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Use of environmental isotopes (^{13}C , ^{15}N , and ^{18}O) for evaluating sources and fate of nitrate and tetrachloroethene in an alluvial aquifer.

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Abstract

Environmental isotopes and geochemical parameters were used to evaluate the sources and fate of nitrate (NO_3^-) and tetrachloroethene (PCE) in an alluvial contaminated aquifer. Isotope data and redox parameters data indicated that biodegradation does not play any role in the attenuation of these compounds along the groundwater flow system. Furthermore, nitrate isotopes and concentration data allowed the authors to distinguish two nitrate inputs and relate them to their possible sources. The primary source originates from septic waste and the secondary source is associated with nitrogenous fertilizer application. Regarding PCE, the $\delta^{13}\text{C}$ values do not change for almost 1000 m along the groundwater flow system despite

large decreases of PCE concentration, thus confirming that physical processes do not alter the isotopic composition of organic compounds; this finding has a significant implication for the use of carbon isotope ratios for fingerprinting sources of PCE in VOC plumes. This study has shown that combined use of environmental isotopes and geochemical parameters is an efficient approach for water resource management studies in sites polluted by various types of contaminants.

1. Introduction

Nitrate and chlorinated organic compounds are among the most common contaminants found in groundwater. High nitrate levels are generally associated with excessive use of inorganic and organic fertilizers. Chlorinated aliphatic hydrocarbons (CAHs), including tetrachloroethene (PCE), have been widely utilized for many years as solvents and degreasing agents and their impact on groundwater is associated with storage tank spills and leakage in industrial areas and dry cleaning facilities in urban areas. Natural attenuation of nitrate and PCE in groundwater anaerobic environments can be controlled by biodegradation reactions because these compounds are used as terminal electron acceptors for denitrifying and dehalogenating microorganisms, respectively. Denitrification starts once available oxygen is consumed and significant PCE biodegradation generally occurs under sulphate reducing or methanogenic conditions (Wiedemeier et al. 1999; Ferguson and Pietari 2000).

Chemical analyses of a limited number of sampling points render it difficult to distinguish the contribution of biotic degradation to natural attenuation from contributions of other physical processes, such as dilution. Much documentation supports the use of environmental isotopes

to evaluate sources and processes that affect nitrate concentration in groundwater (Kendall and Aravena 2000; Widory et al. 2005; Kendall et al. 2007; Aravena and Mayer, 2010). Regarding organic compounds, compound-specific isotope analysis (CSIA) has become a well established tool used to trace the origin of CAHs and for assessing degradation processes that control the fate of these compounds in groundwater (Schmidt et al. 2003; Meckenstock et al. 2004; Blessing et al. 2007; Hunkeler and Aravena, 2010). Previous studies have shown that microbial degradation produces carbon isotope fractionation of chlorinated organic compounds and ^{13}C enrichment in the remaining product compound; in comparison, little fractionation is produced during evaporation, sorption, dilution and transport processes (Huang et al. 1999; Poulson and Drever 1999; Slater et al. 2000; Hunkeler et al., 2004).

Sedimentary alluvial deposits form vulnerable aquifers commonly used as water resources in agricultural, industrial and urban areas. Consequently, many such aquifers are polluted by various contaminants. The aim of this study was to apply CSIA to carbon to evaluate the origin and fate of PCE in an alluvial contaminated aquifer. The rationale for using CSIA for fingerprinting PCE is based on the significant range of $\delta^{13}\text{C}$ values that have been measured for manufactured PCE (van Warmerdam et al. 1995; Beneteau et al. 1999; Jendrzewski et al. 2001). The carbon isotope enrichment pattern associated with biodegradation was used to assess the role of biodegradation in the natural attenuation of PCE along the groundwater flow system.

Various wells in the aquifer under investigation are also affected by nitrate pollution, which reaches concentrations above the drinking water threshold (50 mg/L; EC, 1998). The elevated nitrate concentrations may act as a redox buffer in those parts of the aquifer where oxygen is consumed, thus limiting the occurrence of stronger reducing conditions favourable for PCE

biodegradation. Therefore, this study also investigated the sources and fate of nitrate using geochemical parameters and isotope tracers. Understanding the fates of the contaminants, PCE and nitrate, is crucial for long term management of the study area water resources.

2. Site description

The aquifer under investigation is located approximately 45 km northwest of Barcelona (Spain) between the Catalan Coastal Ranges and the Mediterranean Sea, and consists of alluvial sedimentary deposits related to the Sant Pol de Mar seasonal stream. The stream is usually dry; water flows only after heavy rains or during rainy periods. In this area, groundwater is primarily used for crop irrigation, but some wells are also used to supply water to Sant Pol de Mar village and a camping area (Figure 1). Sant Pol de Mar's population was approximately 5,000 in 2006. The well water supplied approximately 50% of the village's drinking water.

In April 1999, the Catalonia Water Agency (ACA) detected elevated PCE concentrations in several wells in the study area, up to 356 $\mu\text{g/L}$; these values were above the drinking water threshold and resulted in closure of those wells that were part of the drinking water supply system (18PESC1 and 25PESC2, Figure 1). This situation prompted the ACA to commission a more comprehensive study (ACA, 2003) to assess contamination of the aquifer. In November 2001 regular sampling for PCE analysis was initiated in various wells. Furthermore, two boreholes of 18 and 26 m were drilled for core sampling and two single interval monitoring wells (S1 and S2) were installed (Figure 1). Well 21PPK, located in an industrial area at the northern part of the site, showed the highest concentration of PCE,

reaching a value of 753 $\mu\text{g/L}$ in March 2002. No concentration data for this well existed before November 2001. The monitoring well S1 was installed in close proximity to 21PPK with the intention of obtaining information about the location of the source area; however, the point of PCE release remains undetermined. The sparse historical information indicates that PCE releases probably occurred several decades ago.

The alluvial aquifer is unconfined and primarily formed by Quaternary sand and gravel beds developed over Paleozoic granodioritic bedrock. Two layers comprising silt and fine sand, with thicknesses of <1 m, were found in the S2 borehole at depths of 4.2 and 6.0 m. The bedrock was reached at 16 and 21 m below ground surface in S1 and S2, respectively, and it was weathered at the top of the unit. Most of the sampled wells are entirely located within the alluvial unit, with an estimated hydraulic conductivity (K) of from 5 to 10 m/day (ACA, 2003).

3. Materials and Methods

3.1 Field activities

Groundwater flow directions were determined from a potentiometric surface map drawn using the water levels measured in May 2003. The water table depth varies from 8.0 to 10.7 m below ground surface at the north end of the site and from 2.4 to 5.9 m at the south end, and the main groundwater flow direction is approximately parallel to the superficial stream (Figure 2). Groundwater flow velocity values ranging from 0.13 to 0.74 m/day were calculated using the estimated K range, the hydraulic gradients measured in different parts of

the aquifer and an average sand effective porosity of 0.38 (Freeze and Cherry, 1979). These values must be considered as an order of magnitude due to the uncertainties and assumptions used for calculations.

The contaminant distribution was evaluated using ten water supply and irrigation wells and two large screen monitoring wells. Figure 2 shows the sampling points used in this study and the approximate location of the PCE dissolved-phase plume. The water supply and irrigation wells have large diameters ranging from 30 to 280 cm, and depths ranging from 13.0 to 27.8 m (Figure 2). In contrast, the single-interval monitoring wells S1 and S2 have diameters of 16.5 and 7.5 cm, respectively, a depth of 18 m and screen lengths of 6 and 3 m, respectively.

Samples were collected over three sampling campaigns; nine samples were analyzed in May 2003, twelve in September 2003 and four in January 2004. The samples analyzed in January were those with the highest PCE concentrations. For sample collection, water was pumped from the selected depth while water quality indicator parameters (dissolved oxygen [DO] and Eh) were monitored in an in-line flow cell to determine the purge volume in each well.

Pumping was performed using non dedicated electrical submersible pumps with polyethylene discharge tubing (10 mm o.d.) at flow rates of between 1.0 and 2.2 L/min. Sampling was conducted at similar depths in different campaigns. Samples for several wells (10PP, 15CR, 13CR, 16AM, 17CP and 19PI) were collected using electrical high flow pumps installed in the wells. Water samples were dispensed into amber glass bottles for concentration analysis, water isotope (δD and $\delta^{18}\text{O}$) analysis and $\delta^{13}\text{C}_{\text{PCE}}$ analysis; and into polyethylene bottles for nitrate isotope ($\delta^{15}\text{N}$ and $\delta^{18}\text{O}$) analysis. All samples were kept in field coolers until returned to the lab, where they were stored in a cool (4°C) and dark environment until processed.

Furthermore, 30 mg HgCl_2 per liter of sample was added to samples that were stored for

several weeks before undergoing isotopic analysis. On site geochemical data, including pH, conductivity, temperature, Eh and DO, were measured with the in-line flow cell. Aquifer conditions at the time of this study had not been disturbed by any remedial activities.

3.2 Analytical methods

3.2.1. Concentration analysis

Concentrations of chlorinated compounds in groundwater samples were determined by headspace (HS) analysis using a FOCUS Gas Chromatograph coupled with a DSQ II Mass Spectrometer (GC-MS) (Thermo Fisher Scientific, Waltham, MA, USA). The GC was equipped with a split/splitless injector and a 60 m × 0.32 mm i.d. DB-624 capillary column (Agilent, Palo Alto, CA, USA) with a film thickness of 1.8 µm. The following temperature program was used: 2 min at 60°C and then increased to 220°C at intervals of 8°C/min. HS vials of 20 mL were filled with a sample volume of 15 mL, previously diluted with ultra pure water (Milli-Q) if necessary, and immediately closed with open aluminium crimp caps containing a PTFE lined silicone septum. The vials were then placed on the automatic HS injector. The HS procedure was conducted for 30 min at 80°C and a headspace volume of 0.75 mL was injected in split mode (split ratio 1:22) at 250°C and 40 mL/min carrier gas flow. The compounds were identified on the basis of the comparison of the retention times and mass spectrum of selected ions with the calibration standards, and the concentrations were quantified using a set of multi-component external standards at different concentrations. A standard stock solution with a concentration of 10 ppm was made by spiking the multi-component standard in HPLC-grade methanol. Then, aqueous standards at various

concentrations, depending on the approximate concentration of the target compounds in the samples, were prepared by diluting the analytes from the methanolic standard stock solution in Milli-Q water. These aqueous standards were analyzed together with the samples.

Nitrate and other major anion concentrations were determined by High Performance Liquid Chromatography (HPLC). The HPLC system was equipped with an IC-Pak anion column (150 × 4.6 mm, Waters, Yvelines Cedex, France). Conventional chemical analyses, including chlorinated ethene aqueous concentration measurements, were performed at the laboratories of the Serveis Científicotècnics (SCT), University of Barcelona, Spain.

3.2.2. Stable isotope analysis

Carbon isotope ratios of chlorinated ethenes were determined by CSIA using headspace solid-phase microextraction (HE-SPME) and a gas chromatograph coupled to an isotope ratio mass spectrometer through a combustion interface (GC-C-IRMS). The method and equipment used are described in detail in Palau et al. (2007). The GC-C-IRMS system used for samples analyzed in the Environmental Isotope Laboratory (uWEILAB) consisted of a Hewlett-Packard 6890 GC (Agilent), a combustion interface operated at 850°C (Micromass, Manchester, UK), a cold trap cooled to -100°C using liquid nitrogen, and an Isochrom IRMS (Micromass). The GC was equipped with an RTX-5 column (60 m × 0.25 mm, 1.0 µm film thickness, Restek, Bellefonte, PA, USA). The volatile compounds were also extracted by HE-SPME using a 75 µm Carboxen-PDMS fiber (Supelco, Bellefonte, PA, USA). Prior to extraction, all samples with concentrations above 50 µg/L were diluted to 50 µg/L with nanopure water. Samples with concentrations below 50 µg/L were diluted to 20 µg/L and 25% weight NaCl was added to increase the volatilization to the gas phase.

For $^{15}\text{N}_{\text{NO}_3}$ and $^{18}\text{O}_{\text{NO}_3}$ analysis a minimum amount of 5 mg N from NO_3^- was required in the sample (modified method from Silva et al., 2000). Dissolved nitrates were concentrated using anion-exchange columns filled with AG 1-X8 (Cl^-) 100-200 mesh resin (Bio-Rad Laboratories, Hercules, CA, USA) after extracting the sulphates and phosphates by precipitation with $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ and filtration. The total amount of Cl^- added to the sample as $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ must be controlled because it can compete with nitrates, thereby minimizing their retention in the resin. Next, nitrates were eluted with HCl (3M) and converted to AgNO_3 by the addition of silver oxide. The obtained AgNO_3 solution was filtered in two steps at 11 and $0.45 \mu\text{m}$ to remove the precipitated AgCl and then was frozen and lyophilized. The resultant pure AgNO_3 was analyzed in silver capsules. $\delta^{15}\text{N}_{\text{NO}_3}$ analysis was performed using a Carlo Erba EA1108 elemental analyzer (Thermo Fisher Scientific) coupled in continuous flow to a Finnigan MAT Delta C IRMS (Thermo Fisher Scientific). $\delta^{18}\text{O}_{\text{NO}_3}$ was measured in duplicate using on-line pyrolysis with a ThermoQuest-Finnigan TC/EA (Thermo Fisher Scientific) coupled to a Finnigan MAT Delta C IRMS.

Oxygen and hydrogen isotopes of water were analyzed using a dual inlet Finnigan MAT Delta S IRMS (Thermo Fisher Scientific) coupled to an automated line based on the equilibration between the water and H_2 gas, with a Pt catalyst, and between water and CO_2 gas (Finnigan MAT EQ-Unit). Isotope data are reported in the usual delta notation for $\delta^{15}\text{N}$, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$, defined as $\delta = ((R_s/R_r)-1) \times 1000(\text{‰})$, where R_s and R_r are the $^{15}\text{N}/^{14}\text{N}$, $^{18}\text{O}/^{16}\text{O}$ and $^{13}\text{C}/^{12}\text{C}$ ratios of the sample and international standards, i.e., atmospheric N_2 , Vienna Standard Mean Oceanic Water (VSMOW) and Vienna PeeDee Belemnite (VPDB), respectively. The isotopic analyses were conducted in the isotope laboratory of the Serveis Científicotècnics (SCT), University of Barcelona, Spain, except for several samples collected

in May 2003 that were analyzed for $\delta^{13}\text{C}_{\text{PCE}}$ at the EILAB of the University of Waterloo, Canada.

4. Results and discussion

4.1. Groundwater isotope data

Water isotopic analyses were performed on groundwater samples collected in May 2003, September 2003 and January 2004. The average values of $-5.2 \pm 0.2\text{‰}$ for $\delta^{18}\text{O}$ and $-35.0 \pm 1.5\text{‰}$ for δD were similar to the weighted mean isotopic composition of the local rain values of -5.5‰ for $\delta^{18}\text{O}$ and -32.6‰ for δD (IAEA/WMO, 2004), indicating that aquifer recharge was controlled by local precipitation. Groundwater level data collected during the period of November 2001 to January 2004 correlated to precipitation levels measured at a meteorological station located approximately 12 km northwest of the study site (DAR, 2007); this reflects the influence of local rainfalls on aquifer recharge and supports this interpretation based on the isotopic data.

4.2. Groundwater geochemistry

4.2.1. Inorganic data

The groundwater is characterized by pH values ranging from 6.4 to 7.0 and conductivity values around $1000 \mu\text{S}/\text{cm}$, except for a high value of approximately $1400 \mu\text{S}/\text{cm}$ that was

measured in well 19PI. The groundwater is calcium-bicarbonate type and the Stiff diagrams (Figure 1) showed spatial chemical variations that were not significant, except for sample S1, which is characterized by more NO_3^- and less Cl^- and Mg^{2+} , and sample 19PI which has more NO_3^- , Ca^{2+} , Cl^- and less Mg^{2+} . It should be noted that wells 19PI and S1 are located in areas that are affected by input of a secondary groundwater flow component connected with the main groundwater flow system (Figure 2); this input could explain the chemical variations observed in these locations.

Redox conditions in the aquifer were estimated based on measurements of several redox parameters including Eh, DO, Mn (II) and Fe (II) (Table 1). The Eh values ranged from 295 to 442 mV, with the exception of the sample collected in 25PESC2 (185 mV). These values indicate the absence of strong reducing conditions in the aquifer. DO values varied from 0.5 to 3.4 mg/L, but concentrations below 1 mg/L were measured only at the distal part of the plume (18PESC1 and 25PESC2) and S2 in September 2003. The presence of oxygen at concentrations above 1 mg/L indicates that the aquifer is aerobic.

4.2.2. Nitrate concentration data

Nitrate concentration ranged from 27 to 158 mg/L and most values were close to the drinking water threshold (50 mg/L) (Table 1). No significant concentration changes were observed among different sampling campaigns. The lowest value of 27 mg/L was observed in well 17CP in May 2003, and the highest concentrations, reaching a peak value of 158 mg/L, were measured in S1, 19PI and 21PPK in May 2003 (Figure 3). With the exception of these values, nitrate concentrations were also similar along the main groundwater flow direction. The

redox conditions, low levels of Mn (II) and Fe (II), and appreciable concentration of O₂ (Table 1) indicate that aquifer conditions are not suitable for the occurrence of denitrification.

4.3. Isotope data in nitrate

To better understand the fate of nitrate in the aquifer, nitrate isotope ratios were also measured. The $\delta^{15}\text{N}_{\text{NO}_3}$ values ranged from +12.1 to +15.7‰, excepting the nitrate collected in S1 and 19PI which showed lower $\delta^{15}\text{N}_{\text{NO}_3}$ values of approximately +7‰ (Table 1). The water samples from wells S1 and 19PI were also characterized by the highest nitrate concentrations, ranging from 87 to 158 mg/L; this suggests a secondary source of nitrate input with a different isotopic composition (Figure 3). Excepting data from wells S1 and 19PI, the $\delta^{15}\text{N}_{\text{NO}_3}$ data seem to exhibit a slight trend to lower values along the main groundwater flow direction (Figure 3). In accordance with the locations of S1 and 19PI, this pattern might be explained by the influence of a secondary nitrate source characterized by a $\delta^{15}\text{N}_{\text{NO}_3} \sim +7\text{‰}$.

A dual isotope approach using $\delta^{15}\text{N}_{\text{NO}_3}$ versus $\delta^{18}\text{O}_{\text{NO}_3}$ data was used to obtain further information about possible nitrate sources (Table 2, Figure 4). The $\delta^{15}\text{N}$ values of nitrate from animal and domestic waste tend to be more ¹⁵N enriched than those of nitrate from industrial fertilizers (Table 2). The nitrogen source of synthetic fertilizers is atmospheric nitrogen, which is characterized by a $\delta^{15}\text{N}$ of 0‰. It is important to note that $\delta^{15}\text{N}_{\text{NO}_3}$ in soils amended by ammonium fertilizers may not be the same as in soils amended by nitrate fertilizers due to the effect of NH₃ volatilization producing nitrate with higher $\delta^{15}\text{N}$ values (Vitòria et al. 2005). The nitrogen isotopic fractionation associated with the volatilization of

ammonia also controls the $\delta^{15}\text{N}$ values of nitrate from animal and domestic waste.

Volatilization can occur during manure storage in lagoons, stockpiles or in the unsaturated zone (Aravena and Mayer, 2010). Nitrate in groundwater impacted by sewage showed a $\delta^{15}\text{N}$ range between +8.1 and +20‰, which is higher than the $\delta^{15}\text{N}$ range of +5 to +8‰ reported for fresh sewage (Aravena and Mayer, 2010). Depending on the $\delta^{18}\text{O}$ value of the water, nitrate from manure, sewage and ammonium fertilizers produced by nitrification in the unsaturated zone tend to be in the range of 0 and +6‰ (Table 2) (Aravena and Mayer, 2010).

According to the summary data presented on Table 2 and data represented on Figure 4, the $\delta^{15}\text{N}_{\text{NO}_3}$ values of around +14‰ agree well with animal manure and septic waste possibly related to leakage from an underground sewage pipe located parallel to the stream. However, the $\delta^{18}\text{O}_{\text{NO}_3}$ values are higher than the expected value of $\sim +4.4\text{‰}$ based on the laboratory data (Hollocher 1984; Anderson and Levine 1986; Kendall 1998), which show that during nitrification 2/3 of the oxygen comes from the water oxygen, with $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values ranging from -4.7 to -5.4‰, and 1/3 from the atmospheric oxygen, with a $\delta^{18}\text{O}_{\text{O}_2}$ value of +23.5‰ (Kroopnick and Craig 1972; Horibe et al. 1973). Oxygen contents of the AgNO_3 samples were close to 28%, indicating that no major contaminants were present in the precipitate.

The ^{18}O enrichment of groundwater nitrate in comparison with the theoretical value can be explained by several processes, including: 1) nitrification in soil waters with higher $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values due to evaporation or seasonal changes in rain, 2) changes in the proportion of oxygen from H_2O and O_2 sources and 3) nitrification using O_2 that has a high $\delta^{18}\text{O}$ value due to bacterial respiration (Mayer et al. 2001; Mengis et al. 2001; Kendall et al., 2007). Vitoria et al. (2005) studied agriculture contamination in groundwater in this region and also obtained $\delta^{18}\text{O}_{\text{NO}_3}$ values in groundwater nitrate samples; these values ranged from +5.1 to +10.2‰,

which are higher than the theoretical range. The source of groundwater nitrate in their samples was related to synthetic fertilizers, with $\delta^{15}\text{N}_{\text{NO}_3}$ values between +6.8 and +9.4‰. These authors observed in some samples a positive correlation between $\delta^{18}\text{O}_{\text{NO}_3}$ values and nitrate concentrations, suggesting that $\delta^{18}\text{O}_{\text{NO}_3}$ deviations could be explained by a small contribution of nitrate-containing fertilizers characterized by $\delta^{18}\text{O}_{\text{NO}_3}$ values close to +23‰.

The lack of concurrent ^{15}N and ^{18}O enrichment of groundwater nitrate samples discards the occurrence of denitrification at the site (Figure 4), even in those wells characterized by low DO concentrations (< 1 mg/L). The nitrate in wells S1 and 19PI also had different $\delta^{18}\text{O}$ values than nitrate found in other parts of the aquifer. The lower $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ values observed in S1 can be explained by a significant contribution of fertilizers in the form of NH_4SO_4 . In the case of 19PI, the lower $\delta^{15}\text{N}$ and the higher $\delta^{18}\text{O}$ values can be explained by a major contribution of fertilizers in the form of NaNO_3 since these types of fertilizers are characterized by highly enriched $\delta^{18}\text{O}$ values in the range of +21.0 to +48.5‰ (Vitòria et al. 2004 and 2005). The influence of fertilizers in the area of these wells agreed with the presence of crops in the vicinity of the wells (Figure 1) and with their intense use in this region (Vitòria et al. 2005).

4.4 Organic contaminant data

PCE is the main volatile organic compound present in the aquifer and, in general, its degradation products (TCE and 1,2-cisDCE) were found at very low concentrations (< 1 $\mu\text{g/L}$). Regarding PCE distribution, the highest concentrations of up to 753 and 717 $\mu\text{g/L}$ were detected in wells 21PPK and S1, respectively, suggesting that these wells are located

close to the source. These values are much lower than PCE solubility of 200 mg/L (Pankow and Cherry, 1996), indicating that a dense non-aqueous phase liquid (DNAPL) may not be present in the vicinity of these wells. A decrease in PCE concentration is observed downgradient from these wells, reaching values as low as 16 µg/L in the most distant well (25PESC2). However, variations in PCE concentration were observed in the plume; for example, well S1 (situated close to 21PPK) data showed PCE concentration values below 30 µg/L (Table 3). The drops in PCE concentration in S1 could also be the consequence of a dilution process associated with lateral groundwater input (Figure 2).

A possible PCE plume core with a concentration of >0.1 mg/L was delineated according to the PCE concentration distribution and the groundwater flow system based on the data collected in May 2003 (Figure 2). The highest concentrations were observed in 21PPK and S2 (Table 3). The facts that well 21PPK has a depth of 22.4 m (Figure 2) and the screen interval of the monitoring well S2 was situated from 14 to 17 m below the ground surface suggest that the plume is migrating through the lower part of the aquifer. Well 18PESC1, which is located in the distal part of the plume about 900 m downgradient of the suspected source area, showed the highest concentrations of up to 151 µg/L during the last sampling campaigns, with the exception of the sample collected in April 2002; this indicates that the plume could be still expanding.

TCE concentrations above 1 µg/L were observed in 21PPK, S1 and 17CP, reaching 10 µg/L in the latter. 1,2-cisDCE was rarely detected, with the exception of samples collected in 21PPK and 17CP in November 2001 and March 2002 which showed values below 20 µg/L. The maximum total concentration of degradation products corresponds to 3.1% of the PCE concentration, except for 17CP in November 2001 and March 2002 where fractions reaching

approximately 5% were found. The low fractions of TCE and 1,2-cisDCE indicate a low extent of biodegradation of PCE in the aquifer. Moreover, TCE could also be an impurity of the PCE production.

4.3. Seasonal patterns of PCE concentration

Significant variations in PCE concentration were observed during the different campaigns, e.g., in well 21PPK (Table 3). In order to gain insight about the processes controlling the PCE concentration close to the source, the concentration values were represented versus the precipitation data (Figure 5). The lowest PCE concentrations match with periods of high precipitation, indicating the occurrence of a dilution process. Significant increases in PCE concentration were observed from November 2001 to March 2002 and February to May 2003; these timeframes correspond with dry periods. The overall pattern could be explained by assuming the contaminant plume is in the bottom of the aquifer. During the rainy season the water table rises and the water in the well represents water that has been diluted with uncontaminated recharge water. During the dry season, and therefore under lower water conditions, the water sampled in the well contains more water from the PCE plume. Regardless of the observed seasonal concentration changes, a trend to lower values is observed, suggesting that contamination close to the suspected source area is decreasing.

4.5. Isotope data for PCE

The PCE $\delta^{13}\text{C}$ values varied from -22.4 to -20.3‰ (Table 4). No significant variations were observed when comparing the $\delta^{13}\text{C}$ value representing the high concentration areas with downgradient samples (Figure 6), excepting the value obtained in 17CP on May 2003, with a deviation above 1‰ (Table 4). The ^{13}C enrichment observed in this well could be partly explained by biodegradation according to the presence of PCE degradation products, reaching a fraction of 5.4% of PCE concentration in November 2001. Nevertheless, the overall low variation in $\delta^{13}\text{C}$ values along the plume indicates a minimal biodegradation of PCE along the groundwater flow system, which is in agreement with the redox conditions and the near absence of biodegradation products. The standard deviation of $\delta^{13}\text{C}_{\text{PCE}}$ in the samples collected in September 2003 (Figure 6) was similar to the analytical uncertainty (typically in the range of 0.5‰). The observed data scatter is probably characteristic of the general variability in a plume and is within the range of values that would be expected in groundwater not affected by biodegradation. Therefore, the attenuation of PCE in the aquifer is apparently controlled by abiotic processes such as dilution, sorption and dispersion. The fact that the $\delta^{13}\text{C}_{\text{PCE}}$ value is preserved for almost one kilometer from the near source area supports the results of Hunkeler et al. (2004), showing that physical processes do not significantly change the carbon isotopic composition of chlorinated compounds in groundwater. These findings have significant implications for the use of carbon isotopes for fingerprinting sources of PCE in VOC plumes.

The obtained $\delta^{13}\text{C}_{\text{PCE}}$ data do not provide evidence of different PCE sources with distinct isotopic compositions, suggesting that the PCE in the aquifer has a single origin. The $\delta^{13}\text{C}_{\text{PCE}}$ values were above the range of $\delta^{13}\text{C}$ for PCE from known different manufacturers, from -23.2 to -35.8‰ (Table 2). The partitioning of contaminants such as benzene, toluene, ethylbenzene, dichloromethane and TCE between water and gas phases led to an enrichment

of ^{13}C in the gas phase, producing an inverse carbon isotope fractionation (Meckenstock et al, 2004); thus, the higher $\delta^{13}\text{C}_{\text{PCE}}$ could not be explained by evaporation during the spill or from a disposal lagoon. However, similar values were found at a source area of another PCE contaminated site in Spain (Palau, 2008), suggesting a wider range of $\delta^{13}\text{C}_{\text{PCE}}$ values for manufactured PCE.

5. Conclusions

The concentration data showed the aquifer is contaminated with nitrate and PCE levels that are above the permissible drinking water level. The nitrate concentration pattern along the groundwater flow system is controlled by input from a secondary source high in nitrate content associated with a groundwater flow component perpendicular to the main groundwater flow system. Input of this secondary source associated with agricultural activities is confirmed by the $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ data. These data also show that the main source of nitrate in the aquifer is of sewage origin and is associated with leakage of a sewage pipe. The redox and isotope data indicate that denitrification does not play any role in the attenuation of nitrate in the aquifer.

Regarding PCE, a significant decrease in concentration was observed along the groundwater flow system downgradient from the suspected source area. Moreover, significant seasonal variations were observed in PCE concentrations in the plume associated with recharge events during rainy periods. Despite a significant decrease of PCE concentration along the groundwater flow system, no changes were observed in the carbon isotopic composition of the PCE, indicating the isotopic fingerprint is conservative along the groundwater flow system. The $\delta^{13}\text{C}_{\text{PCE}}$ data also indicate that no significant microbial reductive dechlorination

of PCE occurs along the one kilometer plume, and physical processes such as dilution and dispersion are the main processes involved in the attenuation of PCE at the study site. This result agrees with the non-reducing chemical conditions at the site.

This study confirms previous laboratory and field studies which showed that physical processes, which control the attenuation of PCE along the groundwater flow system, do not change the isotopic composition of the PCE. These findings support the use of carbon isotopes as tracers for fingerprinting sources of chlorinated compounds in groundwater. This study has shown that combined use of geochemical parameters and isotopic tracers provides useful insights into the behaviour of groundwater contaminants.

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Figures

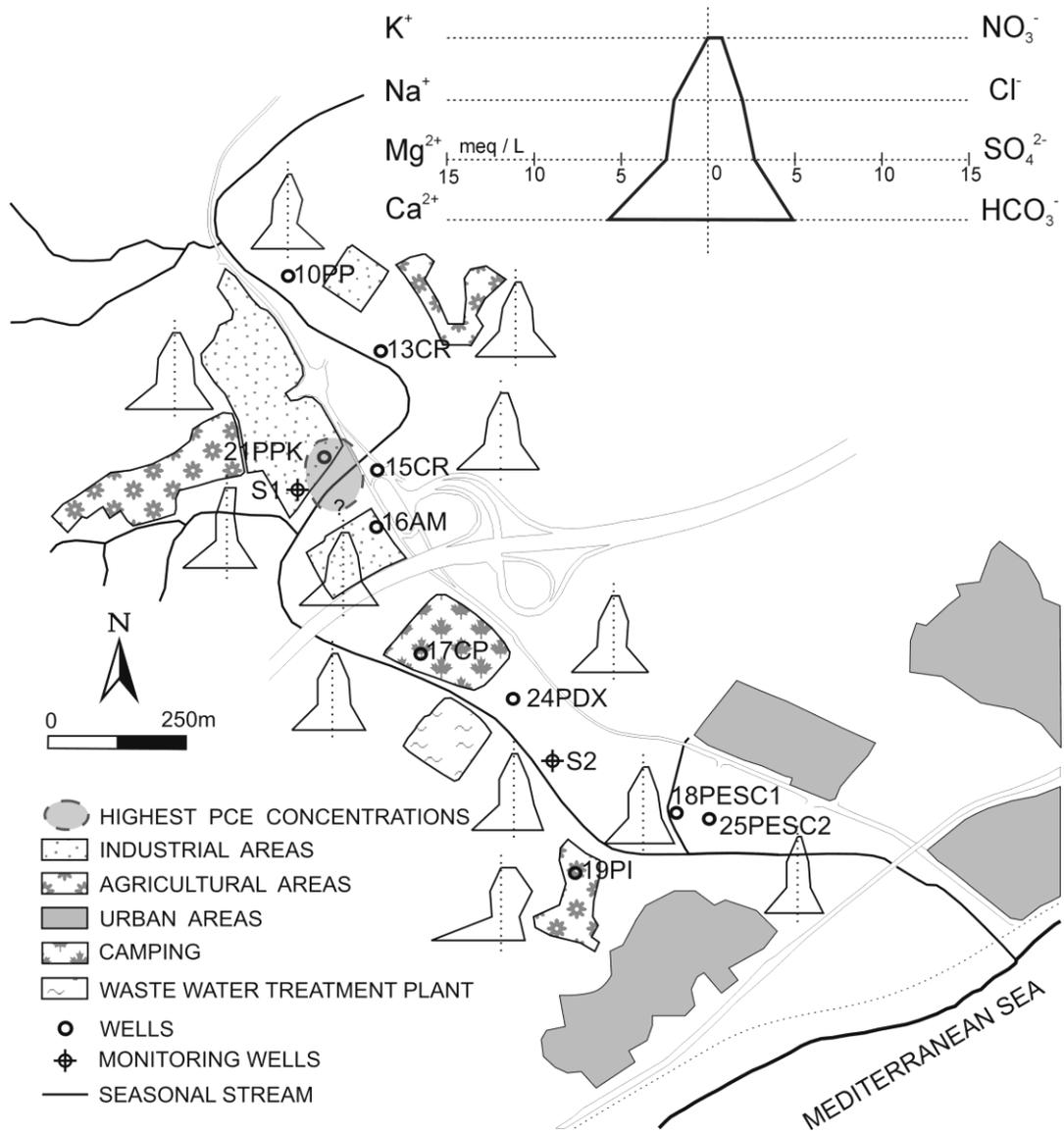


Figure 1. Soil uses, location of groundwater sampling points and chemical compositions of water samples collected in September 2003.

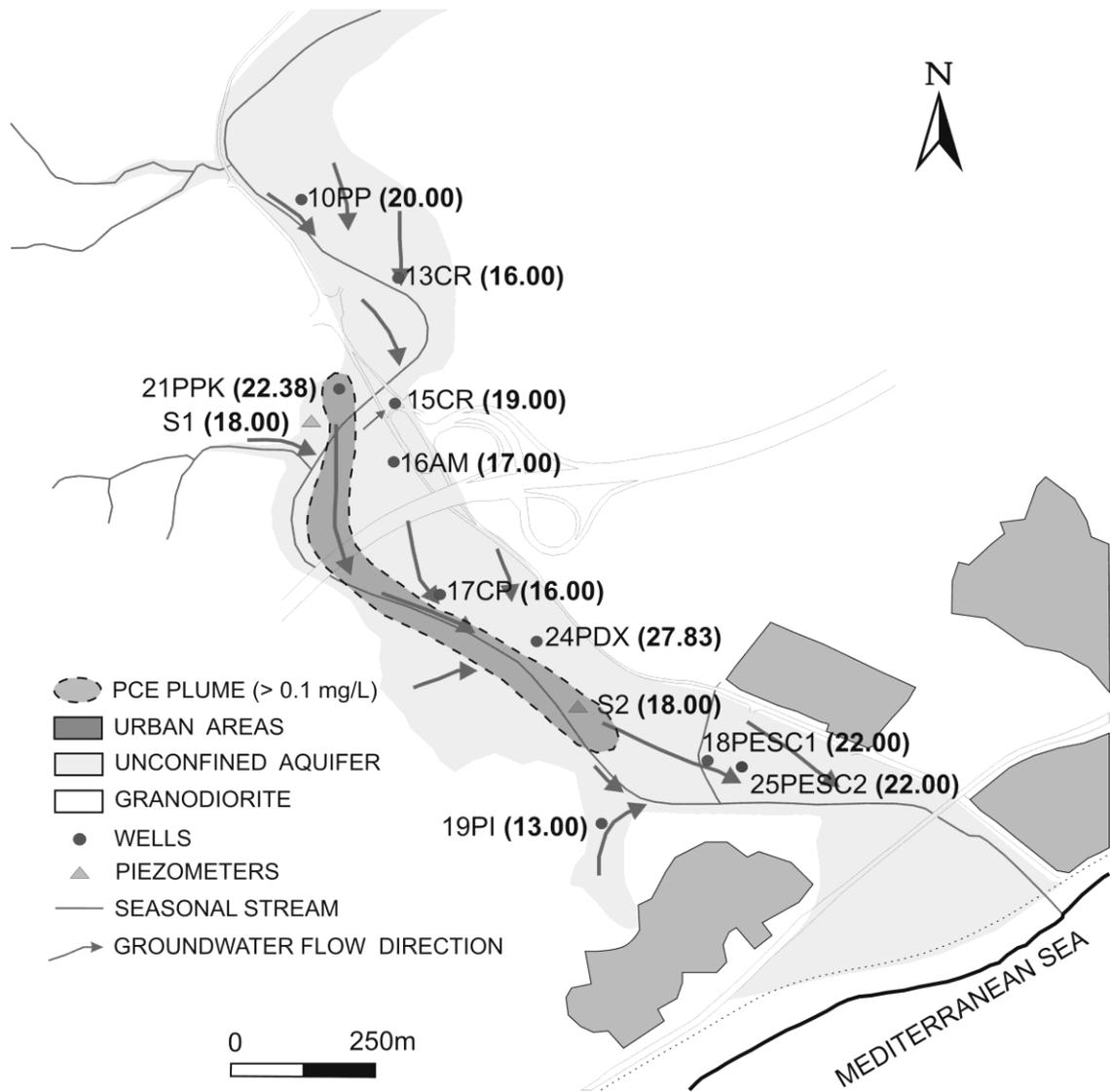


Figure 2. Estimated extent of the PCE plume core. Well depth (in meters) is indicated in brackets next to the well label.

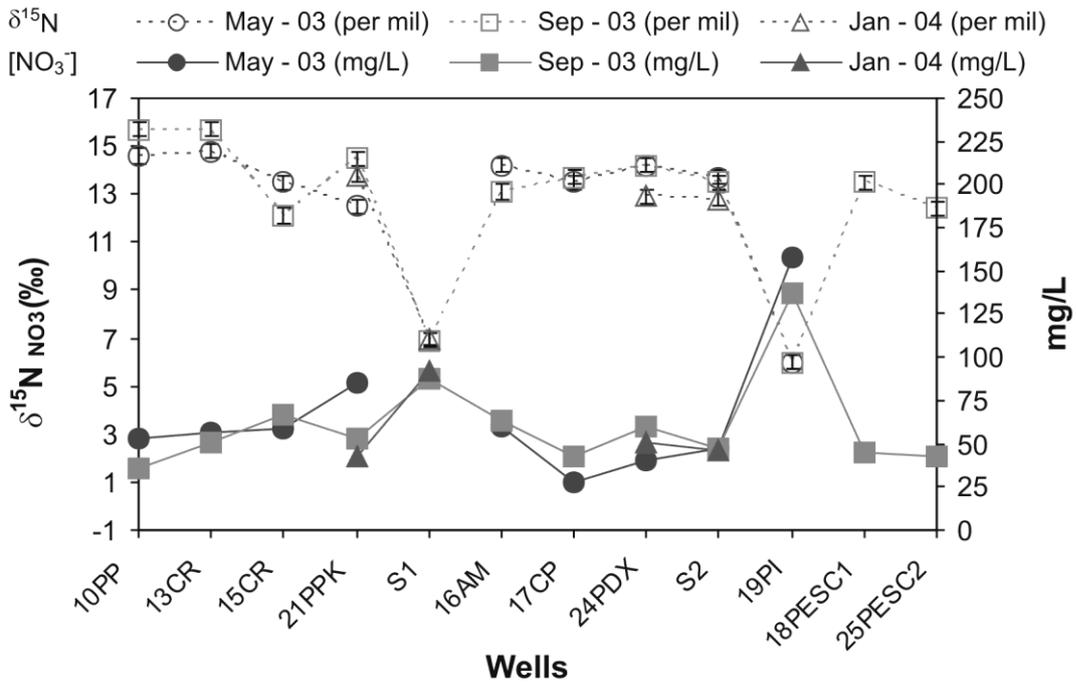


Figure 3. Nitrate concentrations and $\delta^{15}\text{N}_{\text{NO}_3}$ values.

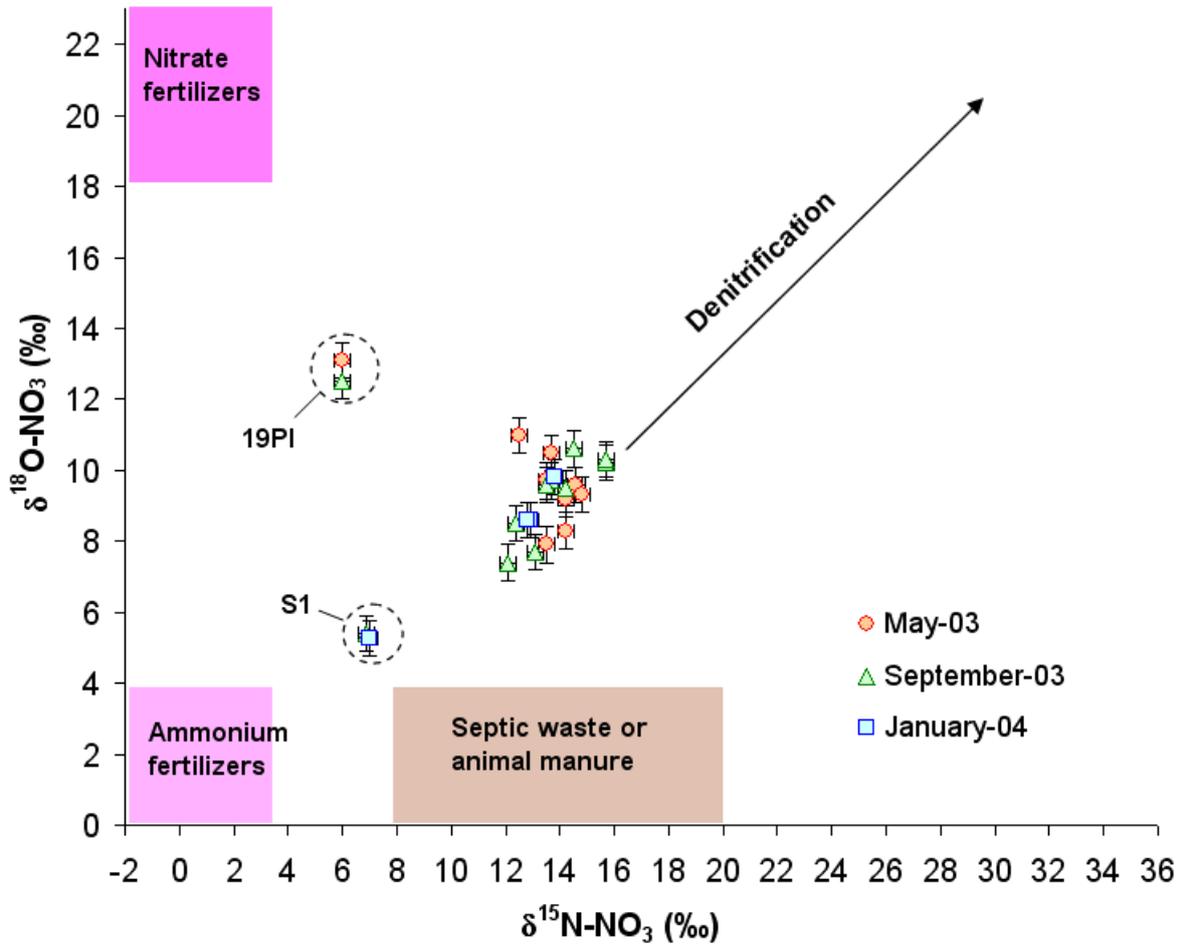


Figure 4. $\delta^{15}\text{N}_{\text{NO}_3}$ versus $\delta^{18}\text{O}_{\text{NO}_3}$ values. Boxes represent the isotopic composition of nitrate from different sources (see Table 2).

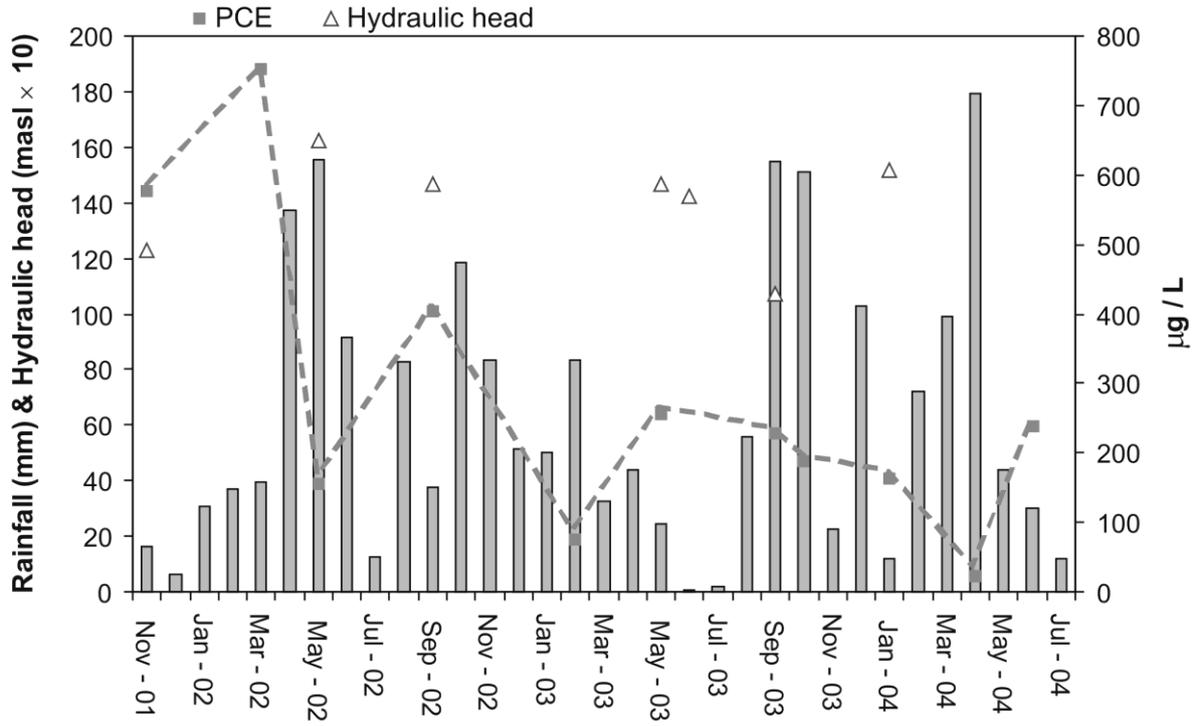


Figure 5. Relationship between PCE concentrations measured in 21PPK and precipitation. Several water level measurements are also indicated.

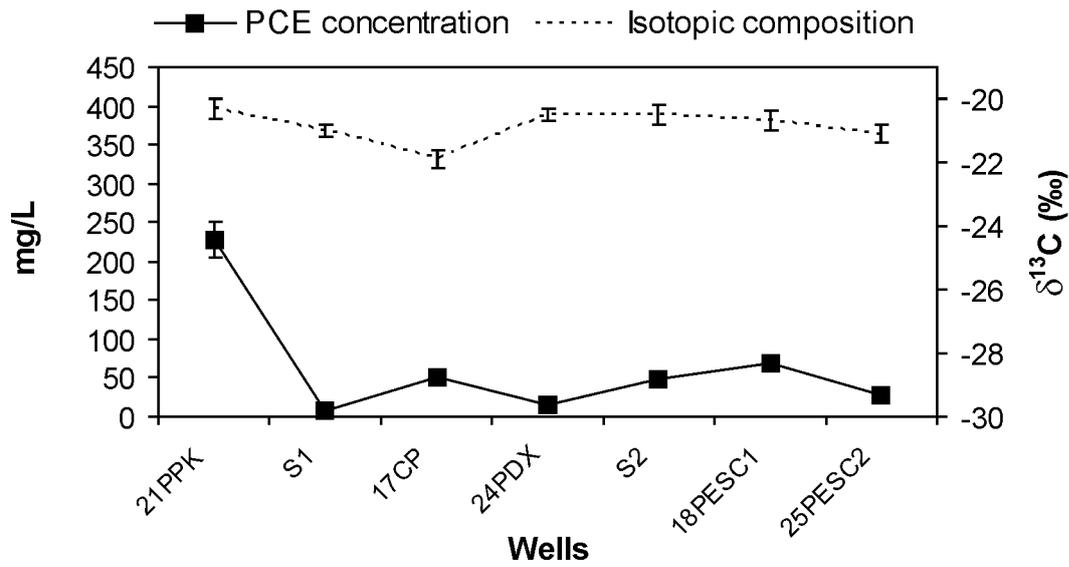


Figure 6. PCE concentration and isotopic composition of the samples collected in September 2003. The symbols of the isotopic data are the size of the $\delta^{13}\text{C}$ error bars, and the error associated to concentration values was $\pm 10\%$.

Tables

Table 1. Redox parameters and nitrate isotopes data.

Well	Date	Eh _{std}	DO	Mn (II)	Fe (II)	NO ₂ ⁻	NO ₃ ⁻	δ ¹⁵ N _{NO3}	δ ¹⁸ O _{NO3}
		(mV)	(mg/L)	(μg/L)	(mg/L)	(mg/L)	(mg/L)	(±0.3 ‰)	(±0.5 ‰)
10PP	May-03	---	---	2.9	0.04	<0.3	53	+14.6	+9.6
13CR	May-03	---	---	4.1	0.04	<0.3	56	+14.8	+9.3
15CR	May-03	---	---	2.7	0.03	<0.3	59	+13.5	+7.9
21PPK	May-03	358	---	2.8	0.01	0.5	85	+12.5	+11.0
16AM	May-03	---	---	2.9	0.04	<0.3	60	+14.2	+9.2
17CP	May-03	---	---	4.4	0.01	<0.3	27	+13.5	+9.7
24PDX	May-03	335	---	7.8	0.01	0.5	40	+14.2	+8.3
S2	May-03	---	---	15.0	0.01	1.0	47	+13.7	+10.5
19PI	May-03	---	---	1.4	0.01	0.8	158	+6.0	+13.1
10PP	Sep-03	---	---	2.6	<0.02	<0.3	36	+15.7	+10.2
13CR	Sep-03	---	---	5.2	<0.02	<0.1	50	+15.7	+10.3
15CR	Sep-03	---	---	0.9	<0.02	<0.1	66	+12.1	+7.4
21PPK	Sep-03	306	---	0.4	<0.03	<0.1	53	+14.5	+10.6
S1	Sep-03	295	2.2	1.6	<0.03	<0.1	87	+6.9	+5.4
16AM	Sep-03	---	---	1.0	<0.02	<0.1	63	+13.1	+7.7
17CP	Sep-03	---	---	1.8	<0.03	0.3	42	+13.7	+9.7
24PDX	Sep-03	307	1.2	0.9	<0.03	<0.1	60	+14.2	+9.5
S2	Sep-03	313	0.5	4.1	<0.03	<0.1	47	+13.5	+9.6
19PI	Sep-03	---	---	0.1	<0.02	<0.3	137	+6.0	+12.5
18PESC1	Sep-03	309	0.6	5.5	<0.03	0.3	45	+13.5	+9.6
25PESC2	Sep-03	185	0.7	88.5	<0.03	<0.3	42	+12.4	+8.5
21PPK	Jan-04	332	1.5	4.8	<0.03	<0.1	43	+13.8	+9.8
S1	Jan-04	417	---	0.6	<0.03	<0.1	92	+7.0	+5.3
24PDX	Jan-04	432	3.3	0.7	<0.03	<0.1	50	+12.9	+8.6
S2	Jan-04	442	3.4	1.0	<0.03	<0.1	46	+12.8	+8.6

---, not measured.

Table 2. Nitrogen and oxygen isotopic values for nitrate of different origin and carbon isotopic values for tetrachloroethene from different manufacturers.

NO ₃ ⁻ origin	Nitrate Fertilizers	Ammonium Fertilizers	Animal and Domestic Waste
δ ¹⁵ N (AIR)	-7.5 - +6.6 ^a	-7.4 - +3.6 ^a	+8.0 - +20.0 ^a +10.0 - +20.0 ^b
δ ¹⁸ O (SMOW)	+17.4 - +25.0 ^a	-5 - +15 ^b	0 - +6 ^a
PCE origin	4 manufacturers (Dow, ICI, PPG and Vulcan)	2 manufacturers (Dow and PPG)	3 manufacturers (Unidentified)
δ ¹³ C (VPDB)	-23.19 - -37.20 ^c	-27.59 - -35.82 ^d	-24.06 - -35.27 ^e

Sources: ^a Aravena and Mayer (2010), ^b Kendall (1998), ^c van Warmerdam et al (1995),

^d Beneteau et al (1999) and ^e Jendrzewski et al (2001).

Table 3. PCE concentrations ($\mu\text{g/L}$).

Well	Sampling date										
	Nov.	Mar.	May.	Sep.	Feb.	May	Sep.	Oct.	Jan.	Apr.	Jul.
	2001	2002	2002	2002	2003	2003	2003	2003	2004	2004	2004
10PP	<i>nd</i>	---	<i>nd</i>	<i>nd</i>	<i>nd</i>	<10	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>
13CR	7	---	2	1	0.3	<10	0.3	8	0.3	0.3	0.2
15CR	9	4	2	0.4	0.4	<10	1	1	0.5	0.3	0.4
21PPK	578	753	155	405	76	256	228	187	163	22	237
S1	---	---	---	---	325	---	<7	29	26	717	19
16AM	36	10	5	2	1	<10	4	2	2	3	1
17CP	149	563	101	20	7	39	50	78	---	98	3
24PDX	---	154	214	64	43	27	16	138	41	35	23
S2	---	---	---	---	85	153	49	38	97	78	77
19PI	10	18	30	7	2	14	8	5	1	1	1
18PESC1	104	---	88	9	65	---	69	151	117	78	132
25PESC2	---	---	---	---	28	---	27	16	28	34	18

Data in italics from Catalan Water Agency. n.d, not detected. ---, not measured.

Table 4. $\delta^{13}\text{C}_{\text{PCE}}$ values (‰).

Well	Sampling date		
	May (2003)	Sep. (2003)	Jan. (2004)
21PPK	-22.4 ± 0.5	-20.3 ± 0.3	-21.4 ± 0.3
S1	---	-21.0 ± 0.2	-20.8 ± 0.2
17CP	-19.6 ± 0.5	-21.9 ± 0.3	---
24PDX	---	-20.5 ± 0.2	-20.7 ± 0.3
S2	-21.4 ± 0.5	-20.5 ± 0.3	-20.4 ± 0.3
18PESC1	---	-20.7 ± 0.3	---
25PESC2	---	-21.1 ± 0.3	---

---, not determined.