SUBSOIL HETEROGENEITIES CONTROLLING CONTAMINANT MASS AND MICROBIAL DIVERSITY IN POREWATER IN MEGA-SITE CONTEXTS

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Abstract

The aim of this study is to gain a better understanding of the conceptual model of contaminant transport and fate in cases of NAPL pollution in mega-site contexts in order to improve the design of remedial strategies. The area where the study was carried out is an unconfined aquifer of alluvial fans in the Tarragona Petrochemical Complex (Spain). Two boreholes were drilled and continuous cores were recovered in order to carry out a geological and hydrogeological testing at centimeter scale. A comprehensive sampling of subsoil materials was also undertaken.

The biogeochemical heterogeneity occurring in the mega-site context is controlled by the existing conjunction of lithological, hydrochemical and microbiological heterogeneities. Biodegradation processes of the lightest compounds take place not only at the level of the dissolved fraction but also at the level of the fraction retained in the fine, less conductive materials. The quantification of this pollutant mass must be taken into account when designing remedial strategies in order to forecast back-diffusion. Sampling the low-conductivity levels contributes to the definition of the conceptual model of transport and fate from the spatial and temporal viewpoints.

Key words: mega-site, chloromethanes, chloroethenes, gasoline, biogeochemistry, biodegradation, porewater, back-diffusion, ecotone, biodegradation halo.

INTRODUCTION

The presence of DNAPLs is common in areas that have traditionally had industrial uses (Cohen and Mercer, 1993). Their low solubility and persistence in the environmental matrices explains why a large number of contaminant episodes originated in the past when the lack of environmental awareness and the absence of appropriate legislation resulted in a poor management of these compounds. The intrinsic characteristics of the sources are responsible for their long life and associated contaminant plumes, affecting both aquifers and soils (Pankow and Cherry, 1996). Their high level of toxicity at low concentrations and the fact that they are compounds whose sorption by mineral particles is low explain why they can pollute large volumes of water for long periods of time (Mackay and Cherry, 1989).

The fact that they are compounds with different physico-chemical properties, such as their hydrophobicity and biodegradability, controls the distribution of their mass in the aquifer media (Pankow and Cherry, 1996). Moreover, if the concentration of porewater is near the solubility limit in water for a pure DNAPL or near the effective solubility limit for a DNAPL mixture, it can be assumed that the DNAPL source (as free or residual phase) is close to the area where the sample was taken. In fact, chemical analysis of

the DNAPL content in the subsoil and partition calculations can contribute to the knowledge of the degree of saturation of the DNAPL in the media (Feenstra et al., 1991). Thus, when characterizing a DNAPL contaminant episode, it is very important to determine the quantity of contaminant mass that has been transferred through partition to the different soil phases, i.e. DNAPL-soil, DNAPL-water and DNAPL-air, DiGiulio and Cho (1990).

DNAPL mass distribution in the subsoil is strongly controlled by the heterogeneities in it (Guilbeault et al., 2005). Many field studies show that the concentrations in the subsoil can vary over few centimeters vertically, while horizontally the change takes place at decimeter scale (Feenstra, 2005). Thus, there is anisotropy in the spatial distribution of the NAPL concentrations, which is controlled by the geological anisotropy of the subsoil (Rivett and Feenstra, 2005).

Various researchers have carried out studies on the physicochemical characteristics of DNAPLs and the multiphase flow processes they involve. A broad description of the physicochemical properties of DNAPLs, especially halogenated solvents, can be found in Mercer and Cohen (1990), Cohen and Mercer (1993), Pankow and Cherry (1996) and Fetter (1996). The significance of heterogeneities in the subsoil in the migration of free-phase DNAPLs has been widely recorded in the aquifer with heterogeneous sands at C.F.B. Borden (Ontario, Canada), where many experiments have been performed with DNAPLs. These experiments have shown that, after its injection, DNAPL is distributed horizontally, forming pools on the horizontal layers with lowest conductivity and vertical trails where the DNAPL free-phase passed during its descent (Kueper et al., 1993 and Brewster et al., 1995).

The heterogeneities of the media are not exclusively geological or hydrogeological. They are also biogeochemical (McMahon and Chapelle, 2008). In fact, physical and geochemical heterogeneities are responsible for the heterogeneities in the distribution and development of microbial communities (Yang and McCarty, 2000) and for their activity (Brockman and Murray, 1997; Hakenkamp et al., 1994 and Russell et al., 1994). A good example is found in the anaerobic micro-habitats where the structure of the microbial communities increases the richness of biological activity (Capuano et al., 1995; Ghiorse et al., 1996 and Santegoeds et al., 1999). The existence of different biogeochemical contexts in the subsoil can play a crucial role in pollutant distribution. Thus, as a result of the biogeochemical heterogeneity, the flow of groundwater crossing an area can give rise to different biodegradation reactions, and this has implications for the risk assessment of each case of pollution.

Subsoil samples in a source area are collected and analyzed in an attempt to determine the presence of pollutants, their vertical and lateral extent of the DNAPL phases (free or residual), and to quantify the pollutant mass. When remedial techniques are applied, the samples are used to verify the achievement of quality targets.

In this sense, the data on the contaminant mass in the samples of geological material from the subsoil are often more important than the data from monitoring wells when delimiting the situation of the pollution source. In fact, it should be noted that the contaminant mass at a NAPL source is much greater than the mass dissolved in the pollution plume. This is another reason that accounts for the duration of the plumes (Feenstra, 2005). Core sampling makes it possible to characterize geochemically the geological formations that are drilled, as well as the chemistry of the porewater. In addition, if undisturbed samples are obtained, it is possible to determine physico-chemical and hydraulic parameters at laboratory level. The geochemical subsoil profiles obtained enables us to differentiate the coarser levels of granulometry from the finer levels that show considerable sorption capacity. They also allow us to identify the

levels rich in organic matter, which is very important when drawing up the conceptual model of reactive transport (Appelo and Postma, 1993).

In the case of geological formations where there are aquitards or levels that show low hydraulic conductivity, intensive sampling of the boreholes cores is required, and this can reach centimeter scale. There are two reasons for this: first, the free phase of a large part of the DNAPLs of the source accumulates here in the form of pools and, second, the diffusion of pollutants inside the matrix of these low conductivity materials is very considerable (Parker et al., 1994 and Parker et al., 2004). Hence, within these materials a large part of the mass of the pollutant initially spilled can be stored, either dissolved or adsorbed by the organic matter in these layers (Cherry et al., 2006). In mature episodes, there can be back-diffusion of this mass to the aquifer. Thus, precise knowledge of the extent of the DNAPL (as trails of residual phase or as pools of free phase above low-permeability layers or stored in these layers) is important when designing the *in situ* remedial strategies to be implemented (Feenstra, 2005).

The determination of the nature and extent of the pollution with special emphasis on the internal anatomy of the contaminant plume is fundamental for understanding the processes governing the contaminant distribution (Parker, 2007). Thus, in the case of plumes, strong spatial variability is also observed (Feenstra et al, 1991). Therefore, an analysis of the vertical distribution of the pollutants in the subsoil material through borehole core and groundwater sampling makes it possible to identify the zones with the largest plume concentrations. These areas are often found associated with a particular vertical and lateral distribution of the DNAPL in the sources located upstream (Feenstra, 2005).

The existence of DNAPL pollution episodes in extensive areas that have been affected by numerous episodes of very different types of pollution for decades (mega-sites) represents a challenge to planning remediation strategies. In these cases, the characterization of the distribution of the pollutant in the subsoil as a function of the heterogeneities becomes a critical point in order to establish the best decontamination method in terms of cost-effectiveness (USEPA, 2000). In this regard, an integrated analysis of the subsoil material can be decisive in shedding light on the complexity of the pollution episodes at these sites.

When the physical medium is partially analyzed, the overall perspective is often lost and it becomes difficult to understand and interpret the reality of what is happening in that medium. This is especially clear in mega-site contexts, where the complex hydrogeochemical background and the presence of characteristic microbial consortia condition the reactions that take place and the natural attenuation.

The hypothesis we seek to demonstrate is that, in mega-site contexts where there are soil and groundwater contaminant episodes of DNAPL and also LNAPL (e.g. chlorinated solvents and gasolines, respectively), the integration of geological, hydrogeological, biogeochemical and microbiological data obtained from continuous core sampling during borehole investigation makes it possible to interpret the complexity of the pollutant distribution in the subsoil and the biogeochemical processes to which they are subjected. The aim of the study is to better understand the conceptual model of pollutant transport in cases of DNAPL pollution in mega-site contexts, making it possible to improve the design of new remedial strategies.

The most important conclusions obtained are that the biogeochemical heterogeneity occurring in a mega-site context is controlled by the conjunction of lithological, hydrochemical and microbiological heterogeneities. The processes of biodegradation of VOCs take place not only at the scale of the dissolved fraction but also at the scale of the fraction retained in the fine, low hydraulic conductive materials. The quantification of this contaminant mass is one of the aspects that should be taken into account when designing remedial strategies to forecast back-diffusion. Sampling the low-conductivity

levels contributes to the definition of the conceptual model of transport not only from a spatial point of view but also from a temporal point of view.

SITE DESCRIPTION

The aquifer chosen to demonstrate the proposed hypothesis is an unconfined aquifer of alluvial fans in the municipalities of Tarragona and Vila-seca, in the La Pineda Petrochemical Complex (Tarragona, Spain), 100 km south of Barcelona. This mega-site complex began its activities by stages, starting in 1960, and is one of the economic driving forces in the region. Many companies installed in this complex are devoted to the manufacture and manipulation of all kinds of oil-derivative products, many of which come into the category of DNAPLs (e.g. chlorinated solvents) and LNAPLs (e.g. gasoline).

From the geological point of view, the area is made up of Plio-Quaternary detritic materials (gravels and clays originating from streams) filling a small sedimentary basin called the Cubeta de La Pineda. This basin is a tectonic depression at the SE end of the Valls-Reus-Montroig tectonic depression, a sedimentary basin filled with Neogen materials in which, as in the case of the Cubeta de La Pineda, there are Plio-Quaternary alluvial fan deposits originating from the dismantling of the adjacent reliefs at the NW end. The two basins are separated by a fault running in a SW-NE direction (fault from L'Hospitalet de l'Infant to La Secuita) which jumps more than 1000 m and is fossilized by the alluvial fan materials.

Below the area where the contaminant source of the studied episode is located, beds of heterometric gravels and sands with average to coarse granulometry predominate, as shown by the various characterization boreholes and electrical tomography studies carried out. These are paleochannels of alluvial origin with a silt-clay matrix, alternating with silt and clay, together with some levels of caliche crust. The thicknesses of this Quaternary formation in the study zone do not exceed 14 m, although in some boreholes drilled by the Spanish Geological and Mining Institute (IGME), values as high as 100 m have been recorded.

The Plio-Quaternary alluvial fan deposits cropping out in the La Pineda area are the materials affected by the pollution. They constitute an unconfined aquifer formation consisting of gravels and sands of different granulometry structured in paleochannels showing alternating silts and clays not exceeding 14 m in thickness. Figure 1 schematically represents the local water table map in October 2008 showing that the main flow is generally towards the SE discharging to the sea along the coastline (which is located some 2 kilometres from the source) and through pumping wells distributed along its entire surface.

The slug tests in the area showed that the hydraulic conductivity ranges, on average, between 20 m and 50 m/day, values that correspond to medium sands. At some piezometers, however, higher values were recorded, ranging between 150 and 245 m/day, corresponding to gravel levels.

As this aquifer is unconfined, it shows a high vulnerability to pollution, especially in this context, where diverse groundwater contaminant episodes by different types of hydrocarbons and other compounds have been detected since the 1970s. The result is a complex pattern of contamination characterized by a variety of compounds from different origins. These compounds, organics and inorganics such as nitrates, sulfates and metals interact, conditioning the terminal electron accepting processes (TEAP) and hindering the fate of the organic contaminants as a function of their reducing potential, especially the natural attenuation of chlorinated solvents.

The pollution episode studied was detected in 1996 in one of the plants in the Petrochemical Complex although it is not known when the episode was initiated. There are two main pollutants associated with this episode: carbon tetrachloride (CT) and chloroform (CF). Both products are used in refrigerant production. CF is still used in the plant's production process, but CT ceased to be used in 1998. CT and CF were stored independently in two tanks. The spillage occurred repeatedly as a result of leaks and spills varying in duration in tank auxiliary structures such as valves, pipes and pumps, which were directly above the ground a few meters from the tanks. This unsatisfactory practice ended when the pollution was detected. However, despite the disappearance of the main cause, the source remains in the subsoil, which is why the groundwater continues to be polluted.

As a result of the detection of CT and CF pollution in 1996 and because of the sale of the plant's industrial facilities to another company, characterization studies and monitoring and control of the groundwater quality were initiated. During these studies, carried out by ADVENT-PRODENAL in June 1996, boreholes were drilled throughout the study area, recovering and sampling continuous cores. These studies showed that the chloromethanes that had spilled, affected materials consisting of clay and clayey silt with intercalated beds of sand and gravel (levels with low hydraulic conductivity with beds of higher conductivity) in the upper part of the subsoil. Chloromethanes affected sands and gravels with beds of silt and clay (levels of high hydraulic conductivity with beds of lower conductivity) in the lower part. From the source zone, the free-phase DNAPL descended vertically and, on finding levels with low conductivity as it went down, formed pools which eventually migrated laterally in a SE direction because of the slight dip shown by the sediments in this direction.

These studies led to a cleanup scheme in 1997 with the installation of a series of wells for initial gas extraction, and for injection of water vapor into the source zone. Finally, a pump and treat (air-stripping) system was implemented in 1998. Despite the substantial reduction in concentrations in groundwater between 1997 and 2006 (Table 1), the pollution continues to be above parametric values.

Table 1: Variation in concentrations of CF and CT in groundwater in 1997 and 2006.

	1997	2006	1997	2006
	CT (µg/L)		CF(µg/L)	
Max	771	160	19,370	960
Min	7	ND	843	1
Average	196	26	11,700	79

Figure 1 also shows the CF plume situation in October 2008. Most of the control points were conventional piezometers with depths between 11 and 20 m and diameters varying between 28.75 and 110 mm.

Because of the persistence of the pollution, we proposed new characterization tasks including boreholes with the recovery and sampling of continuous cores in the pollution source zone. However, the need for dismantling the insulating cover on which the tanks causing the contamination where placed prevented us from drilling boreholes in the area of the source. For this reason, in April 2008, it was decided to drill the S1UB and S2UB boreholes, located 220 m downstream of the pollution source (Figure 1). The boreholes crossed a paleochannel that was identified by electrical tomography in February 2007 and that was affected by the pollution plume. They are located 2.5 m from each other on either side of piezometer P8. The depths attained were 22 m in the case of the S1UB borehole and 16.37 m in the S2UB borehole. In addition, they were

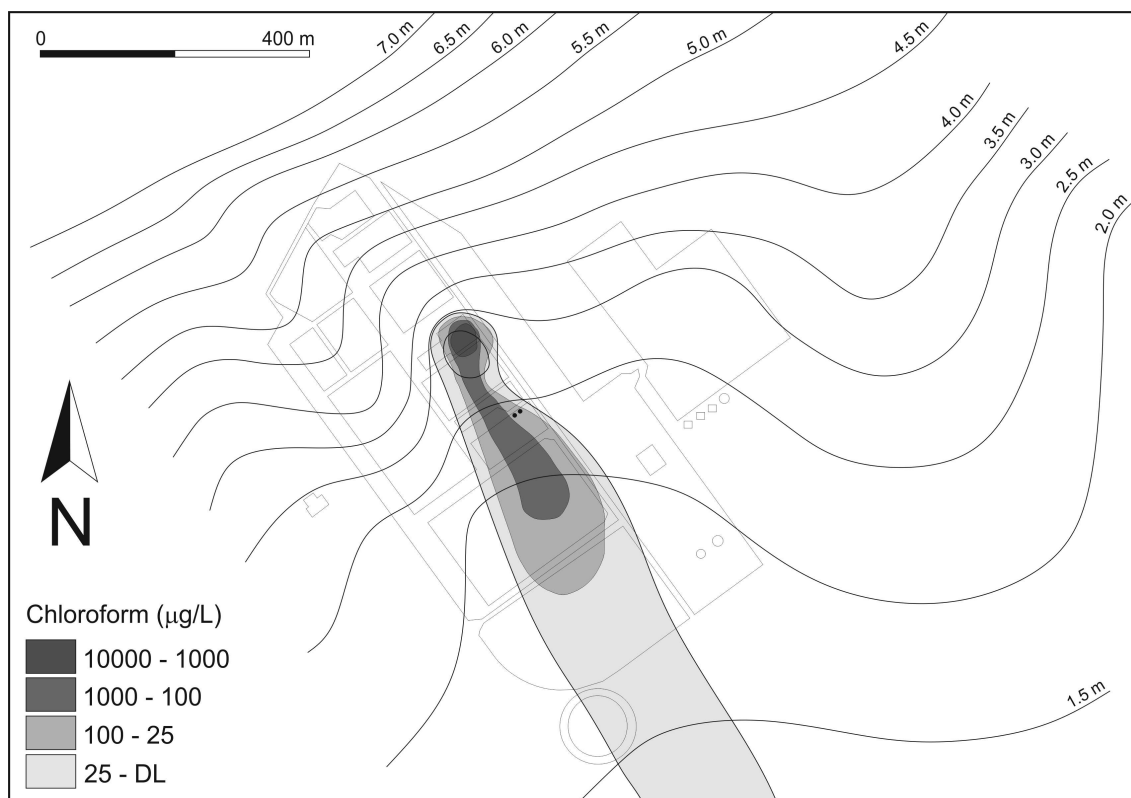equipped as multi-level CTM-type (Solinst) piezometers. Port 7 of these piezometers is 12.5 m deep.

Figure 1: Water level map (masl) and contaminant CF plume map in October 2008. DL: detection limit. Black dots are S1UB borehole (left) and S2UB borehole (right).

MATERIALS AND METHODS

The two boreholes were carried out by rotation with a diamond crown, with a provisional metal sleeve casing with an external diameter of 127 mm and an 85 mm core diameter was obtained. To recover the continuous core, a tool was designed to maintain the stratigraphy of the core, especially when this consisted of unconsolidated material from the non-saturated zone (NSZ). This enabled us to carry out the geological and hydrogeological testing at centimeter scale and the sampling of the soil and subsoil materials.

In this mega-site context, an integrated approach with geological, physico-chemical and chemical parameters was crucial for an improved understanding of the processes governing the removal of chloromethanes. Thus, in addition to the chlorinated solvents in the soil and subsoil samples, a variety of electron donors and electron acceptors, such as organic carbon, sulfates, nitrates, iron, manganese and other metals as well as the compounds of BTEX group were analyzed. Moreover, it was necessary to study the effect of hydrogeochemical and microbial indicators of degradation in order to characterize the processes controlling the fate of chlorinated solvents. Data on the relationship between the development of microorganisms and environmental factors such as characteristic patterns of redox conditions were essential for improving our understanding of subsoil heterogeneities in contaminant attenuation.

Sampling consisted of obtaining 65 soil and subsoil samples from the S1UB borehole and 71 from S2UB, with one duplicate for every 20 samples and the corresponding

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field, transport, reactant and instrumentation blanks. Based on the study and analysis of these samples, textural parameters such as color, physico-chemical parameters of the soil, such as electrical conductivity (EC), oxidation-reduction potential (Eh), pH and Cation Exchange Capacity (CEC) were determined, together with the concentration of elements such as total carbon (C_T), organic carbon (C_{org}), total nitrogen (N_T) and total sulphur (S_T); and the concentration of trace elements, such as Fe, Mn, Cu, As, Pb and Cd, and Volatile Organic Compounds (VOCs). As regards the samples collected to determine microbial diversity and development, 10 soil samples were collected from the S1UB borehole and 10 from S2UB, in all cases in the saturated zone (SZ).

A sterilized spatula was used for sampling the material from the recovered core. The samples taken were stored in different types of container depending on the determinations to be made: 40 and 20 mL glass vials (Supelco), sterile 100 mL pots and aluminium trays. To determine the bulk density, special capsules (Eijelkamp) were used for the purpose.

The reactants used during sampling were methanol (MeOH, Merck, ISO Pro analysis), Sudan IV (Fluka) and MilliQ® water.

A rotary agitator (Heidolph), an ultrasound bath (SELECTA) and a digital grain balance were required for pretreating the samples for analyzing the VOCs in the porewater in low-conductivity materials and in the fine matrix of coarser materials.

To determine the physico-chemical and organic parameters (C_{org}) and to extract metals with *aqua regia*, HCl (37%, Sigma-Aldrich), HNO_3 (90%, Sigma-Aldrich), 100 μm filters (Ashless, Whatman), $CaCl_2$ at 0.01M (99% Sigma-Aldrich), shaker-agitator (SELECTA), orbital-agitator (SELECTA), KCl (99%, Sigma-Aldrich), EC, pH and Eh electrodes (CRISON) were used.

To carry out the PCR tests, a premixture of PuRe Taq Ready-To-GoTM (GE Healthcare, Little Chalfont, UK) was used together with an Eppendorf thermal cycler (New York, USA). For the DGGE (Denaturing Gradient Gel Electrophoresis) tests, acrylamide was used at 6% (Biorad 30 %), urea 7M (BioUltra ≥ 99.5%), formamide at 40% (BioUltra ≥ 99.5%), a buffer solution of Tris-acetate-EDTA (TAE) 1X and an SBR Gold dye (Molecular Probes Europe BV, Leiden, The Netherlands). The photographs obtained were taken with a Chemidoc XRS (Brored) camera using Image Capture software Quantity One. Finally, to extract the DNA of the microorganisms present, the Power Soil DNA Isolation kit (MoBio Laboratories, Carlsbad, CA) was used together with 0.2 μm membranes (Millipore).

All testing and sampling activities were carried out *in situ*. Testing consisted of a detailed description (at centimeter scale) of the materials from the cores following the Unified Soil Classification System (USCS) criteria. Special attention was paid to depth at which the lithological changes were located, low conductivity levels and definition of the textural characteristics of the materials and their color in each section according to the Munsell color system code.

Sampling began immediately after testing each section of the core and describing each sample. Given the vulnerability of the quality of the samples, they were collected in the following order: microorganisms, VOCs and Sudan IV to determine the presence of free-phase NAPLs, metals and physico-chemical parameters. The samples for carrying out microbiological tests were all taken from the cores from to the saturated zone (SZ). The criteria followed for taking the samples were the existence of changes in the core and whether these were lithological or due to environmental conditions such as redox changes indicated by color changes. But the transition zones between the different materials were also sampled to determine whether there were differences in the microorganism communities.

To determine VOCs, the presence of free phase and metals, samples were taken from both the NSZ and the SZ. The main lithologies observed were sampled taking into account the changes in hydraulic conductivity and grain size (following Guilbeault et al., 2005). Special emphasis was placed on low hydraulic conductivity levels. Areas showing alteration haloes and interesting sedimentary structures were also sampled. In cases where the core showed a high level of homogeneity at first sight, samples were taken with a minimum interval of 0.5 m.

The sampling and conservation protocol as well as the calculations of porewater concentrations are an adaptation of the protocol followed by Parker et al. (2003) developed for granular contexts. Identification of organic compounds was made in two ways: i) screening methods were used to visually identify free phase of NAPL by using Sudan IV (Cohen et al., 1992), and ii) laboratory quantification through VOC analysis.

In order to minimize volatilizations we used a methanol (MeOH) trap in accordance with EPA SW-846, Method 5035. Every 20 samples a duplicate was taken and blanks collected. The extraction of VOCs sorbed in the subsoil materials was carried out by adapting the protocol described in Dincutoiu et al. (2003). Gas Chromatography-Mass Spectrometry (GC-MS) was used to determine the VOCs at the Scientific-Technical Services at the University of Barcelona.

The pH of the subsoil samples was determined, according to the ISO/DIS 10390:2005 protocol. For electrical conductivity (EC), the ISO/DIS 11265:1994 protocol was followed. Finally, the potential redox (Eh) of the sample was determined according to the ISO/DIS 11271:2002 protocol. In order to control quality in the measurements, the measuring instruments were calibrated every 25 samples. The CEC analysis was carried out following the ISO 11260:1994 protocol and the instrument used was a flame photometer.

The trace element content was determined by attacking with *aqua regia* the sample fraction selected according to the ISO/DIS 11466:1995 protocol. Inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma optical emission spectroscopy (ICP-OES) were used as analytical techniques.

As for the determination of total carbon (C_T), organic carbon in the subsoil (C_{org}), total nitrogen (N_T) and total sulphur (S_T), the ISO 10693:1995, ISO 10694:1995, ISO 11261:1995 and ISO 15178:2000 standards were followed, respectively. These parameters and elements were analyzed by gas chromatography with thermal conductivity detector (TCD).

To determine the microorganisms in the SZ, DNA was extracted from 0.25 g of a homogeneous sediment sample using the Power Soil DNA Isolation kit (MoBio Laboratory, Carlsbad, CA). The V3 region of the bacterial rDNA 16S from the extracted DNA was then amplified using the Polymerase Chain Reaction (PCR) technique. The products obtained from this application were analyzed using the denaturing gradient gel electrophoresis (DGGE) technique to determine the presence of microbial consortia.

RESULTS AND DISCUSSION

Geological heterogeneities controlling the DNAPL distribution in the subsoil

Lithostratigraphic testing of the recovered cores showed that the paleochannel crossed is very heterogeneous internally since, in both boreholes, there are a large number of interstratified layers of materials with different granulometries.

Geological testing of the S1UB borehole (Figure 2) showed that clays predominate from 0 to 1.50 m deep. From 1.50 m to 3.50 m deep, the principal lithology corresponds

to clayey and sandy silt showing interstratified crusts of caliche. From 3.50 to 4.10 m, gravels are found with a sandy-silty matrix and caliche crusts between 3.65 and 4.00 m. Between 4.10 m and 5.75 m, fine sand predominates, with interstratified layers of medium sand, caliche crusts and silt. From 5.75 to 6.15 m, clay to sandy silts are found with interstratified layers of medium to fine sand. Then, between 6.15 and 7.90 m, there are materials showing a coarsening-up pattern varying from sand and silt at the bottom to medium to coarse gravel at the top. From 7.90 to 8.85 m, there is once again a coarsening-up pattern, similar to that described above.

During the drilling, the water table was found at a depth of 7.90 m. In the SZ, between 8.85 and 9.55 m there is coarse gravel with interstratified levels of sand. Between 9.55 and 9.70 m the most distinctive feature is a layer of silt and below this between 9.70 and 11.70 m deep, heterometric gravels predominate with interstratifications of levels of blocks with a diameter exceeding 30 cm and, to a lesser extent, sand levels.

At the base of the aquifer formation, between 11.70 and 12.90 m, there are heterometric gravels with interstratified layers of clayey to sandy silts, below which there is a transition to the aquitard of the base with a level of clayey silts from 12.90 to 14.00 m down. This is a transition zone to the aquitard of a type similar to those described by Parker et al. (2003). From 14.00 m to 22.00 m, where the drilling ends, clays predominate, with interstratified levels of medium gravel with clayey matrix at centimeter scale.

The S2UB borehole (Figure 2), which also shows caliche crusts, presents clayey silts from 1.20 to 1.35 m and from 1.35 to 2.00 m there are sandy clays. From 2.00 m to 3.30 m, sandy clay and sandy silt predominates and between 3.30 and 6.00 m there are materials showing a fining-up pattern with gravel and some caliche crusts in the lower part to medium to fine sand with interstratified layers of silt and some caliche crust in the upper part. Between 6.00 and 6.90 m layers of fine sands and gravels are observed, and, from 6.90 to 7.30 m there is a level of fine gravel. From 7.30 m to 8.00 m, where the water table was crossed, a zone with a coarsening-up pattern of fine silt to medium sand to gravel is present. Between 8.00 and 8.80 m, another zone with a coarsening-up pattern of sand in the lower part and medium gravels in the upper part is observed. There follows a level of medium to silty sand with interstratifications of medium gravel between 8.80 and 9.50 m downwards.

Below these levels, between 9.50 and 9.80 m, coarse gravels are found; and from 9.80 to 10.02 m, alternating layers of medium sand and medium gravel predominate. Above the base aquitard, between 10.02 and 13.30 m deep, heterometric gravels with interstratifications of levels of medium to fine sand and pebbles with a diameter exceeding 30 cm predominate. Some caliche crusts are present between 11.50 and 11.60 m deep and at the bottom between 13.00 and 13.10 m deep. This borehole does not, therefore, detect a transition zone to the aquitard, as the S1UB borehole does. From 13.30 m there is the aquitard clay formation, with interstratifications of medium gravels.
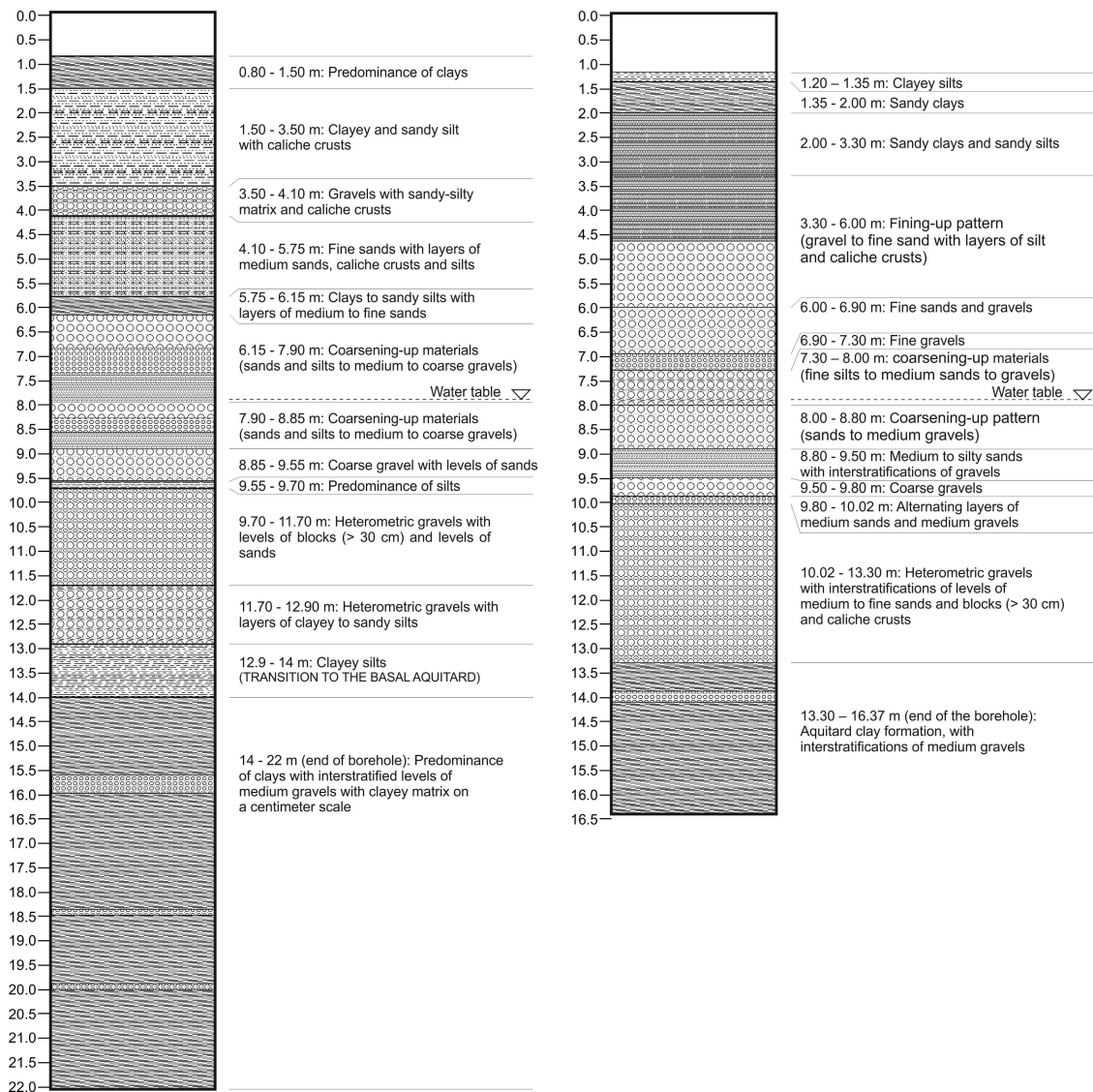
Figure 2: Geological testing of boreholes. A: S1UB. B: S2UB (distance between these boreholes is 5 m). Water table in October 2008.

The S1UB borehole is more heterogeneous than the S2UB borehole, as shown by its number of vertical lithological changes (Table 2), i.e. alternating layers of gravels, sands, silts, clays and caliche crusts. Moreover, gravels and sands show textural differences ranging from sands or gravels with no matrix to sands or gravels with silty-clayey or clayey matrix.

Table 2: Number of lithological changes of layers per meter of total thickness of the Non Saturated Zone (NSZ), Saturated Zone (SZ) and basal aquitard (BA) in the in the two boreholes S1UB and S2UB.

	NSZ	SZ	BA
S1UB	5.4	4.2	0.9
S2UB	3.4	3.5	0.6

The presence of a significant proportion of fine matrix affects the conductivity of the sand and gravel layers. Thus, despite the fact that the total thickness of sands and

gravels in the S2UB borehole is slightly larger than that in the S1UB borehole (Table 3), the percentage of layers with no matrix is more significant in the S1UB, especially in the SZ (Table 4). As a result the hydraulic conductivity of gravels and sands of the SZ in the S1UB borehole is greater.

Table 3: Total thickness (m) of layers of the different lithologies in the Non Saturated Zone (NSZ) and in the Saturated Zone (SZ) of the two boreholes S1UB and S2UB.

	S1UB		S2UB	
	NSZ	**SZ**	**NSZ**	**SZ**
Gravel	0.46	3.91	0.68	4.27
Sand	1.48	0.66	2.12	0.61
Silt	2.29	2.16	2.60	0.29
Clay	1.54	0.00	1.53	0.00
Caliche	0.75	0.00	0.78	0.26

Table 4: Percentage of matrix type in gravel and sand layers of the Non Saturated Zone (NSZ) and Saturated Zone (SZ) of the two boreholes S1UB and S2UB.

		S1UB		S2UB	
		No matrix present	**Silty to clayey matrix**	**No matrix present**	**Silty to clayey matrix**
NSZ	**Sand layers**	0.0	100.0	33.5	66.5
	Gravel layers	16.2	83.8	6.6	93.4
SZ	**Sand layers**	27.6	72.4	2.2	97.8
	Gravel layers	34.3	65.7	5.5	94.5

At this site, the discontinuous layers of clay and silt interstratified with levels of gravel and sand form heterogeneities at centimeter and millimeter scales. These heterogeneities determined the geometry of the distribution of the pollutant in the source leading to the migration of free-phase DNAPL laterally and downwards from the source. The pollutants also remained above the low conductivity levels as pools of DNAPL. Over time, part of the pollutant mass penetrated these levels from the plume owing to migration through molecular diffusion.

The basal aquitard consists of unconforming clays with some intercalations of levels of coarse sand to gravel, with a certain dipping towards the SE, which facilitates the migration of dissolved pollutants along these levels. On the other hand, as the free phase of the initially spilled DNAPL reached the aquitard, it also became a store of the contaminant mass as described by Cherry et al. (2006).

Biogeochemical heterogeneities controlling the bioavailability of pollutants

Physico-chemical parameters and color characteristics

The subsoil materials are highly alkaline, with a pH ranging between 8.07 and 8.89 and between 8.31 and 9.69 in the S1UB and S2UB boreholes, respectively (Table 5). These intervals show that the S1UB borehole is less alkaline than S2UB. These pH differences are related to the textural nature of the subsoil. In this way, the existence of a greater heterogeneity in the S1UB borehole (Table 2) accompanied by the larger conductivity caused by the lower proportion of fine matrix (Table 4) contributes to a shorter time of residence for groundwater than in the case of S2UB. This means there is less possibility of an equilibrium being established between the groundwater and subsoil material in the S1UB borehole zone than in S2UB. By contrast, the longer time

of residence for water in the borehole S2UB probably enables the carbonates in the areas where crusts of caliche are present to neutralize the porewater in the sediment.

Table 5: Statistical values of diverse Physico-chemical and chemical parameters in the two boreholes S1UB and S2UB. Total carbon (C_T), total nitrogen (N_T), organic carbon (C_{org}), Cd and Cu.

S1UB	pH	EC (µS/cm)	Eh (mV)	C_T (ppm)	N_T (ppm)	C_{org} (ppm)	Cd (ppm)	Cu (ppm)
Max	8.89	523	155	88.51	0.97	0.97	13.33	75
Min	8.07	107.9	128	0.46	0.09	0.14	3.33	5
Geom. mean	8.65	183.51	138.76	44.8	0.22	0.32	7.18	12.22
Std Dev	0.17	76.67	8.53	21.18	0.12	0.17	2.76	11.29
S2UB	pH	EC (µS/cm)		C_T (ppm)	N_T (ppm)	C_{org} (ppm)		
Max	9.69	320		91.98	0.45	0.59		
Min	8.31	15.8		0.8	0.05	0.11		
Geom. mean	9.3	142.02		46.29	0.19	0.28		
Std Dev	0.26	48.64		21.56	0.07	0.11		

The Eh (measured only in borehole S1UB) shows little variability (range between 128 and 155 mV), which contrasts with the variability in color observed *in situ*. In fact, this parameter shows how, no substantial changes are recorded in the NSZ (in the absence of edaphic materials) and the predominant color is 5YR (Munsell scale), in contrast with that observed in the SZ.

In borehole S1UB, in the NSZ between 5.08 and 5.35 m deep, coinciding with levels of sand with clayey silt matrix, a more reddish color is observed (2.5YR) indicating conditions of greater oxidization. By contrast, between 6.08 and 7.14 m deep, coinciding with an increase in the proportion of sand and gravel layers, the coloration is generally more yellowish (7.5YR), suggesting more reductive conditions. When the proportion of silt levels increases, between 7.14 and 7.99 m deep, the color becomes more reddish although more yellowish areas are detected, indicating more reductive conditions. In fact, the capillary ascent and piezometric oscillation zones are characterized by an increase in yellowish coloration. This change in coloration is attributed to the fact that in a mega-site context such as this petrochemical complex, the environmental conditions become reductive as a consequence of the significant quantity of organic matter used as an energy source by microorganisms, which leads to depletion of oxygen.

In the SZ, the colorations are also quite variable in terms of color, lightness and chroma. In general, the existence of areas with high levels of hydraulic conductivity, which is the case of sand and gravel acting as the preferred path for water flow, coincides with the zones where colorations ranging between 7.5YR and 10YR predominate. For example, between 8.20 and 9.91 m deep, the color 7.5YR predominates, while deeper down, between 10 and 13.87 but within the granular aquifer formation, the color 10YR predominates, indicating more reductive conditions. In fact, when comparing colors with the DO groundwater profile, obtained from the multilevel piezometers, it can be assessed that, deep down, the reductive character of groundwater increases. However, the interstratified levels of silts of the transition zone to the aquitard detected in S1UB show colorations varying between 2.5YR and 7.5YR. By contrast, in the aquitard zone clays promote reddish colorations, suggesting the presence of oxidized species, such as Fe^{3+}. At the same time, these materials show

stains of different colors indicating sharp changes in redox conditions and even levels rich in organic matter.

In the case of the S2UB borehole it is observed that, as with S1UB, the first few meters of the NSZ show colorations of around 5YR. By contrast, deeper down, from 4.16 m, clear changes in coloration are observed. Thus, between 4,16 and 4.86 m more yellowish colorations predominate (between 7.5YR and 10YR), while between 4.86 and 6.27 m reds prevail (5YR), with some levels indicating more reductive conditions (7.5YR and 10YR). The capillary ascent and piezometric oscillation zones, between 6.49 and 8 m deep, show a predominance of 7.5YR colorations, although many interstratified levels of 10YR and 5YR are detected, coinciding with contrasts in hydraulic conductivity. In the SZ, between 8 and 13.16 m, there is a predominance of sand layers with 10YR colorations. On the other hand, compared with the transition zone of the S1UB borehole, in S2UB, interstratified levels of silt and sand before the aquitard show greater color uniformity. As in S1UB, in the aquitard zone, a predominance of reddish colorations is observed, ranging from 2.5YR to 5YR.

The observations of the variability of coloration indicates that the medium presents predominantly oxidizing conditions in silty zones, while in the areas where materials with high levels of hydraulic conductivity predominate, more reductive conditions are detected. However, in transition or aquitard zones, the presence of stains with sharp changes in coloration show variations in the redox status of the media linked to the presence of organic matter and to biogenic activity.

The EC of the soil in both boreholes does not exceed 200 µS/cm, with the exception of the first few meters, where the existence of a more silty topsoil places this parameter near 500 and 300 µS/cm in the S1UB and S2UB boreholes, respectively. As regards the S1UB borehole, between 8.17 and 10 m down, there is an increase in EC, ranging between 275 and 523 µS/cm. These levels correspond to sandy silt and gravel with a silty-sandy matrix close to the water table, which could indicate a pollution plume which today moves, or in the past moved, near this water table.

Distribution of C_T, N_T, C_{org}, and trace elements in the subsoil

Concentration of C_T and N_T varies similarly with depth (Figure 3). It should be noted that near the soil surface, the concentration of N_T is greater, particularly in the S2UB borehole. The concentration of inorganic C is strongly correlated with the presence of abundant levels of caliche in the NSZ.

The C_{org} concentration variation profile shows that, at a surface level, there are greater concentrations in the S1UB borehole. This tendency is inverted from 4 m down according to a greater proportion of fine materials in the S2UB borehole as a result of more interstratified layers of silt and clay between the levels of sand and gravel. In the C_{org} profile from the S1UB borehole, an increase in concentration in the transition zone to the aquitard can be detected from 11.7 m to 12.76 m, as the concentration varies from below the detection limit (BDL) to above this limit (ADL) in the interstratified clay levels.

Metals and other trace elements sorbed in the soil and subsoil showed, in general, low concentrations. Arsenic, for example, was below the DL, as, in general, was Pb. For this reason, only samples from the S1UB borehole were analyzed. In the case of Pb (not shown in Figure 3), only one sample located approximately 20 m deep in the clays of the aquitard shows a concentration of 0.16 ppm. This anomaly coincides with a significant N_T anomaly. The existence of interstratified gravels between the aquitard clays allows pollutants, such as the detected Pb, to reach this zone via a lateral connection from its source area. The origin of this Pb could be related to the existence, in this mega-site context, of an old pollution plume from gasoline, to which, in the past,

organo-metal compounds like tetraethyl lead (TEL) and tetramethyl lead (TML) were added as anti-knock agents (Zayed et al., 2003). Lead is an element which is not very mobilized in the subsoil between alkaline to neutral pH levels (Merino and Garcia-Rodeja, 1997), which explains why its presence in areas far downgradient from the potential sources (such as the location of the S1UB and S2UB boreholes) is low.
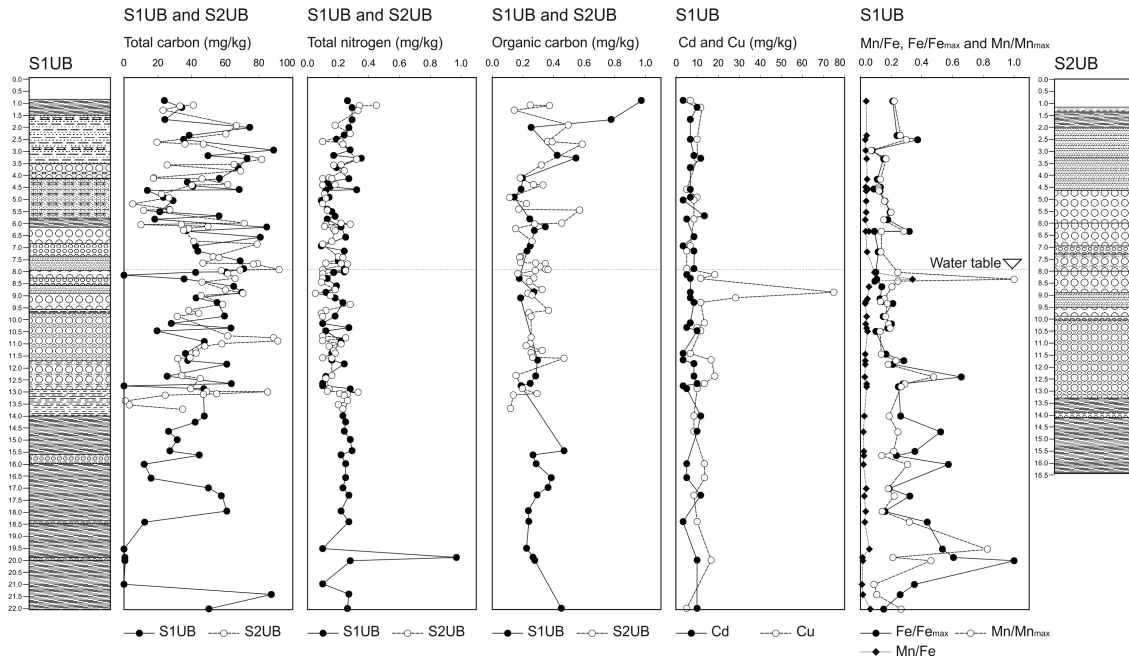

Figure 3: Soil profiles of total carbon (C_T), organic carbon (C_{org}) and total nitrogen (N_T) in the S1UB and S2UB boreholes; and Cd, Cu, Mn/Fe, Fe/Fe$_{max}$ and Mn/Mn$_{max}$ in S1UB borehole. Water table in October 2008.

Cd and Cu were also detected in the subsoil (Figure 3). Their maximums tend to correlate with maximums of C_{org}. They are probably complexed with the organic matter. The concentration of Cu shows an increase at 8.83 m down (the value reaches 75 mg/kg), where the silts are abundant, and another increase between 11.41 and 12.36 m. This increase is accompanied by an increase in the concentration of Cd and C_{org} coinciding with a gravel zone with interstratifications of silts above the transition zone towards the base aquitard in S1UB (Figure 2). The origin of these metals could be mainly associated with the existence of the old gasoline pollution mentioned above, as they can be present in the composition of many gasolines, as indicated in Saint Pierre et al. (2004). However, their presence together with their greater affinity for forming complexes with humic acids from the soil is not ruled out (Kerndorff and Schnizer, 1980).

As for the Fe and Mn values in the S1UB borehole, it can be seen that the Mn/Fe relationship remains fairly constant above the water table, while below it, 8.33 m down, a Mn anomaly is detected, coinciding with the zone where an increase in the EC was detected. As for the relative variation of the Fe and Mn content with respect to the maximum concentrations recorded, Fe$_{max}$ and Mn$_{max}$ (Figure 3), a progressive increase below the water table in accordance with the stability fields of these two elements was observed (Krauskopt, 1979) as the alkalinity diminishes (although pH is never below 8). This increase is most notable in the gravel zone above the transition zone towards the base aquitard owing to the increase in the proportion of silty-clayey type fine materials. Notwithstanding the natural causes, the increasing values for Mn deep down and its anomaly at 8.33 m could be attributed in part to the aforementioned gasoline pollution

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as, in the past, organo-metal Mn compounds like methylcyclopentadienyl manganese tricarbonyl (MMT) could also have been added to gasoline (Smargiassi et al., 2000 and Zayed et al., 2003).

Ranges of VOC variation in the subsoil

Table 6 shows that the highest percentage of detectable chloromethane concentrations (% ADL), i.e. the percentage of samples in which the concentration in the methanol trap is above the DL, corresponds to the S1UB borehole. Of the chloromethanes, the one showing the highest % ADL is CF, followed by DCM and then CT. The fact that CT is the one with the lowest % ADL is attributable to the fact that the boreholes were drilled 220 m from the DNAPL source. It may therefore be assumed that the largest mass of CT is concentrated in the area of the source because of its greater hydrophobic nature. On the other hand, a substantial part of the pollutant stored in the matrix by molecular diffusion was transported in the pollution plume to the area of the boreholes. This accounts for the fact that the plume has shown a greater concentration of CF over time. Moreover, the greater solubility of CF with respect to CT has promoted the preferential dissolution of CF in the plume in accordance with Rault's law. Part of the CT initially stored in the finer levels could also have been degraded to CF by the microbial consortia present in the zone.

The average CT values are similar, 11.3 and 7.3 µg/L, respectively, for the S1UB and S2UB boreholes, while, in the case of CF, they range between 88 and 123 µg/L, the latter value corresponding to the S2UB borehole. This corroborates the greater presence of CF circulating in a dissolved form, as a result of which a large part has penetrated the matrix by molecular diffusion. However, the highest CF concentration recorded appears in the S1UB borehole (1470 µg/L). In the case of DCM, the geometric mean ranges between 31.6 and 23.5 µg/L, respectively, for the S1UB and S2UB boreholes, and the maximum concentration is recorded in S2UB (9054 µg/L).

As for the chloroethane concentrations, the highest values of % ADL recorded correspond to 1,1,2,2 PCA in borehole S1UB and 1,1,1,2 PCA in S2UB, and the lowest to 1,1,1 TCA in boreholes S1UB and S2UB. The average concentrations for 1,1,1,2 PCA, 1,1,2,2 PCA, 1,1,1 TCA and 1,1,2 TCA range between 8.6 and 20; 5.4 and 6.2; 5 and 6.3 and 8 and 7 µg/L, respectively, for boreholes S1UB and S2UB.

Chloroethene concentrations record a higher % ADL for PCE and a lower one for 1,1 DCE. In this case, the presence of PCE in sediments corresponds to the concentrations recorded at piezometer P8 owing to a one-off spill that occurred in a nearby lorry park for trucks transporting liquid chemical products. The average values range, respectively, for the S1UB and S2UB boreholes, between 11.3 and 20.3 µg/L (PCE) and 5.6 and 6.8 µg/L (TCE); and, in both cases, they are approximately 6 µg/L (tDCE) and 5 µg/L (cDCE). In most cases, the maximum concentrations of PCE and TCE correspond to the values recorded in the S2UB borehole, with 997 and 101 µg/L, respectively, and the value of 153 µg/L for tDCE in the S1UB borehole.

The highest % ADL for compounds from the BTEX group corresponds to toluene and xylenes. The average concentrations, in the two piezometers, respectively, correspond to benzene (3.7 to 4.6 µg/L), toluene (60 to 89 µg/L), ethylbenzene (6.2 to 9.5 µg/L) and xylenes (12 to 15.3 µg/L), with maximum values corresponding to toluene (10,060 µg/L) in the S1UB borehole. The high concentrations in the BTEX group compounds are closely linked to the activities at the petrochemical complex where the DNAPL contaminant episode was detected.

Table 6: Main statistical parameters of VOCs in porewater from sediment samples of S2UB S1UB boreholes. DL detection limit. La Pineda (April-May, 2008).

	S1UB (µg/L)																
	Chloromethanes			Chloroethanes				Chloroethenes					BTEX group				
% ADL	**33.3**	**81.0**	**41.3**	**25.4**	**15.9**	**17.5**	**33.3**	**42.9**	**17.5**	**6.3**	**22.2**	**20.6**	**20.6**	**87.3**	**42.9**	**71.4**	**71.4**
Compounds	CT	CF	DCM	1,1,1,2 PCA	1,1,2,2 PCA	1,1,1 TCA	1,1,2 TCA	PCE	TCE	1,1 DCE	tDCE	cDCE	Benzene	Toluene	Etilbenzene	m-Xilene	p-Xilene
Max	564.00	1470.00	5730.00	132.00	2260.00	79.00	98.50	139.00	79.00	15.30	153.00	25.00	50.40	593.00	98.00	181.00	355.00
Min	1.14	3.83	1.46	1.67	1.38	1.47	1.55	1.34	1.59	1.34	1.38	2.35	0.96	1.86	0.97	0.94	0.95
Geometric mean (GM)	11.30	88.00	31.60	8.60	5.40	5.00	8.00	11.30	5.60	4.16	5.64	4.79	3.70	60.00	6.20	12.00	12.95
Standard deviation (SD)	113.00	251.00	1357.00	27.00	294.00	11.30	21.00	32.00	11.40	2.80	20.30	4.73	7.20	145.00	19.10	36.11	54.00

	S2UB (µg/L)																
	Chloromethanes			Chloroethanes				Chloroethenes					BTEX group				
% ADL	**25.4**	**73.1**	**35.8**	**52.2**	**19.4**	**22.4**	**19.4**	**58.2**	**23.9**	**11.9**	**14.9**	**16.4**	**22.4**	**77.6**	**58.2**	**71.6**	**59.7**
Compounds	CT	CF	DCM	1,1,1,2 PCA	1,1,2,2 PCA	1,1,1 TCA	1,1,2 TCA	PCE	TCE	1,1 DCE	tDCE	cDCE	Benzene	Toluene	Etilbenzene	m-Xilene	p-Xilene
Max	406.37	1286.29	9054.00	848.62	1782.11	98.91	214.93	997.00	101.00	50.61	72.12	52.35	117.71	10060.00	215.33	263.04	713.28
Min	1.38	2.69	2.57	2.80	2.19	2.26	2.61	1.63	2.51	2.30	2.32	2.25	1.61	1.35	1.31	1.15	1.35
Geometric mean (GM)	7.30	123.00	23.50	20.00	6.20	6.30	7.00	20.30	6.80	5.14	5.58	5.19	4.60	89.00	9.50	15.30	15.57
Standard deviation (SD)	60.93	340.31	1606.59	164.58	238.60	18.22	32.30	193.27	17.80	8.12	12.13	7.20	20.41	1279.53	40.35	59.06	141.54

<u>Chloromethanes distribution profile in the subsoil</u>

Chloromethane depth distribution (Figure 4) shows that carbon tetrachloride (CT) in the NSZ presents peaks that coincide in the two boreholes, although it is observed in a larger number of samples in the S2UB borehole, where chloromethane concentrations in the methanol trap is above the DL.
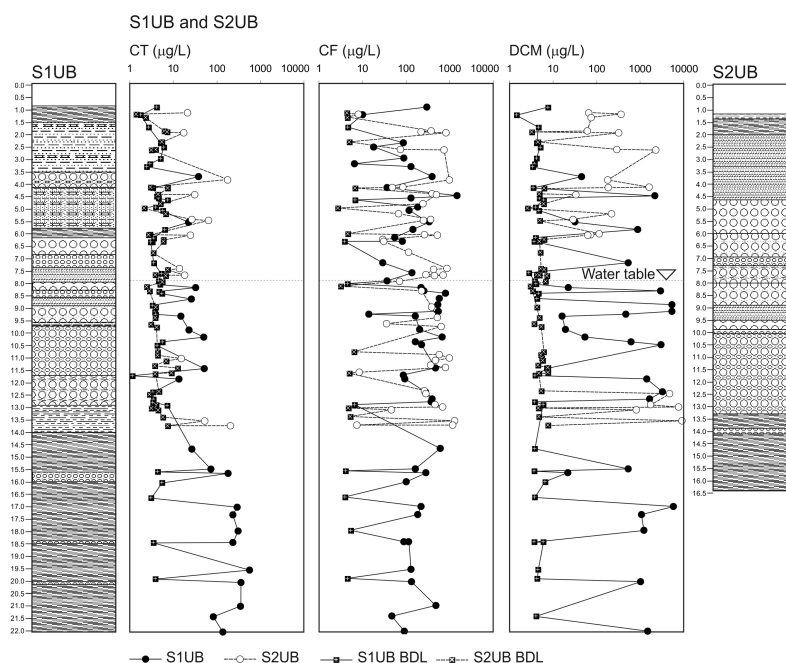

Figure 4: Chloromethanes porewater profiles (CT, CF and DCM). BDL samples below the detection limit. Water table in October 2008.

In the SZ, on the other hand, the S2UB borehole shows few samples in which concentrations in the methanol trap are above the DL, always coinciding with clayey-silty levels. The fact that CT was lower in the S2UB borehole than in the S1UB borehole may be attributed to a greater degradation rate of this compound in the S2UB borehole zone owing to a higher proportion of fine materials (or fine matrix in coarser materials), nutrients and bioconsortiums.

In the S1UB borehole, in the SZ, the maximums found for CT are between 8.2 and 8.64 m; between 9.3 and 10.18 m and at 11.43 m deep, coinciding with silty levels. In fact, the presence of CT in silty levels is also shown in the aquitard, where maximums are detected at 15.63 m, between 17 and 17.94 m and at 18.4 m. This behavior is clearly controlled by the hydrophobic nature of CT and by the molecular diffusion process towards the interior of the clays, which also controls its bioavailability, as this depends, among other factors, on the chemical structure of the compound (Bossert et al., 1986) and on the possible sorption that can take place, particularly in organic matter and, to a certain degree, also in the clayey mineral matrix.

In addition, as shown in the S1UB borehole, the dissolved phase affected the aquitard. It is therefore reasonable to assume that, in the area of the source, the DNAPL free phase reached this aquitard. Then, after moving downgradient along the contact with the aquifer, the dissolved phase reached the area of the boreholes, penetrating the aquitard by molecular diffusion. Although the depth of penetration in the aquitard is at least 8 m, the exact penetration is unknown, and the total mass of pollutant remaining in the aquitard is still significant (Figure 4).

The distribution of CF over depth indicates that the concentrations in the NSZ are higher in the S2UB borehole. In addition, this compound shows that although CF is detected in the greater part of the profile, the maximums coincide with clayey-silt layers, as in the case of CT.

DCM also shows a greater concentration in the NSZ in the S2UB borehole, whereas in the SZ it is essentially detected in the S1UB, and most particularly in the levels closest to the water table where there are many silt stratifications. For this reason, it could be related to microbe activity since the most important ecotone in an aquifer media is located in the area of capillary ascent and in the zones where lithological changes occur (Goldscheider et al., 2006).

On the other hand, in the S2UB borehole, DCM appears especially in the zone near the aquitard, where there are also many lithological changes. Moreover, as is the case of CT and CF, in the S1UB borehole it has also been detected inside the clay aquitard, which demonstrates that this formation is also vulnerable.

Chloroethanes distribution profile in the subsoil

Chloroethanes show a behavior similar to that observed in DCM. The maximums in the S1UB borehole are given in the first few meters of the SZ, where there are abundant levels of silts interstratified in gravels. In S2UB they appear near the aquitard. This behavior is observed in the two isomers of TCA and in 1,1,1,2 PCA.

In addition, 1,1,1,2 PCA shows a progressive increase in the S2UB borehole, whereas 1,1,2,2 PCA shows concentration peaks at 8.64; 11.43 and 14.65 m. These three peaks coincide with gravel levels in the first two cases and with a gravel level interstratified in clays in the last case.

Chloroethenes distribution profile in the subsoil

Chloroethenes (Figure 5) show evidence of biodegradation; e.g., although tDCE is mainly found in concentrations below the DL in the methanol trap, at 10.18 m down in the SZ, a high peak is observed in the S1UB borehole in heterometric gravels with silty sandy matrix, giving rise to a concentration halo centered in these gravels (Figure 5). This tDCE peak coincides with a lower peak of PCE and with a higher peak in TCE indicating that part of the mass of PCE stored in the matrix has been biotransformed successively into tDCE and some cDCE.

As for cDCE, it is most frequently found above the DL in the methanol traps. In the S1UB borehole, tDCE and cDCE usually do not coincide and their peaks are separated by a short distance. However, these compounds show similar tendencies except for the capillary ascent fringe, which constitutes an ecotone promoting biodegradation (Goldscheider et al., 2006), where cDCE shows high values. In addition, cDCE is often detected in zones where there are gravels with a silty matrix (e.g. S2UB). This means that this compound is often associated with zones that are well provided with bioavailable electrons and/or nutrients.
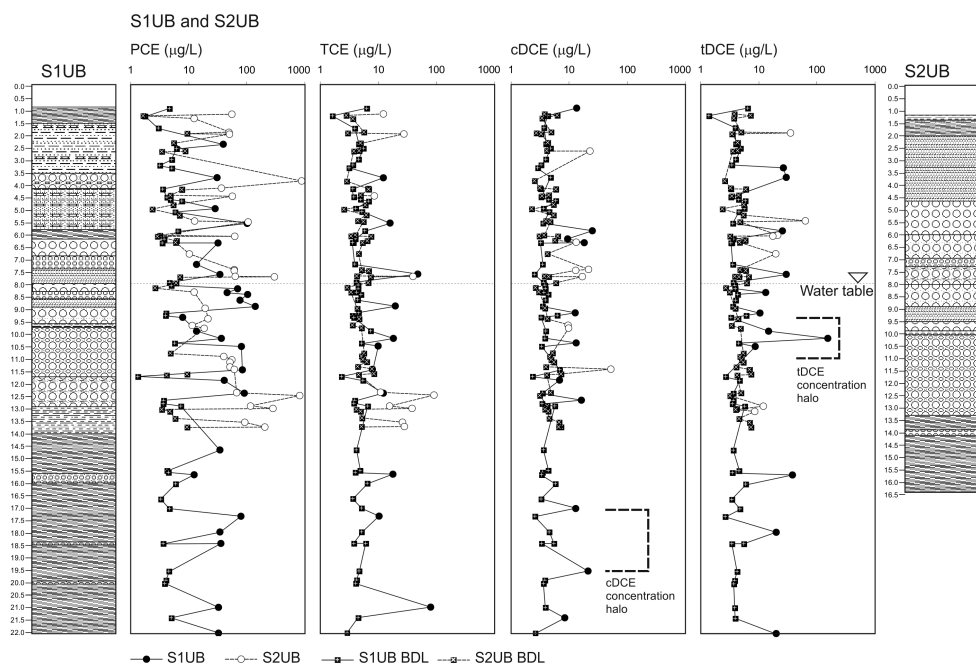
Figure 5: Chloroethenes porewater profiles. tDCE, cDCE, TCE and PCE. BDL, samples below the Detection Limit. Water table in October 2008.

Another example of concentration halo is in the aquitard, where the tCDE is detected in interstratified gravel levels, which would indicate that it has migrated via these levels, acting as a preferred migration path for pollutants, while the concentrations of cDCE increase towards the interior of the aquitard clays. The fact that cDCE is more hydrophobic than tDCE does not account for the increase in concentrations of the former in the aquitard. This increase could then be attributed to PCE and TCE biodegradation processes taking place in this aquitard owing to the higher proportion of organic carbon acting as electron donor. As a result of these processes a concentration halo displaced with respect to each side of an adjacent gravel level is produced (Figure 5). Then, in such aquitard contexts the detection of cDCE concentration halos is a good indicator of the existence of biodegradation (Bradley, 2003).

As for TCE, certain similarities with the distribution of cDCE are observed, although in general it is not abundant. Its presence in the S2UB borehole, in the zone near the aquitard, and the low concentrations recorded in the aquitard zone of the S1UB borehole should be noted.

PCE shows the highest concentrations, with maximum values in the piezometric oscillation zone, and in the zone near the aquitard. If its evolution is compared with that of cDCE, it may be seen that their peaks are displaced, which could indicate the presence of biodegradation. All these PCE maximums are related to silt levels.

BTEX distribution profile in the subsoil

The porewater concentration profiles of the BTEX group show a high variability of concentration over depth and greater concentrations in the NSZ (Figure 6). The S2UB borehole presents greater concentrations than the S1UB borehole in the profiles of the different compounds, especially in the NSZ, accordingly with his lithological and textural predominant features by reference to the S1UB borehole (Table 3 and Table 4), and in the capillary ascent fringe and piezometric oscillation zone, as corresponds o the behavior of a LNAPL (Pankow and Cherry, 1996; USEPA, 1999).
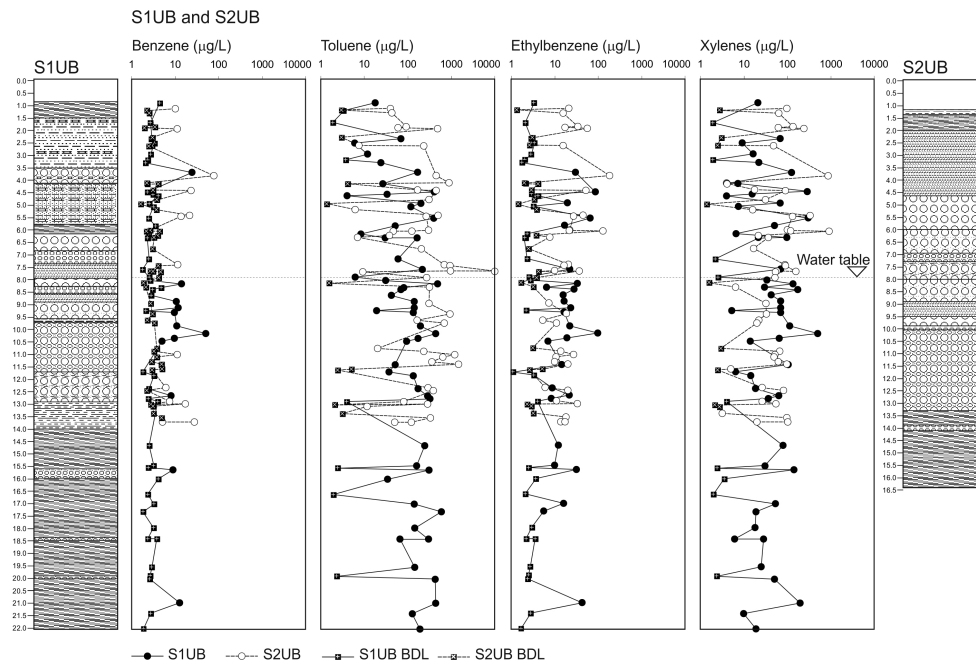
Figure 6: BTEX porewater profiles. Benzene, toluene, ethylbenzene and xylenes. BDL, samples below the Detection Limit. Water table in October 2008.

Toluene, ethylbenzene and xylenes tend to correlate very well with benzene but concentrations are higher than those of the latter. In the S1UB borehole maximum concentrations of benzene are mainly concentrated in the first few meters of the SZ between 8.19 and 10.18 m. These maximums coincide with interstratified levels of silts in sands and gravels. The reason for these concentrations could be that, in the past, this sector was affected by a sub-surface pollution plume which is no longer detected.

On the other hand, the maximum concentrations of benzene in the S2UB borehole are in the NSZ between 3.87 and 5.46 m down, while in the SZ the maximums are concentrated in the zone near the aquitard at 13 m. In the basal aquitard maximums are found in the gravel interstratifications and at a short distance of the Pb anomaly, which has already been mentioned. One explanation is the past existence of a distant pollution source consisting of leaded gasoline (the old gasoline pollution mentioned above) which, through transversal dispersion, reached the aforementioned gravel levels, allowing them to be transported to the drilled zone. Another possibility is the existence of a NAPL resulting from the mixture of DNAPL and LNAPL (made up of leaded gasoline) that migrated to the bottom of the aquifer formation. This led to the penetration of these pollutants into the interstratified gravel levels in the aquitard.

Microbial heterogeneity

Based on samples from the SZ obtained from the cores, it was possible to make a semi-quantitative estimate of the diversity and degree of development of the different bacterial communities present in the aquifer media. The two boreholes are also characterized by a large degree of heterogeneity from the microbiological point of view.

Figure 7 shows that samples with the least diversity and development of microbial communities are located below the piezometric oscillation zone (samples M1, M2, corresponding to the S1UB borehole and samples M12 and M14 corresponding to S2UB). Despite the low microbial diversity of these samples with respect to other samples situated in deeper parts of the core, a greater diversity is found in levels of

lower granulometry (M1 at 9.6 m deep in a level of clayey silts from the S1UB borehole). The existence of different diversity and development of microbial communities that depend on the granulometric and textural characteristics of the media highlights the need to analyze the samples of different granulometries (Albrechtsen, 1994 and Hurst et al., 2002).
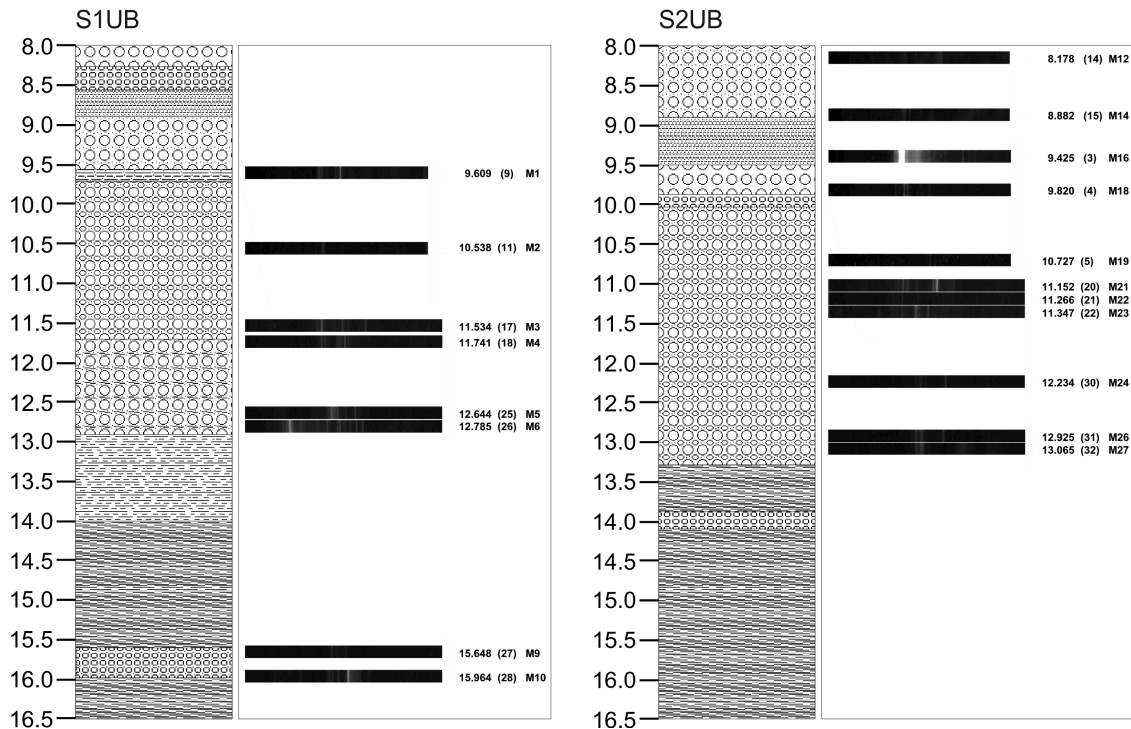

Figure 7: DGGE results in the S1UB and S2UB cores.

Further down, microbial diversity increases and there is greater variability depending on the predominant lithology and the geochemical characteristics (Cozzarelli and Weiss, 2007). Thus, the microbial diversity is greater and the communities are often more developed where fine granulometry levels predominate (silt and clay, as in the case of samples M4 and M5). These are zones with less hydraulic conductivity and a greater capacity of organic matter (and even bacteria cells) to sorb organic pollutants (Scholl et al., 1990; Scholl and Harvey, 1992 and Mills et al., 1994).

The role of granulometry in microbial diversity and development can also be seen at centimeter scale in samples M21, M22 and M23, situated between 11.15 and 11.35 m deep in the S2UB borehole. Thus, in sand levels with clayey-silty matrix (samples M21 and M23) there is greater microbiological diversity than in the levels where the pebble content increases (M22).

On the other hand, at greater depth (samples M24, M26 and M27 in the S2UB borehole) there is a certain homogeneity in the diversity and degree of development of the microbe communities with respect to the other zones. This behavior is due to greater homogeneity in the materials and in the concentrations of available organic compounds.

Microbial diversity and development, however, are also controlled by other elements. For example, in areas where gravels predominate (sample M6 from the S1UB borehole) microbe populations are much more developed owing to a greater bioavailability of nutrients and contaminants. The increase in grain size can be

accompanied by an increase in the size of pores. Nutrients, pollutants or electron donors reach the microorganisms and the Terminal Electron Accepting Processes can take place because of this porosity (Chapelle, 1993 and Fredrickson et al., 1997). In fact, several studies show a greater bacterial abundance and activity in sandy rather than clayey sediments (Fredrickson et al., 1989; Hicks and Fredrickson, 1989; Chapelle and Lovley, 1990 and Phelps et al., 1989 and 1994).

However, a high bioavailability of pollutants also controls microbial diversity and development. Microbial populations are more specialized in the areas where the communities are least diverse and least develop (samples M3 and M4 of the S1UB borehole) because of the maximum concentrations of chloromethanes. This phenomenon has been observed 8.4 m further down (sample M16 from S2UB), where the relative concentrations of DCM, CF and CT are high and where a bacterial community is well developed (Figure 7).

An example related to a low bioavailability of pollutant organic compounds can be found in samples M9 and M18 from the S1UB and S2UB boreholes, respectively, where there are low concentrations of organic contaminants, accounting for the low bacterial diversity and development.

Finally, the existence of centimeter levels of medium gravel and sand interstratified in the clays of the aquitard favors the development of the microbial communities (sample M10 from S1UB). This confirms the greater microbial development in zones with lithological changes (Goldscheider et al., 2006).

CONCLUSIONS

In a mega-site context such us the episode under study, the existence today and in the past of various pollution plumes has given rise to a geochemical background formed by many organic compounds, parent and metabolites in addition to organo-metal compounds and metals. These compounds, in a dissolved phase, are transferred by sorption processes and by molecular diffusion to the solid phase and to the porewater of the silty-clayey levels and to the fine matrix of coarser layers.

Detailed testing and sampling of borehole cores make it possible to describe i) granulometric heterogeneity and the transitional changes occurring in the subsoil, and ii) the physico-chemical characteristics conditioning the biochemical processes taking place in the environment. Heterogeneity conditions the mass of VOCs transferred to the materials with low conductivity as well as the geometric distribution of the pollutants. This is of significance since the quantification of this mass enables us to predict back-diffusion processes that can occur once remedial work has been carried out on the more conductive levels of the aquifer. This is of paramount importantce when designing the remedial strategies.

The piezometric oscillation zone, the capillary zone and, especially, the zones where there are granulometric contrasts constitute ecotones in which levels with fine granulometry or levels of sand with a clayey-silty matrix generally show greater microbial diversity and often more developed communities. At these levels, there is a lower flow velocity and VOCs are present through sorption by the organic material and molecular diffusion from the more conductive levels that are adjacent. Under these conditions, the supply of nutrients, pollutants and electron donors through the more conductive layers leads to the biodegradation of VOCs due to the microbe communities. However, if the concentrations of contaminants are high, e.g. chloromethanes and/or chloroethanes, there is less bacterial development and diversity; i.e. the species are more specialized and the number is lower. Biogeochemical heterogeneity is therefore controlled by the conjunction of lithological

and hydrogeochemical heterogeneities and the large microbiological heterogeneity both in terms of depth and space.

The detection of concentration halos of parent compounds and metabolites on both sides of some of the more conductive levels shows that the VOC biodegradation processes occur not only at the level of the fraction dissolved in the aquifer but also at the level of the fraction retained in the fine materials and in the fine matrix of coarser materials.

The sampling of low-conductivity levels contributes to the definition of the conceptual model of transport not only from a spatial dynamic point of view but also from a temporal view point. As a result, it is possible to identify compounds (e.g. associations of BTEX and metals) that are the remaining traces of the passage of old contaminant plumes at a mega-site whose sources have now disappeared. This is a matter of special interest given that such identification enables us to describe past biogeochemical processes and to partially account for the processes occurring today.

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