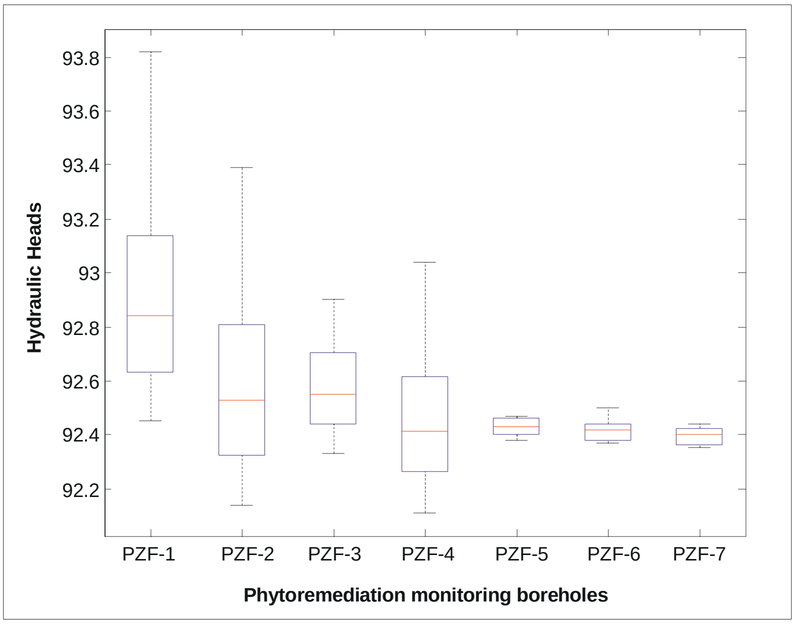

Figure 4.11 - Box and whiskers diagram of the water levels measured in the phytoremediation boreholes.

The groundwater flow directions show two distinct patterns throughout the different seasons. Groundwater contours for the source and phytoremediation areas are shown in Figure 4.12 and Figure 4.13.

After the wet seasons, which are characterized by periods of large recharge, the groundwater gradients range between 1 and 5% and flow directions are clearly towards the lake and local drains, which act as outflow zones to the aquifer.

After the dry seasons, which are characterized by low recharge rates, groundwater gradients are notably decreased, ranging from 0 to 2.5% and occasionally some flow inversion from the lake to up-gradient areas is observed. This fact possibly indicates some contribution from the lake to the aquifer during the dry seasons. Figure 4.14 illustrates the inversions in flow directions that occurred near the lake and Figure 4.15 shows the groundwater level gradient magnitudes.

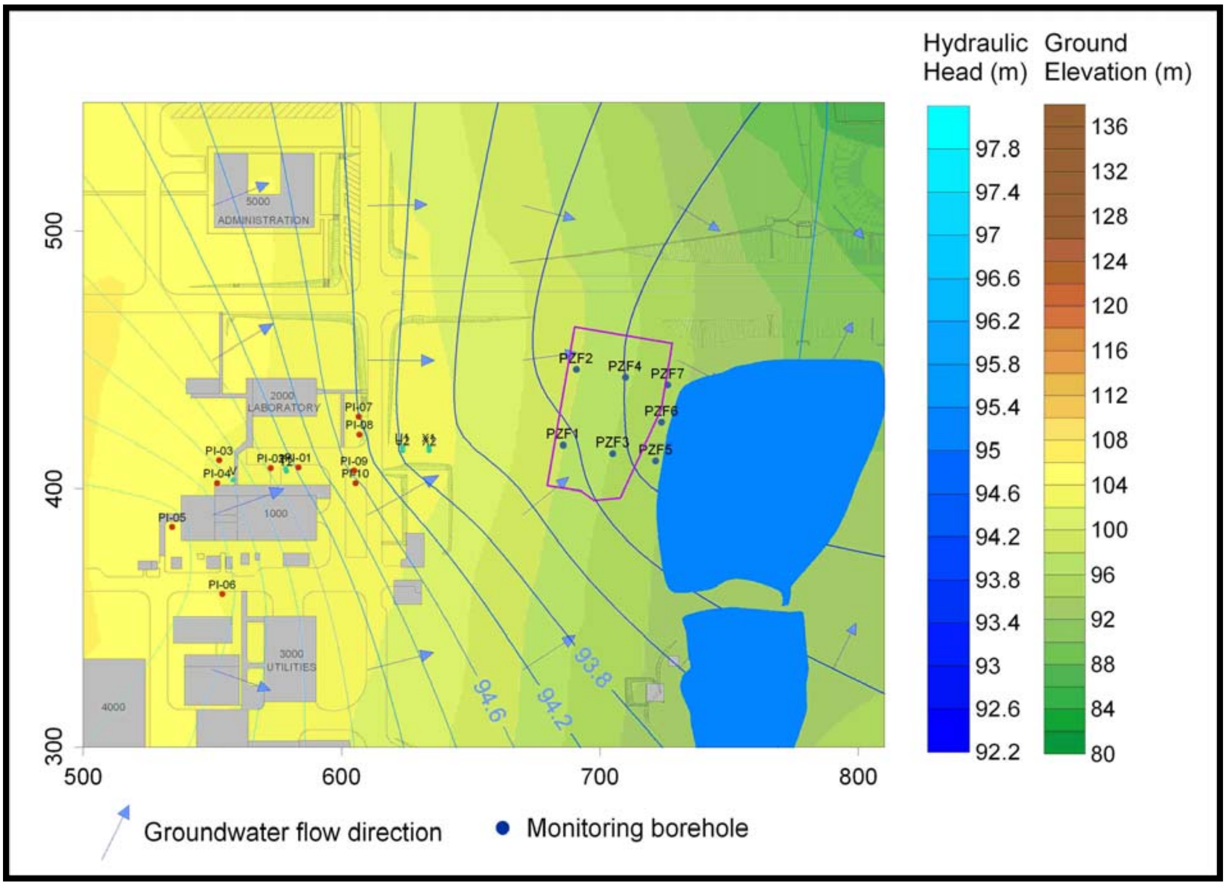

Figure 4.12 - Interpolated groundwater contours for phytoremediation and source areas - May 2002.

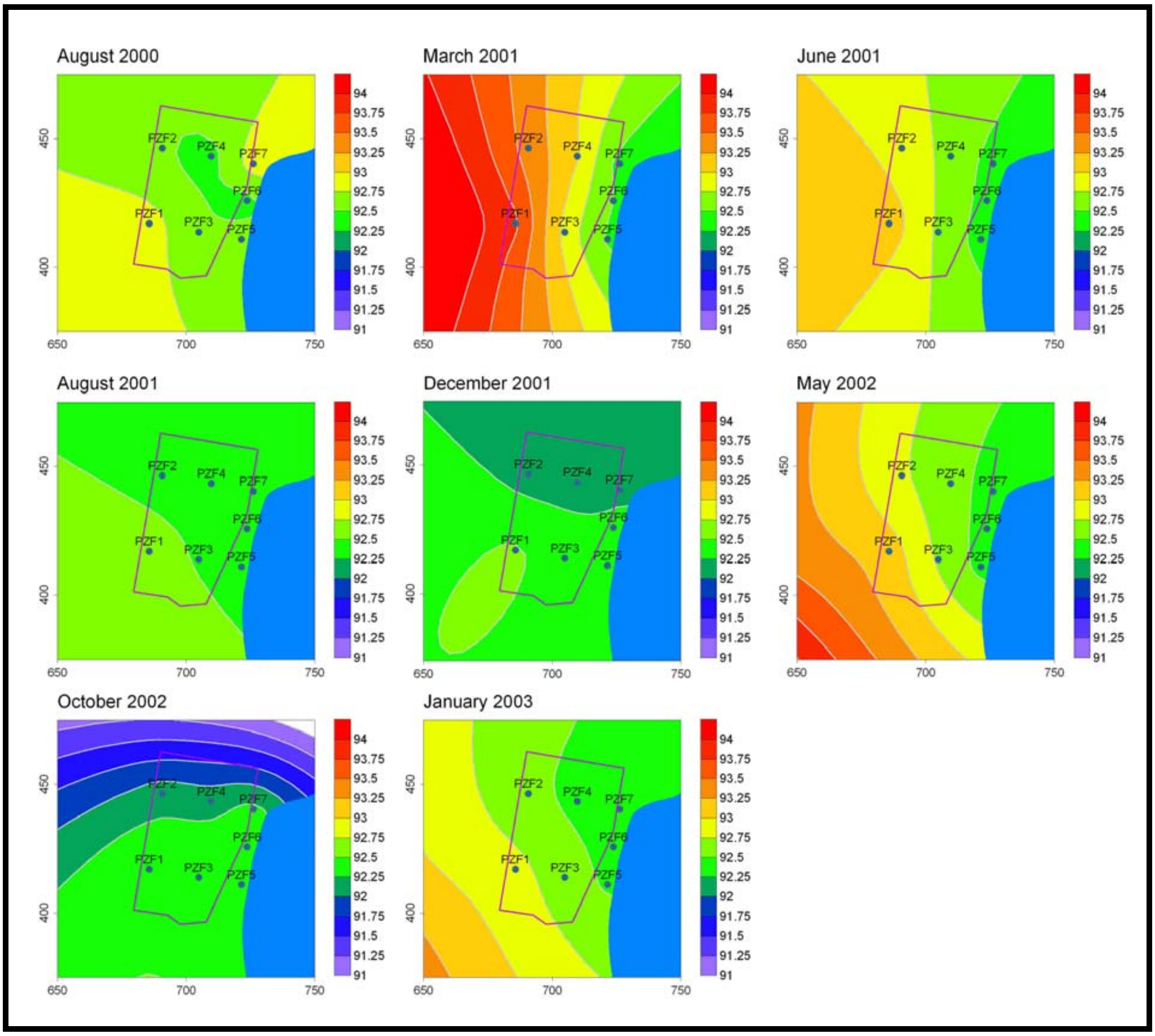

Figure 4.13 - Groundwater level contours - Phytoremediation area.

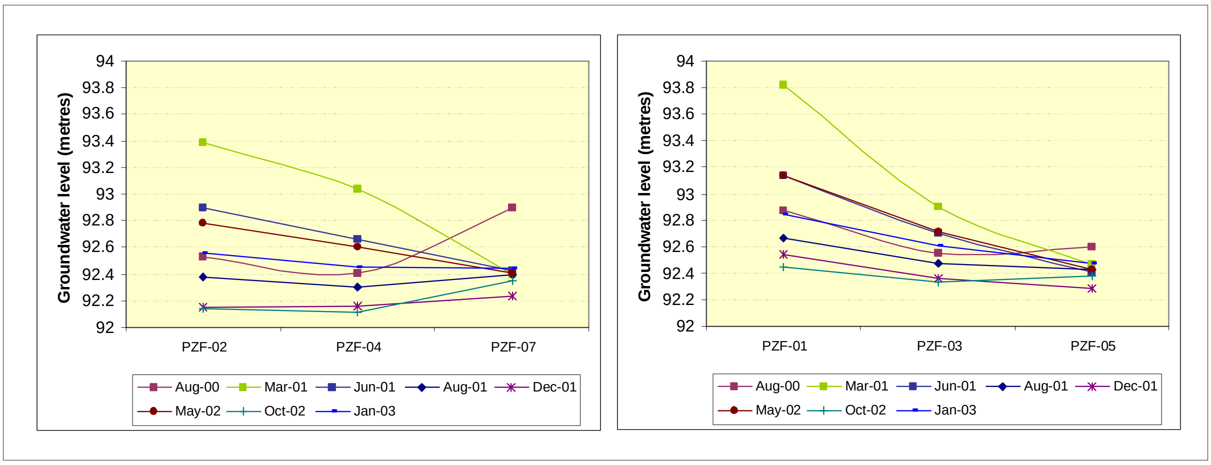

Figure 4.14 - Groundwater level profiles for sections PZF-01-03-05 and PZF-02-04-07.

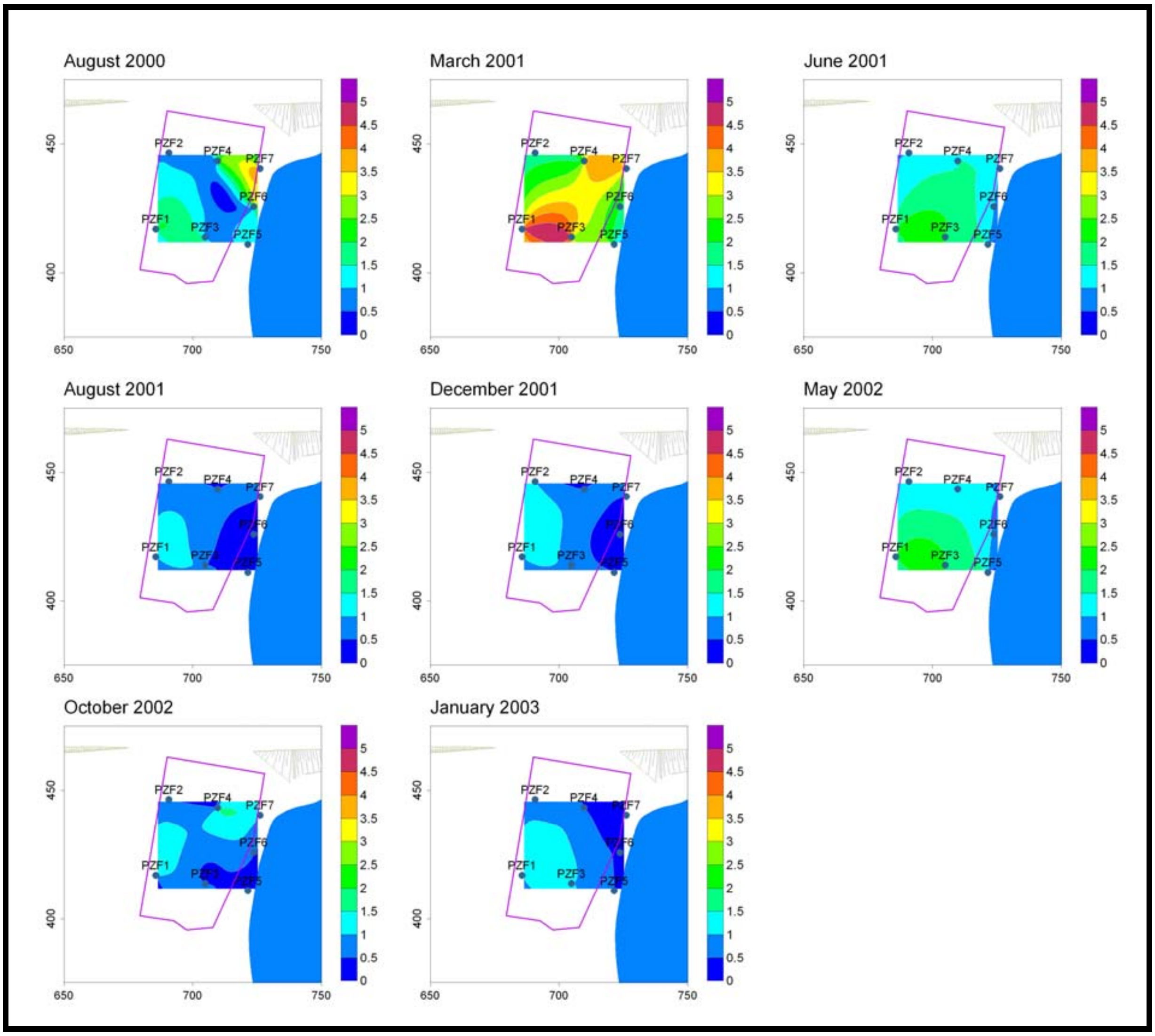

Figure 4.15 - Groundwater level gradient magnitude (%) - Phytoremediation area.

4.5.4. Groundwater use

The groundwater use in the areas close to the site is essentially industrial. A hydrocensus was undertaken in 2000, when 46 boreholes were identified within a radius of 2 kilometres from the site. Data obtained during the hydrocensus was restricted to borehole locations, depth, water levels and water use. No groundwater use for domestic supply was identified. Most of the obtained water levels are deeper than 50 metres, indicating that these measurements reflect deeper aquifers and not the studied aquifer described in the previous sections. The locations of the hydrocensus boreholes are shown in Figure 4.16.

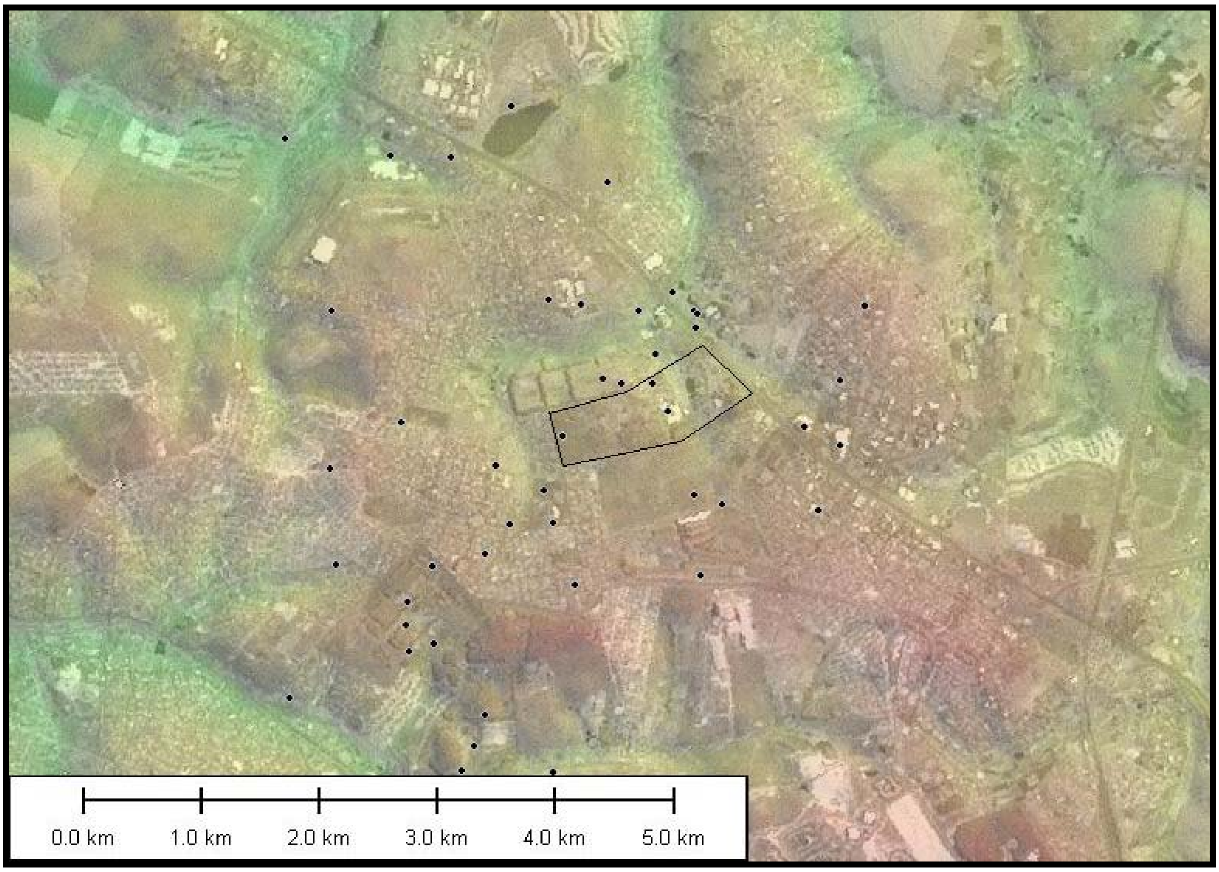

Figure 4.16 - Hydrocensus boreholes (blue dots).

4.5.5. Groundwater quality

The groundwater quality will be discussed only in terms of contamination and biodegradation parameters. During the phytoremediation monitoring program, groundwater samples from the monitoring boreholes were collected on average, on a three-monthly basis for *in-situ* measurements, analysis of VOC (Volatile Organic Compounds) and biodegradation parameters.

Figure 4.17 shows the time series of the most relevant monitoring parameters. Figure 4.18 to Figure 4.24 show the compilation of monitoring data for the monitoring boreholes, and Figure 4.25 to Figure 4.27 show interpolated contours for the most relevant contaminants.

4.5.5.1. Contamination parameters

The contaminants that significantly exceeded the detection limits throughout the monitoring period are:

- Benzene [C_6H_6],
- Chloride [Cl],
- Chlorobenzene [C_6H_5Cl],
- Chloroform [$CHCl_3$],
- 1,2 Dichloroethane [$C_2H_4Cl_2$],
- Methylene chloride [CH_2Cl_2].

The monitoring analytical results indicate a very irregular pattern of contamination migration and evolution. Different compounds in different concentrations and monitoring points were found. This irregular pattern is likely associated with one or more of the following processes:

- Multiple pulses of contamination;
- Different transport rates of contaminants;
- High biodegradation rates;
- Contamination of unsaturated zone due to water level oscillation;
- Changes in flow direction due to water level oscillation;
- Dilution due to recharge processes;
- Dilution due to lake inflow after dry season periods; and
- Anisotropy effects.

Significant concentrations of chloroform, benzene and 1,2 dichloroethane were detected in the monitoring borehole PZF-02 before the phytoremediation implementation (August 2000), indicating that the plume had likely reached the phytoremediation area before the phytoremediation start-up.

Unlike borehole PZF-02, significant concentrations of chlorobenzene were identified in the monitoring borehole PZF-01 before the implementation, while significant concentrations of chloroform and benzene were only identified in August 2001. This fact suggests the possibility of two different plumes migrating through the boreholes. The first plume likely originated from leaching events in the building 2000 and the second plume from the building 1000.

The down-gradient monitoring boreholes PZF-06 and PZF-07 also showed two chloroform concentration peaks in March 2001 and May 2002 and are likely related to two different contamination events.

High benzene concentrations were identified only in the middle and up-gradient monitoring boreholes (PZF-01, PZF-02, PZF-03 and PZF-04). The very low benzene concentration found in the down-gradient boreholes may indicate that only the plume edge has reached these boreholes, or that biodegradation rates are higher in the plume edges, once the biodegradation capacity is likely to be more favourable (such as high dissolved oxygen concentrations and oxidant redox) in the areas where little or no biodegradation has yet occurred.

It is important to emphasize that benzene is more susceptible to biodegradation and volatilization processes, if compared with the other mentioned contaminants. Biodegradation and volatilization effects are therefore likely to be more evident in the benzene concentrations than of the other contaminants.

Methylene chloride results do not indicate high concentrations of this compound, with the exception of monitoring borehole PZF-03, which showed peaks between 1 and 1.8 mg/l from March to August 2001 and again in January 2003. Although methylene chloride can be a product originated from chloroform biodegradation, its concentrations show a high correlation with chloroform only in the earlier stages. One hypothesis that could explain this phenomenon is that as chloroform has higher mobility, it can migrate faster than methylene chloride, promoting the lack of correlation in the later stages.

The up-gradient boreholes PZF-01 and PZF-02 showed a slightly negative correlation of chloride and chlorobenzene concentrations with the water levels. This correlation could indicate dilution related to the recharge processes. These correlations can be masked in the other boreholes due to the influence of other processes such as increased biodegradation in the phytoremediation area and water inflow from the lake.

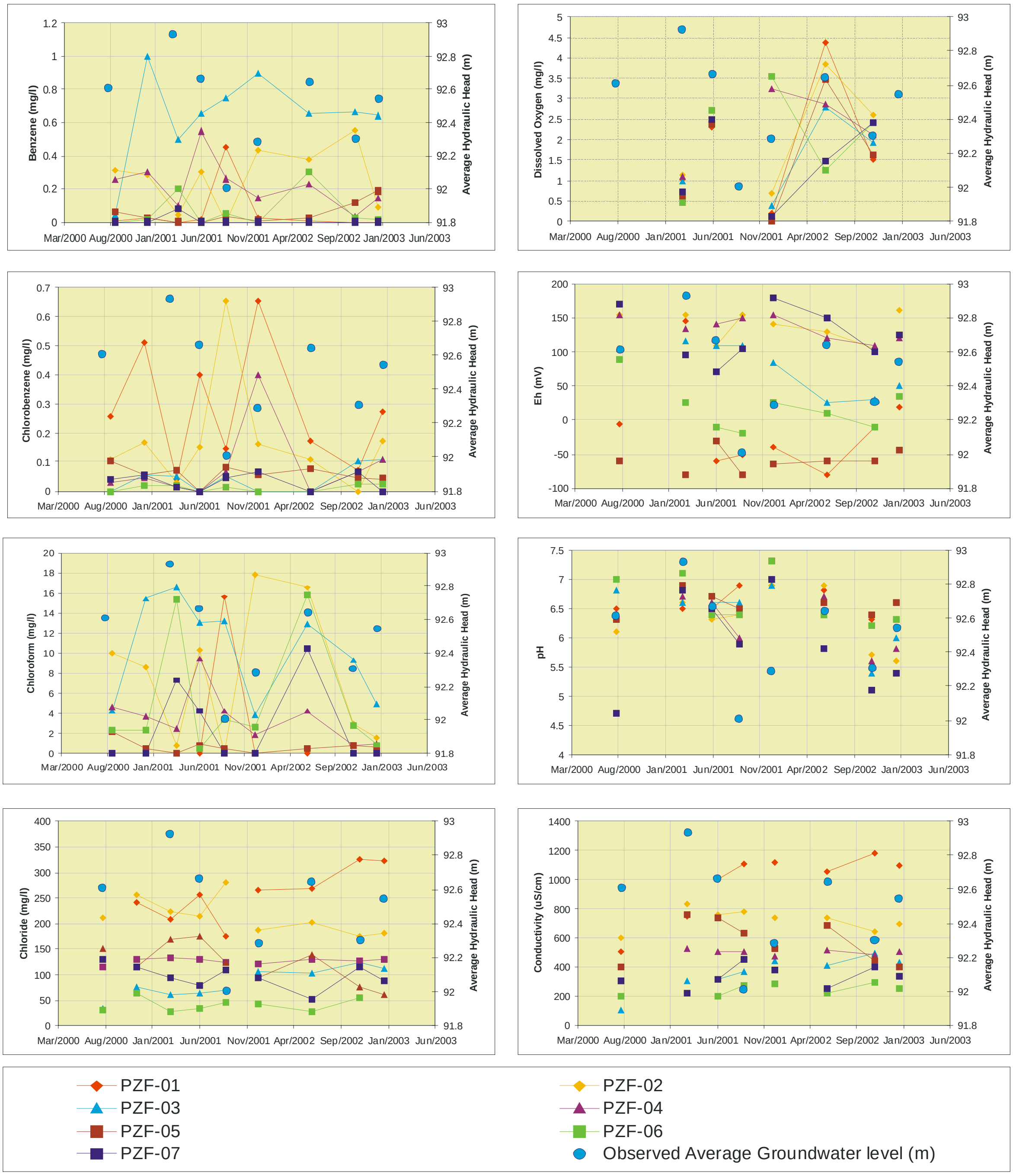

Figure 4.17 - Time series graphics of the most relevant contamination and biodegradation parameters.

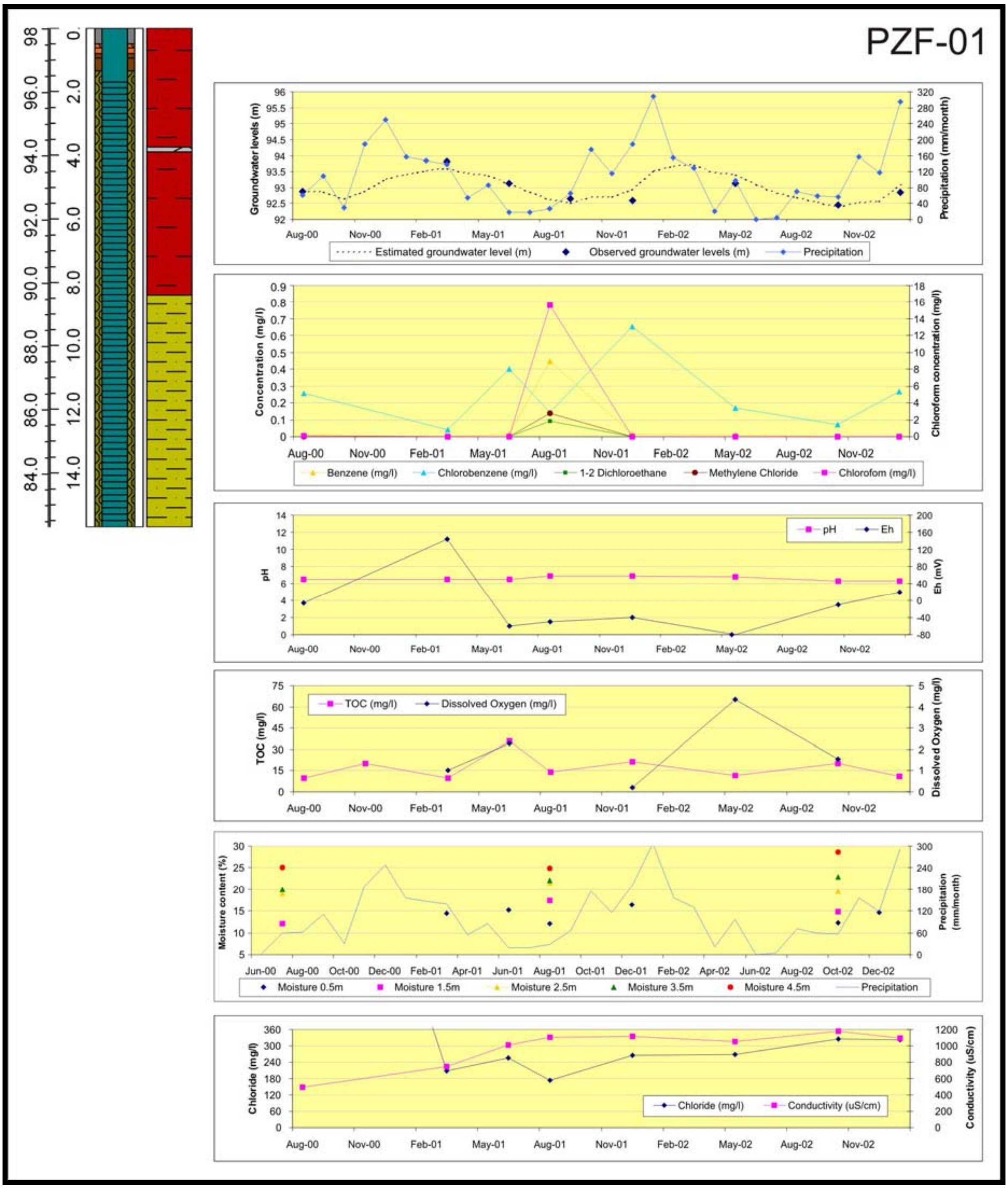

Figure 4.18 - Monitoring data compilation of PZF-01.

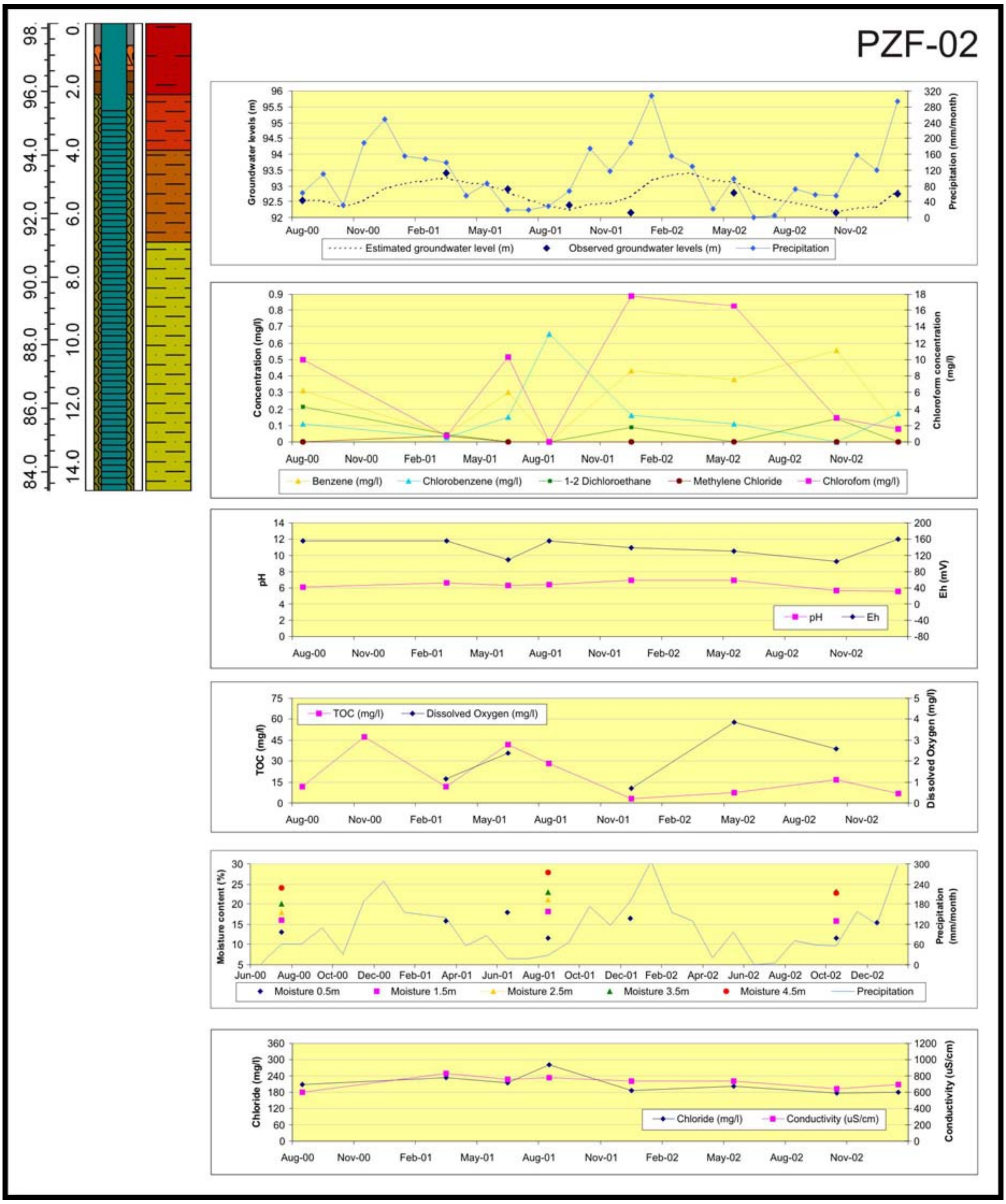

Figure 4.19 - Monitoring data compilation of PZF-02.

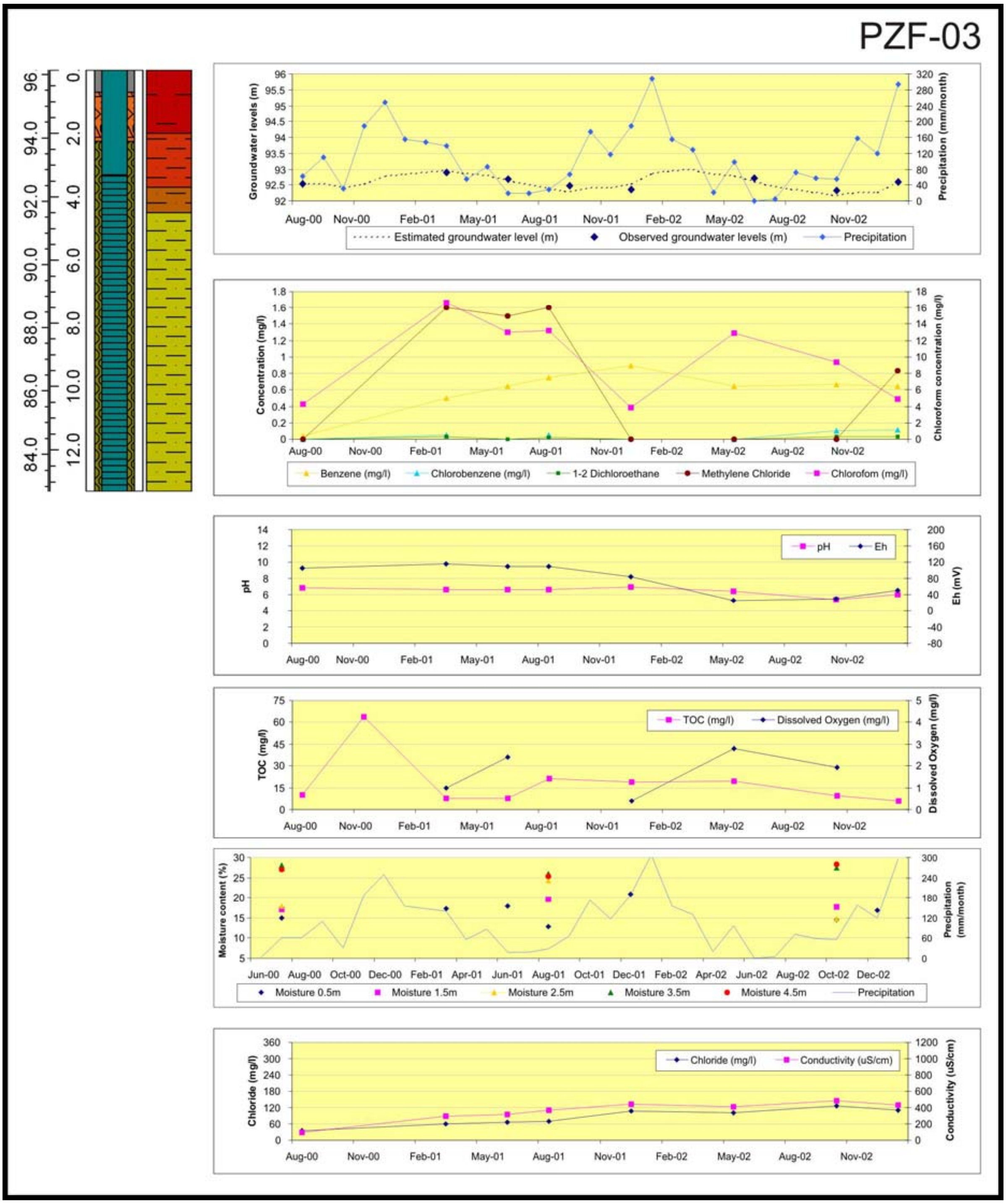

Figure 4.20 - Monitoring data compilation of PZF-03.

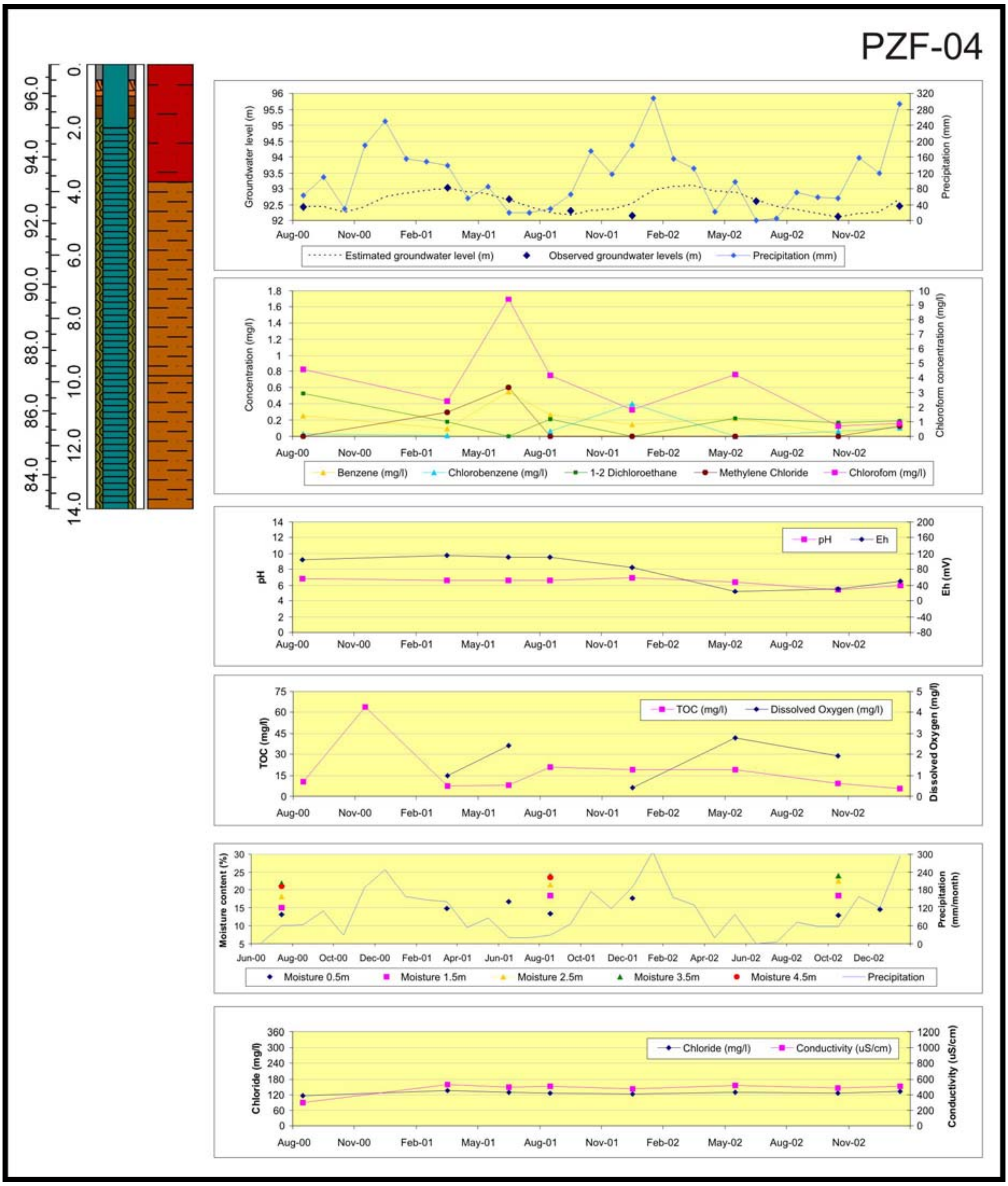

Figure 4.21 - Monitoring data compilation of PZF-04.

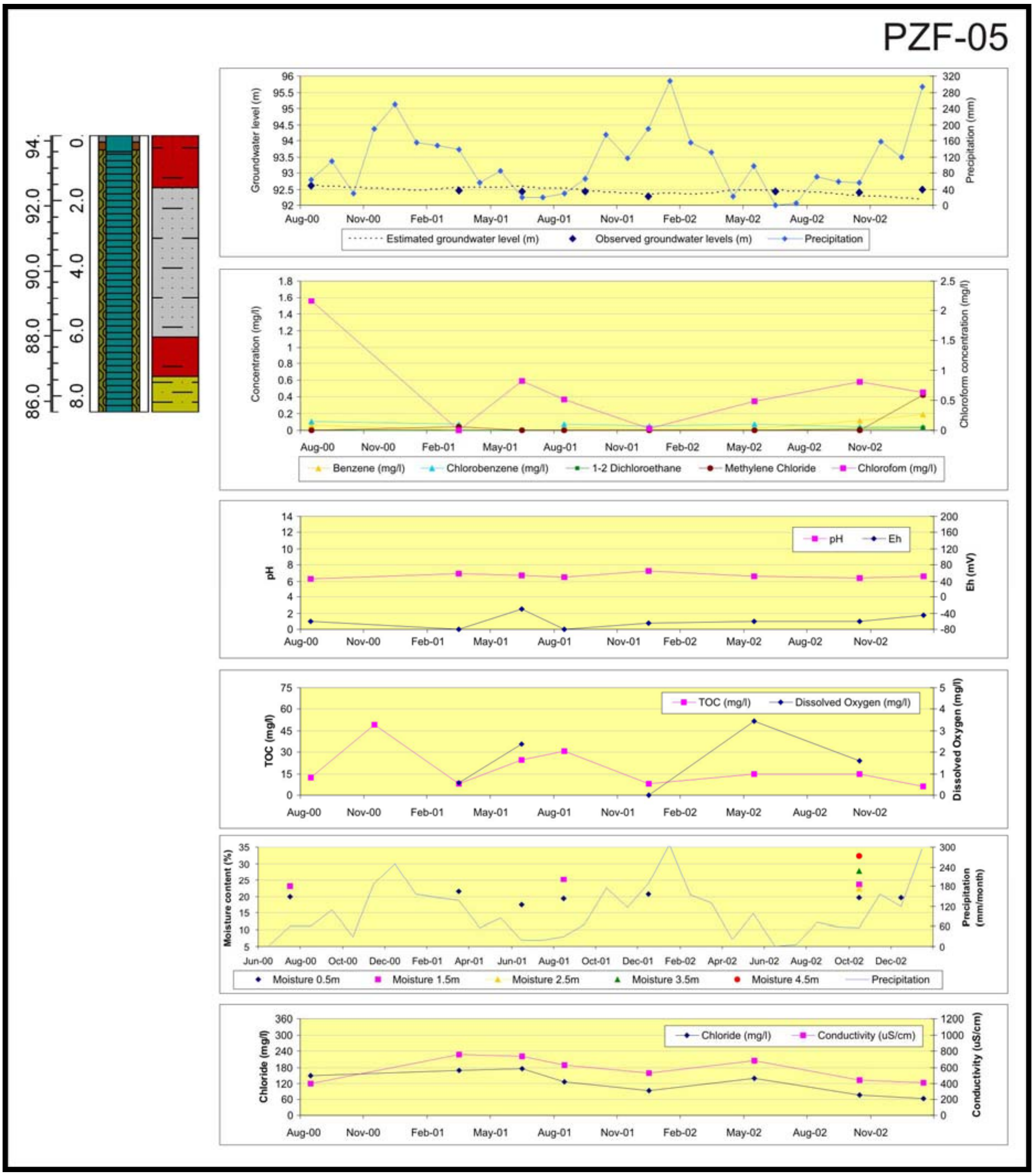

Figure 4.22 - Monitoring data compilation of PZF-05.

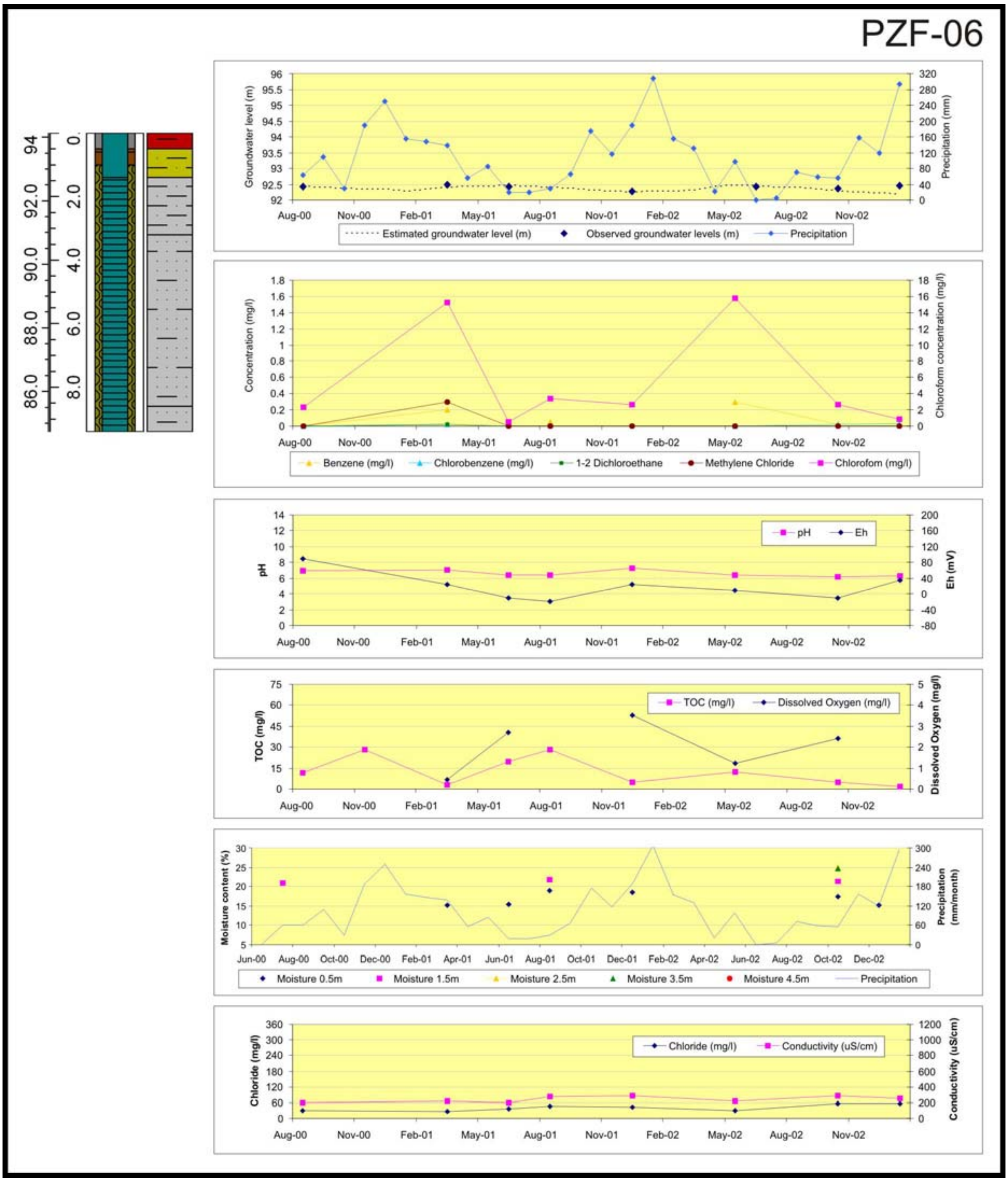

Figure 4.23 - Monitoring data compilation of PZF-06.

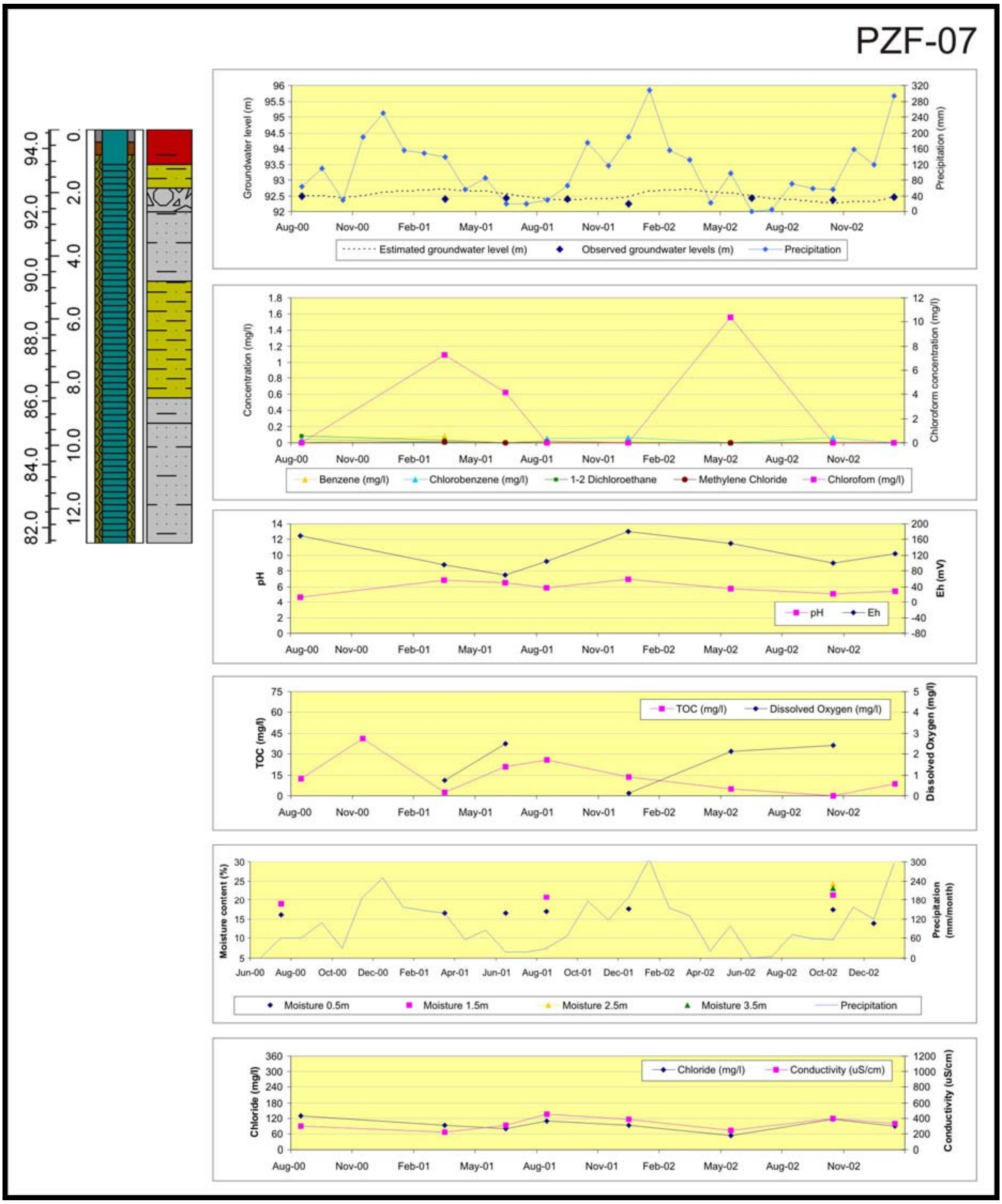

Figure 4.24 - Monitoring data compilation of PZF-07.

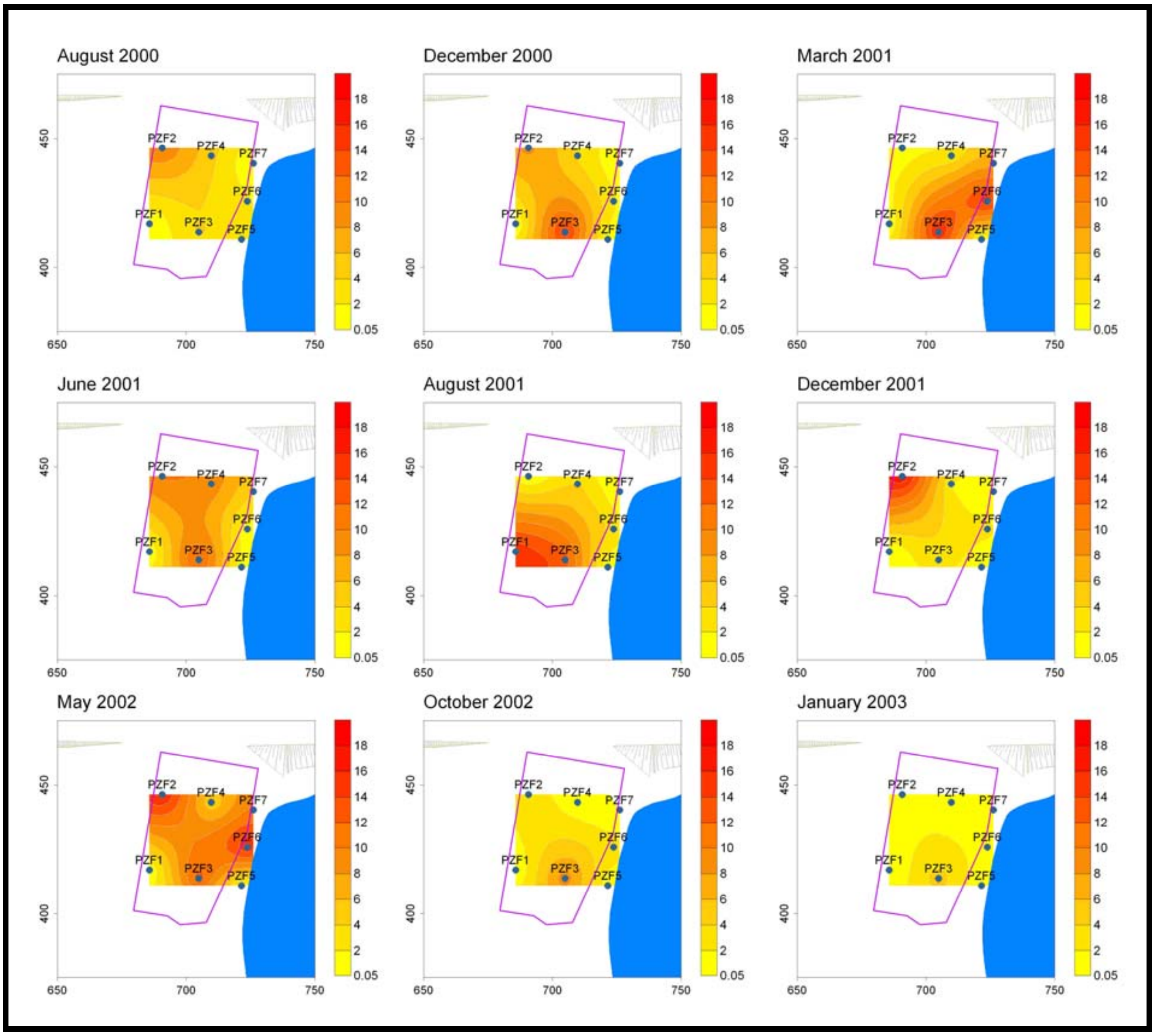

Figure 4.25 - Dissolved chloroform contours (mg/l).

The iso-concentration contours for chloroform also reflect the irregular pattern observed in the time series graphs. No evidence of a systematic migration of the contaminants can be observed. This lack of systematic migration evidence may indicate that the transport rates are too low to be observed in a period of two years, and that changes in the chloroform processes are related to smearing processes in the unsaturated zone due to groundwater level oscillation.

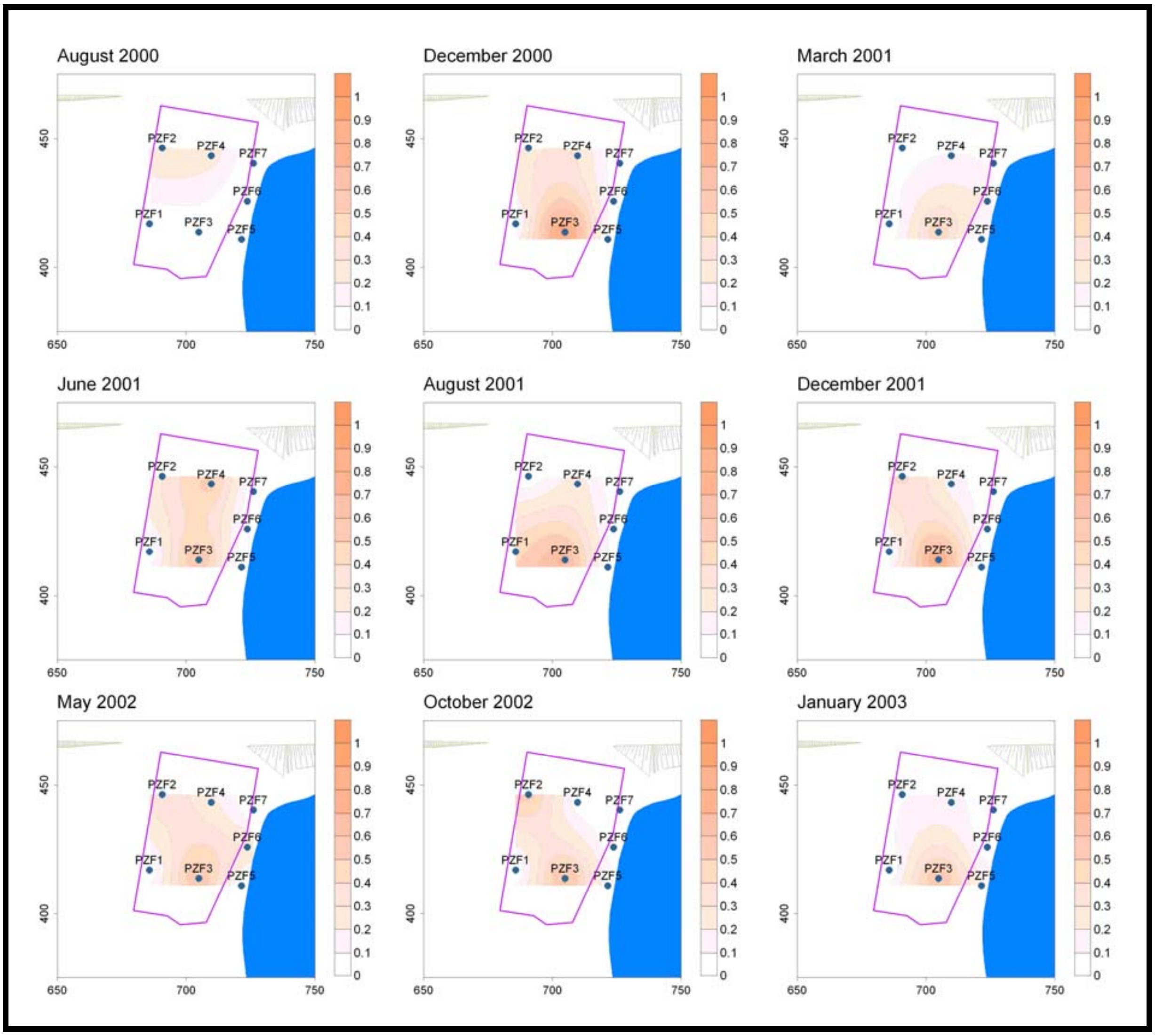

Figure 4.26 - Dissolved benzene contours (mg/l).

The iso-concentration contours for benzene show a relatively stable plume with relatively small changes. These changes are likely to be related to groundwater level oscillations. It is also observed in the iso-contours that the down-gradient boreholes show low benzene concentrations. As previously mentioned, this pattern could be related to the fact that only the plume edge has reached the down-gradient areas, or that high biodegradation rates have occurred in the plume edge areas.

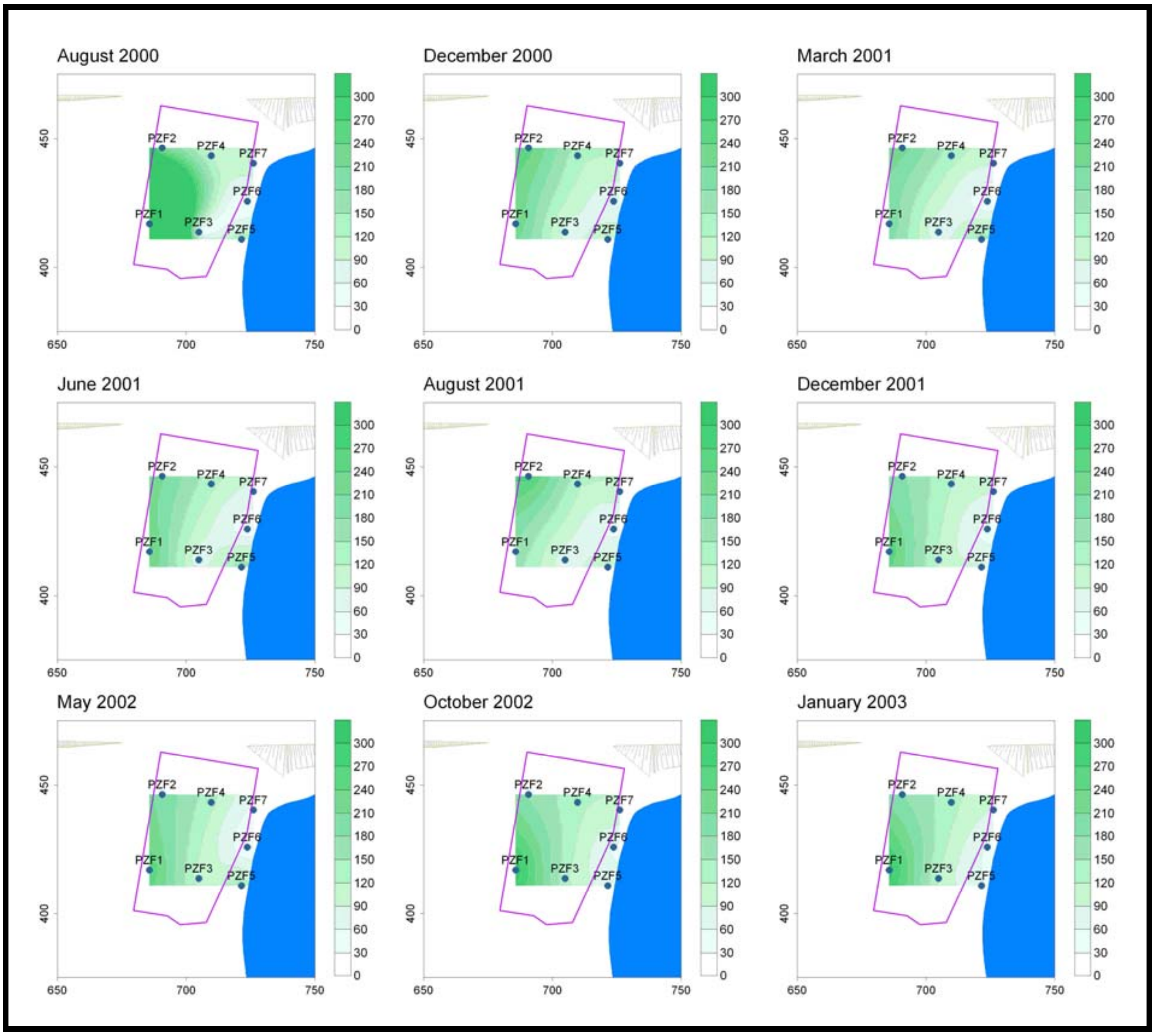

Figure 4.27 - Dissolved chloride contours (mg/l).

The iso-concentration contours for chloride showed the best evidence of a slow progressive migration towards the down-gradient areas. This can be explained by the fact that chloride is the more conservative contaminant, as it is not strongly affected by adsorption and volatilization processes, and is not affected by biodegradation.

Based on the observed results, it becomes evident that contaminant migration occurs at very slow rates within the phytoremediation areas. The irregular patterns observed in the monitoring boreholes are likely to be related to oscillation in the groundwater levels, which would cause two different processes: the first one, related to the smearing of contaminants in the unsaturated zone; and the second one related differential dilution of contaminants with recharge water, due to the different recharge rates.

4.5.5.2. Biodegradation parameters

Dissolved oxygen concentrations exceeded 1 mg/l in most of the monitoring events, indicating that the aquifer was able to promote aerobic biodegradation reaction throughout the phytoremediation process. These concentrations also show a weak correlation with the water levels, mainly in the later stages of the phytoremediation, and can be related to a dissolved oxygen input through recharge.

With the exception of monitoring boreholes PZF-1 and PZF-5, the boreholes showed positive values for redox potential (Eh), indicating a predominant oxidant environment in the phytoremediation area and, thus, favourable conditions for aerobic biodegradation.

Concentrations of total organic carbon (TOC) were expected to be higher in the advanced stages of the phytoremediation, due to the release of plant exudates into groundwater. However, the concentrations in the later stages are slightly lower than the concentrations obtained in the baseline. One of the reasons for this decrease is that sometimes organic contamination can also be taken into account for the TOC analysis and thus, the contaminants might be interfering in the TOC results.

4.5.5.3. Compliance to target levels

Regarding contaminant concentration limits, site-specific target levels were established by a risk assessment performed on the site during the environmental assessment performed in 2000. The risk assessment was undertaken following the ASTM-RBCA (Risk Based Corrective Action) procedures and will not be discussed in this study. The site-specific target levels are shown in Table 4.6.

Table 4.6 - Site specific target levels for groundwater.

Compound	Site Specific Target Levels – SSTL (mg/l)
Acetone	3.02
Benzene	0.01
Chlorobenzene	0.05
Chloroform	1.00
1,2 Dichloroethane	0.01
Methylene chloride	0.05
Toluene	6.04
Xylenes	60.04

Comparing the analytical results with the site specific target levels, the contaminants chloroform, chlorobenzene, benzene, 1,2 dichloroethane and methylene chloride remained in concentrations above the target levels until the later monitoring stages, indicating that the phytoremediation system was not effective in the sense that it potentially allowed groundwater inflow into the lake with concentrations above the target levels.

5. CONCEPTUAL MODEL

The hydrogeological conceptual model was built based on the available data and its main objective is to promote a qualitative understanding of the site in terms of hydrology, hydrogeology and water balance.

As shown in the previous sections, available data include:

- Borehole logs;
- Groundwater levels;
- Hydrological monitoring data;
- Groundwater monitoring data;
- Geological maps; and
- Slug-test analysis results.

In order to provide an appropriate description of both flow and transport models, they will be described separately below.

5.1. Conceptual flow model

As described in previous sections, the aquifer of interest is composed by the weathering zones of sedimentary and intrusive rocks existing in the area. This weathered zone constitutes an aquifer with unconfined behaviour and an average thickness of 20 metres. The base of the aquifer is the unweathered basalt sills which act as a barrier to vertical flow.

The aquifer can be divided into two layers according to its soil textures and hydraulic parameters. The upper layer is composed basically by a sandy-clay soil while the lower layer is composed of silty-clay or clayey soil. It is expected that the lower layer has lower hydraulic conductivity values and higher specific yield, due to its more clayey composition.

The aquifer on the infiltration ponds area was originated from the weathering of sedimentary rocks, while in the phytoremediation area the aquifer is composed mostly from the weathering of the underlying basalt sill, which may cause a difference in the conductivities of these two areas. Due to the relatively higher clay content, the weathered basalt horizons are expected to have slightly smaller and more homogeneous conductivity values than the weathered horizons of the infiltration ponds, constituted by weathering of sedimentary rocks and where the slug test data was obtained.

The topographic highs that exist up-gradient of the industrial facilities constitute a water divide, separating groundwater that flows towards the lake and down-gradient drains from groundwater that flows towards other drainage systems. The exact position of this water divide may show small changes throughout periods of different recharge rates. However, these changes are not likely to be significant, since the water levels are expected to show relatively similar changes during the periods of different recharge rates and, thus, the gradients that define the water divide are expected to remain constant. Furthermore, draw-down depressions caused by the phytoremediation area are very unlikely to reach the water divide nearby areas and will therefore not affect the position of the water divide.

Aquifer inflow occurs by direct recharge from rainfall infiltration and, for the local soil type, is expected to be between 1 and 10% of the mean annual rainfall. Impermeable surfaces such as the industrial facilities and roads tend to have lower recharge rates compared with vegetated and uncovered surfaces, although horizontal flow processes through the unsaturated zone are likely to attenuate this effect.

The groundwater flow is, regardless of the water oscillations, overall towards the lake and down-gradient drainages, which act as an outflow zone to the aquifer. After periods of low recharge, the lake can also act as an inflow zone, promoting seepage from the lake into the aquifer.

The phytoremediation area constitutes an outflow zone, due to the plant uptake and transpiration of groundwater from unsaturated and, possibly, saturated zones. Groundwater uptake in the unsaturated zone can also influence the recharge rates by decreasing the amount of water that flows from the unsaturated zone to the saturated zone.

Vegetated areas other than the phytoremediation area are unlikely to have some influence zone, due to the shallow root systems of these vegetations. In addition most of these areas are composed by adult plants and the major water uptake in plants occurs in their growing stages. A schematic representation of the conceptual model is presented in Figure 5.1.

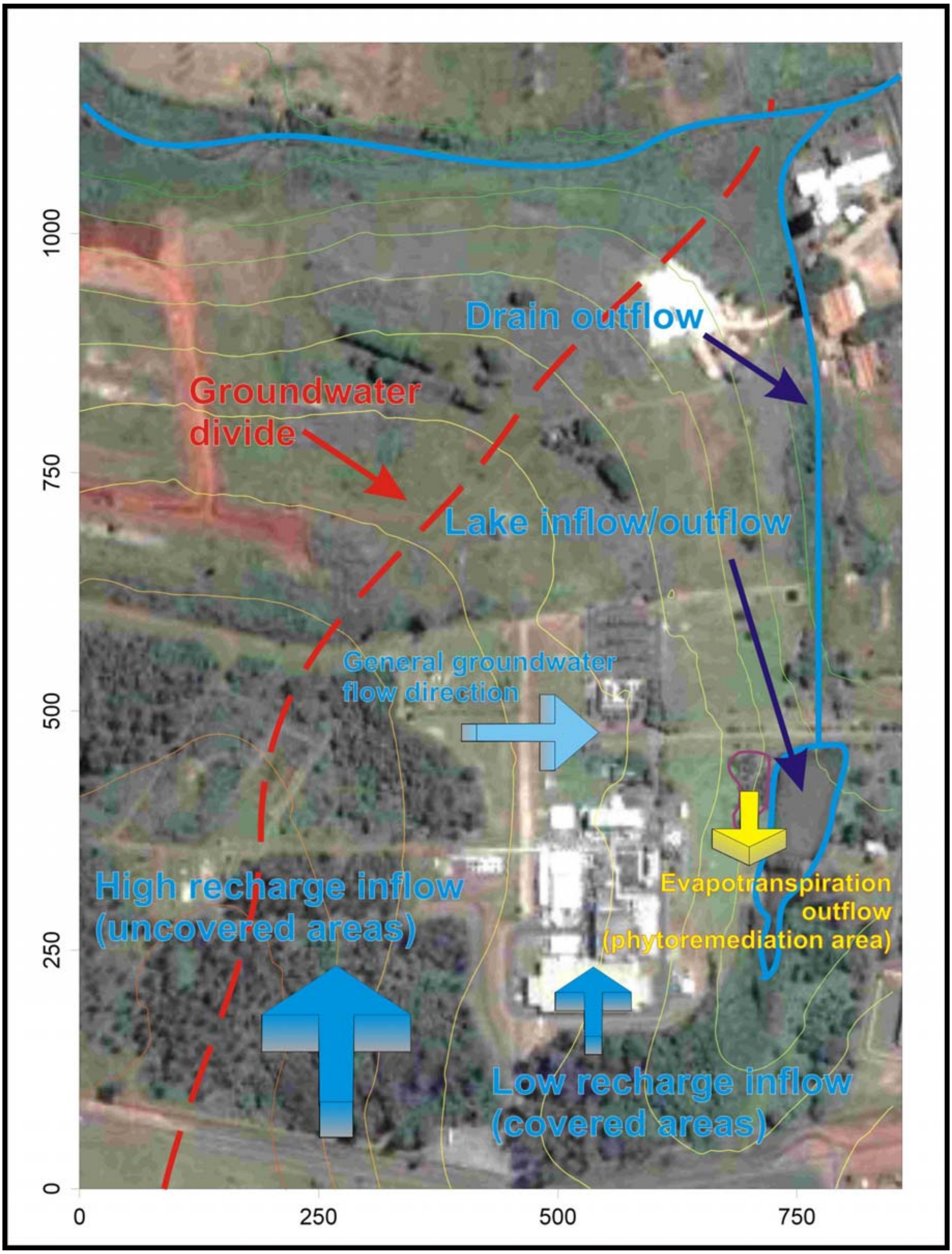

Figure 5.1 - Schematic representation of the conceptual model.

5.2. Conceptual hydrogeochemical model

A conceptual hydrogeochemical model was elaborated for the area in terms of contamination that occurred in the industrial areas and biodegradation of this contamination, due to the lack of data regarding major anions, major cations and baseline data prior to the contamination events. In this regard the conceptual model can be described in terms of sources, pathways and chemical processes that occurred throughout the contamination transport.

The main sources of contamination are related to leakages that occurred in the industrial area facilities, namely buildings 1000 and 2000. The composition of the original leakage is not well-known, as it originated from the effluent of the industrial activities. The analytical results from soil and groundwater samples collected throughout the environmental assessment and remediation processes indicates that the original leakage effluent is mostly composed of chlorinated compounds and benzene.

These leakage events did not occur simultaneously and their composition is not expected to be similar. Three major events were reported and it is likely that more minor secondary events may have occurred.

The contaminants that originated from the leakage events migrated vertically within the unsaturated zone until they reached the saturated zone, when horizontal migration due to advection and dispersion processes started to take place.

The first environmental assessment indicated high concentrations of contaminants in the groundwater and low concentrations in soil samples. This assessment was conducted eight years after the last reported leakage event occurred, and may indicate that most of the contamination that remained in the unsaturated zone as residual phase may have volatilized.

Significant contaminant concentrations in the unsaturated zone are likely to have occurred essentially in the immediate vicinity of source areas or in the horizons where groundwater level oscillation occurs.

The first remediation actions of chemical oxidation were conducted in the year 2000, eleven years after the last reported leakage event took place. Significant transport may have therefore occurred prior to the first remediation actions. Due to the high contamination levels, low biodegradation may have occurred, since these high levels possibly exhausted the aerobic biodegradation capacity of the aquifer quickly, by the consumption of all dissolved oxygen and secondary compounds required by biodegradation.

The injections of peroxide conducted from 2000 until 2003 contributed to the rebuilding of favourable biodegradation conditions, by oxidation of contaminants, addition of oxygen into the saturated zone, and by changing the general aquifer redox to a more oxidant condition.

Although the peroxide injections are deemed to be a strong remediation method, the remediation was not enough to provide effective reduction in the concentrations to the site-specific target levels. Reasons for the ineffectiveness of the peroxide injections may be related to the extremely high contaminant concentrations, or to the ineffective spreading of the peroxide within the saturated zone.

The contaminants that were not affected by the biodegradation continued their horizontal migration towards the down-gradient areas, where the phytoremediation area is situated. The results from groundwater samples collected from the downgradient phytoremediation monitoring boreholes indicated significant benzene and chloroform concentrations prior to the phytoremediation implementation, which means that the contamination had already reached the phytoremediation area before the remediation started.

Phytoremediation effects on the contaminant concentrations may have started significantly later than the implementation time, due to the low depth of the tree's root systems. Once the phytoremediation effects started to take place, some limited contamination extraction may have occurred due to the groundwater abstraction from the trees, as well as enhanced biodegradation due to the increasing or stabilization of dissolved oxygen concentrations and the releasing of exudates, which might have contributed to the biodegradation. Increase of the microbial activity near to the root systems of the trees may have also occurred and contributed to the increase in the biodegradation rates.

Dilution processes occurred to a lesser extent throughout the contaminant migration due to groundwater recharge. The recharge water also may have a small contribution in keeping favourable biodegradation conditions by adding dissolved oxygen into the aquifer.

A schematic representation of the hydrogeochemical conceptual model is presented in Figure 5.2.

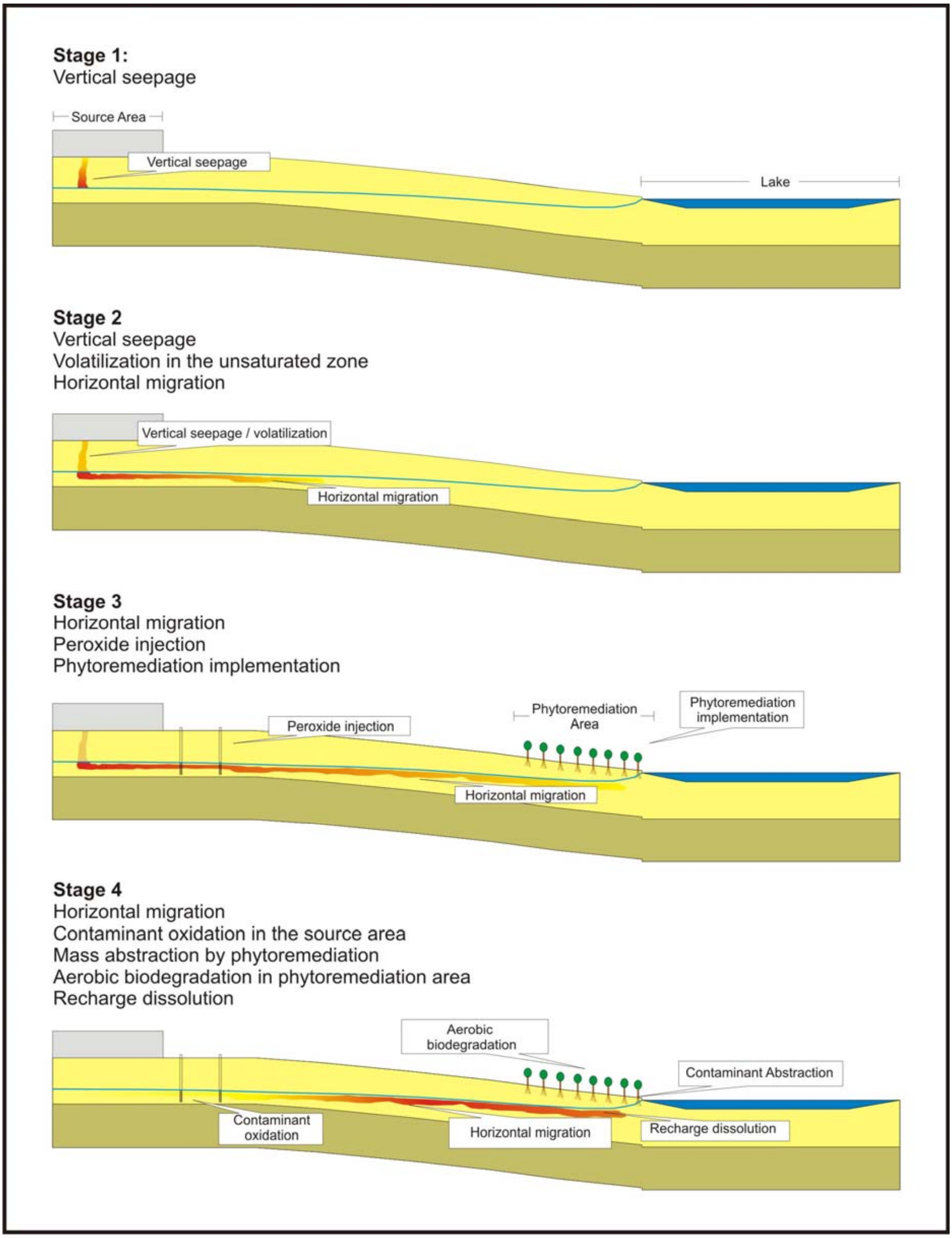

Figure 5.2 - Schematic representation of the hydrogeochemical conceptual model throughout the different contamination stages.

6. NUMERICAL MODELLING OF THE PHYTOREMEDIATION SYSTEM

The numerical groundwater modelling was undertaken in order to quantify the hydrogeological processes that occurred in the study area and to evaluate the effectiveness of the phytoremediation system in terms of evapotranspiration rates and groundwater drawdown. From all the processes investigated and quantified in the modelling exercise, evapotranspiration rates and draw-down imposed by the phytoremediation system are the most important processes, considering the objective of evaluating the effectiveness of the system.

The following sections describe the procedures adopted during the groundwater modelling and modelling results.

6.1. Model description

The model used for the saturated groundwater modelling was the modular three-dimensional finite-difference groundwater model MODFLOW-2000, Version 1.15.01, released by the United States Geological Survey – USGS in April 2005. The graphic user interface used to generate the model input files and analyse the output file is the software Processing Modflow pro, Version 7.0.31, released by Webtech 360 in 2005.

MODFLOW-2000 is a free open-source model and is one of the most world-widely used groundwater flow models. It was first released in 1984 and, since then, has been constantly updated and new capabilities have been added. This model has a modular structure, which makes it quite adaptable and easy to modify for specific applications, if necessary.

MODFLOW-2000 simulates saturated steady and transient flow of irregularly shaped aquifers and flow systems. Simulated aquifer layers can be confined, unconfined or a combination of both. External sources of stress, such as wells, drains, recharge, rivers and evapotranspiration processes can be simulated.

In this model, the groundwater flow equation is solved using a numerical finite difference approximation. The simulated region is subdivided in orthogonal blocks, which within properties are assumed to be uniform. To each block, different aquifer properties and stress conditions can be assigned, allowing the model to simulate heterogeneous and anisotropic flow regions. A flow equation is written for each block, creating a matrix problem that can be solved by several solvers provided in the model.

Data requirements for MODFLOW-2000 use include initial and boundary conditions, aquifer properties and hydraulic stresses. The output data is calculated hydraulic heads. Based on these heads, secondary output such as drawdown and water budgets can be calculated.

A detailed explanation of all calculations and procedures adopted by the model is presented by McDonald and Harbaugh (1988 and 1996), Harbaugh and McDonald (1996), Hill *et al*. (2000) and Harbaugh et al. (2000).

6.2. Assumptions and limitations

During the modelling processes, several assumptions had to be made due to the model code and data limitations.

As MODFLOW-2000 solves the groundwater flow equation exclusively for the saturated zone, groundwater flow was simulated and was assumed to occur only in the saturated zone. Water changes in inflow and outflow zones were assumed to occur exclusively through the saturated zone. Thus, no unsaturated flow process was directly simulated.

Based on borehole logs, two weathered zones could be defined as different layers in the model. However, in order to avoid issues with dry-cells, only one layer was defined for the model and no vertical heterogeneity was taken into account.

Recharge zones were defined only in terms of covered and non-covered/vegetated areas, regardless of soil type, slope and runoff calculations, as no infiltration data was available and the model is only capable of simulating saturated flow processes. In summary, the recharge in non-covered and vegetated areas was assumed to be spatially constant, while the recharge in covered areas was assumed to be zero.

Evapotranspiration was considered to be effective exclusively in the phytoremediation area, due to two reasons. The first reason is that most of the local vegetation has shallow root systems and should take up water mostly from the unsaturated zone. The second reason is that no wind speed, daylight measurements and temperature data was available.

Although the borehole logs confirmed the existence of an intrusive sill in the phytoremediation and source areas, it is likely that this sill does not exist in the whole model domain and vertical flow to underlying rocks, especially in the up-gradient areas, can occur.

Due to the lack of lake water level measurements, the water level of the lake was assumed to be constant throughout the simulation period.

Few zones with different aquifer properties were assigned based on the borehole log descriptions and no specific pumping/slug test data was available for the study area.

6.3. Model input parameters

6.3.1. Model grid

The model grid was built in order to incorporate the study area and natural boundaries. The grid has a total of 215 columns and 300 rows, with a regular 4-metre spacing and cell size of 16 square metres. In addition, the model grid was aligned to the overall groundwater flow direction. Figure 6.1 shows the model grid used in the simulations.

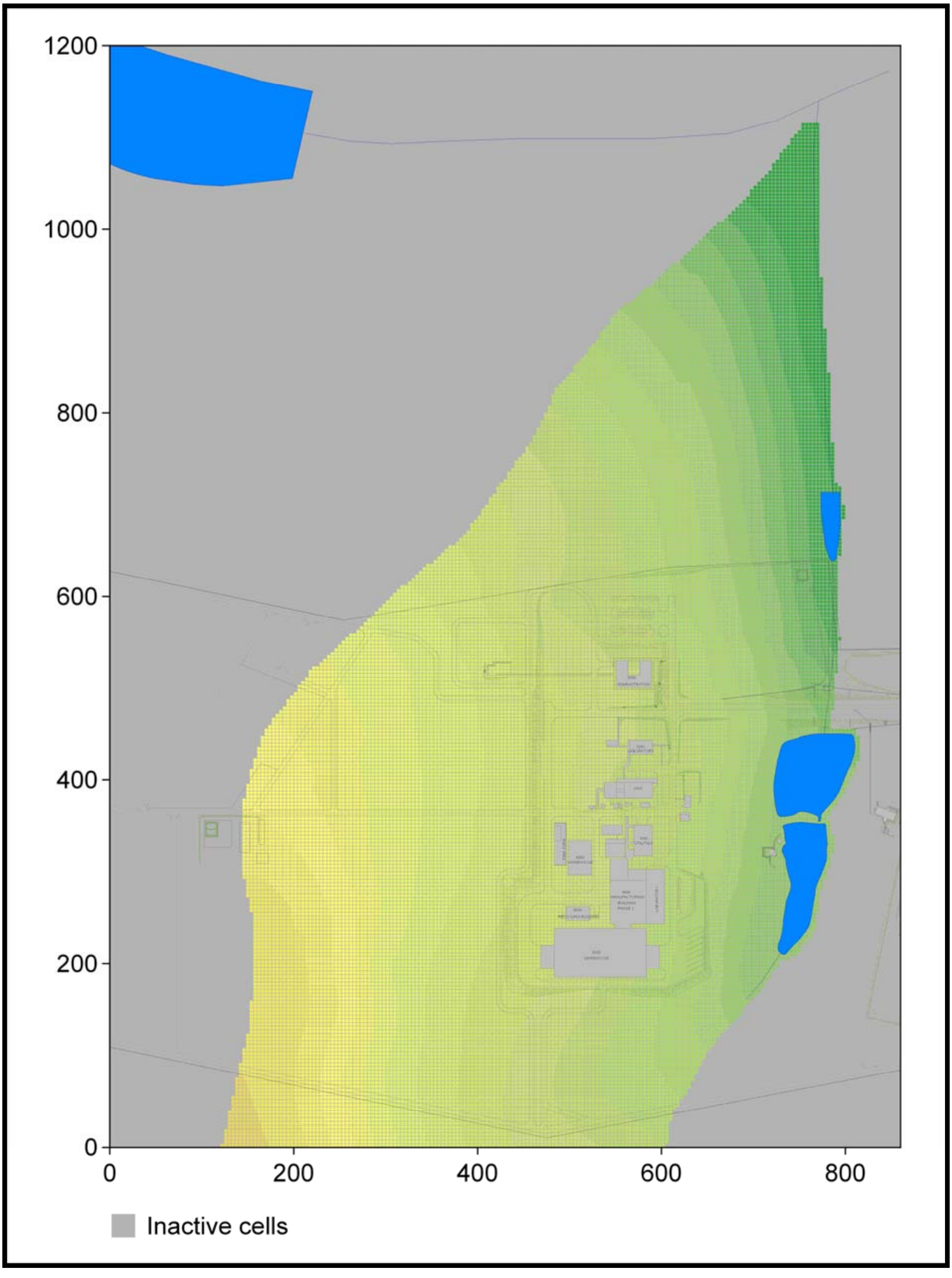

Figure 6.1 - Model grid.

6.3.2. Boundary conditions

The boundary conditions used in the modelling were used to represent the inflow and outflow zones described in the conceptual model section.

Topographical highs existing up-gradient from the source were considered to be water divides and, thus, no-flow cells were assigned. Topographical valleys existing along the lake and drainage extension also act as water divides, in the sense that groundwater does not flow from one side of the divide to the other. No-flow cells were therefore defined to the right side (other than the study area) of the lake and drainage area.

In order to simulate effects of inflow and outflow from the lake and down-gradient dams and drainages, river boundary cells were assigned. The thickness of the river and drainages, obtained by subtraction of the river head and river bottom elevation, was defined to be one metre due to the lack of bathymetrical data. The river head for the drainage and dam was assigned as one metre below the ground surface. Due to the lack of river head monitoring data, the river head was assigned as 92.7 metres.

The inflow from rainfall was simulated with the use of recharge conditions. Recharge conditions were assigned to all the active cells with the exception of those where river conditions were assigned. Simulated recharge rates varied on a monthly basis, based on the rainfall data.

Effects of evapotranspiration promoted by the phytoremediation area were simulated using evapotranspiration conditions. The evapotranspiration conditions were assigned to all the cells within the phytoremediation area. As the evapotranspiration from the plants other than those in the phytoremediation area was considered to be exclusively from the unsaturated zone, evapotranspiration conditions were not assigned to other areas. Figure 6.2 shows the distribution of the boundary conditions.

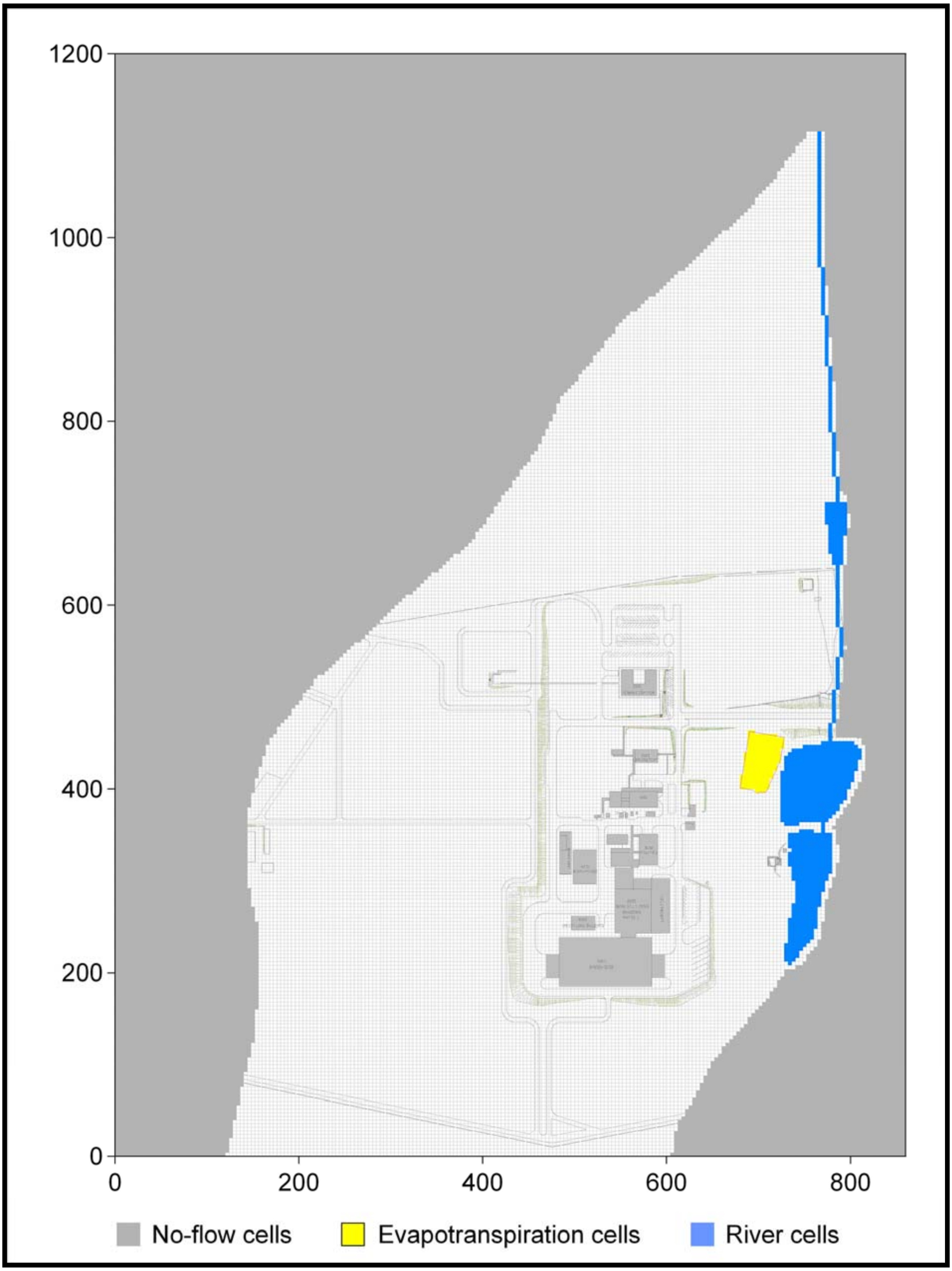

Figure 6.2 - Boundary conditions.

6.3.3. Aquifer parameters

Due to the lack of pumping test data on the monitoring boreholes in the phytoremediation area, the adopted aquifer parameters, such as hydraulic conductivity and specific yield, were defined based on the values obtained from pumping test data performed on the monitoring boreholes located near the deactivated infiltration ponds.

Based on the borehole logs from the phytoremediation and source areas, three property zones were defined in order to characterise possible heterogeneities existing on the site. The distribution of the property zones are shown in Figure 6.3.

As no transport simulation was performed, no values for effective porosity were assigned. Values for vertical hydraulic conductivity were also not assigned as the model has only one layer and, thus, no value for this parameter is required.

The initial aquifer parameters adopted prior to the model calibration were estimated based on the results of the slug tests performed in the infiltration pond areas and on the reported lithologies from the borehole logs. Initial values for horizontal hydraulic conductivity were assigned to be between 0.01 and 1 m/day, since most of the results from slug tests performed in nearby areas were within this range (Figure 4.9). Specific yield values were chosen according to the soil profile. The initial values are shown in the Table 6.1 below.

Table 6.1 - Initial aquifer parameters used prior to the calibration process.

Properties Zone	Horizontal Hydraulic Conductivity (m/day)	Specific Yield
Zone 1	0.03	0.02
Zone 2	0.07	0.03
Zone 3	0.4	0.04

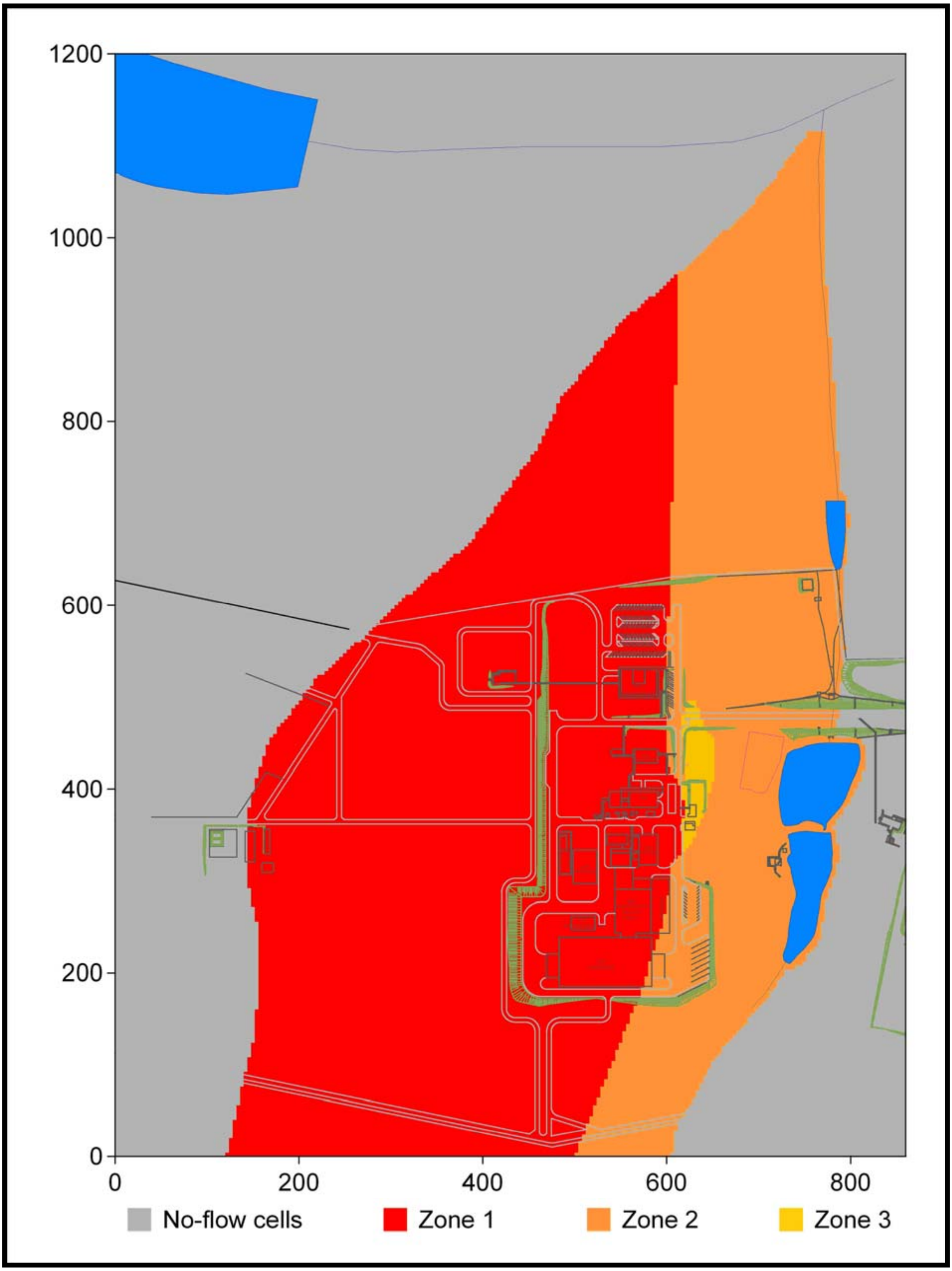

Figure 6.3 - Aquifer property zones assigned to the model.

6.3.4. Initial conditions

The definition of appropriate initial conditions was probably one of the more challenging tasks during the modelling process. The difficulty to assign the appropriate initial conditions relies basically on two reasons. Firstly, most of the groundwater level data came from the source and phytoremediation areas, which constitute a small fraction of the modelled area and, thus, create difficulties to generate appropriate initial heads in areas without data. Secondly, only water level data from the phytoremediation monitoring boreholes was available at the time of initial conditions (August 2000).

Geostatistical procedures were performed in order to overcome these difficulties. The first issue to be solved was to estimate proper heads in areas where no boreholes were available. A Bayesian krigging procedure was undertaken through the correlation between ground and groundwater levels.

As the groundwater levels measurements in August 2000 were conducted only in the seven phytoremediation boreholes, measurements taken during of May 2002, which included measurements in the phytoremediation and source area boreholes, were taken to perform the Bayesian krigging.

Once groundwater levels were estimated for the whole area from data measured in May 2002, another Bayesian krigging was performed through the correlation between the measurements of August 2000 and May 2002.

The Bayesian krigging procedures were performed using the software Tripol, Version 1.0, developed by the Institute of Groundwater Studies – IGS in 1996. In order to fit the estimated initial heads to the model grid, the Shepard's Inverse Distance algorithm from the Processing Modflow module Field Generator was used. Figure 6.4 shows the estimated initial head contours.

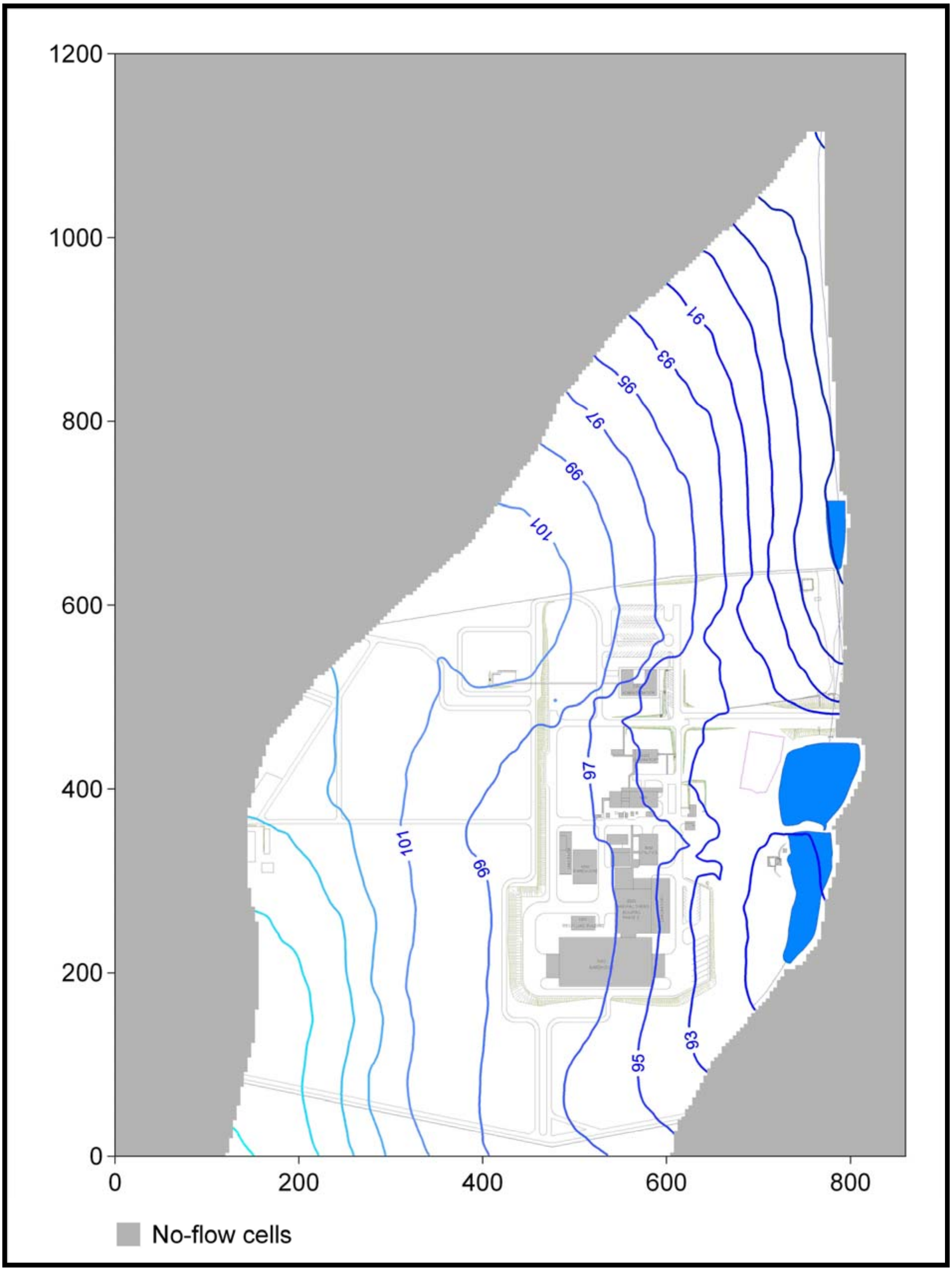

Figure 6.4 - Estimated initial head contours (metres).

6.3.5. Running conditions and transient parameters

The model was built to simulate the first two years of the phytoremediation process, from August 2000 to July 2002. As the objective of modelling was to simulate the evolution of evapotranspiration rates throughout the phytoremediation process, a transient simulation was conducted. The use of transient simulations allows the simulation of non-equilibrium conditions in the aquifer.

Most of the available rainfall rate data between 2000 and 2002 is on a monthly basis. Therefore, the model was divided in 24 stress periods to represent the monthly oscillations in rainfall-dependent recharge rates. Each stress period was divided in four time-steps of approximately one week intervals in order to provide a better approximation of the non-equilibrium state. In addition, in order to keep the time-steps regularly spaced, no time-step multiplier was used. Table 6.2 and Table 6.3 summarize the simulated stress periods, time-steps and corresponding periods.

Table 6.2 - Stress periods used in the simulation - Year 1.

Stress period	Simulated period (days)	Number of time-steps	Simulated period per time-step (days)	Corresponding month
1	31	4	7.75	August 2000
2	30	4	7.50	September 2000
3	31	4	7.75	October 2000
4	30	4	7.50	November 2000
5	31	4	7.75	December 2000
6	31	4	7.75	January 2001
7	28	4	7.00	February 2001
8	31	4	7.75	March 2001
9	30	4	7.50	April 2001
10	31	4	7.75	May 2001
11	30	4	7.50	June 2001
12	31	4	7.75	July 2001

Table 6.3 - Stress periods used in the simulation - Year 2.

Stress period	Simulated period (days)	Number of time-steps	Simulated period per time-step (days)	Corresponding month
13	31	4	7.75	August 2001
14	30	4	7.50	September 2001
15	31	4	7.75	October 2001
16	30	4	7.50	November 2001
17	31	4	7.75	December 2001
18	31	4	7.75	January 2002
19	28	4	7.00	February 2002
20	31	4	7.75	March 2003
21	30	4	7.50	April 2003
22	31	4	7.75	May 2003
23	30	4	7.50	June 2003
24	31	4	7.75	July 2003

The model layer was assigned to be type 1, unconfined, where the transmissivities used during the calculation are based on the saturated thickness, i.e. the distance between the groundwater level and the base of the layer. No anisotropy within the layer was considered.

The MODFLOW Preconditioned Conjugate Gradient Package 2 (PCG2) was the solver used during the simulations. The solver parameters are summarized in the table below.

Table 6.4 - Solver parameters used throughout the simulation.

Solver parameter	Value / method
Preconditioning parameters	
Preconditioning method	Modified Incomplete Cholesky.
Relaxation parameter	1
Allowed iteration numbers	
Outer Iteration	50
Inner Iteration	30
Convergence criteria	
Head Change (metres)	0.001
Residual (metres)	0.001
Damping	
Damping Parameter	1

6.4. Model results

6.4.1. Calibration

The strategy used to perform and appropriate calibration included three stages, namely:

- Average steady-state calibration;
- Source area transient calibration; and
- Phytoremediation area calibration.

The calibration was conducted manually and using the PEST (Parameter Estimation) software developed by Watermark Computing. The PEST software uses an optimization algorithm where the residuals of calibrated and observed heads are minimized varying the model parameters within realistic ranges. A detailed description of PEST structure and calculations are described by Doherty et al. (1994).

In order to obtain first approximations of calibrated hydraulic conductivity parameters, a steady-state calibration was performed. This procedure was adopted due to the lack of hydraulic conductivity data, and was performed based on the average groundwater levels, calculated from the water level measurements.

Monitoring boreholes from which water level data was used in the steady state calibration are shown in the table below.

Table 6.5 - Monitoring boreholes used in the steady-state calibration.

Area	Monitoring boreholes
Up-gradient area	PZ-H, PZ-O, PZ-Q1, PZ-Q2.
Source area[7]	PI-01, PI-02, PI-03, PI-04, PI-05, PI-07, PI-08, PI-09, PI-10, PZV-01, PZT-01, PZT-02, PZU-01, PZU-02, PZX-01, PZX-02.
Phytoremediation area	PZF-1, PZF-2, PZF-3, PZF-4, PZF-5, PZF-6, PZF-7.
Down-gradient area	PE-2.1/P, PE-2.2/P.

A scatter plot diagram comparing calculated and observed hydraulic heads is shown in Figure 6.5. The mean residual between calculated and observed heads is -0.08 metres,

[7] The borehole series PZV, PZT, PZU and PZX are multi-level boreholes. Borehole description and construction details are illustrated in the Appendix 3.

which indicates that the calculated hydraulic heads are, on average, 0.08 metres lower than the observed heads.

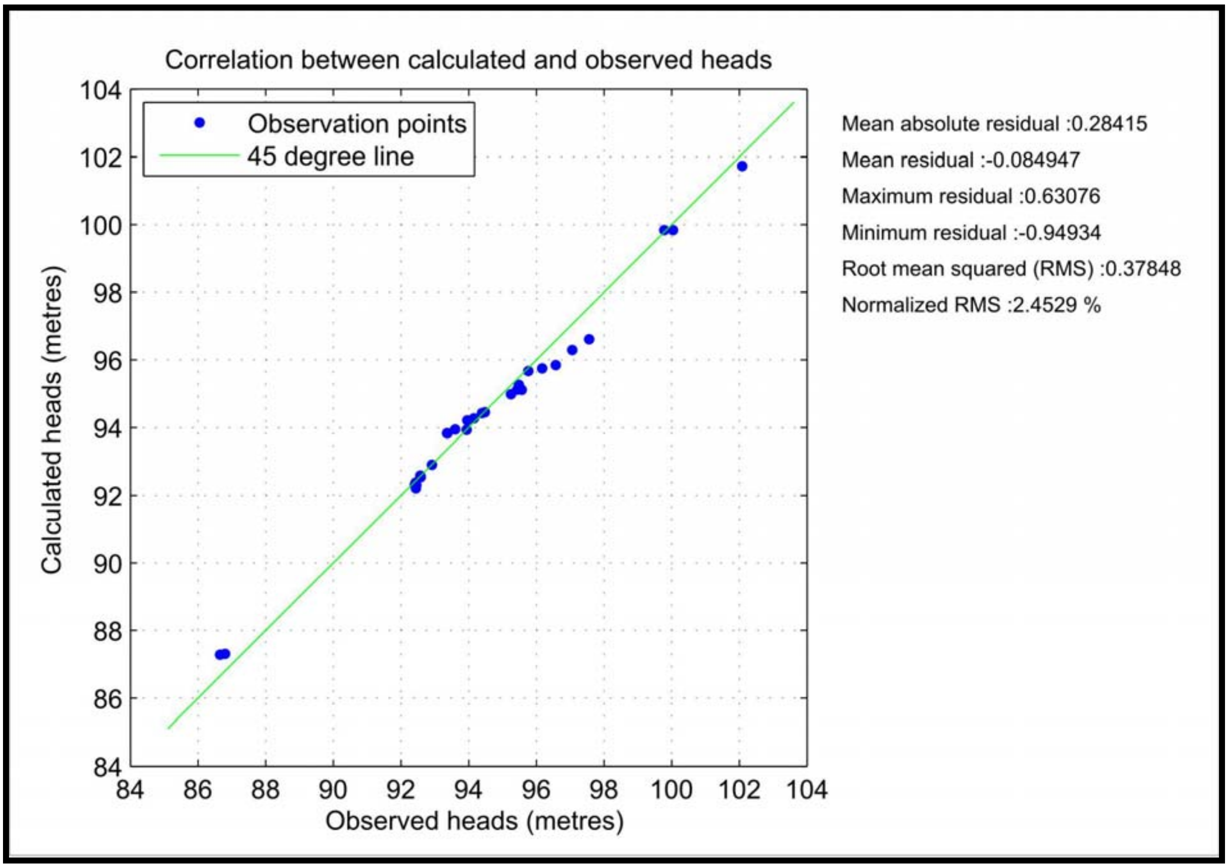

Figure 6.5 - Scatter diagram of calculated and observed heads - Steady-state calibration.

The normalised RMS (Root Mean Squared) residual for the steady-state calibration is approximately 2.5%, which is considered to be reasonable, considering the available data. The parameter values obtained during the steady-state calibration are shown in Table 6.6.

Table 6.6 - Parameter values obtained during the steady-state calibration.

Parameter	Unit	Value
Horizontal hydraulic conductivity		
Zone 1	m/day	0.08
Zone 2	m/day	0.114
Zone 3	m/day	0.3
Recharge rates		
Covered areas	mm/year	0
Uncovered areas	mm/year	36.5[8]
River conductance		
Lake	m^2/day	0.3
Down-gradient drainages	m^2/day	0.3

Once the steady-state calibration was concluded, the transient model was calibrated, using the parameters calibrated in the steady-state simulation as first guesses.

The transient calibration was first performed using only the water level data from the boreholes in the source area, where no significant influence of the evapotranspiration was expected to occur. Thus, in this stage, evapotranspiration from the phytoremediation area was not considered.

After the model was calibrated with the data from the source area, evapotranspiration rates of the phytoremediation area were calibrated using the water level data from the phytoremediation monitoring boreholes. The transient calibration results are summarized in the scatter plot diagram shown in Figure 6.6.

[8] The calibrated recharge value of 36.5 mm/year corresponds to 2.64% of the average annual rainfall.

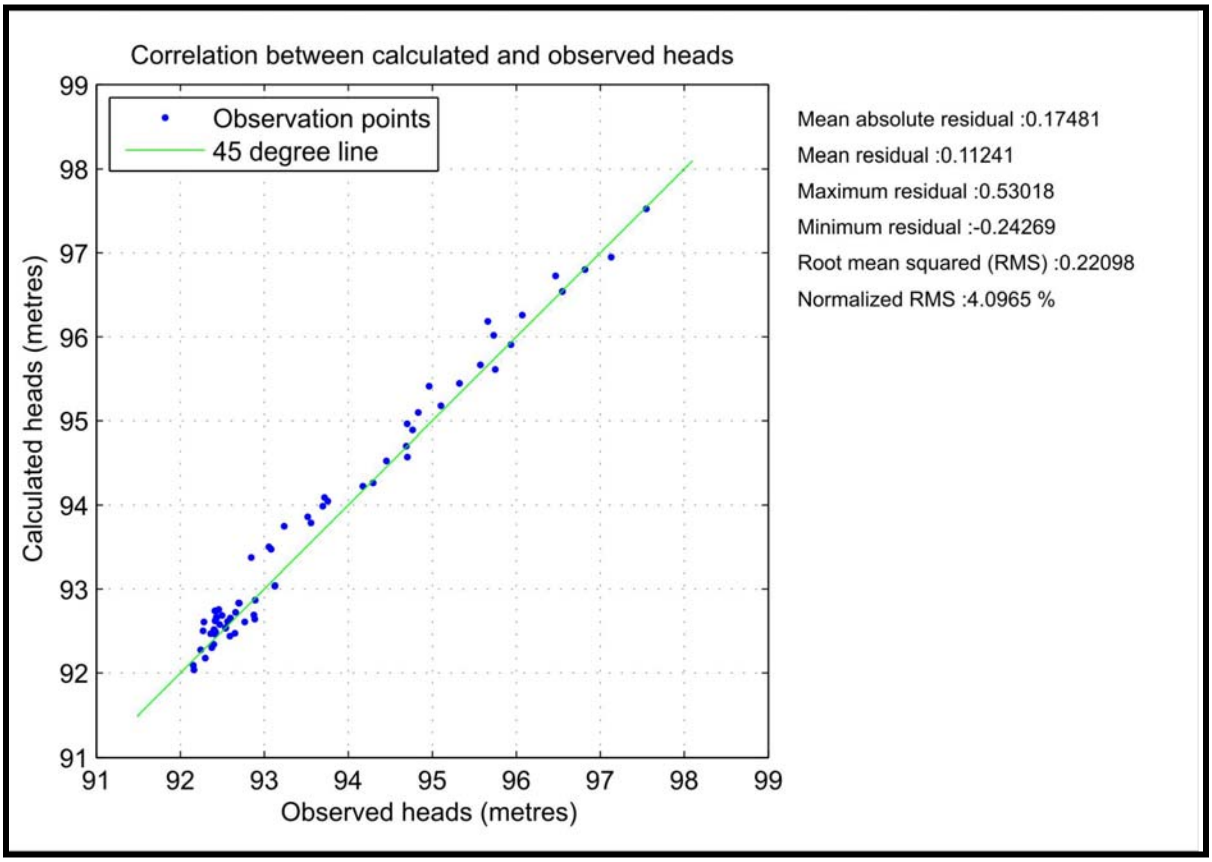

Figure 6.6 - Scatter diagram of calculated and observed heads - Transient simulation.

The calibration indexes for the transient simulation showed values slightly higher than those obtained in the steady-state simulation. The mean absolute residual was 0.174 metres while the normalised RMS index was 4.09%, which is considered appropriate.

The parameter values obtained during the transient calibration are summarized in Table 6.7 and Table 6.8. Comparing these values with those obtained from the steady-state simulations, hydraulic conductivity and recharge values are slightly higher in the transient simulation. Reasons for this are due to the fact that the steady state calibration was made based on average values of an irregular time-series data, which could not represent the annual average properly. Another possible hypothesis is that as the recharge/rainfall rations are not constant throughout the whole year, the wet seasons could show higher run-off rates and, thus, smaller recharge/rainfall ratios.

The hydraulic conductivity values range between 0.1 to 0.43 m/day, which are compatible with those obtained in the deactivated infiltration ponds area. The storage parameters (specific yield) showed better calibration for constant values of 0.03.

Table 6.7 - Parameter values obtained during the transient calibration.

Parameter	Unit	Value
Horizontal hydraulic conductivity		
Zone 1	m/day	0.1
Zone 2	m/day	0.236
Zone 3	m/day	0.43
Specific yield		
Zone 1	-	0.03
Zone 2	-	0.03
Zone 3	-	0.03
Recharge rates		
Covered areas	mm/month	0
Uncovered areas	mm/month	See Table 6.8
Evapotranspiration in the phytoremediation area		
Extinction depth	m	10
Evapotranspiration	mm/month	See Table 6.8
River conductance		
Lake	m^2/day	0.25
Down-gradient drainages	m^2/day	0.25

Table 6.8 - Calibrated recharge and evapotranspiration values with corresponding rainfall rates.

Stress period	Time	ET Rates[9] (mm/month)	Corresponding rainfall rates (mm/month) t-90 days	Calibrated recharge rates (mm/month)	Corresponding rainfall ratio (%)
1	August 2000	26.3	3	0.2	6.4
2	September 2000	8.3	3	0.2	6.4
3	October 2000	6.4	60	3.8	6.4
4	November 2000	0.0	62	3.8	6.2
5	December 2000	0.0	110	7.2	6.6
6	January 2001	0.0	30	1.9	6.4
7	February 2001	0.0	188	11.2	5.9
8	March 2001	4.2	249	15.8	6.4
9	April 2001	13.0	156	9.6	6.2
10	May 2001	8.9	147	10.4	7.0
11	June 2001	30.0	139	8.6	6.2
12	July 2001	52.3	55	3.6	6.6
13	August 2001	83.2	86	5.5	6.4
14	September 2001	77.1	19	1.2	6.4
15	October 2001	78.7	19	1.2	6.4
16	November 2001	85.3	28	1.7	6.2
17	December 2001	83.9	66	4.3	6.6
18	January 2002	80.5	174	11.1	6.4
19	February 2002	51.2	116	6.9	5.9
20	March 2002	51.3	188	12.0	6.4
21	April 2002	63.9	308	19.0	6.2
22	May 2002	35.5	155	10.9	7.0
23	June 2002	47.3	130	8.0	6.2
24	July 2002	52.7	21	1.4	6.6

Calculated and observed head-time curves of the phytoremediation monitoring boreholes are shown in Figure 6.7. The head-times curves in this Figure show that the simulation could reasonably represent the water levels oscillation that occurred in the phytoremediation area.

[9] Presented evapotranspiration rates were obtained from the water budget calculations instead of the values inserted in the model input, since the values inserted in the boundary conditions represent the maximum imposed evapotranspiration, when the water level depth is equal to zero.

The monitoring boreholes that showed the worst fit between the calculated and observed heads are boreholes PZF-05 and PZF-06. This could be due to the fact that the water level of the lake was considered to be constant throughout the simulation period. Boreholes PZF-05 and PZF-06 are those nearest to the lake and, thus, are expected to be more sensitive to the river parameters.

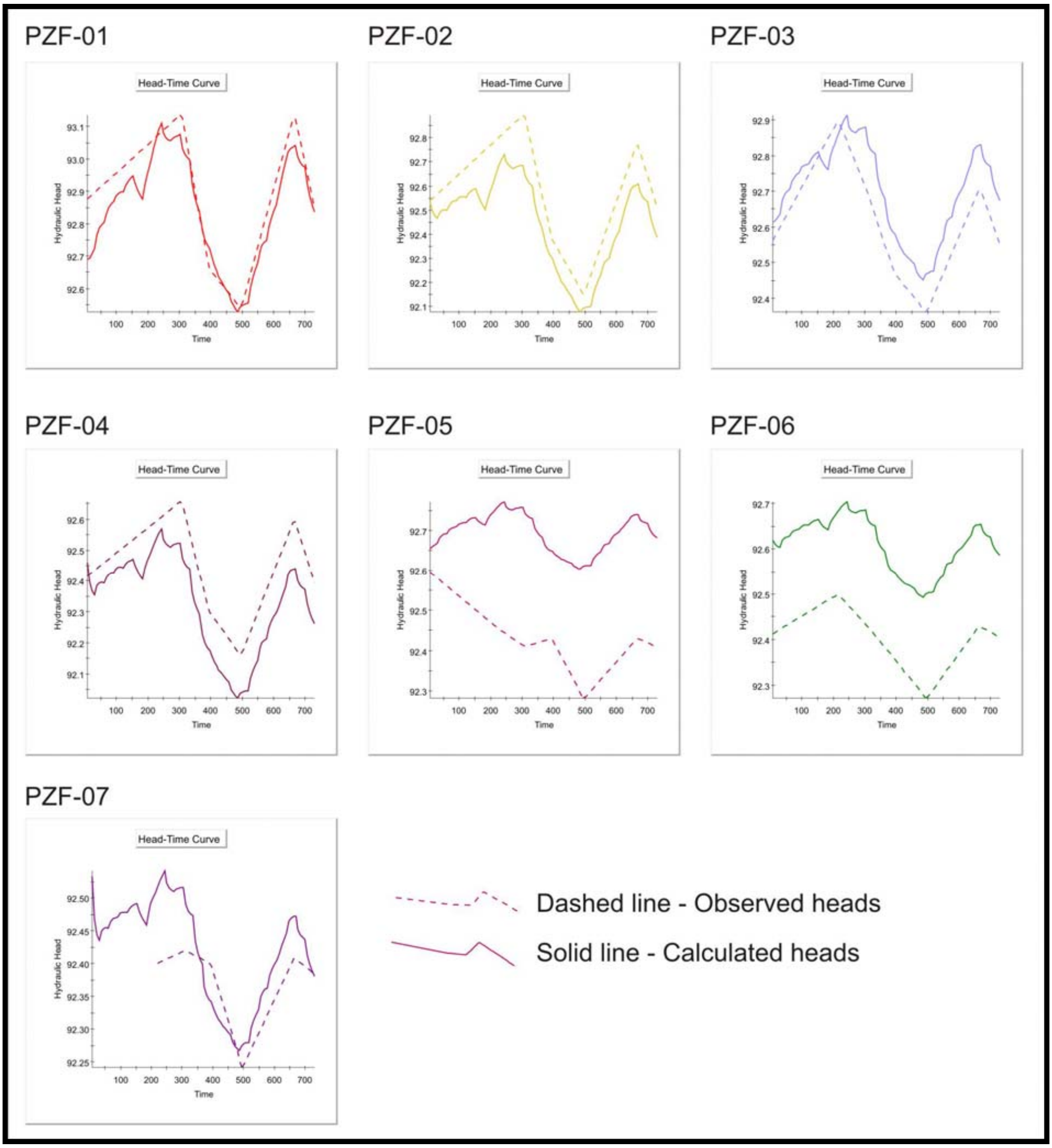

Figure 6.7 - Comparison of calculated and observed head-time curves.

6.5. Analysis of the effectiveness of the phytoremediation system

6.5.1. Evapotranspiration rates

The evapotranspiration rates were calculated based on the model results, using the Sub regional Water Budget Code developed by CHIANG (1993).

The estimated evapotranspiration rates ranged from 0 to 90 mm/month, which equates to abstraction rates of between 0 to 190 m^3/month. The higher evapotranspiration rates were only observed from July 2001, one year after the phytoremediation system was implemented. This phenomenon can be explained by the fact that the root systems of the phytoremediation trees were not deep enough to abstract water from the saturated zone in the first year of the phytoremediation. Figure 6.8 shows the simulated evapotranspiration rates and the A-pan measured evaporation rates.

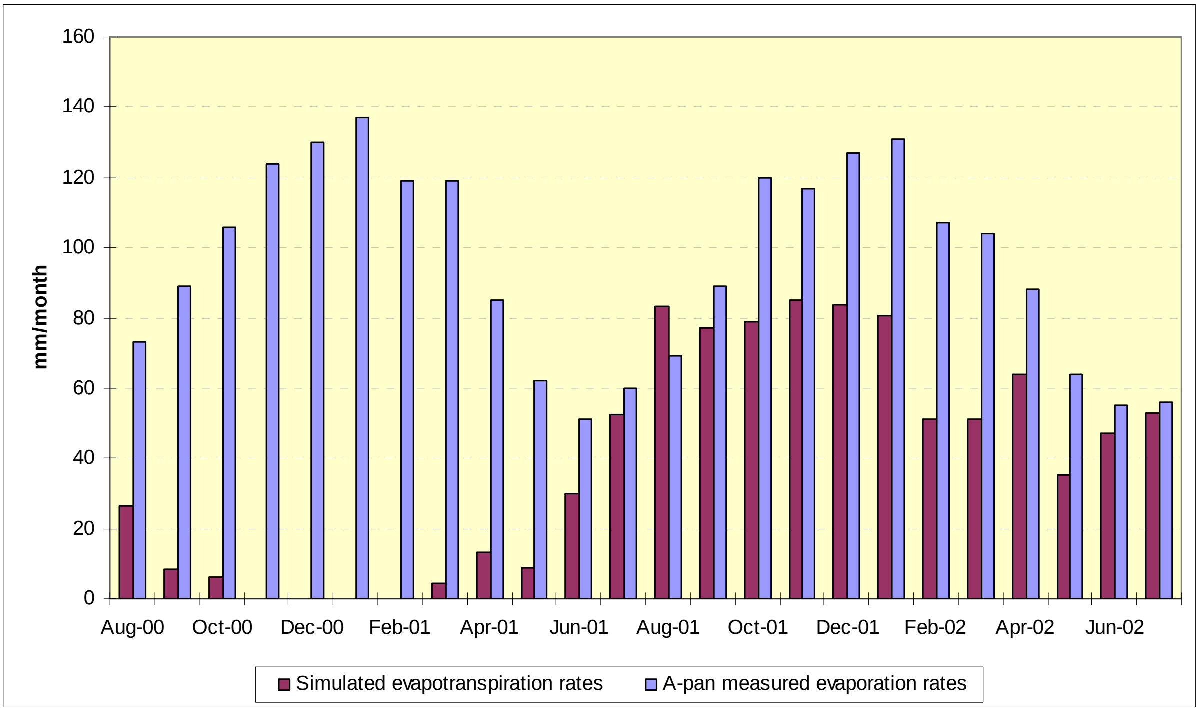

Figure 6.8 - Comparison between the simulated evapotranspiration rates and A-pan measured potential evapotranspiration rates (mm/month).

Comparing the simulated evapotranspiration and recharge rates, it is noted that the evapotranspiration rates are higher than the recharge rates throughout most of the simulation period. This fact indicates that the phytoremediation system evapotranspirated all the clean water provided by recharge and contaminated water from the up-gradient source areas. Figure 6.9 shows the comparison between the evapotranspiration and recharge rates.

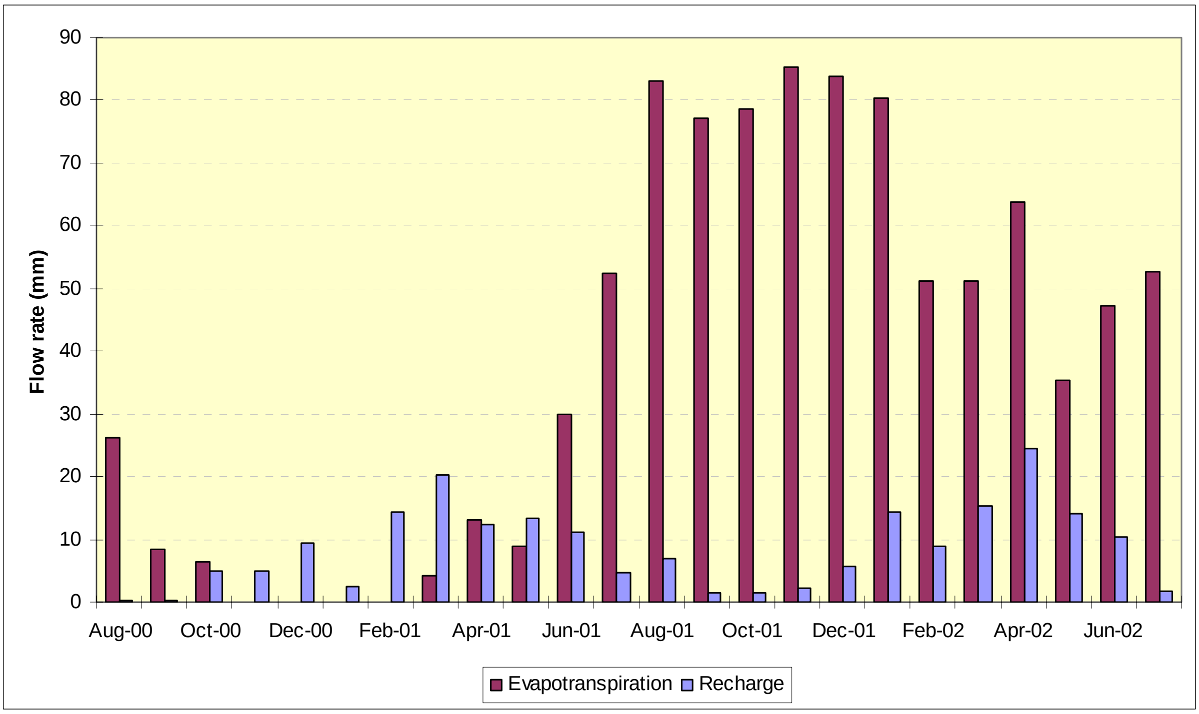

Figure 6.9 - Comparison between simulated evapotranspiration and recharge rates.

Within the phytoremediation area, the higher evapotranspiration rates were observed in the down-gradient areas near the lake. Reasons for this can be explained by the fact that groundwater levels are shallower in down-gradient areas and the fact that wetland trees, which are expected to have higher evapotranspiration rates, were planted only in the down-gradient areas. Figure 6.10 shows the evapotranspiration contours within the phytoremediation area.

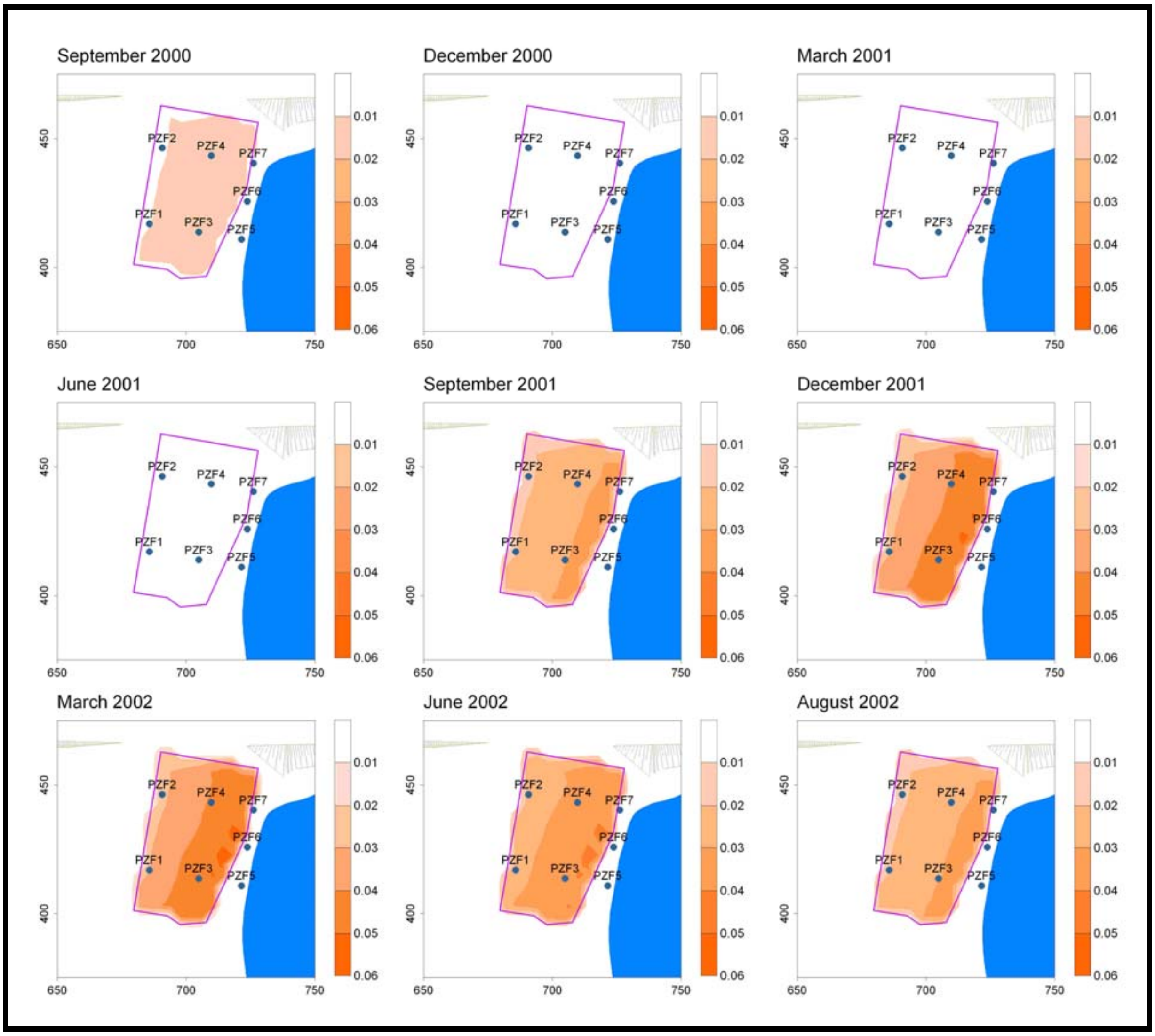

Figure 6.10 - Evapotranspiration rate contours (m^3/day/cell).

6.5.2. Simulated groundwater levels

In order to evaluate the effects of the groundwater abstraction imposed by the phytoremediation on the groundwater level contours and gradients, simulated groundwater level contours were plotted for the two scenarios, considering the effects of the phytoremediation, and not considering the effects of phytoremediation. The generated contours for the both scenarios are presented in Figure 6.11 and Figure 6.12.

Considering the scenario that included the effects from evapotranspiration, the groundwater contours showed very small changes and these are more likely to be related to the various recharge rates imposed in the model than the effects from evapotranspiration. The scenario that did not include evapotranspiration effects also showed very similar contours, indicating that evapotranspiration imposed by the phytoremediation area does not have a significant effect on the groundwater levels.

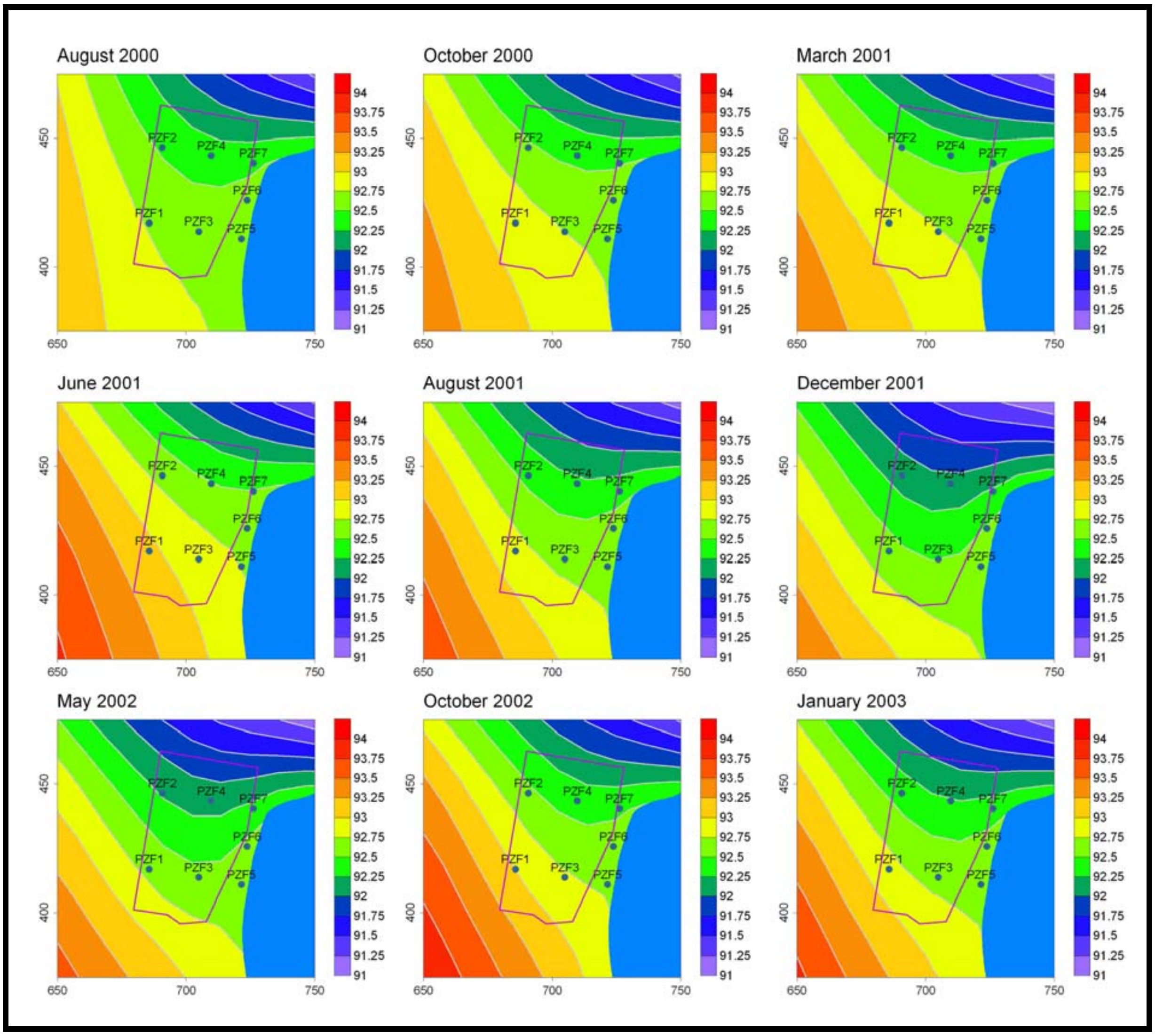

Figure 6.11 - Simulated water level contours (metres).

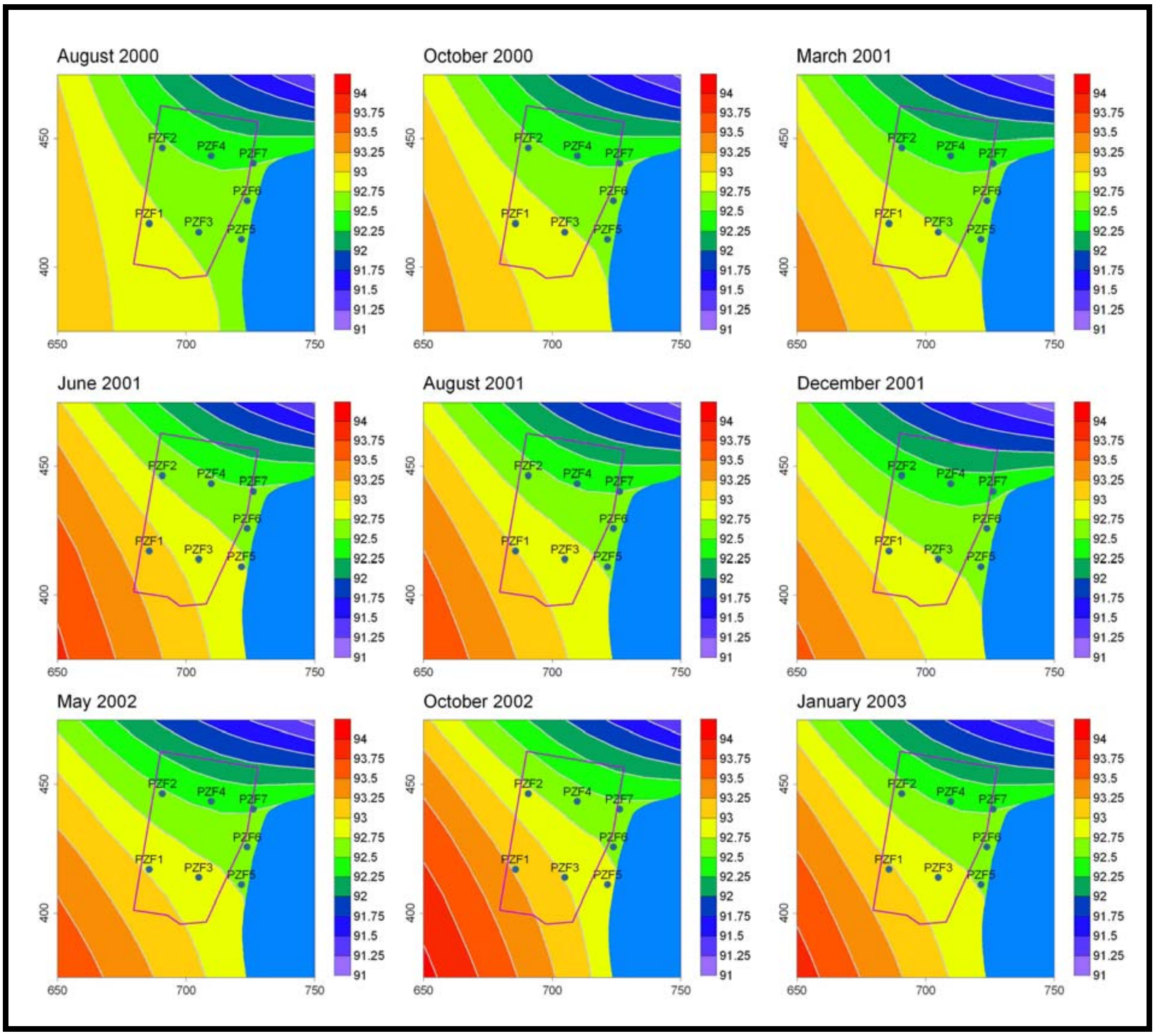

Figure 6.12 - Simulated water levels without evapotranspiration abstraction (metres).

6.5.3. Draw-down

General procedures to estimate drawdown include subtracting the simulated groundwater levels from the initial conditions (groundwater levels). However these procedures would not be appropriate for these simulations, as the groundwater levels show oscillation due to different recharge rates, regardless of phytoremediation effects.

The draw-down was estimated by running the whole simulation time (two years) in two scenarios, the first scenario considering the evapotranspiration effects (calibrated model), and the second scenario considering no evapotranspiration caused by the phytoremediation.

The groundwater levels from scenario 2 were subtracted from the respective groundwater levels from scenario 1, generating the groundwater draw-down grids. Figure 6.13 shows the simulated draw-down contours.

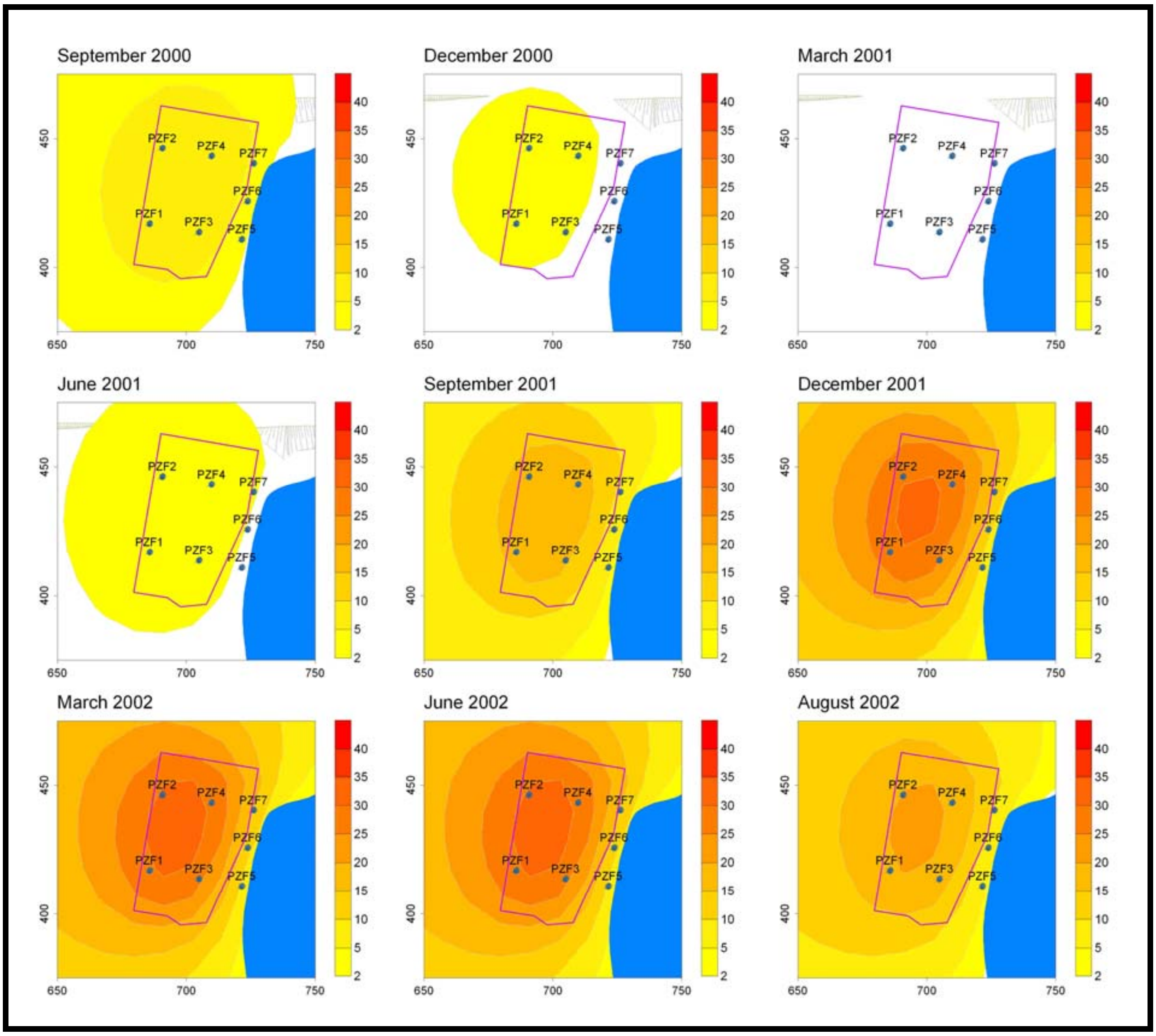

Figure 6.13 - Simulated draw-down cone contours (centimetres).

The estimated drawdown ranged between 0 and 40 centimetres, with maximum values occurring between the intermediate and up-gradient monitoring boreholes (PZF-01, PZF-02, PZF-03 and PZF-04).

It is noted that draw-downs higher than 15 centimetres only occurred from September 2001, one year after the phytoremediation start-up. This can be explained by the fact that the plant roots were not deep enough to take up significant amounts of water in the first year.

The simulated draw-downs for August 2002 showed lower values than those simulated from December 2001 up to 2002. The lowering of groundwater levels as a result of low recharge rates in dry seasons may be a possible reason for this decrease in the draw-down, as the plants should have been abstracting less groundwater from the saturated zone.

The draw-downs near the down-gradient boreholes are lower than 15 centimetres for the whole simulation period, which could indicate that inflow from the lake into the aquifer may have counter-acted the evapotranspiration effects.

The draw-down cones extend up to 50 metres from the phytoremediation area considering draw-downs higher than 10 centimetres.

6.5.4. Water balance

Based on the results from the sub-regional Water Budget Code (CHIANG, 1993), a water balance was built including the main exchange processes between the phytoremediation area and the down-gradient lake. The balance was calculated essentially in terms of inflow and outflow as follows:

- Inflow terms
  - Storage;
  - Horizontal exchange;
  - Recharge;
  - River leakage[10]; and
  - Total inflow.
- Outflow terms

[10] The term river leakage corresponds to leakage from the lake, and was used since the lake was represented in the groundwater model by a river condition (3rd type).

- o Storage;
- o Horizontal exchange;
- o Evapotranspiration;
- o River leakage; and
- o Total outflow.

The results of the water balance are summarized in Table 6.9. Graphs illustrating the relationship of the various water balance terms are presented in Figure 6.14 and Figure 6.15.

According to the water balance results, the major inflow into the phytoremediation area occurs through horizontal exchange from the surrounding areas, with rates ranging between 4 and 8 m^3/day. Lake leakage (river leakage) is also significant with rates ranging between 1 and 3.5 m^3/day. Storage and recharge are less significant and showed inflow rates of up to 1.5 m^3/day.

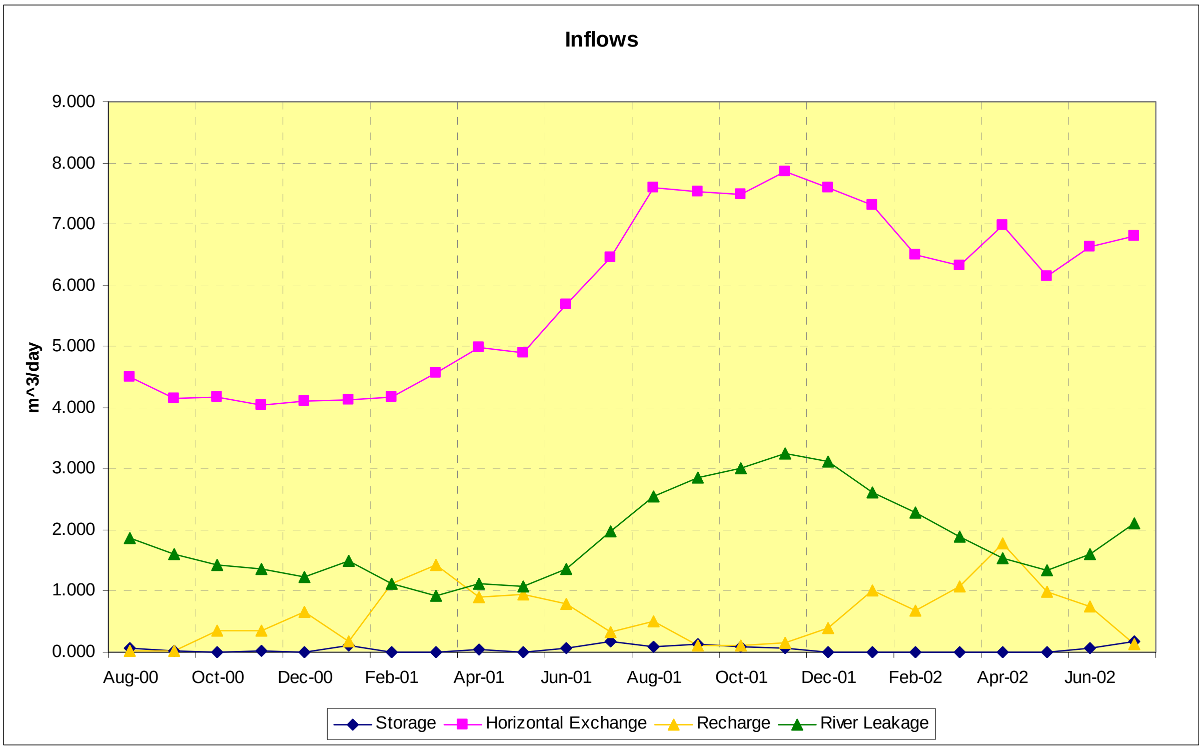

Figure 6.14 - Time series of calculated water balance flow terms (inflows).

The most relevant output flow term throughout the simulation period was horizontal exchange with downgradient areas, showing outflow rates between 4.5 and 6 m^3/day. Evapotranspiration started to show significant outflow rates from July 2000, exceeding the horizontal exchange outflows between August 2001 and January 2002. Storage and river leakage is of low significance, with outflow rates lower than 0.5 m^3/day.

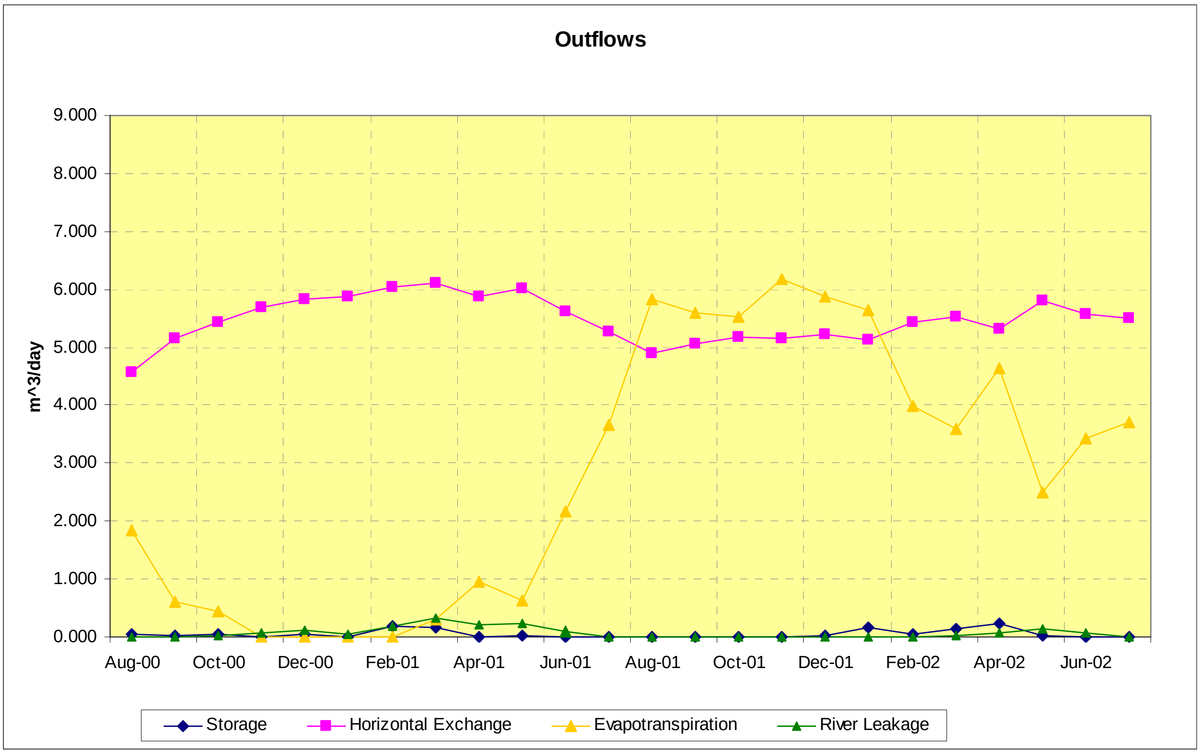

Figure 6.15 - Time series of calculated water balance flow terms (outflows).

Comparing the lake inflow and outflow rates, it is noted that the inflow rates exceed the outflow rates throughout the whole simulation period, which means that the lake acts more as an inflow zone than a discharge zone and, thus, any contamination due to the aquifer seepage into the aquifer is highly unlikely to occur. Figure 6.16 illustrates this relationship.

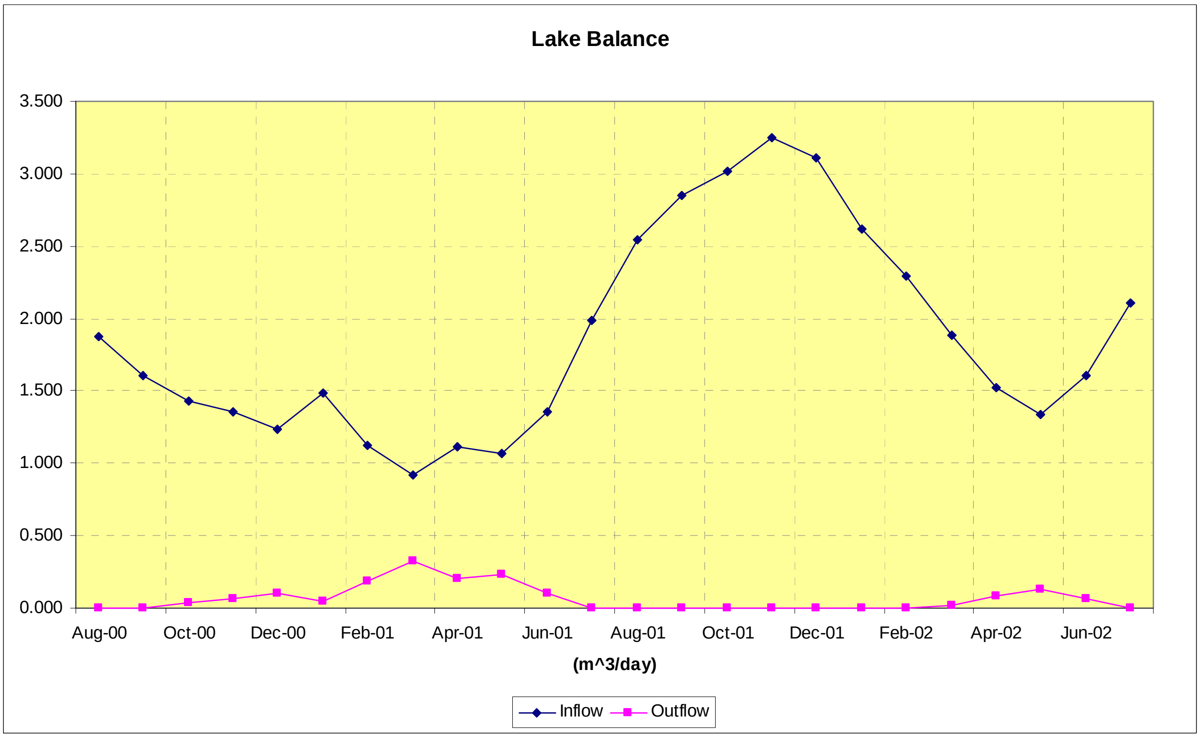

Figure 6.16 - Comparison of lake inflow and outflow terms.

Using an average groundwater level of 3.5 metres below the ground level, effective porosity of 0.3 and the phytoremediation area of 2,175 m^2, it is estimated that the saturated groundwater volume of approximately 10766 m^3 within the phytoremediation area.

Using the maximum outflow rate of 11.34 m^3/day, it can be calculated that the aquifer within the phytoremediation area would need a minimum of 944 days (10766m^3/ 11.34m^3/day) to outflow all of its groundwater volume, considering that no inflow within this period would leave the aquifer by outflow. This indicates that the contamination that migrated throughout the phytoremediation area in the simulated period possibly originated before the peroxide injections in the source area were conducted and, thus, the peroxide injections did not affect this contamination.

Table 6.9 - Summary of the water balance calculations.

YEAR 1													
Time	**Stress Period**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
	Elapsed Time (days)	**31**	**61**	**92**	**122**	**153**	**184**	**212**	**243**	**273**	**304**	**334**	**365**
	Corresponding Date	Aug/2000	Sep/2000	Oct/2000	Nov/2000	Dec/2000	Jan/2001	Feb/2001	Mar/2001	Apr/2001	May/2001	Jun/2001	Jul/2001
Inflow (m^3/day)	**Storage**	0.073	0.011	0.000	0.012	0.000	0.117	0.000	0.000	0.042	0.000	0.058	0.171
	Horizontal Exchange	4.501	4.138	4.164	4.032	4.103	4.130	4.169	4.560	4.979	4.898	5.685	6.451
	Recharge	0.017	0.018	0.345	0.356	0.653	0.172	1.116	1.431	0.896	0.935	0.799	0.327
	River Leakage	1.874	1.610	1.431	1.358	1.235	1.488	1.126	0.915	1.110	1.068	1.359	1.985
	Total Inflow	6.465	5.778	5.940	5.758	5.991	5.908	6.411	6.906	7.028	6.900	7.900	8.935
Outflow (m^3/day)	**Storage**	0.057	0.028	0.037	0.006	0.044	0.000	0.178	0.170	0.000	0.017	0.000	0.000
	Horizontal Exchange	4.562	5.143	5.421	5.690	5.840	5.866	6.050	6.115	5.881	6.024	5.623	5.262
	Evapotranspiration	1.847	0.603	0.446	0.002	0.001	0.000	0.000	0.297	0.946	0.626	2.176	3.669
	River Leakage	0.000	0.003	0.035	0.061	0.106	0.042	0.182	0.324	0.201	0.234	0.101	0.003
	Total Outflow	6.465	5.778	5.940	5.758	5.991	5.908	6.410	6.906	7.028	6.900	7.900	8.934
YEAR 2													
Time	**Stress Period**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**	**23**	**24**
	Elapsed Time (days)	**396**	**426**	**457**	**487**	**518**	**549**	**577**	**608**	**638**	**669**	**699**	**730**
	Corresponding Date	Aug/2001	Sep/2001	Oct/2001	Nov/2001	Dec/2001	Jan/2002	Feb/2002	Mar/2002	Apr/2002	May/2002	Jun/2002	Jul/2002
Inflow (m^3/day)	**Storage**	0.095	0.140	0.091	0.073	0.000	0.000	0.000	0.000	0.000	0.000	0.059	0.182
	Horizontal Exchange	7.591	7.536	7.489	7.857	7.603	7.308	6.493	6.311	6.981	6.136	6.638	6.797
	Recharge	0.494	0.113	0.109	0.161	0.392	1.000	0.689	1.080	1.770	0.986	0.747	0.125
	River Leakage	2.540	2.851	3.016	3.252	3.114	2.621	2.289	1.885	1.526	1.336	1.610	2.109
	Total Inflow	10.721	10.640	10.705	11.342	11.109	10.929	9.471	9.277	10.277	8.458	9.054	9.212
Outflow (m^3/day)	**Storage**	0.000	0.000	0.000	0.000	0.013	0.157	0.056	0.138	0.244	0.025	0.000	0.000
	Horizontal Exchange	4.887	5.052	5.183	5.161	5.212	5.128	5.438	5.522	5.321	5.812	5.565	5.513
	Evapotranspiration	5.834	5.588	5.522	6.181	5.883	5.645	3.977	3.600	4.632	2.487	3.428	3.698
	River Leakage	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.017	0.080	0.133	0.061	0.002
	Total Outflow	10.721	10.640	10.705	11.343	11.109	10.929	9.471	9.276	10.277	8.458	9.054	9.212

6.6. Final remarks on groundwater modelling

From the findings of the groundwater modelling exercise, it was found that numerical models have great potential as tools to evaluate and quantify the effectiveness of phytoremediation systems, especially in terms of hydrodynamic processes.

In regard to the phytoremediation system modelled in this study, the model could make reasonable estimates of the major processes that occurred in the saturated zone, such as recharge and evapotranspiration rates. Important processes hypothesised in the conceptual model were confirmed by the modelling, such as the delay time between rainfall and effective recharge and inflow from the lake.

The model results indicated appropriate calibration indexes for both steady-state and transient simulations, which allowed for quantifying of draw-down and evapotranspiration rates, indicators of phytoremediation effectiveness. In this regard, the model showed that the phytoremediation was not effective in terms of promoting a hydraulic barrier to contaminant migration. Furthermore, the results also helped to achieve a better understanding of the hydrogeochemistry, showing that the groundwater flow velocities are too slow to relate the irregular concentration patterns to multiple sources.

The modelling exercise also indicated some misconceptualisation during the phytoremediation design stage, especially with respect to the lake-aquifer relationship, as at the design stage the lake was considered to be a groundwater outflow zone. The results from field measurements and the model water balance demonstrated that the lake acts more as a recharge zone to the aquifer than a discharge zone, as previously conceptualised.

The MODFLOW code was able to accurately represent the saturated process and incorporated some unsaturated processes to a certain extent, such as decreased evapotranspiration and recharge rates when groundwater levels become deeper. However, if the aim of the modelling exercise is to quantify unsaturated processes accurately, unsaturated codes must be used. Alternative unsaturated codes include MODFLOW-VSF, SURFACT and MIKE-SHE, but technical points must be addressed, especially regarding the complete unsaturated zone monitoring.

7. Conclusions

Based on the results obtained by the groundwater study and groundwater modelling, the following conclusions were reached:

Groundwater numerical models can be useful tools to evaluate phytoremediation systems and have excellent potential to quantify major phytoremediation water balance processes. In the phytoremediation site where the groundwater modelling was performed, the modelling results contributed to a better understanding of major hydrogeologic processes, allowing qualifying and quantifying these processes.

The groundwater study performed in the phytoremediation area identified two important processes. The first on is the delay between rainfall and recharge on the saturated zone, and the second one is the change in flow regime throughout dry and wet seasons. These two processes are critical to understand the water balance processes that occurred in the study area.

The analysis of groundwater contaminant results identified a very irregular distribution and evolution pattern of the contaminants. The contaminant concentrations showed very high oscillations when compared to the estimated groundwater flow velocities, which could indicate that the results are likely to be related to groundwater level oscillation and smearing processes. Furthermore, contaminant concentrations exceeded the target levels in the up-gradient and down-gradient boreholes until later monitoring stages.

Regarding the modelling results, the calibration indexes indicated that the model was properly calibrated for both steady-state and transient simulations. Furthermore, the calibrated model was able to provide estimations of evapotranspiration rates and draw-downs, which were then used to evaluate the effectiveness of phytoremediation.

Transient simulations indicated draw-downs ranging from 0 up to 40 centimetres throughout the simulation period. No relevant flow change due to the draw-down cones was observed.

Simulated abstraction rates caused by the phytoremediation area range between 0 and 200 m^3/month and are in most of the simulated period higher than the recharge rates, indicating that not only recharge water, but also contaminated water from the source areas was abstracted by the phytoremediation system.

Although the higher draw-down were identified in the intermediate and up gradient phytoremediation areas, the higher groundwater abstraction occurred in the down gradient area near the lake, where groundwater levels are shallower and thus, the saturated zone was closer to the phytoremediation plant root systems.

Monitoring data from the multi-level piezometers showed no significant change on hydraulic heads along the different monitoring levels, indicating that the one-layer modelling approach was appropriate.

Water balance calculations based on the average groundwater levels, calibrated porosity values and the extent of the phytoremediation area indicated an approximate volume of 10766m^3 of groundwater within the phytoremediation area. Using this value with the maximum outflow rates, it was possible to establish that the aquifer within the phytoremediation area would require a minimum of 944 days to renew all the groundwater volume within. This fact has several implications regarding the age of contamination within the phytoremediation area, which indicates that contaminants that migrate throughout the phytoremediation area during the simulated period (August 2000 up to July 2002) probably originated before the peroxide injections were conducted. Therefore, the peroxide injections probably did not affect the contamination observed in the phytoremediation area during the simulation period.

The measurement water levels in the lake would have been critical to precisely define the water balance relationships between the phytoremediation area and the lake. The sensitivity of the lake elevation becomes clear in the transient calibration, where the monitoring boreholes near the lake (PZF-05 and PZF-06) showed the fit between calibrated and observed heads, related to the use of constant river elevation throughout the simulation.

Transport modelling was not conducted for the area basically for three reasons, being:

- Lack of appropriate initial conditions;
- Peroxide injection events that occurred in the source area would require a reactive transport modelling code; and
- Contaminant mass gains and losses to unsaturated zone due to the water level oscillations.

The studied phytoremediation system was not effective as a hydraulic barrier, as no significant draw-down and change in groundwater flow direction occurred. Reasons for the ineffectiveness of the phytoremediation system include:

- Groundwater concentrations were underestimated;
- Aquifer conductivity was underestimated;
- Lack of site-specific data;
- Misconceptualisation;
- Inadequate monitoring program; and
- Inappropriate plant selection.

Stronger alternative techniques such as extended peroxide oxidation and air sparging would probably have been more effective if used instead of the phytoremediation method over time. However, the concept at the design stage was that most of the contamination would be controlled by the peroxide injections conducted in the source area, and only a low-cost polishing technique would be required as a last barrier to protect the lake. This is, thus, the main reason why phytoremediation was the chosen technique.

Although the phytoremediation was not effective, the contamination scenario would probably be worse if the phytoremediation was not been implemented. The biodegradation results indicate dissolved oxygen concentrations above 1 mg/l and positive Eh values throughout most of the phytoremediation process, which indicates that the phytoremediation system could have acted in maintaining favourable conditions for biodegradation.

8. RECOMMENDATIONS

The results from the studied phytoremediation site indicate a draw-down of 40 centimetres over a period of two years, which might indicate that phytoremediation systems can be used as hydraulic barriers, using a detailed time frame assessment regarding contamination migration and plant growth rates.

To maximize the effectiveness of phytoremediation systems (regarding hydraulic aspects), a detailed groundwater investigation must be conducted in order to provide a complete understanding of the aquifer water balance and contamination scenario, which is critical for the design stages. A groundwater investigation must at the very least address the following points:

- Aquifer geometry;
- Distribution of hydraulic parameters;
- Groundwater levels distribution;
- Definition of boundary conditions;
- Groundwater / surface water interactions; and
- Contaminant distribution.

Due to the complexity of aquifers and their relationships with surface water and other hydrological parameters, it is extremely difficult to delineate a general phytoremediation monitoring program regarding parameters and frequency, since the monitoring must deal with the site-specific aquifer conditions.

In this regard, the use of groundwater modelling can play a major role in the phytoremediation design stage, not only for the prediction of the phytoremediation method itself, but also to identify parameters with higher sensitivity and, therefore, higher influence on the remediation effectiveness. In the study area, the model of the studied site showed that the lake level, which was not monitored, was the most sensitive parameter. Thus the measurement of the lake levels would have therefore substantially improved the accuracy of the modelling results and system design.

Several modelling codes can be used to evaluate effectiveness and parameter sensitivity of phytoremediation systems. This study has shown that MODFLOW can accurately represent the main processes that occur in the saturated zone and, to some extent, processes that occurred in the unsaturated zone. However, when the unsaturated zone imposes high sensitivity to aquifer conditions or plays a major role in the system effectiveness, unsaturated codes, such as MODFLOW-VSF, FEMWATER and SURFACT, should be used. It is also important to emphasize that the use of unsaturated modelling codes has several implications on the monitoring, since a more detailed assessment and monitoring of the unsaturated zone would be required.

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APPENDIX 1 - Photographic record of the plants used in the phytoremediation system – October 2003.

A1 – Sangra d’água (*Croton urucuana*).

B1 – Ingá-feijão (*Inga marginata*).

A2 – Pau-santo (*Kielmeyera cariacea*).

B2 – Pau-terra-mirim (*Qualea dichotoma*).

D2 – Canafístula (*Peltophorum dubium*).

A3 – Angico-vermelho (*Anadaranthera macrocarpa*).

B3 – Angico-do-cerrado (*Anaderanthera falcate*)

C3 – Angico-branco-da-mata (*Anaderanthera columbrina*).

D3 – Deadaleiro (*Lafoensia pacari*).

APPENDIX 2 - Groundwater monitoring results.

Borehole	Target level (mg/l)	Chloroform concentrations (mg/l)								
		August 2000	**December 2000**	**March 2001**	**June 2001**	**August 2001**	**December 2001**	**May 2002**	**October 2002**	**January 2003**
PZF-01	1.00	0.075	ND	ND	ND	15.6	0.01	ND	0.006	ND
PZF-02	1.00	10	8.6	0.78	10.3	ND	17.8	16.5	2.96	1.6
PZF-03	1.00	4.25	15.4	16.6	13	13.2	3.8	12.95	9.319	4.9
PZF-04	1.00	4.6	3.7	2.4	9.4	4.2	1.85	4.25	0.689	0.9
PZF-05	1.00	2.17	0.4	ND	0.83	0.51	0.029	0.487	0.815	0.63
PZF-06	1.00	2.3	2.3	15.3	0.5	3.35	2.6	15.8	2.696	0.89
PZF-07	1.00	0.016	ND	7.3	4.2	0.006	ND	10.4	ND	ND

* ND – Non detected.

Borehole	Target level (mg/l)	Chlorobenzene concentrations (mg/l)								
		August 2000	**December 2000**	**March 2001**	**June 2001**	**August 2001**	**December 2001**	**May 2002**	**October 2002**	**January 2003**
PZF-01	0.05	0.256	0.51	0.041	0.4	0.145	0.651	0.169	0.07	0.27
PZF-02	0.05	0.107	0.164	0.028	0.15	0.655	0.16	0.11	ND	0.17
PZF-03	0.05	ND	0.056	0.051	ND	0.05	ND	ND	0.101	0.11
PZF-04	0.05	0.032	0.049	0.014	ND	0.066	0.4	ND	0.064	0.11
PZF-05	0.05	0.104	0.054	0.069	ND	0.079	0.055	0.073	0.044	0.043
PZF-06	0.05	0.001	0.022	0.019	ND	0.015	ND	ND	0.026	0.027
PZF-07	0.05	0.04	0.053	0.015	ND	0.048	0.067	ND	0.064	ND

* ND – Non detected.

Borehole	Target level (mg/l)	Benzene concentrations (mg/l)								
		August 2000	**December 2000**	**March 2001**	**June 2001**	**August 2001**	**December 2001**	**May 2002**	**October 2002**	**January 2003**
PZF-01	0.01	0.012	0.018	ND	0.013	0.45	0.018	0.01	ND	ND
PZF-02	0.01	0.31	0.28	0.041	0.3	ND	0.43	0.38	0.555	0.088
PZF-03	0.01	0.044	1.0	0.5	0.65	0.75	0.9	0.65	0.668	0.64
PZF-04	0.01	0.258	0.3	0.1	0.55	0.26	0.15	0.225	0.037	0.15
PZF-05	0.01	0.059	0.023	ND	ND	0.031	0.009	0.023	0.119	0.19
PZF-06	0.01	ND	0.017	0.203	ND	0.05	ND	0.3	0.022	0.016
PZF-07	0.01	ND	ND	0.08	ND	ND	ND	ND	ND	ND

* ND – Non detected.

Borehole	Target level (mg/l)	Methylene chloride concentrations (mg/l)								
		August 2000	December 2000	March 2001	June 2001	August 2001	December 2001	May 2002	October 2002	January 2003
PZF-01	0.05	ND	ND	ND	ND	0.141	ND	ND	ND	ND
PZF-02	0.05	ND	0.029	0.034	ND	ND	ND	ND	ND	ND
PZF-03	0.05	ND	1.1	1.6	1.5	1.6	ND	ND	ND	0.83
PZF-04	0.05	ND	0.143	0.3	0.6	ND	ND	ND	ND	0.13
PZF-05	0.05	ND	0.017	0.039	ND	ND	ND	ND	ND	0.42
PZF-06	0.05	ND	ND	0.3	ND	ND	ND	ND	ND	ND
PZF-07	0.05	ND	ND	0.015	ND	ND	ND	ND	ND	ND

* ND – Non detected.

Borehole	Target level (mg/l)	1,2 – Dichloroethane concentrations (mg/l)								
		August 2000	December 2000	March 2001	June 2001	August 2001	December 2001	May 2002	October 2002	January 2003
PZF-01	0.01	ND	ND	ND	ND	0.093	ND	ND	ND	ND
PZF-02	0.01	0.212	0.103	0.0454	ND	ND	ND	ND	0.143	ND
PZF-03	0.01	ND	0.021	0.036	ND	0.025	ND	ND	0.029	0.03
PZF-04	0.01	0.53	0.35	0.181	ND	0.214	ND	0.225	0.169	0.19
PZF-05	0.01	ND	0.005	ND	ND	ND	ND	ND	0.024	0.035
PZF-06	0.01	ND	ND	0.026	ND	0.005	ND	ND	ND	ND
PZF-07	0.01	0.087	ND	0.03	ND	0.021	ND	ND	ND	ND

* ND – Non detected.

Borehole	Target level (mg/l)	Chloride concentrations (mg/l)								
		August 2000	November 2000	March 2001	June 2001	August 2001	December 2001	May 2002	October 2002	January 2003
PZF-01	-	1835	241	208	255	175	265	269	325	322
PZF-02	-	210	255	223	215	280	187	201	176	181
PZF-03	-	35	75	59.8	65	70	106	102	125	111
PZF-04	-	115	130	134	130	125	121	130	127	131
PZF-05	-	150	115	170	175	125	93	140	75	62
PZF-06	-	30	65	27.1	35	45	43	29	55.5	55
PZF-07	-	130	115	93.4	80	110	92.5	53	116	88.5

Borehole	Target level (mg/l)	pH								
		August 2000	December 2000	March 2001	June 2001	August 2001	December 2001	May 2002	October 2002	January 2003
PZF-01	-	6.5	NM*	6.5	6.5	6.9	6.9	6.8	6.3	6.3
PZF-02	-	6.1	NM*	6.6	6.3	6.4	6.9	6.9	5.7	5.6
PZF-03	-	6.8	NM*	6.6	6.6	6.6	6.9	6.4	5.4	6
PZF-04	-	6.3	NM*	6.7	6.6	6	7	6.7	5.6	5.8
PZF-05	-	6.3	NM*	6.9	6.7	6.5	7.3	6.6	6.4	6.6
PZF-06	-	7	NM*	7.1	6.4	6.4	7.3	6.4	6.2	6.3
PZF-07	-	4.7	NM*	6.8	6.5	5.9	7	5.8	5.1	5.4

* NM – Not measured.

Borehole	Target level (mg/l)	Eh (mV)								
		August 2000	December 2000	March 2001	June 2001	August 2001	December 2001	May 2002	October 2002	January 2003
PZF-01	-	-5	NM*	145	-60	-50	-40	-80	-10	20
PZF-02	-	155	NM*	155	110	155	140	130	105	160
PZF-03	-	105	NM*	115	110	110	85	25	30	50
PZF-04	-	155	NM*	135	140	150	155	120	110	120
PZF-05	-	-60	NM*	-80	-30	-80	-65	-60	-60	-45
PZF-06	-	90	NM*	25	-10	-20	25	10	-10	35
PZF-07	-	170	NM*	95	70	105	180	150	100	125

* NM – Not measured.

Borehole	Target level (mg/l)	Dissolved oxygen (mg/l)								
		August 2000	December 2000	March 2001	June 2001	August 2001	December 2001	May 2002	October 2002	January 2003
PZF-01	-	NM*	NM*	1.03	2.29	NM*	0.21	4.36	1.53	NM*
PZF-02	-	NM*	NM*	1.13	2.39	NM*	0.07	3.84	2.59	NM*
PZF-03	-	NM*	NM*	0.99	2.41	NM*	0.4	2.8	1.94	NM*
PZF-04	-	NM*	NM*	1.11	2.37	NM*	3.24	2.88	2.1	NM*
PZF-05	-	NM*	NM*	0.56	2.63	NM*	0.02	3.45	1.61	NM*
PZF-06	-	NM*	NM*	0.46	2.71	NM*	3.54	1.25	2.42	NM*
PZF-07	-	NM*	NM*	0.74	2.49	NM*	0.12	1.48	2.41	NM*

* NM – Not measured.

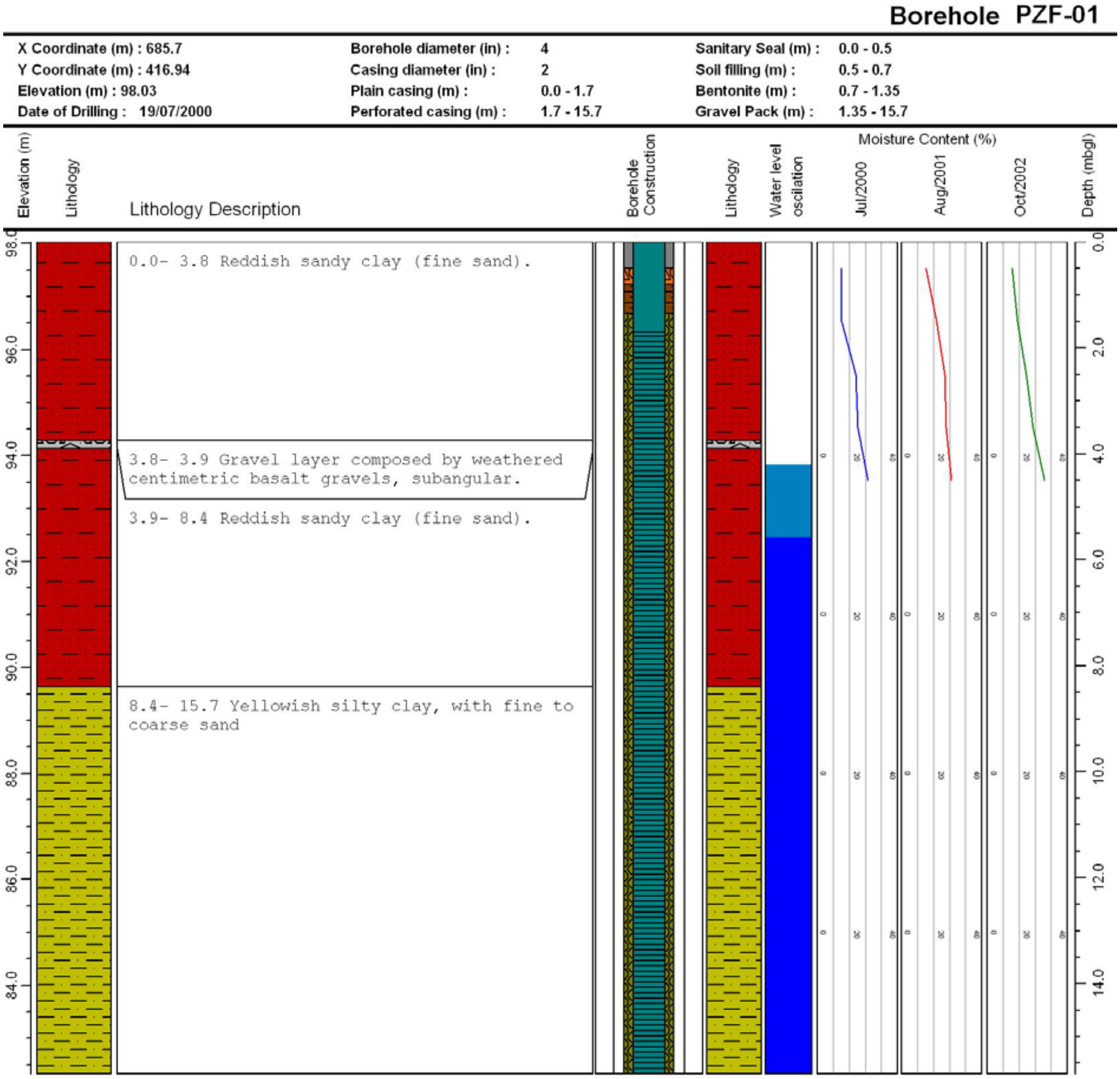
Borehole	Target level (mg/l)	Electric conductivity (uS/cm)								
		August 2000	December 2000	March 2001	June 2001	August 2001	December 2001	May 2002	October 2002	January 2003
PZF-01	-	500	NM*	750	1006	1108	1116	1052	1181	1091
PZF-02	-	600	NM*	829	760	776	735	733	647	693
PZF-03	-	100	NM*	300	312	365	438	411	489	430
PZF-04	-	300	NM*	526	500	507	468	513	483	501
PZF-05	-	400	NM*	762	742	630	529	683	443	403
PZF-06	-	200	NM*	224	200	273	282	217	291	250
PZF-07	-	300	NM*	223	312	452	383	247	399	334

* NM – Not measured.

Borehole	Target level (mg/l)	Groundwater temperature (ºC)								
		August 2000	December 2000	March 2001	June 2001	August 2001	December 2001	May 2002	October 2002	January 2003
PZF-01	-	24.5	NM*	23.8	25.3	NM*	27.1	27.6	26.6	27.3
PZF-02	-	23.9	NM*	24.2	25.6	NM*	25.5	24.7	24.5	26.1
PZF-03	-	25.0	NM*	24.6	25.6	NM*	26	25.4	27.4	26.1
PZF-04	-	25.1	NM*	24.8	24.9	NM*	25.6	25.3	25.8	25.5
PZF-05	-	24.2	NM*	26.2	25.0	NM*	27.9	24.6	27.9	26.5
PZF-06	-	23.0	NM*	24.8	24.8	NM*	28.1	23.6	25.7	26.9
PZF-07	-	22.3	NM*	24	24.4	NM*	29.3	24.6	24.8	27.2

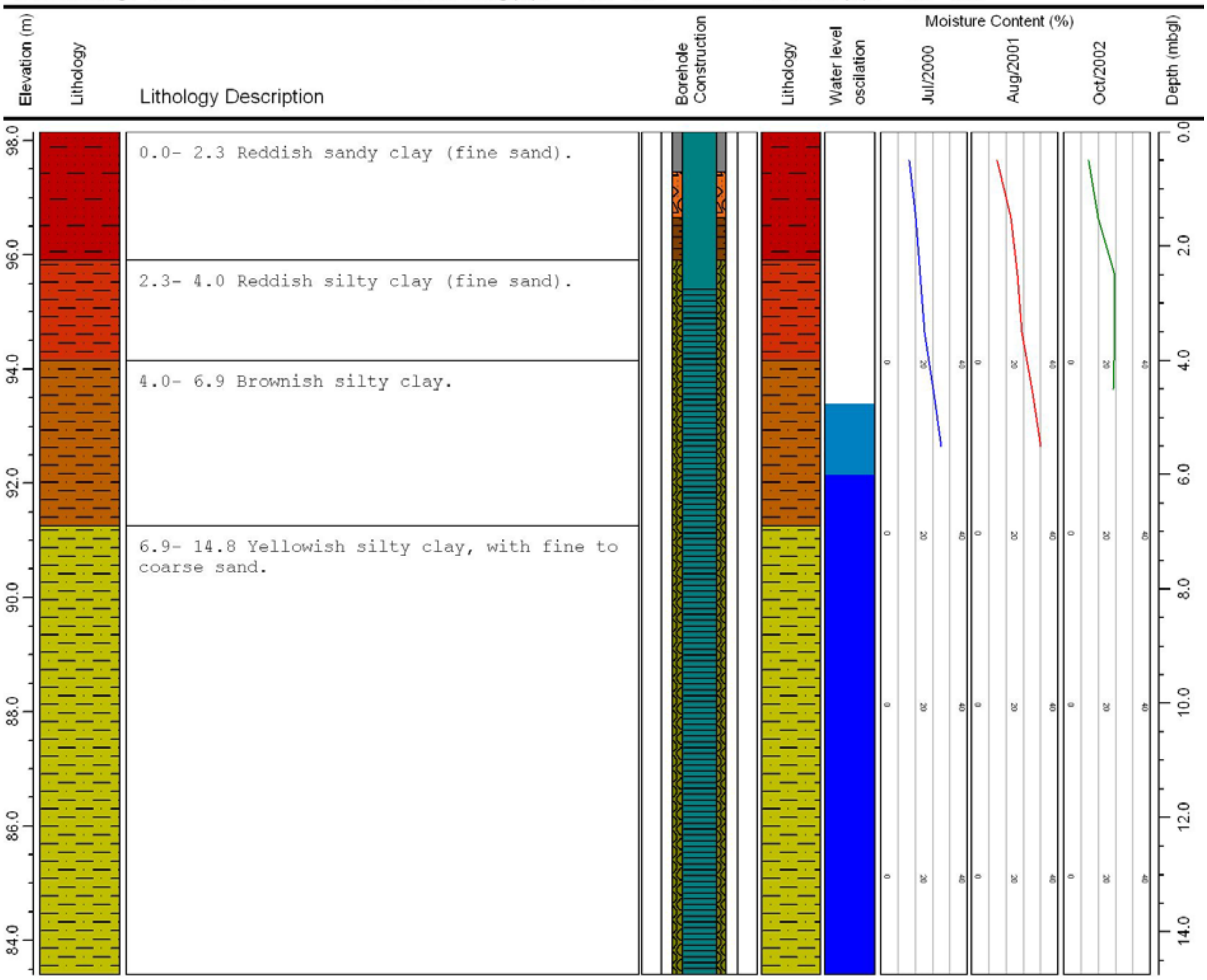
* NM – Not measured.

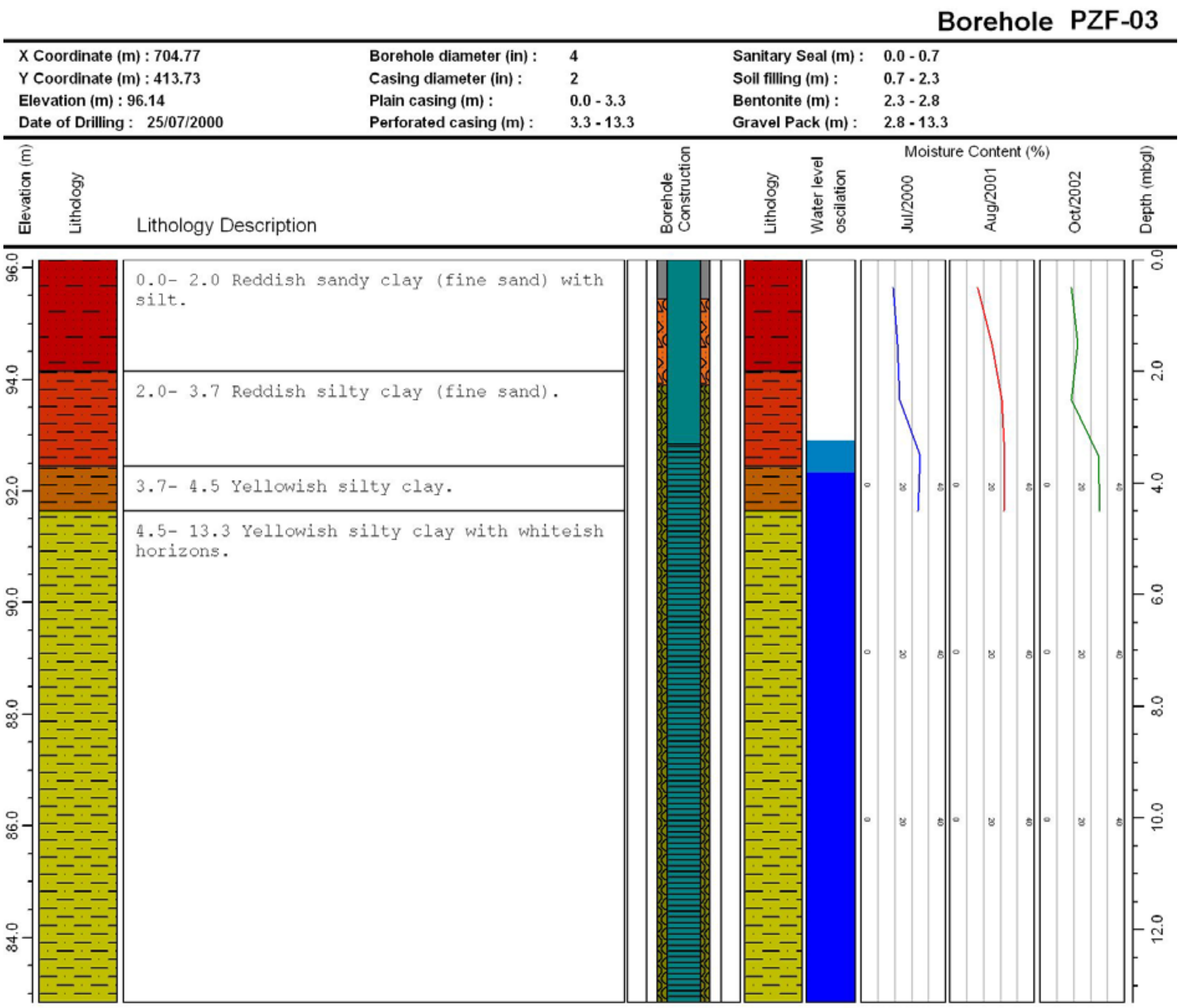
APPENDIX 3 - Borehole logs.

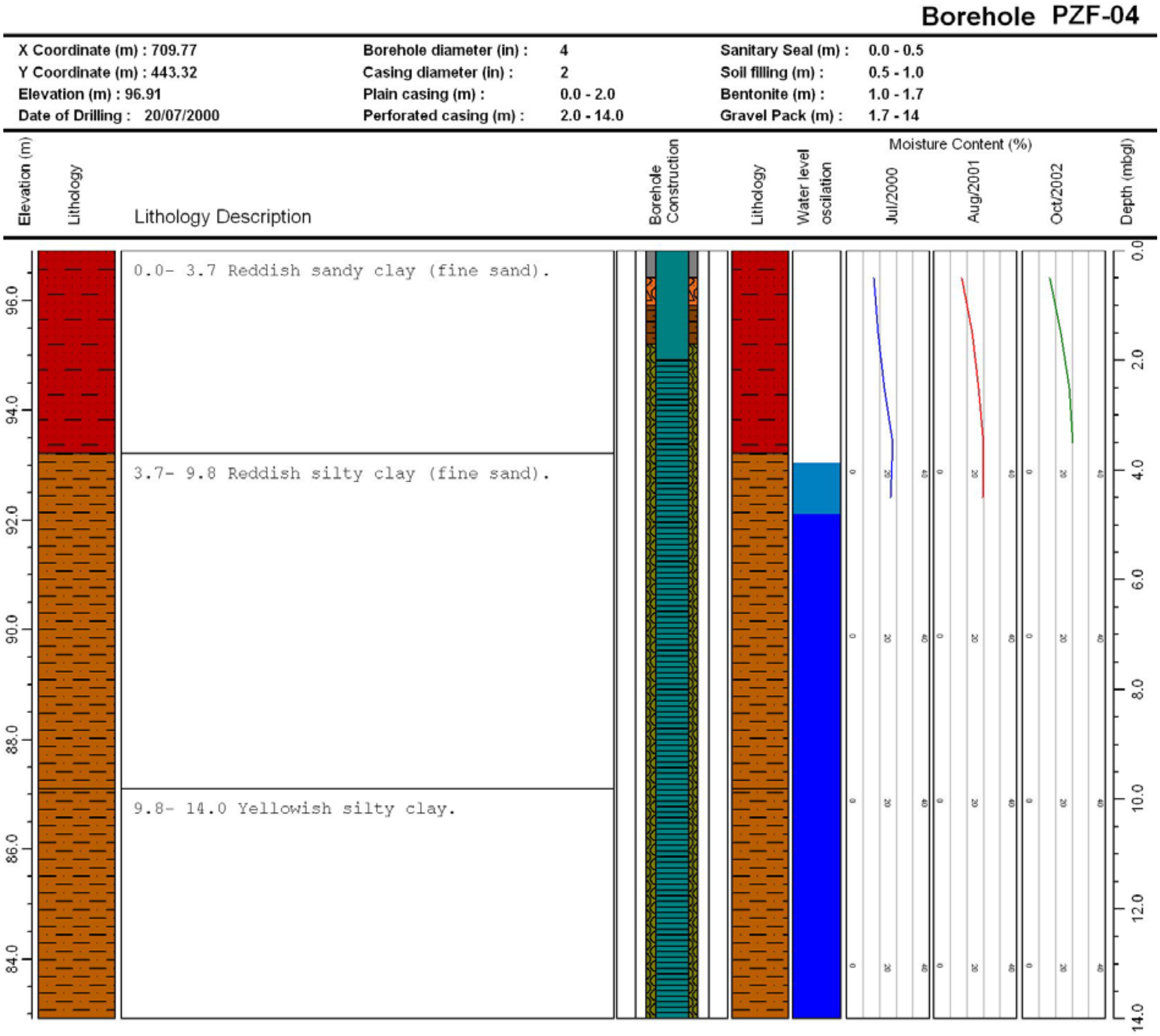

Borehole PZF-01
X Coordinate (m) : 685.7
Y Coordinate (m) : 416.94
Elevation (m) : 98.03
Date of Drilling : 19/07/2000
Borehole diameter (in) : 4
Casing diameter (in) : 2
Plain casing (m) : 0.0 - 1.7
Perforated casing (m) : 1.7 - 15.7
Sanitary Seal (m) : 0.0 - 0.5
Soil filling (m) : 0.5 - 0.7
Bentonite (m) : 0.7 - 1.35
Gravel Pack (m) : 1.35 - 15.7
Elevation (m)
Lithology
Lithology Description
Borehole Construction
Water level oscillation
Moisture Content (%)
Jul/2000
Aug/2001
Oct/2002
Depth (mbgl)
0.0- 3.8 Reddish sandy clay (fine sand).
3.8- 3.9 Gravel layer composed by weathered centimetric basalt gravels, subangular.
3.9- 8.4 Reddish sandy clay (fine sand).
8.4- 15.7 Yellowish silty clay, with fine to coarse sand

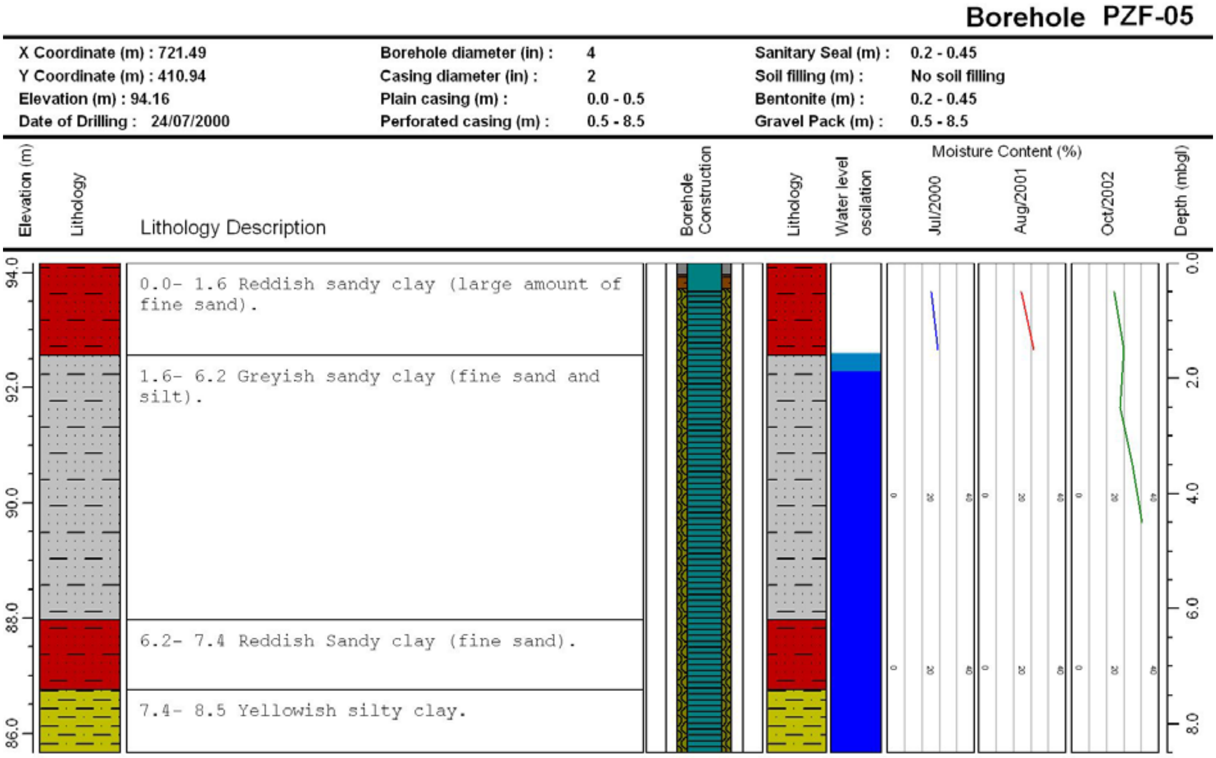
Borehole PZF-02

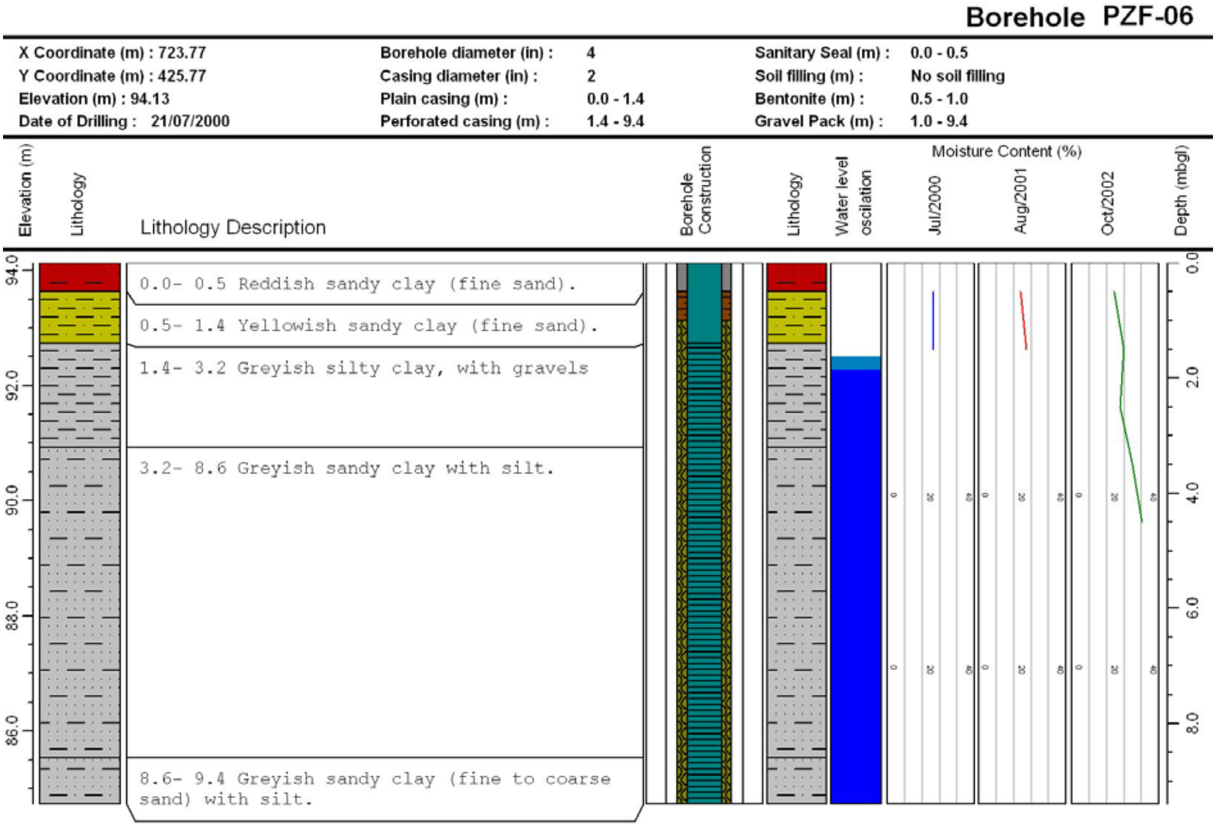
X Coordinate (m) : 690.74		Borehole diameter (in) :	4	Sanitary Seal (m) :	0.0 - 0.7
Y Coordinate (m) : 446.38		Casing diameter (in) :	2	Soil filling (m) :	0.7 - 1.5
Elevation (m) : 98.15		Plain casing (m) :	0.0 - 2.75	Bentonite (m) :	1.5 - 2.25
Date of Drilling :	20/07/2000	Perforated casing (m) :	2.75 - 14.75	Gravel Pack (m) :	2.25 - 14.75




Borehole PZF-03
X Coordinate (m) : 704.77
Y Coordinate (m) : 413.73
Elevation (m) : 96.14
Date of Drilling : 25/07/2000
Borehole diameter (in) : 4
Casing diameter (in) : 2
Plain casing (m) : 0.0 - 3.3
Perforated casing (m) : 3.3 - 13.3
Sanitary Seal (m) : 0.0 - 0.7
Soil filling (m) : 0.7 - 2.3
Bentonite (m) : 2.3 - 2.8
Gravel Pack (m) : 2.8 - 13.3
Elevation (m)
Lithology
Lithology Description
Borehole Construction
Water level oscilation
Moisture Content (%)
Jul/2000
Aug/2001
Oct/2002
Depth (mbgl)
0.0- 2.0 Reddish sandy clay (fine sand) with silt.
2.0- 3.7 Reddish silty clay (fine sand).
3.7- 4.5 Yellowish silty clay.
4.5- 13.3 Yellowish silty clay with whiteish horizons.
96.0
94.0
92.0
90.0
88.0
86.0
84.0
0.0
2.0
4.0
6.0
8.0
10.0
12.0


Borehole PZF-04
X Coordinate (m) : 709.77
Y Coordinate (m) : 443.32
Elevation (m) : 96.91
Date of Drilling : 20/07/2000
Borehole diameter (in) : 4
Casing diameter (in) : 2
Plain casing (m) : 0.0 - 2.0
Perforated casing (m) : 2.0 - 14.0
Sanitary Seal (m) : 0.0 - 0.5
Soil filling (m) : 0.5 - 1.0
Bentonite (m) : 1.0 - 1.7
Gravel Pack (m) : 1.7 - 14
Elevation (m)
Lithology
Lithology Description
Borehole Construction
Lithology
Water level oscilation
Moisture Content (%)
Jul/2000
Aug/2001
Oct/2002
Depth (mbgl)
0.0- 3.7 Reddish sandy clay (fine sand).
3.7- 9.8 Reddish silty clay (fine sand).
9.8- 14.0 Yellowish silty clay.
96.0
94.0
92.0
90.0
88.0
86.0
84.0
0.0
2.0
4.0
6.0
8.0
10.0
12.0
14.0


Borehole PZF-05
X Coordinate (m) : 721.49
Y Coordinate (m) : 410.94
Elevation (m) : 94.16
Date of Drilling : 24/07/2000
Borehole diameter (in) : 4
Casing diameter (in) : 2
Plain casing (m) : 0.0 - 0.5
Perforated casing (m) : 0.5 - 8.5
Sanitary Seal (m) : 0.2 - 0.45
Soil filling (m) : No soil filling
Bentonite (m) : 0.2 - 0.45
Gravel Pack (m) : 0.5 - 8.5
Elevation (m)
Lithology
Lithology Description
Borehole Construction
Lithology
Water level oscillation
Moisture Content (%)
Jul/2000
Aug/2001
Oct/2002
Depth (mbgl)
0.0- 1.6 Reddish sandy clay (large amount of fine sand).
1.6- 6.2 Greyish sandy clay (fine sand and silt).
6.2- 7.4 Reddish Sandy clay (fine sand).
7.4- 8.5 Yellowish silty clay.
94.0
92.0
90.0
88.0
86.0
0.0
2.0
4.0
6.0
8.0

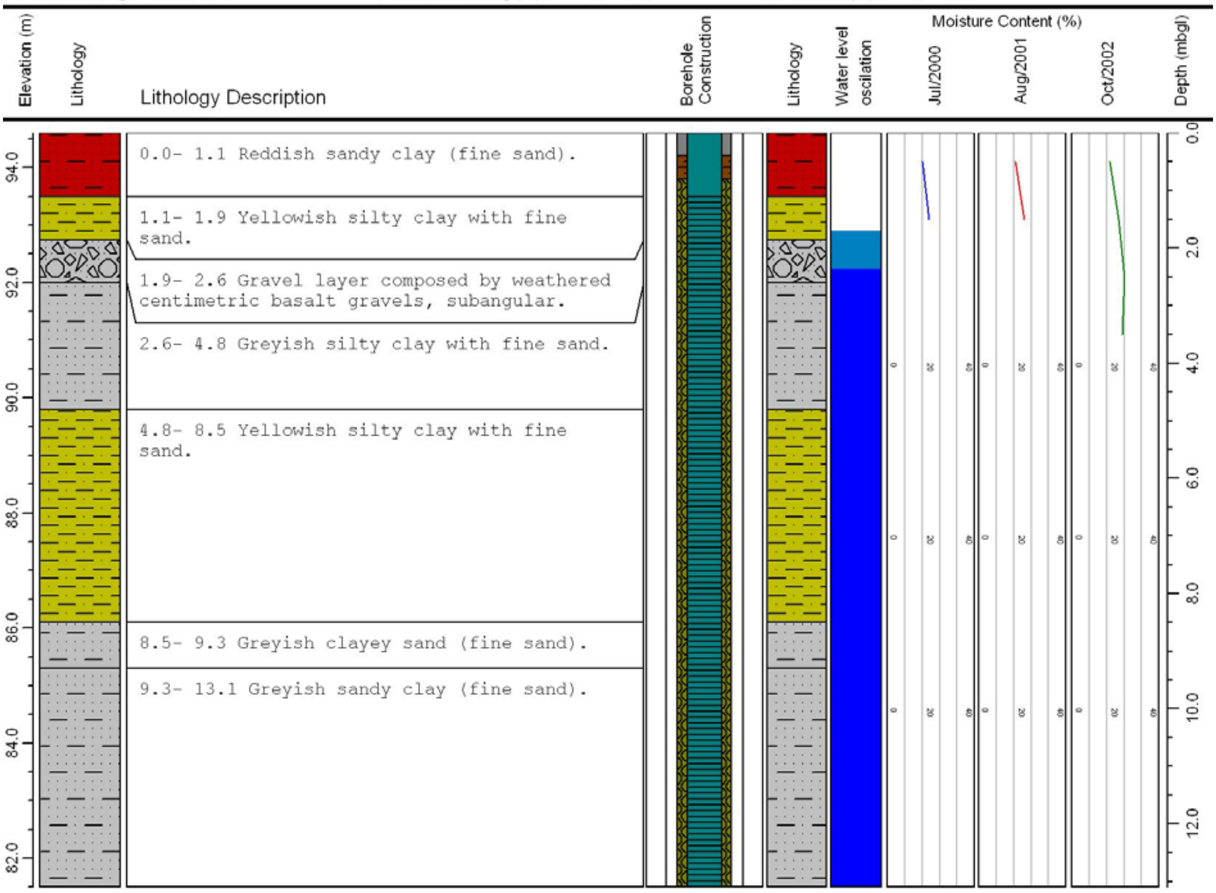

Borehole PZF-06
X Coordinate (m) : 723.77
Y Coordinate (m) : 425.77
Elevation (m) : 94.13
Date of Drilling : 21/07/2000
Borehole diameter (in) : 4
Casing diameter (in) : 2
Plain casing (m) : 0.0 - 1.4
Perforated casing (m) : 1.4 - 9.4
Sanitary Seal (m) : 0.0 - 0.5
Soil filling (m) : No soil filling
Bentonite (m) : 0.5 - 1.0
Gravel Pack (m) : 1.0 - 9.4
Elevation (m)
Lithology
Lithology Description
Borehole Construction
Lithology
Water level oscilation
Moisture Content (%)
Jul/2000
Aug/2001
Oct/2002
Depth (mbgl)
0.0- 0.5 Reddish sandy clay (fine sand).
0.5- 1.4 Yellowish sandy clay (fine sand).
1.4- 3.2 Greyish silty clay, with gravels
3.2- 8.6 Greyish sandy clay with silt.
8.6- 9.4 Greyish sandy clay (fine to coarse sand) with silt.
94.0
92.0
90.0
88.0
86.0
0.0
2.0
4.0
6.0
8.0

Borehole PZF-07

X Coordinate (m) : 726.18
Y Coordinate (m) : 440.38
Elevation (m) : 94.6
Date of Drilling : 21/07/2000

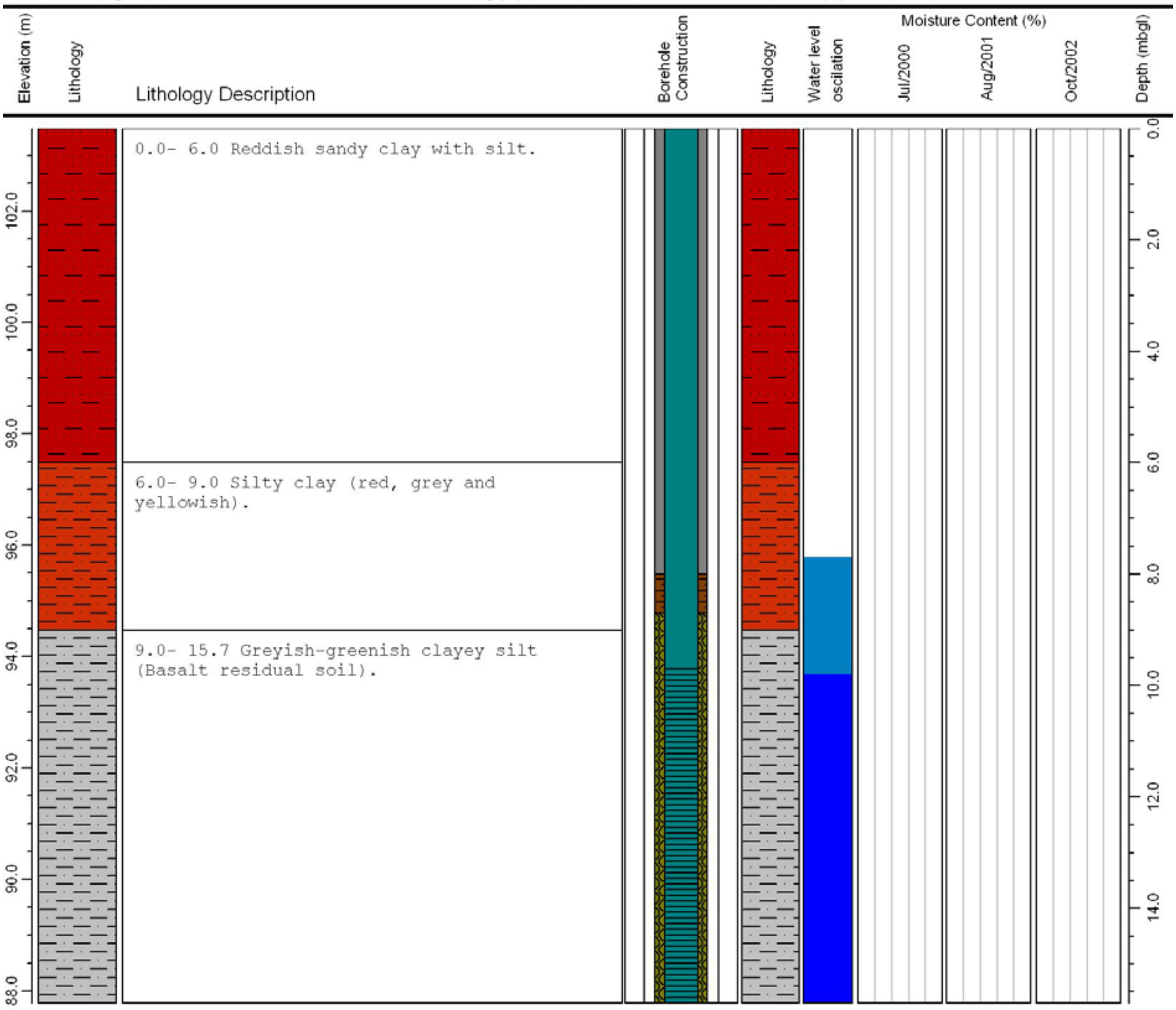
Borehole diameter (in) : 4
Casing diameter (in) : 2
Plain casing (m) : 0 - 1.1
Perforated casing (m) : 1.1 - 13.1

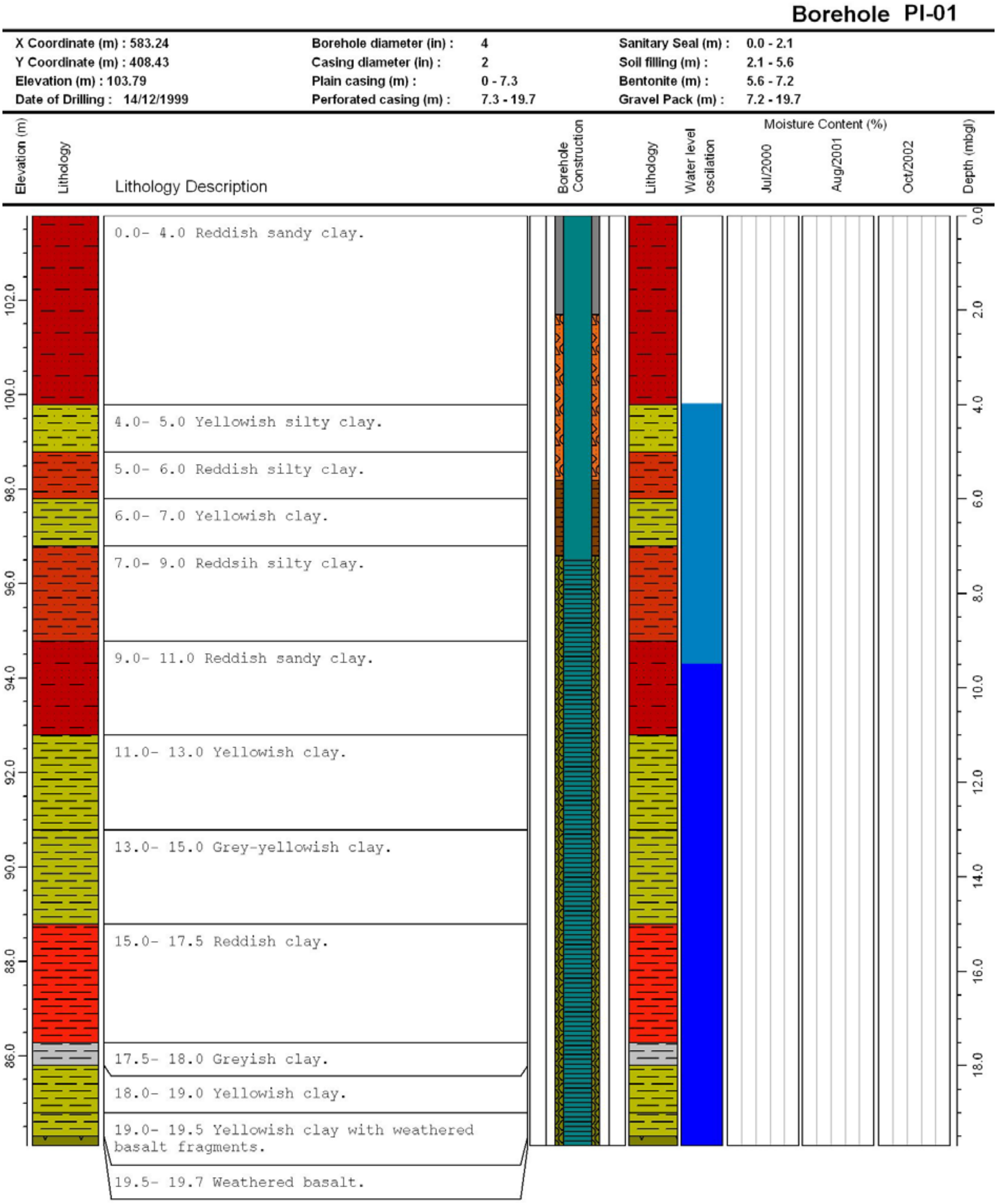
Sanitary Seal (m) : 0.0 - 0.4
Soil filling (m) : No soil filling
Bentonite (m) : 0.4 - 0.8
Gravel Pack (m) : 0.8 - 13.1

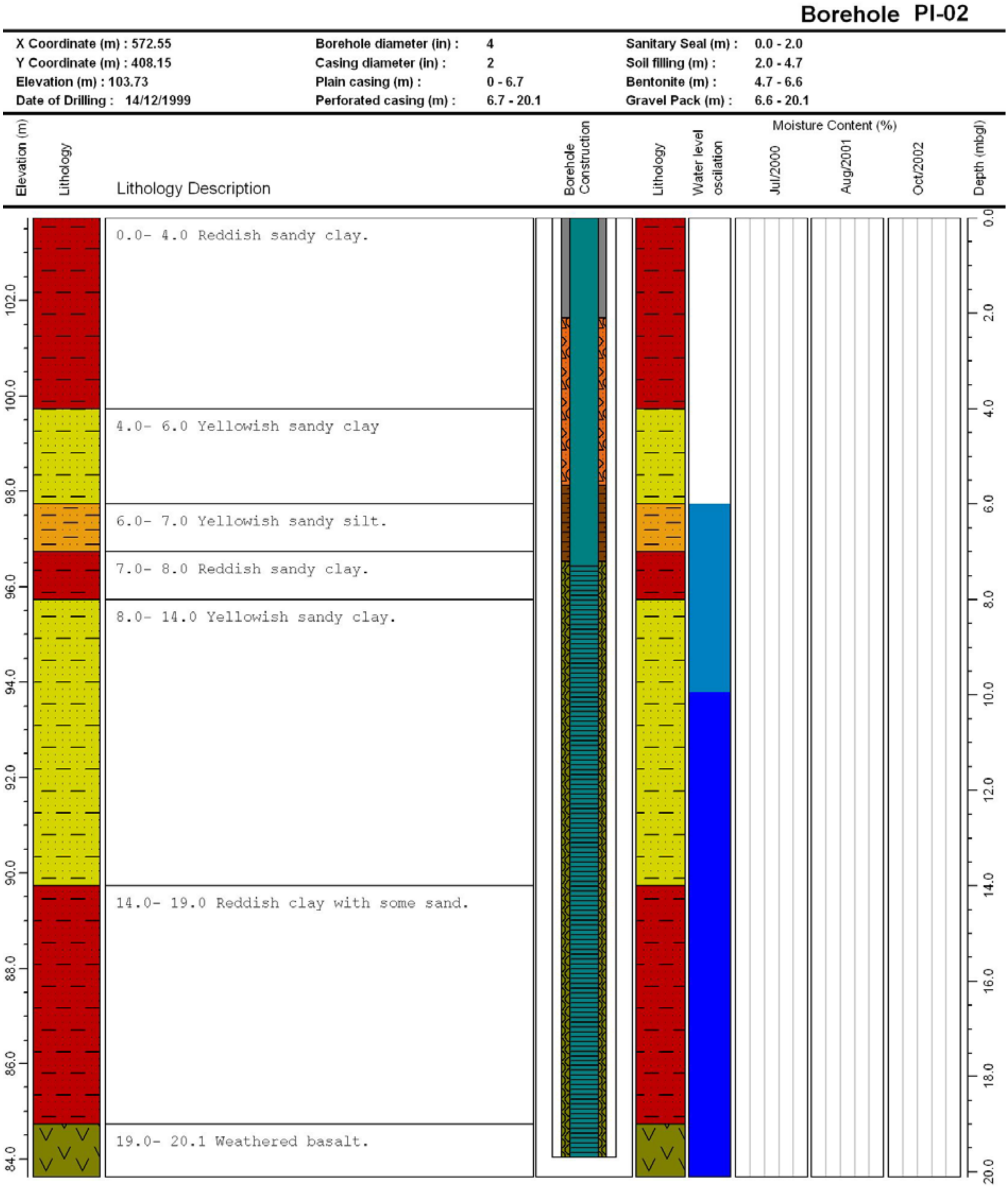


Borehole PI-10

X Coordinate (m) : 605.31	Borehole diameter (in) :	4	Sanitary Seal (m) :	0.0 - 8.0
Y Coordinate (m) : 402.27	Casing diameter (in) :	2	Soil filling (m) :	No filling
Elevation (m) : 103.48	Plain casing (m) :	0.0 - 9.7	Bentonite (m) :	8.0 - 8.7
Date of Drilling : 12/06/2001	Perforated casing (m) :	9.7 - 15.7	Gravel Pack (m) :	8.7 - 15.7

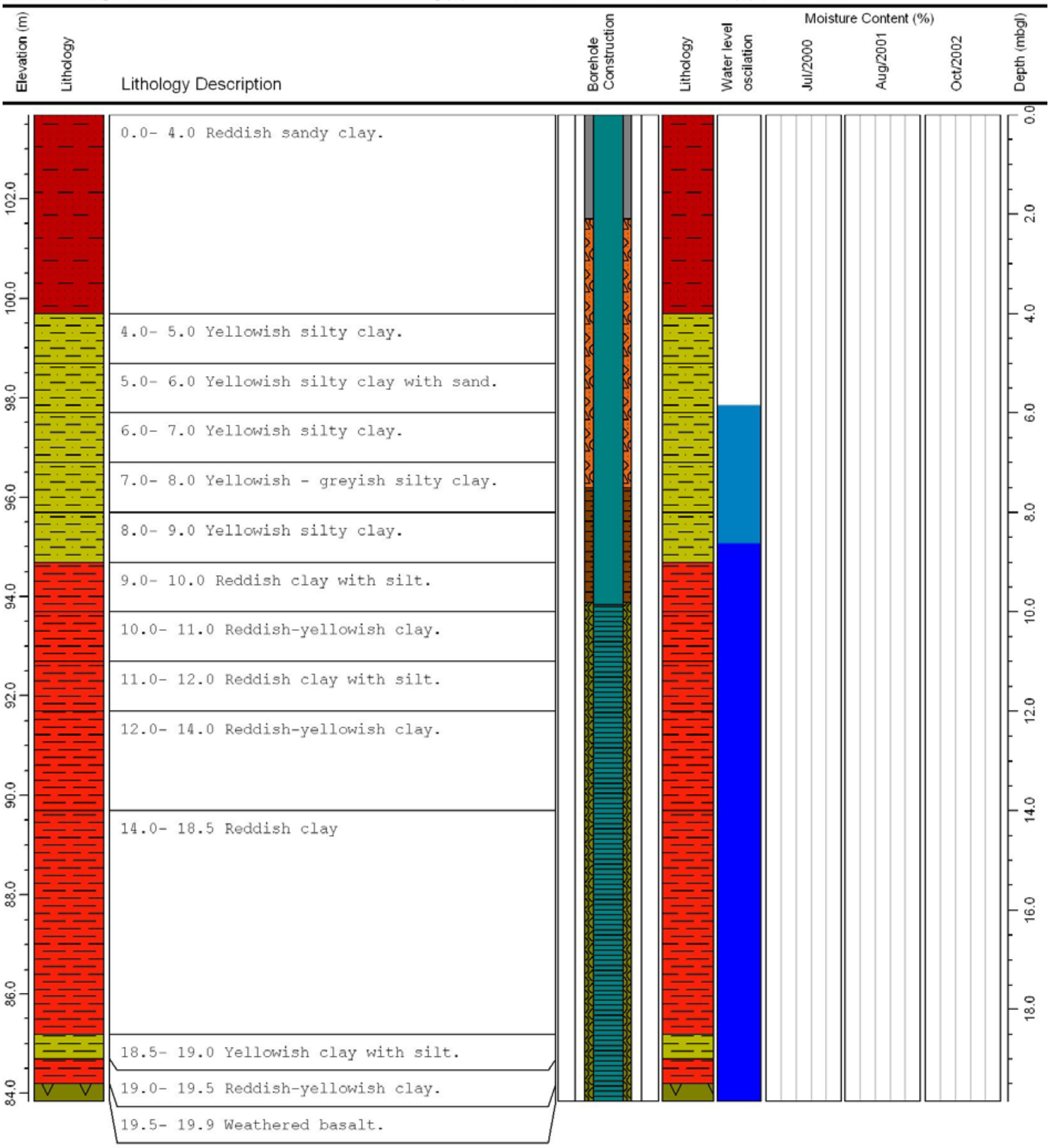


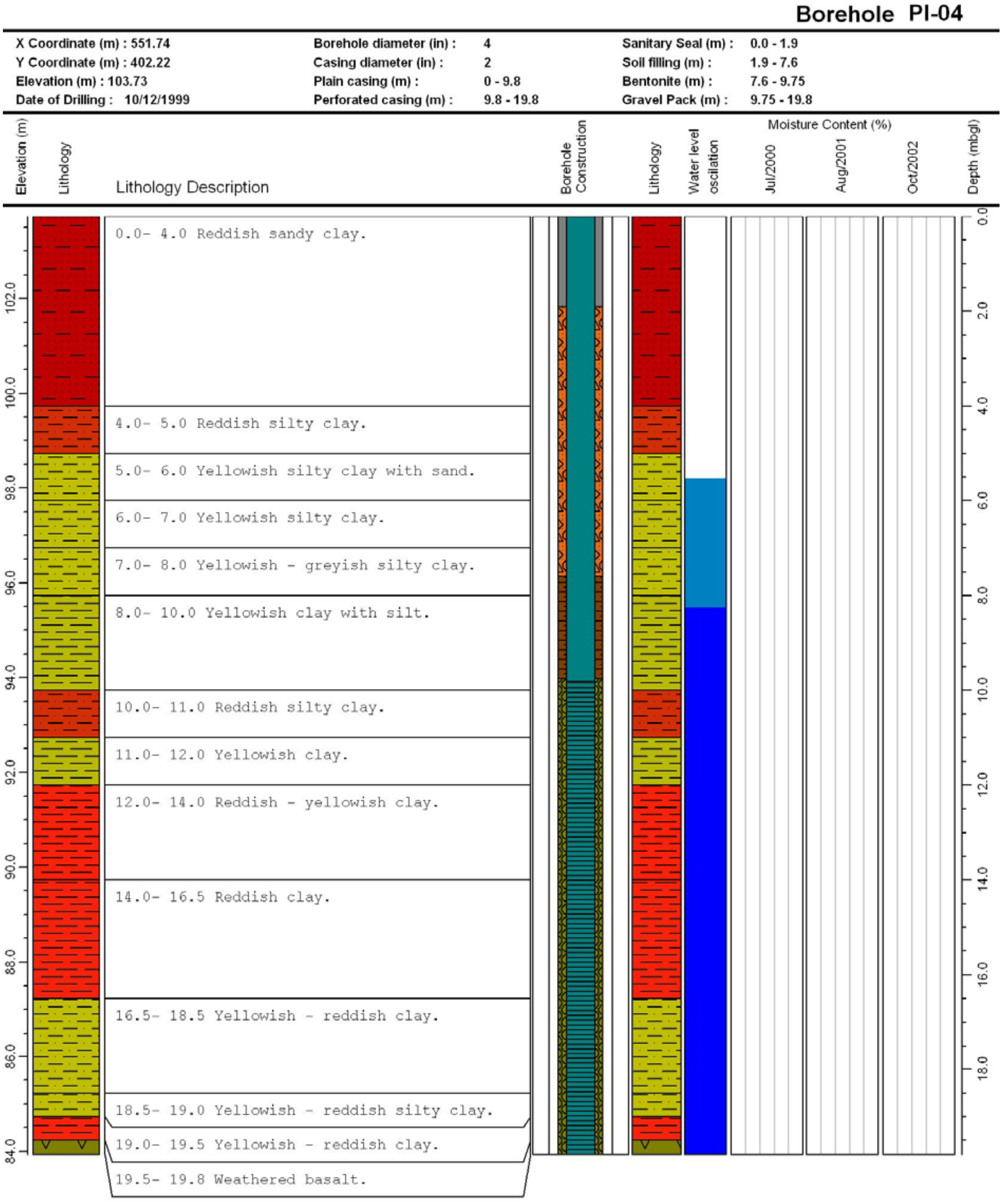

Borehole PI-01
X Coordinate (m) : 583.24
Y Coordinate (m) : 408.43
Elevation (m) : 103.79
Date of Drilling : 14/12/1999
Borehole diameter (in) : 4
Casing diameter (in) : 2
Plain casing (m) : 0 - 7.3
Perforated casing (m) : 7.3 - 19.7
Sanitary Seal (m) : 0.0 - 2.1
Soil filling (m) : 2.1 - 5.6
Bentonite (m) : 5.6 - 7.2
Gravel Pack (m) : 7.2 - 19.7
Elevation (m)
Lithology
Lithology Description
Borehole Construction
Lithology
Water level oscilation
Moisture Content (%)
Jul/2000
Aug/2001
Oct/2002
Depth (mbgl)
0.0- 4.0 Reddish sandy clay.
4.0- 5.0 Yellowish silty clay.
5.0- 6.0 Reddish silty clay.
6.0- 7.0 Yellowish clay.
7.0- 9.0 Reddsih silty clay.
9.0- 11.0 Reddish sandy clay.
11.0- 13.0 Yellowish clay.
13.0- 15.0 Grey-yellowish clay.
15.0- 17.5 Reddish clay.
17.5- 18.0 Greyish clay.
18.0- 19.0 Yellowish clay.
19.0- 19.5 Yellowish clay with weathered basalt fragments.
19.5- 19.7 Weathered basalt.
102.0
100.0
98.0
96.0
94.0
92.0
90.0
88.0
86.0
0.0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
18.0

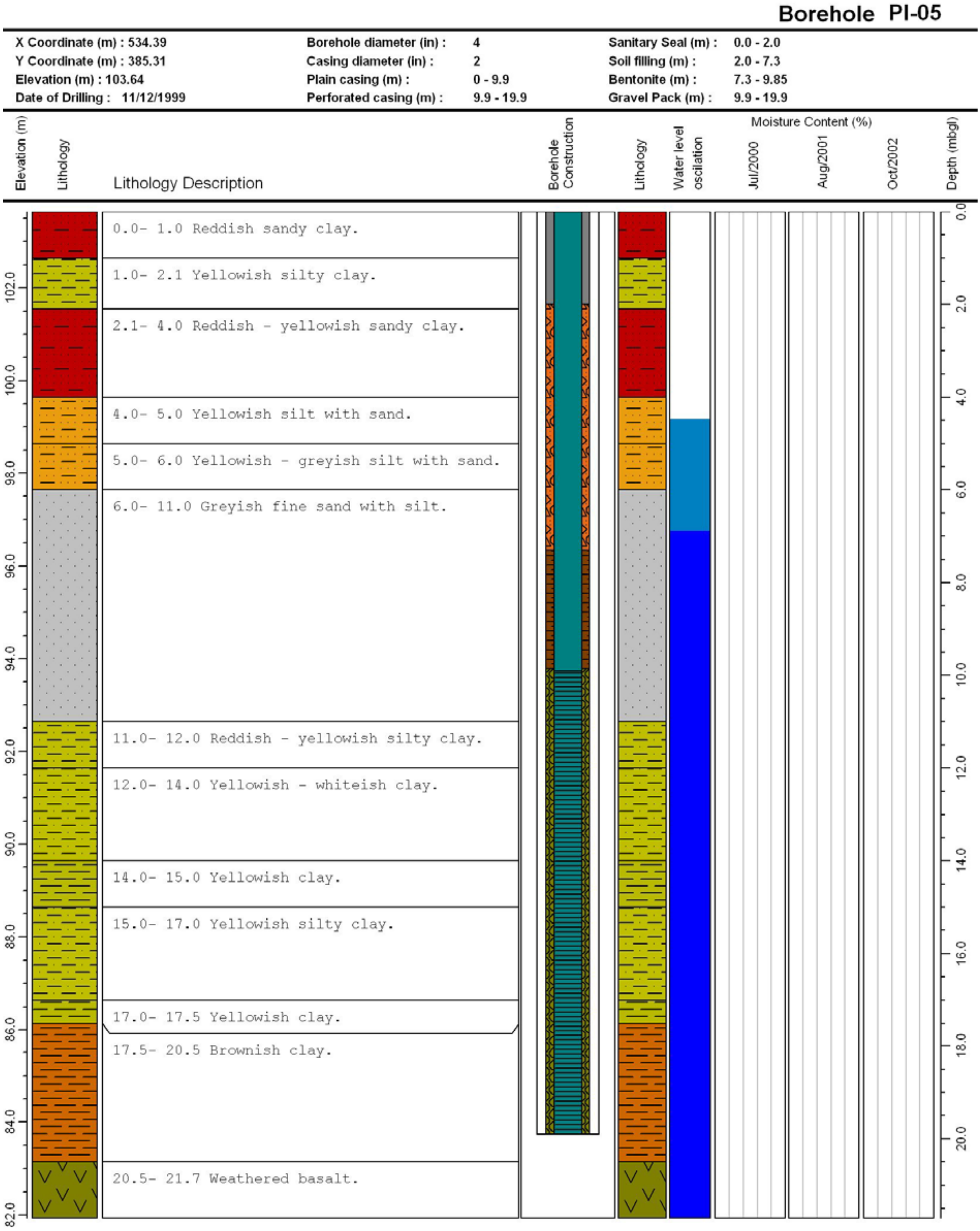

Borehole PI-02
X Coordinate (m) : 572.55
Y Coordinate (m) : 408.15
Elevation (m) : 103.73
Date of Drilling : 14/12/1999
Borehole diameter (in) : 4
Casing diameter (in) : 2
Plain casing (m) : 0 - 6.7
Perforated casing (m) : 6.7 - 20.1
Sanitary Seal (m) : 0.0 - 2.0
Soil filling (m) : 2.0 - 4.7
Bentonite (m) : 4.7 - 6.6
Gravel Pack (m) : 6.6 - 20.1
Elevation (m)
Lithology
Lithology Description
Borehole Construction
Lithology
Water level oscilation
Moisture Content (%)
Jul/2000
Aug/2001
Oct/2002
Depth (mbgl)
0.0- 4.0 Reddish sandy clay.
4.0- 6.0 Yellowish sandy clay
6.0- 7.0 Yellowish sandy silt.
7.0- 8.0 Reddish sandy clay.
8.0- 14.0 Yellowish sandy clay.
14.0- 19.0 Reddish clay with some sand.
19.0- 20.1 Weathered basalt.
102.0
100.0
98.0
96.0
94.0
92.0
90.0
88.0
86.0
84.0
0.0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
18.0
20.0

Borehole PI-03

X Coordinate (m) : 552.62		Borehole diameter (in) :	4	Sanitary Seal (m) :	0.0 - 2.1
Y Coordinate (m) : 411.13		Casing diameter (in) :	2	Soil filling (m) :	2.1 - 7.5
Elevation (m) : 103.69		Plain casing (m) :	0 - 9.85	Bentonite (m) :	7.5 - 9.8
Date of Drilling :	10/12/1999	Perforated casing (m) :	9.85 - 19.85	Gravel Pack (m) :	9.8 - 19.85

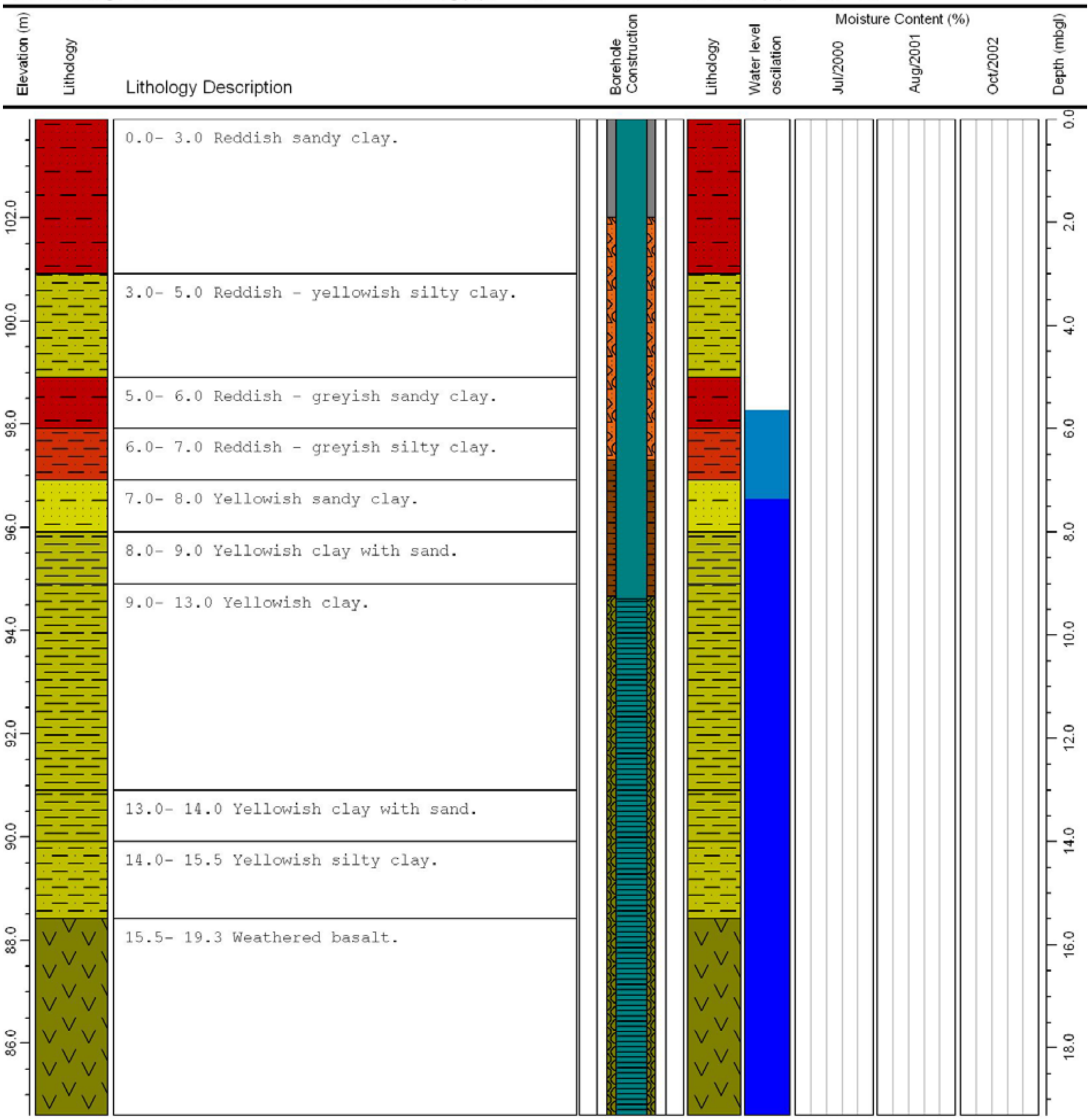


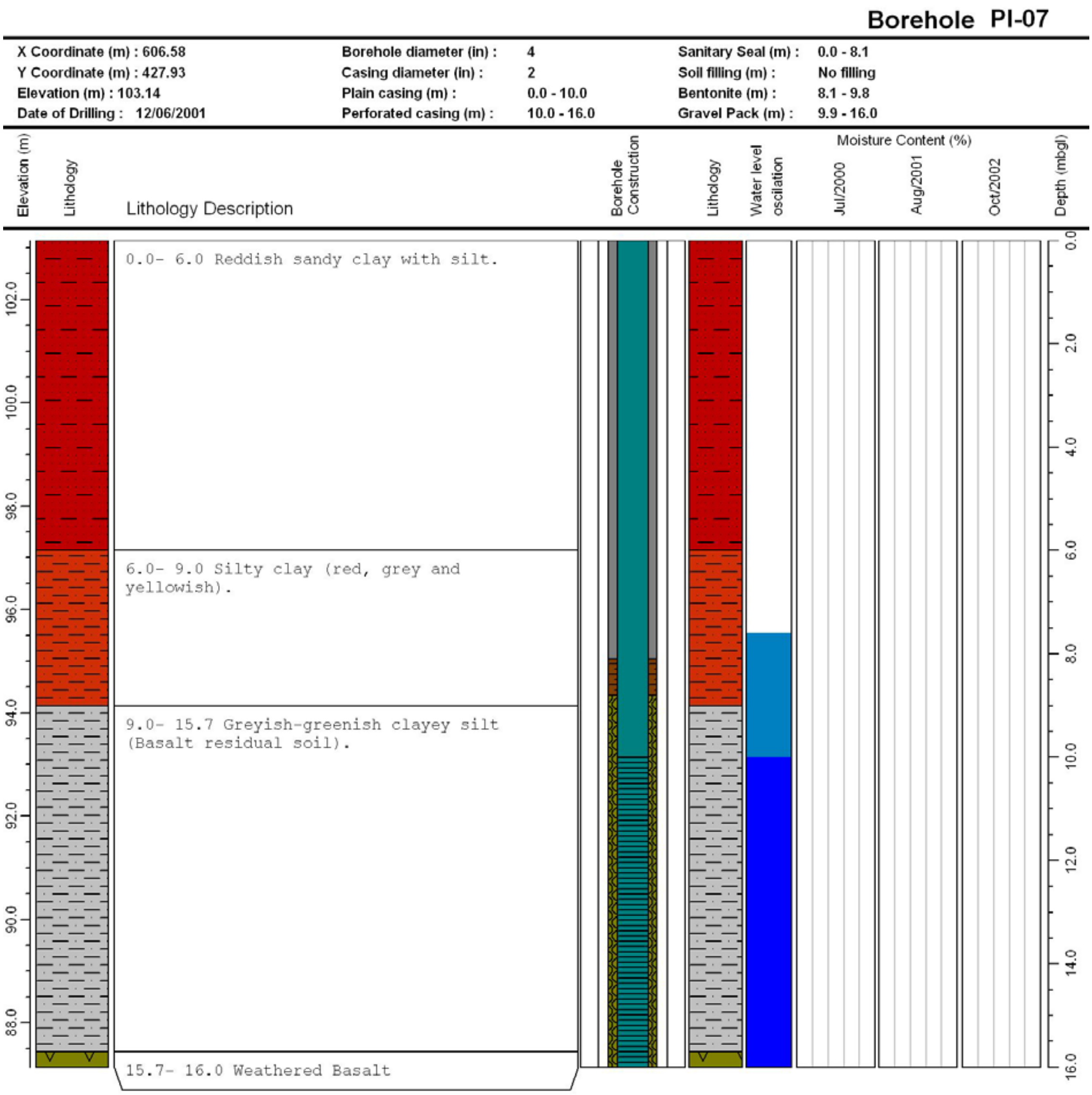

Borehole PI-04
X Coordinate (m) : 551.74
Y Coordinate (m) : 402.22
Elevation (m) : 103.73
Date of Drilling : 10/12/1999
Borehole diameter (in) : 4
Casing diameter (in) : 2
Plain casing (m) : 0 - 9.8
Perforated casing (m) : 9.8 - 19.8
Sanitary Seal (m) : 0.0 - 1.9
Soil filling (m) : 1.9 - 7.6
Bentonite (m) : 7.6 - 9.75
Gravel Pack (m) : 9.75 - 19.8
Elevation (m)
Lithology
Lithology Description
Borehole Construction
Lithology
Water level oscilation
Moisture Content (%)
Jul/2000
Aug/2001
Oct/2002
Depth (mbgl)
0.0- 4.0 Reddish sandy clay.
4.0- 5.0 Reddish silty clay.
5.0- 6.0 Yellowish silty clay with sand.
6.0- 7.0 Yellowish silty clay.
7.0- 8.0 Yellowish - greyish silty clay.
8.0- 10.0 Yellowish clay with silt.
10.0- 11.0 Reddish silty clay.
11.0- 12.0 Yellowish clay.
12.0- 14.0 Reddish - yellowish clay.
14.0- 16.5 Reddish clay.
16.5- 18.5 Yellowish - reddish clay.
18.5- 19.0 Yellowish - reddish silty clay.
19.0- 19.5 Yellowish - reddish clay.
19.5- 19.8 Weathered basalt.
102.0
100.0
98.0
96.0
94.0
92.0
90.0
88.0
86.0
84.0
0.0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
18.0

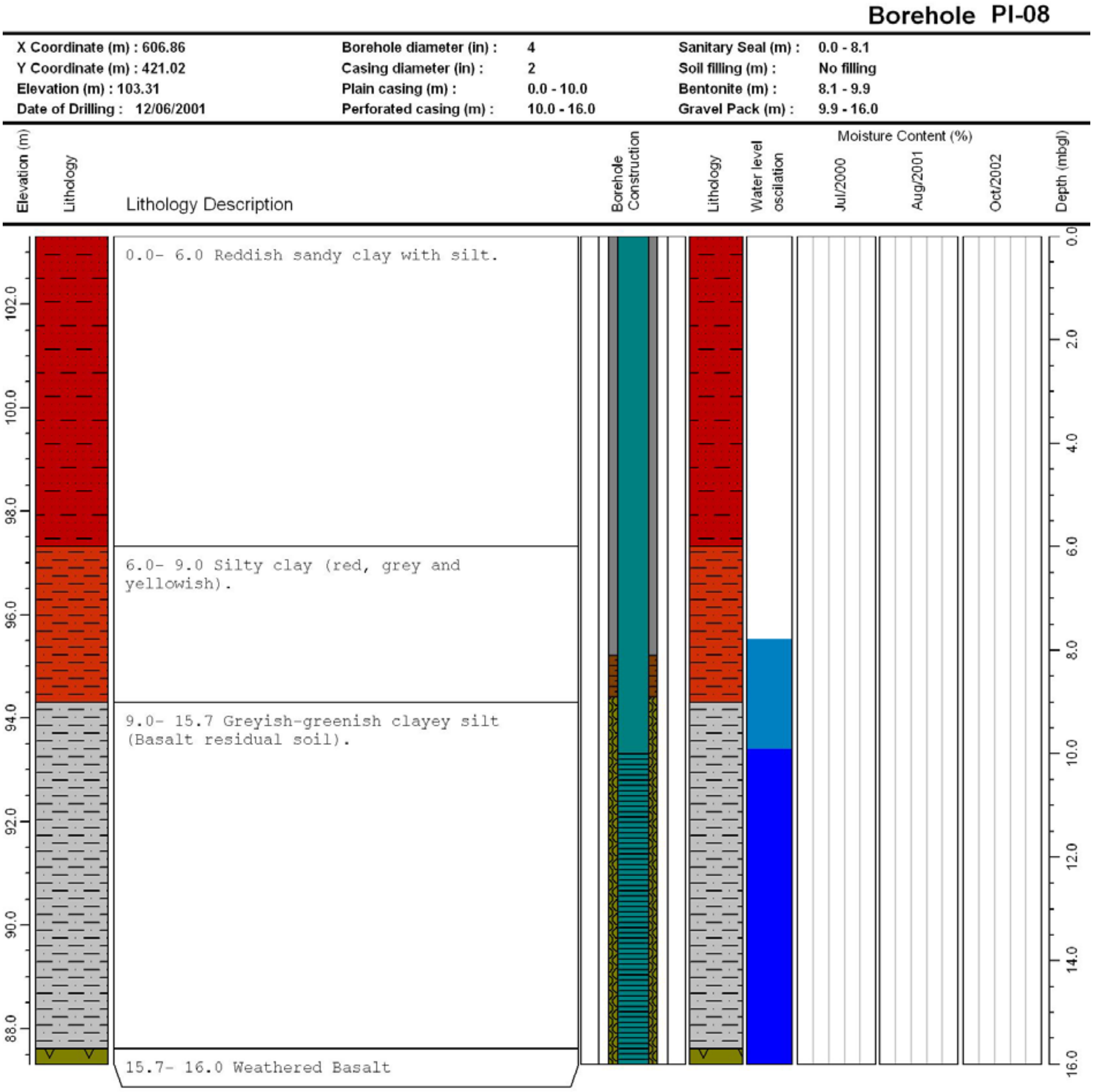

Borehole PI-05
X Coordinate (m) : 534.39
Y Coordinate (m) : 385.31
Elevation (m) : 103.64
Date of Drilling : 11/12/1999
Borehole diameter (in) : 4
Casing diameter (in) : 2
Plain casing (m) : 0 - 9.9
Perforated casing (m) : 9.9 - 19.9
Sanitary Seal (m) : 0.0 - 2.0
Soil filling (m) : 2.0 - 7.3
Bentonite (m) : 7.3 - 9.85
Gravel Pack (m) : 9.9 - 19.9
Elevation (m)
Lithology
Lithology Description
Borehole Construction
Lithology
Water level oscilation
Moisture Content (%)
Jul/2000
Aug/2001
Oct/2002
Depth (mbgl)
0.0- 1.0 Reddish sandy clay.
1.0- 2.1 Yellowish silty clay.
2.1- 4.0 Reddish - yellowish sandy clay.
4.0- 5.0 Yellowish silt with sand.
5.0- 6.0 Yellowish - greyish silt with sand.
6.0- 11.0 Greyish fine sand with silt.
11.0- 12.0 Reddish - yellowish silty clay.
12.0- 14.0 Yellowish - whiteish clay.
14.0- 15.0 Yellowish clay.
15.0- 17.0 Yellowish silty clay.
17.0- 17.5 Yellowish clay.
17.5- 20.5 Brownish clay.
20.5- 21.7 Weathered basalt.
102.0
100.0
98.0
96.0
94.0
92.0
90.0
88.0
86.0
84.0
82.0
0.0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
18.0
20.0

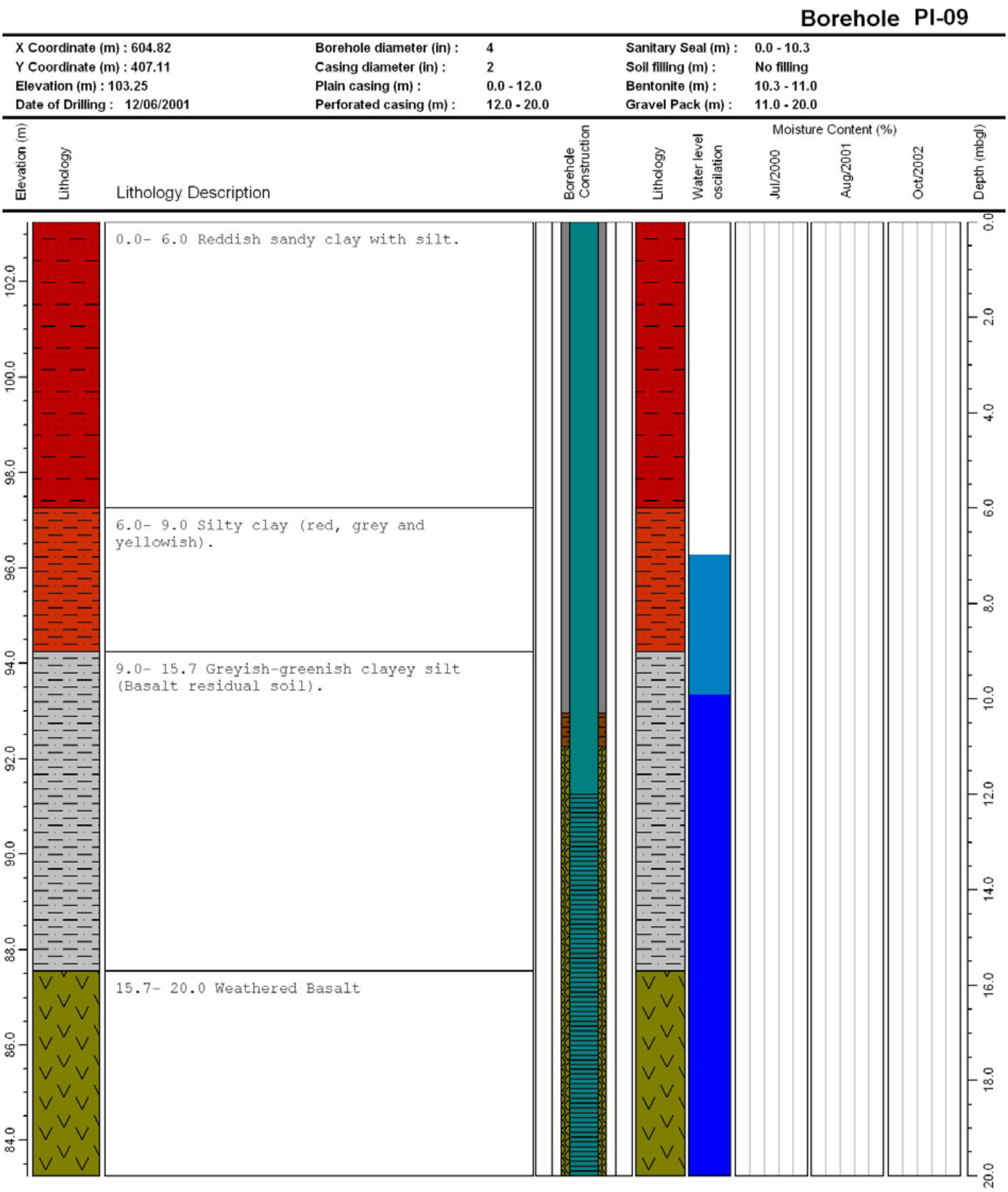
Borehole PI-06

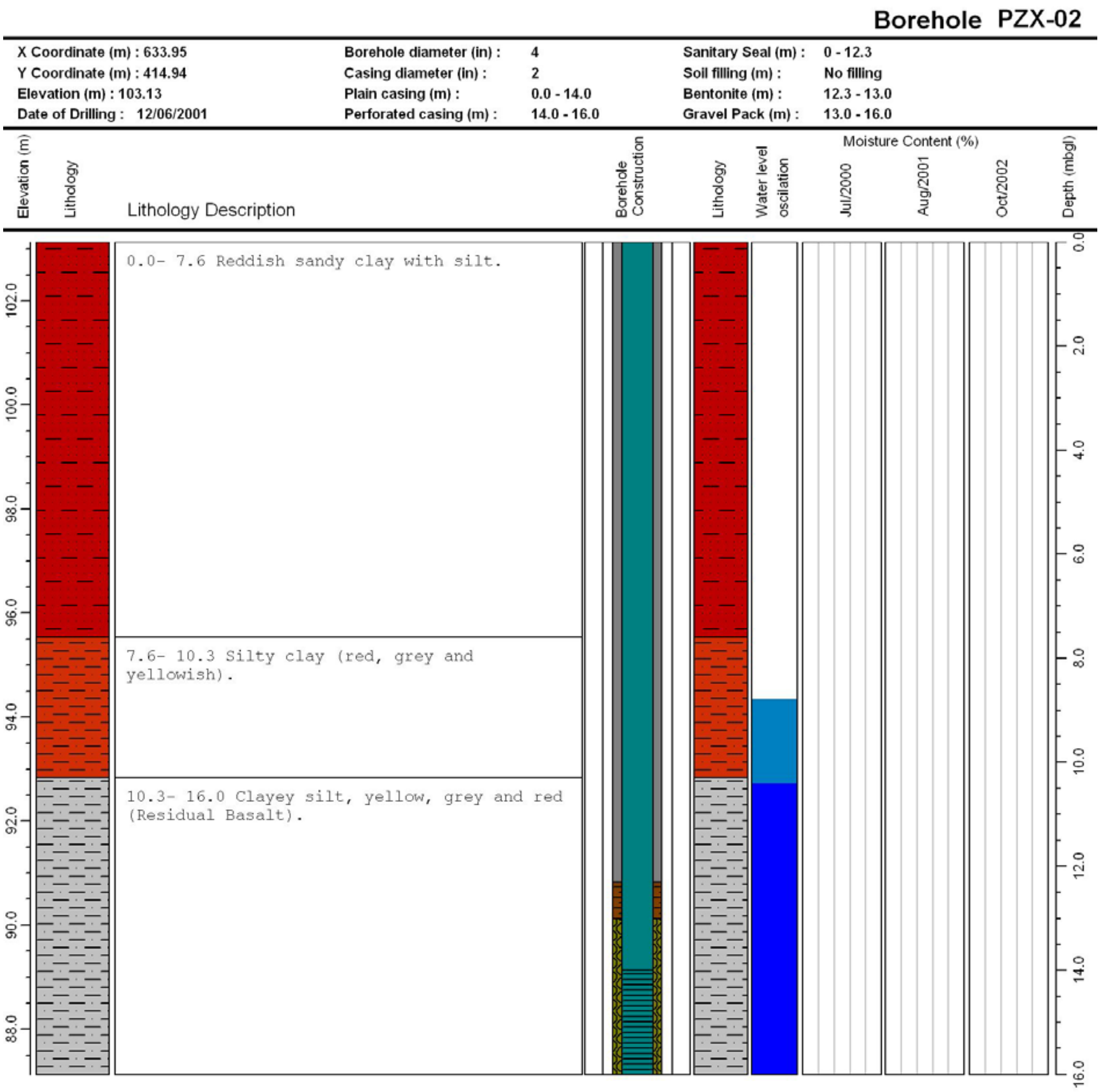
X Coordinate (m) : 553.75	Borehole diameter (in) :	4	Sanitary Seal (m) :	0.0 - 1.9
Y Coordinate (m) : 359.27	Casing diameter (in) :	2	Soil filling (m) :	1.9 - 6.6
Elevation (m) : 103.91	Plain casing (m) :	0 - 9.3	Bentonite (m) :	6.6 - 9.25
Date of Drilling : 13/12/1999	Perforated casing (m) :	9.3 - 19.3	Gravel Pack (m) :	9.25 - 19.3

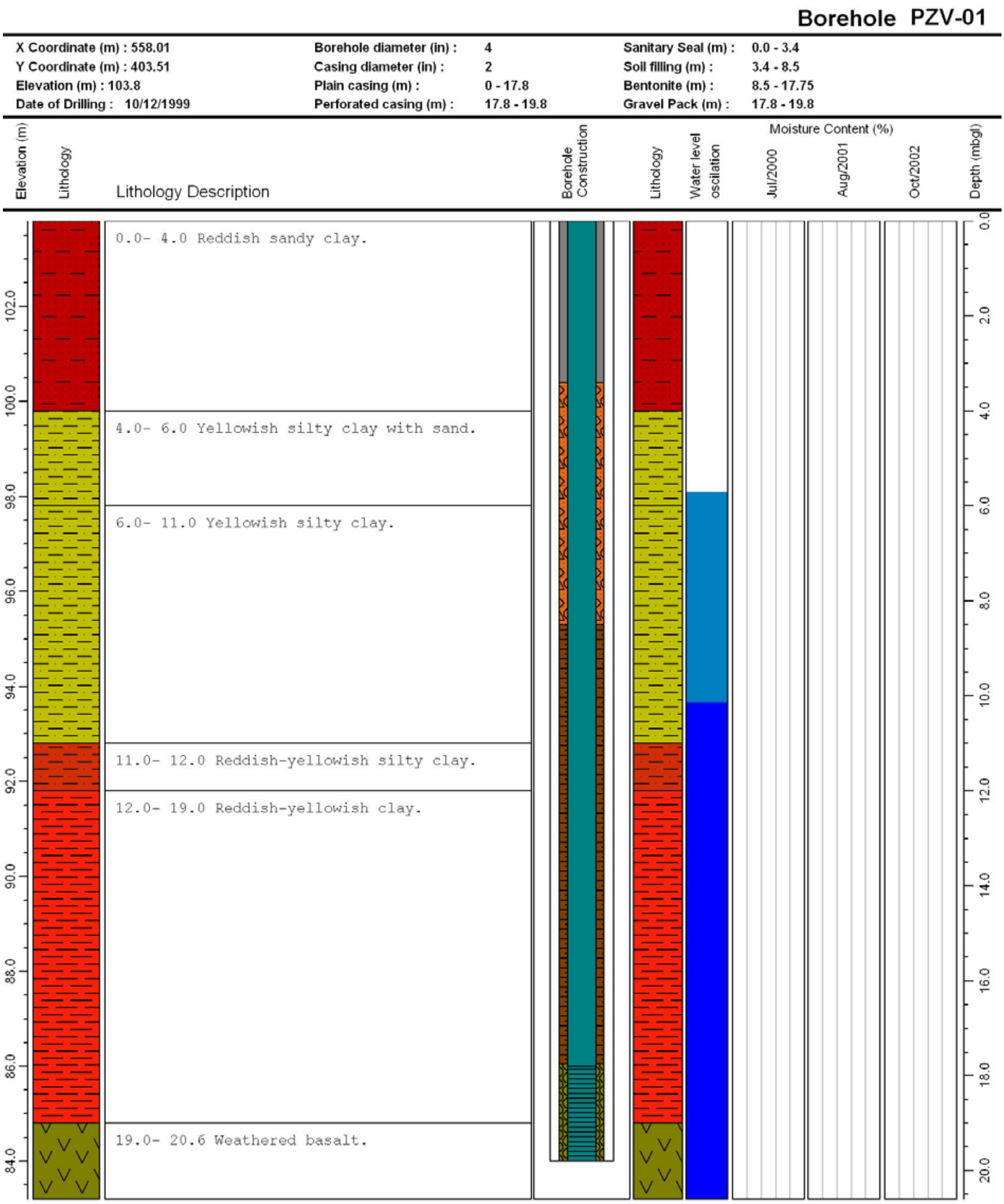



Borehole PI-07
X Coordinate (m) : 606.58
Y Coordinate (m) : 427.93
Elevation (m) : 103.14
Date of Drilling : 12/06/2001
Borehole diameter (in) : 4
Casing diameter (in) : 2
Plain casing (m) : 0.0 - 10.0
Perforated casing (m) : 10.0 - 16.0
Sanitary Seal (m) : 0.0 - 8.1
Soil filling (m) : No filling
Bentonite (m) : 8.1 - 9.8
Gravel Pack (m) : 9.9 - 16.0
Elevation (m)
Lithology
Lithology Description
Borehole Construction
Lithology
Water level oscillation
Moisture Content (%)
Jul/2000
Aug/2001
Oct/2002
Depth (mbgl)
0.0- 6.0 Reddish sandy clay with silt.
6.0- 9.0 Silty clay (red, grey and yellowish).
9.0- 15.7 Greyish-greenish clayey silt (Basalt residual soil).
15.7- 16.0 Weathered Basalt
102.0
100.0
98.0
96.0
94.0
92.0
90.0
88.0
0.0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0


Borehole PI-08
X Coordinate (m) : 606.86
Y Coordinate (m) : 421.02
Elevation (m) : 103.31
Date of Drilling : 12/06/2001
Borehole diameter (in) : 4
Casing diameter (in) : 2
Plain casing (m) : 0.0 - 10.0
Perforated casing (m) : 10.0 - 16.0
Sanitary Seal (m) : 0.0 - 8.1
Soil filling (m) : No filling
Bentonite (m) : 8.1 - 9.9
Gravel Pack (m) : 9.9 - 16.0
Elevation (m)
Lithology
Lithology Description
Borehole Construction
Lithology
Water level oscilation
Moisture Content (%)
Jul/2000
Aug/2001
Oct/2002
Depth (mbgl)
0.0- 6.0 Reddish sandy clay with silt.
6.0- 9.0 Silty clay (red, grey and yellowish).
9.0- 15.7 Greyish-greenish clayey silt (Basalt residual soil).
15.7- 16.0 Weathered Basalt
102.0
100.0
98.0
96.0
94.0
92.0
90.0
88.0
0.0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0

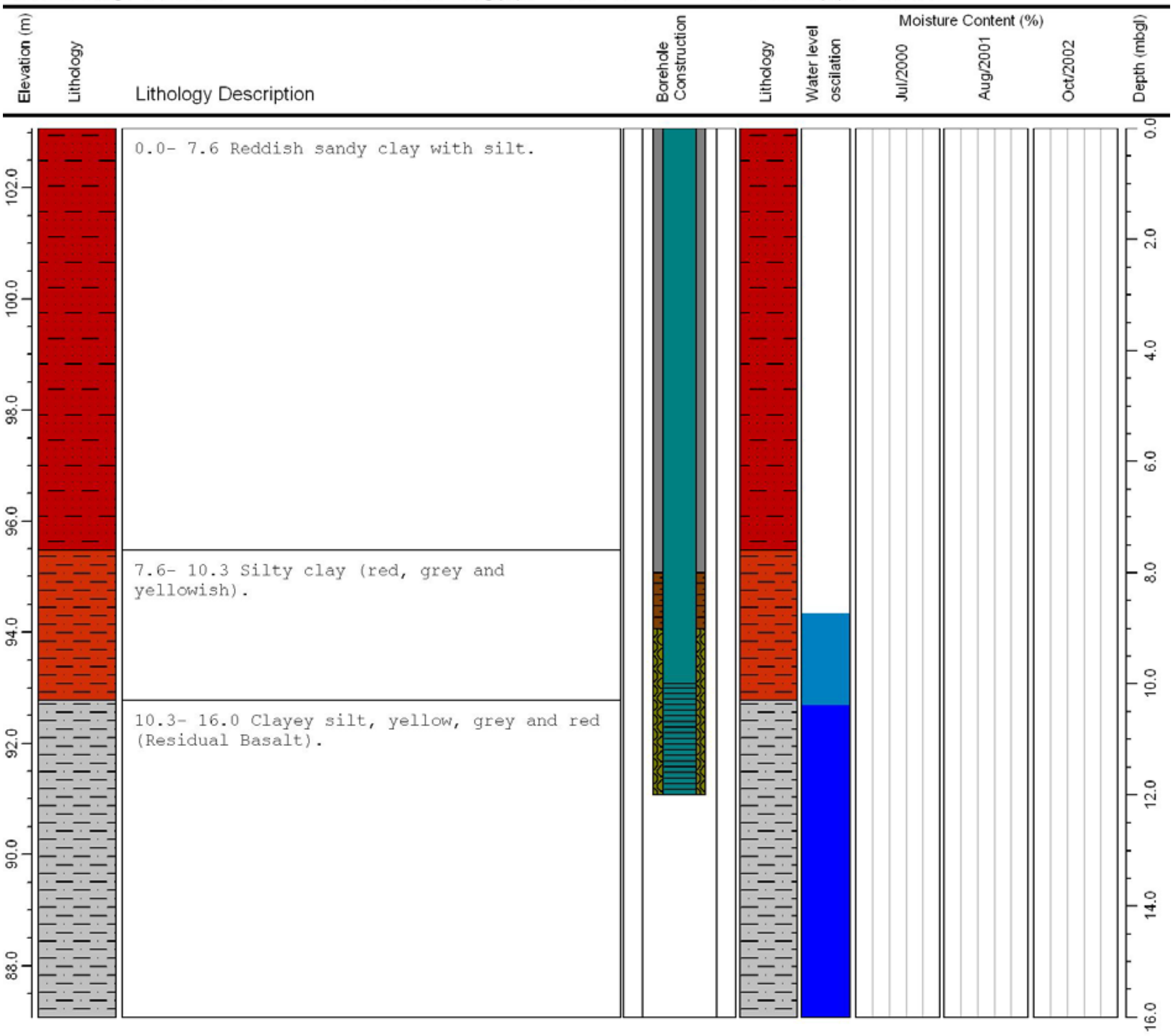

Borehole PI-09
X Coordinate (m) : 604.82
Y Coordinate (m) : 407.11
Elevation (m) : 103.25
Date of Drilling : 12/06/2001
Borehole diameter (in) : 4
Casing diameter (in) : 2
Plain casing (m) : 0.0 - 12.0
Perforated casing (m) : 12.0 - 20.0
Sanitary Seal (m) : 0.0 - 10.3
Soil filling (m) : No filling
Bentonite (m) : 10.3 - 11.0
Gravel Pack (m) : 11.0 - 20.0
Elevation (m)
Lithology
Lithology Description
Borehole Construction
Water level oscilation
Moisture Content (%)
Jul/2000
Aug/2001
Oct/2002
Depth (mbgl)
0.0- 6.0 Reddish sandy clay with silt.
6.0- 9.0 Silty clay (red, grey and yellowish).
9.0- 15.7 Greyish-greenish clayey silt (Basalt residual soil).
15.7- 20.0 Weathered Basalt
102.0
100.0
98.0
96.0
94.0
92.0
90.0
88.0
86.0
84.0
0.0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
18.0
20.0


Borehole PZX-02
X Coordinate (m) : 633.95
Y Coordinate (m) : 414.94
Elevation (m) : 103.13
Date of Drilling : 12/06/2001
Borehole diameter (in) : 4
Casing diameter (in) : 2
Plain casing (m) : 0.0 - 14.0
Perforated casing (m) : 14.0 - 16.0
Sanitary Seal (m) : 0 - 12.3
Soil filling (m) : No filling
Bentonite (m) : 12.3 - 13.0
Gravel Pack (m) : 13.0 - 16.0
Elevation (m)
Lithology
Lithology Description
Borehole Construction
Water level oscilation
Moisture Content (%)
Jul/2000
Aug/2001
Oct/2002
Depth (mbgl)
0.0- 7.6 Reddish sandy clay with silt.
7.6- 10.3 Silty clay (red, grey and yellowish).
10.3- 16.0 Clayey silt, yellow, grey and red (Residual Basalt).
102.0
100.0
98.0
96.0
94.0
92.0
90.0
88.0
0.0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0


Borehole PZV-01
X Coordinate (m) : 558.01
Y Coordinate (m) : 403.51
Elevation (m) : 103.8
Date of Drilling : 10/12/1999
Borehole diameter (in) : 4
Casing diameter (in) : 2
Plain casing (m) : 0 - 17.8
Perforated casing (m) : 17.8 - 19.8
Sanitary Seal (m) : 0.0 - 3.4
Soil filling (m) : 3.4 - 8.5
Bentonite (m) : 8.5 - 17.75
Gravel Pack (m) : 17.8 - 19.8
Elevation (m)
Lithology
Lithology Description
Borehole Construction
Water level oscilation
Moisture Content (%)
Jul/2000
Aug/2001
Oct/2002
Depth (mbgl)
0.0- 4.0 Reddish sandy clay.
4.0- 6.0 Yellowish silty clay with sand.
6.0- 11.0 Yellowish silty clay.
11.0- 12.0 Reddish-yellowish silty clay.
12.0- 19.0 Reddish-yellowish clay.
19.0- 20.6 Weathered basalt.
102.0
100.0
98.0
96.0
94.0
92.0
90.0
88.0
86.0
84.0
0.0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
18.0
20.0

Borehole PZX-01

X Coordinate (m) : 633.76		Borehole diameter (in) :	4	Sanitary Seal (m) :	0.0 - 8.0
Y Coordinate (m) : 416.12		Casing diameter (in) :	2	Soil filling (m) :	No filling
Elevation (m) : 103.07		Plain casing (m) :	0.0 - 10.0	Bentonite (m) :	8.0 - 9.0
Date of Drilling :	12/06/2001	Perforated casing (m) :	10.0 - 12.0	Gravel Pack (m) :	9.0 - 12.0



APPENDIX 4 – Summary of hydrocensus data

Table 1 - Summary of the data obtained during the hydrocensus.

Borehole ID	Owner	Elevation (mamsl)	Depth (mbgl)	Static water level (mbgl)
1	3M do Brasil Ltda.	597	150.00	14.00
2	DAE Sumaré / Silva & Cia Ltda.	554	127.00	1.00
3	Dersa	593	.	.
4	Honda motor do Brasil	575	180.00	15.00
5	Agostinho Rosa Machado	599	100.00	10.00
6	Buckman Laboratórios	573	102.00	5.00
7	Sumaré Ind. Química Ltda.	615	173.00	21.80
8	DAE Sumaré	643	20.00	.
9	Sumaré Ind. Química Ltda.	606	267.00	24.00
10	Inst. Quim. Campinas	590	.	.
11	Granito Ltda.	580	120.00	25.64
12	Constr Sama SA / Stowe Woodward	590	150.00	1.00
13	DAE Hortolândia / S Silva & Cia.	626	125.00	18.00
14	Inst. Quimico de Campinas SA	589	212.00	9.50
15	Granito Ltda.	586	173.00	29.47
16	Posto 9 de Julho	630	38.00	11.00
17	Granito Ltda.	607	118.00	.
18	Johnson & Johnson	602	87.00	.
19	Granito Ltda.	607	103.00	28.21
20	Johnson & Johnson	602	126.00	35.69
21	Wabco Brasil Equip. Ltda.	621	250.00	1.50
22	CPFL	615	57.00	5.00
23	Johnson & Johnson	613	310.00	10.00

Table 2 - Summary of the data obtained during the hydrocensus.

Borehole ID	Owner	Elevation (mamsl)	Depth (mbgl)	Static water level (mbgl)
24	Minasa SA Ind. Milho Óleos Vegetais	626	230.00	30.00
25	DAE Hortolândia	609	160.00	.
26	DAE Hortolândia	644	220.00	40.00
27	Ind, Plast. Cipla / Tamplasa	615	330.00	.
28	DAE Sumaré	628	106.00	.
29	DAE Sumaré	634	180.00	20.00
30	DAE Sumaré	627	341.50	8.00
31	Ind, Plast. Cipla / Tamplasa	625	300.00	.
32	Ind, Plast. Cipla / Tamplasa	616	140.00	.
33	DAE Hortolândia / S Silva & Cia.	622	140.00	8.00
34	DAE Hortolândia	633	200.00	25.00
35	DAE Hortolândia	596	123.00	.
36	DAE Hortolândia	645	.	.
37	DAE Sumaré	642	150.00	25.00
38	Cobrasma SA Ind. E Com.	626	246.00	22.00
39	Cobrasma SA Ind. E Com.	613	230.00	20.00
40	Cobrasma SA	617	250.00	15.00
41	Cobrasma SA Ind. E Com.	595	224.00	10.00
42	DAE Hortolândia / S Silva & Cia.	575	316.00	1.00
43	Braseixos SA	608	281.00	41.40
44	Braseixos SA	604	244.00	37.50
45	Granito Agroavic Hort SA	603	124.00	40.00
46	Braseixos SA	590	250.00	15.00

ABSTRACT

Phytoremediation is defined by the set of technologies used for soil, surface water or groundwater clean-up through the use of plants. This technology has been developed during the last twenty years and has created great interest from environmental agencies, consultants and researchers. Although huge efforts have been made in order to research the potential of phytoremediation, there are still some difficulties regarding its effectiveness quantification.

The objective of this study was to evaluate the use of groundwater models to evaluate the effectiveness of phytoremediation systems. In order to achieve this objective, groundwater modelling was conducted for a phytoremediation system implemented on a site contaminated by chlorinated compounds in South Eastern Brazil. The phytoremediation system was implemented in August 2000 on an industrial site contaminated mainly by benzene and chlorinated compounds with the objective to promote a last barrier for the dissolved phase before groundwater discharge reached an artificial lake located approximately 200 metres down-gradient from the contamination source.

The study site is located close to the 22^{o} latitude. A-pan evapotranspiration rates ranges from 25 mm in the colder months up to 150 mm/month during the summer. Average rainfall rates range between 1100 and 1200 mm/year. Plants from mesophytic tropical wet forests and plants from the Cerrado climate were selected for the phytoremediation system, with a total of 179 trees being planted in an area of approximately 2175 m^2. The contaminated aquifer is composed essentially composed from the weathering horizon of local outcropping basalt and sedimentary rocks. This aquifer has an unconfined behaviour, with groundwater levels ranging from 0.5 to 7 m, and an average thickness of 20 metres.

A groundwater model using USGS MODFLOW-2000, Version 1.15.01, was built in order to quantify the main hydraulic effects imposed by the phytoremediation system in terms of draw-down, changes in the groundwater flow direction and evapotranspiration rates in the saturated zone. The simulated period started in August 2000, prior to the phytoremediation implementation, and ended in July 2002, two years after the implementation of the phytoremediation. Calibrated parameters showed hydraulic conductivities ranging between 0.1 and 0.5 metres/day, specific yields of 0.3 and a recharge rate of approximately 6% of the monthly rainfall. The conceptual model indicated a possible delay between rainfall and effective recharge, which was confirmed by the model calibration and showed a delay time of approximately 90 days.

The calculated evapotranspiration rates ranged from 0 to 190 mm/month, which equates to abstraction rates between 0 to 190 m^3/month. Calculated draw-down values ranged from 0 to 40 centimetres. Higher evapotranspiration rates and draw-downs were observed from July 2001, one year after the implementation of the phytoremediation. This is likely to be related to the fact that the phytoremediation plant root systems probably have not reached the saturated zone in the first year.

The groundwater modelling results showed that the effects imposed by the phytoremediation system were not enough to provide significant draw-down and, thus, changes in the groundwater flow direction. Groundwater models, however, have throughout this exercise shown to be a useful tool in the management of phytoremediation systems. The use of these models cannot be restricted to evaluate effectiveness but also need to be used in the design stage, where it can delineate the most sensitive aquifer parameters and, therefore, parameters that must be monitored to ensure the effectiveness of the system.

Keywords: Groundwater modelling, phytoremediation, evapotranspiration, hydrogeology.