Assessing TNT and DNT groundwater contamination by compound-specific isotope analysis and ^{3}H-^{3}He groundwater dating: A case study in Portugal

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Abstract

Trinitrotoluene (TNT) and dinitrotoluene (DNT) originating from 50 years of explosives production have heavily contaminated two stacked aquifers in the vicinity of Lisboa, Portugal. To assess if these poly-nitroaromatic compounds (P-NACs) are being degraded in the subsurface, tracer-based groundwater dating techniques combined with compound-specific isotope analyses (CSIA) were applied.

The groundwater residence times were distinctly different in the two aerobic aquifers, as determined by the tritium (^{3}H)-^{3}He method. In the contaminated zones, the upper aquifer exhibited groundwater ages of 25 years, whereas the lower (presumably confined) aquifer contained hardly any tritium which indicates water ages >55 years. P-NACs-containing waste waters are known to have leaked into the upper, unconfined aquifer. However, P-NACs were present in both aquifers in high concentrations (up to 33,000 μg/L TNT), which implies a hydraulic connection, although tritium concentrations and chemical data suggest two separated aquifers. Based on the ^{3}H-^{3}He groundwater dating and the presence of very high P-NAC concentrations, the contamination of the lower aquifer must have happened during the early stage of the explosive production, i.e. >50 years ago. Despite this 'old' contamination, TNT and DNT have not been transformed until to date as is demonstrated by the

negligible changes in their carbon isotopic signatures ($\delta^{13}C$). Thus, P-NACs are very recalcitrant to degradation at the investigated site. If the aquifers remain aerobic, TNT and DNT are expected to persist in the subsurface for many decades to centuries.

The presented approach of assessing time scales of natural attenuation at the field scale by the combination of CSIA and ^3H-^3He water dating has the potential to be applied to any other groundwater contaminants, such as e.g., chlorinated hydrocarbons, gasoline components, heterocyclic carbenes, or polyaromatic hydrocarbons.

1. Introduction

The contamination of the environment by explosives, such as trinitrotoluene (TNT) and dinitrotoluene (DNT), is a worldwide problem. During World War I and II, enormous amounts of TNT and DNT were produced and the majority of contaminated sites are located at (former) ammunition factories and other places where nitroaromatic explosives were manufactured and used (Rodgers and Bunce, 2001). Such a 'typical' case is located in the vicinity of Lisboa, Portugal, where the former Portuguese Society of Explosives (SPEL) caused the contamination of groundwater and soils by the long-term handling (~50 years) of TNT and DNT. Albeit the fact that the two contaminated aquifers have intensely been exploited for irrigation, industry and drinking water purposes, and although it is known that the most important human exposure to P-NACs derives from the ingestion of contaminated (drinking) water (ATSDR, 1998), a detailed evaluation of this TNT and DNT contamination was not undertaken until to date. Hence, in this study we present the first quantitative data of the occurrence and persistence of P-NACs for this site.

The assessment of the SPEL site is urgent because TNT and DNT are toxic and carcinogenic (ATSDR, 1995). Also, some of their metabolite products, particularly partially reduced amino-nitrobenzenes are equal or even more toxic (Suhanara et al., 1998). On the other hand, microbial transformations may degrade P-NACs and thus remove the compounds from water resources. In anaerobic aquifers, TNT and DNT are known to be reduced by abiotic transformation (Haderlein et al., 2000). Under aerobic conditions, P-NACs are much more persistent, although they may be microbiologically transformed by oxidation and/or reduction (Nishino et al.,

2000; Hofstetter et al., 2008). Physical processes affecting the fate of NACs in the environment are dispersion, photolysis, volatilization (ATSDR, 1995), and particularly specific adsorption to clay mineral surfaces (Haderlein et al., 2000). In the absence of clays and due to the rather polar character of TNT and DNT, these compounds are transported relatively fast in the subsurface (ATSDR, 1998).

Thus, it is important to determine if along a groundwater flow path, i.e. increasing groundwater residence time, the P-NACs contamination is being attenuated by transformation or by physical processes. Biochemical transformation reactions are mass dependent and are therefore often accompanied by a kinetic isotopic effect that leads to an isotopic (reaction-specific) fractionation of the compound (Schmidt et al., 2004; Meckenstock et al., 2004; Zwank et al., 2005; Elsner et al., 2005). This is in contrast to physical processes (i.e., sorption or volatilization) that only cause negligible isotopic fractionation (Hunkeler et al., 1999; Slater et al., 2000). Hence, as contaminants are biochemically transformed along a groundwater flow path, a progressive isotopic enrichment in the heavier isotopes occurs (Galimov, 1985). This allows to assess the extent of transformation from measurements of isotopic signatures, by means of compound-specific stable isotope analyses (CSIA) (Vieth et al.; 2003, Kirtland et al., 2003; Zwank et al., 2003; Morrill et al., 2005; Hunkeler et al., 1999; Hartenbach et al., 2008). Hofstetter et al. (2008) showed that under aerobic conditions, the biotic oxidation of nitrobenzene (NB) strongly fractionates the C-isotopes, whereas in contrast, the reduction of NB shows little fractionation of the C-isotopes.

To determine P-NAC transformation rates, knowledge on the residence time of the compounds in groundwater is required. Such information can be obtained by determining water ages. Therefore, to assess if transformation is occurring and to quantify rates of transformation at the field scale, we combined carbon-CSIA with ^{3}H (tritium)-^{3}He groundwater dating. The ^{3}H-^{3}He method is based on the radioactive decay of ^{3}H to the noblegas ^{3}He (Tolstikhin and Kamenskiy, 1969; Torgersen et al., 1979). Tritium entered the hydrological cycle after being released by atmospheric thermonuclear bomb tests during the early 1960's. Once the recharge water reaches the water-saturated part of the aquifer, the 'clock' starts as ^{3}He accumulates over time in the groundwater.

An advantage of our approach, i.e. the combined use of CSIA and tracer-based water dating, is that based on a few sampling locations, an understanding of a complex hydrogeological contaminated site can be developed. This approach was recently applied to determine the degradation rates of chlorinated ethenes of several contaminated sites by applying carbon-CSIA (Amaral et al., 2009; Aeppli et al., 2009).

2. Description of the field site

2.1 History

The studied site south of Lisboa (Portugal) covers a heavily urbanized area, where many groundwater wells in the vicinity of the SPEL area abstract large amounts of water from the two aquifers (Fig. 1). During 50 years (1949-1998), SPEL produced TNT and DNT for military and industrial purposes, using raw materials that included DNT, sulphuric and nitric acids, toluene and ethylene glycol (INETI and ITA, 1996). Production waste waters containing TNT and DNT (originating from the production of explosives) were disposed in open permeable sandy-clayish soil pits close to the production site (5000 m^2 and 10 m^2 for TNT and DNT containing wastes, respectively) (INETI and ITA, 1996). Although these disposal pits were located on the premises of SPEL, their exact number and locations are unknown. It is estimated that 300-900 tons/yr DNT and 400 tons/yr TNT were produced (INETI and ITA, 1996). It is, however, uncertain whether such annual explosive production was kept throughout the 50 years of SPEL's operation. Environmental impact studies estimated that about 0.2 tons/yr of DNT and 10 tons/yr of TNT were lost to the soil in form of production waste (INETI and ITA, 1996).

In the early 1980's, the eastern part of SPEL's terrain (about ¼ of the total SPEL area) was sold to a sand-exploitation company, which has mined the Pliocene sand of the upper aquifer, including its unsaturated zone. This extensive sand exploitation disrupted the natural hydraulics at the SPEL site. As sand mining reached the water table of the upper aquifer, it forced springs to form that fed small ponds close to the most contaminated area. Moreover, these activities altered the topography of the area considerably, i.e., by removing the unsaturated zone of the upper aquifer which enhanced its susceptibility to contamination.

[FIGURE 1]

2.2 Hydrogeology

The studied area is part of the River Tejo Left Margin aquifer system, which comprises structurally complex porous multi-layered aquifers (Almeida et al., 2002). Two major aquifers are distinguished (Fig. 2). The upper unconfined sandy aquifer consists of heterogeneous fluvial deposits of Pliocene age (Azevêdo, 1983). The lower semi-confined/confined aquifer develops at the base of the Pliocene formation and at the top of the early (marine) Miocene consisting of multi-layered fluvial sediments and calcarenetic layers. Clay lenses and a 2

m thick clay layer at the base of the Pliocene separate both aquifers, as documented by sediment logs (Fernandes et al., 1999). However, this 'sealing' is not complete as the aquifers are locally in hydraulic contact. The thickness of the unsaturated zone varies between 20 and 40 m. The upper aquifer reaches down to 40-50 m, whereas the lower aquifer has an average depth of 150 m (min-max: 125-185 m).

Since the late 1980's and the beginning of the 1990's, the lower aquifer has been exploited by various wells pumping at rates of 20 to 100 L/s (in total about 700 L/s). The pumping reduced the piezometric heads in the lower aquifer to such an extent, that the hydraulic potential of the upper aquifer is nowadays higher than that of the lower one (Fernandes et al., 1999). This leads to an enhanced leakage of water from the upper aquifer into the lower aquifer. Furthermore, the extensive groundwater abstraction from the lower aquifer strongly alters the flow of groundwater that is naturally directed towards NNE to the Tejo Estuary. The high and unequal pumping rates are expected to influence the spread of the P-NACs. The much smaller abstraction rates (household level) from the upper aquifer are assumed to have a negligible influence on the regional groundwater flow directed also towards NNE.

[FIGURE 2]

3. Methods

3.1 Water sampling and water composition

Water samples were collected from 29 groundwater wells and 2 ponds located in an area of about 25 km^2 that covers the SPEL and its up- and downstream zones (Fig. 1). The wells are private or public owned whereas the ponds are located in the sand exploitation area. The pond water is occasionally used to wash the exploited sand. The ponds and 7 wells tap the upper aquifer. These wells reach 40 m deep and are either screened over the entire depths or between 25-40 m. The remaining 22 wells abstract water from the lower aquifer at different depths (125-185 m, typically 140 m) and have varying screen lengths.

All water samples were analyzed for major anions (Cl$^-$, NO$_3^-$, NO$_2^-$, SO$_4^{-2}$) and cations (Na$^+$, Mg^{+2}, K$^+$, Ca^{+2}), which were measured by ion chromatography. Dissolved Fe and Mn were quantified by inductively coupled plasma optical emission spectroscopy. NH$_4^+$ was measured by photometry. Total and dissolved organic carbon was measured by infrared spectrometry after being oxidised to CO$_2$. Dissolved oxygen, electrical

conductivities, pH and temperature were measured in the field by multi-parameter electrodes.

3.2 Groundwater dating

Groundwater residence times were determined by the ^{3}H-^{3}He dating method (Tolstikhin and Kamenskiy, 1969; Torgersen et al., 1979). Tritium decays to (tritiogenic) ^{3}He with a half-life ($T_{\frac{1}{2}}$) of 4500 days (Lucas and Unterweger, 2000). Large amounts of ^{3}H were released by nuclear bomb testing during the early 1960's and increased the terrestrial ^{3}H budget by about 3 orders of magnitude (IAEA/WMO, 2001). In the atmosphere, ^{3}H is immediately oxidized to tritiated water, and consequently enters the natural water cycle. The atmospheric ^{3}H input function (i.e., the ^{3}H concentration in atmospheric water) shows a prominent ^{3}H maximum in 1963-1964 when up to several 1000 tritium units (TU) were present in precipitation of the northern hemisphere (Ferronsky and Polyakov, 1982). This high concentration is referred to as the 'bomb-peak' (IAEA/WMO, 2001). Waters recharged prior to 1955 ('pre-bomb' water) have ^{3}H concentrations close to the natural background of ≤1-5 TU (Craig and Lal, 1961). Hence today such waters contain virtually no ^{3}H (due to decay), whereas post-1959 waters still have ^{3}H in measurable amounts. The dating method ^{3}H-^{3}He is based on the indirect measurement of ^{3}H from the in-growth of tritiogenic ^{3}He in a water sample that was previously measured for ^{3}He and other noble gases (Kipfer et al., 2002). Thus, it is independent on the knowledge of the atmospheric ^{3}H input function.

The method has been widely applied in surface and groundwater studies (see for example, Hohmann et al., 1997; Beyerle et al., 1999; Schlosser et al., 1988). This dating method allows determining groundwater ages, i.e. when the last air-water gas exchange occurred during groundwater recharge, from several months up to about 55 years (Beyerle et al., 2000). The ^{3}H-^{3}He age τ is calculated according to Schlosser et al. (1988):

$$\tau = \frac{T_{1/2}}{\ln 2} \bullet \left(1 + \frac{^3H_{tri}}{^3H}\right) \qquad (1)$$

where ^{3}He$_{tri}$ and ^{3}H are the concentrations of the tritiogenic ^{3}He and ^{3}H in water and $T_{1/2}$ is the half-life of ^{3}H. For details on how to determine the ^{3}He$_{tri}$ concentrations and the ^{3}H-^{3}He ages from noble gases and ^{3}H analysis see Kipfer et al. (2002), Aeschbach-Hertig et al. (1999) and Beyerle et al. (2000).

3.3 CSIA applied to P-NACs contaminated groundwater

CSIA to assess carbon and hydrogen isotopic compositions of environmental contaminants has been successfully applied in several studies and is becoming a routine analytical tool for investigations of natural transformation of organic compounds at the field scale (Hunkeler et al., 1999; Zwank et al., 2003; Schmidt et al., 2004; Zwank et al., 2005; Sherwood Lollar et al., 2001; Van Stone et al., 2005; Vieth et al., 2003). CSIA methods for nitrogen and chlorine isotope analysis were recently developed (Berg et al., 2007; Hofstetter et al., 2007) and applied in laboratory studies to assess the isotopic behaviour of nitrogen- and chlorine containing contaminants (Hartenbach et al., 2006; Tobler et al., 2007; Hartenbach et al., 2008; Hofstetter et al., 2008).

Compound-specific isotopic signatures of P-NACs have so far not been assessed at field sites, apart from source allocation (Coffin et al., 2001). A robust analytical CSIA protocol for the determination of C as well as N isotopic signatures of P-NACs was only recently developed (Berg et al., 2007). This method allows to assess transformation of P-NACs in the field, provided that concentration levels are in the mg/L-range (Berg et al., 2007). In this study, the samples with highest P-NACs concentrations were analysed for C- and N-isotopic composition. However, only the C-isotopic analyses could be considered because the uncertainties of N-isotopic measurements were too large to draw conclusions.

The stable isotopic ratios obtained from CSIA are reported in the δ deviation (in per mil) from an international standard (Craig, 1957; Hoefs, 1997):

$$\delta^h E = \left(\frac{R_{sample}}{R_{reference}} - 1 \right) \bullet 1000 \ (^0/_{00}) \qquad (2)$$

where R_{sample} and $R_{reference}$ are the heavy to light isotope ratios of element E ($^h E / ^l E$) in the sample and reference material, respectively. If the bulk enrichment factor ε_E of the element E (reported in ‰) is known for a particular reaction, the extent of transformation B of a compound can be quantified (see e.g. Zwank et al. 2005; Elsner et al., 2005):

$$B = 1 - f = 1 - \left(\frac{1000 + \delta^h E}{1000 + \delta^h E_0} \right)^{1000/\varepsilon_E} \qquad (3)$$

where, f is the remaining fraction of the reacting compound, and $\delta^h E$ and $\delta^h E_0$ are the isotopic signatures of the compound in the plume and at the source, respectively (or times t and zero, respectively). For details on the analytical protocols of CSIA see for example (Zwank et al. 2005; Aeppli et al. 2008).

4. Results

The two aquifers showed distinct chemical compositions in NO_3^-, SO_4^{-2}, Mg^{+2}, K^+, DOC and TOC, with the upper aquifer being more mineralized than the lower one (Table 1). However, both aquifers had similar water temperatures, electrical conductivities, pH and oxygen contents. Three samples were highly mineralized, one sample from the upper (560) and two samples from the lower aquifer (G06 and 564). These three samples also showed distinct field parameters: low oxygen concentrations (10-20% saturation), high electrical conductivity (1790-4470 µS/cm) and very low pH (pH~3.7). The other samples showed higher oxygen concentrations, less electrical conductivity and had neutral pH. Additionally, these three samples showed much higher concentrations in DOC (up to 50 mg/L; other wells in upper aquifer: 1.2-4.3 mg/L, in lower aquifer: <1.5 mg/L), NO_3^- (50-100 mg/L; other wells in upper aquifer: 5-40 mg/L, in lower aquifer: 1-8 mg/L), and SO_4^{-2} (1200-3800 mg/L; other wells in upper aquifer: 25-100 mg/L, lower aquifer: 4-20 mg/L).

[TABLE 1]

The aquifers contained ^3H concentrations in the range of 0.1-3.6 TU (Tables 2 and 3). In the upper aquifer, the youngest water (7 years) was present upstream of SPEL, whereas ages up to 28 years were found near the P-NACs source (Fig. 3). All water samples from the lower aquifer near and downstream of SPEL contained virtually no ^3H (<0.3 TU), indicating water recharged before the ^3H bomb-peak prior to 1955. Another (younger) groundwater mass was identified in the lower aquifer. This groundwater body developed to the northwest of SPEL and its water residence time (18 to 41 years) increased in the direction of the Tejo Estuary.

TNT, DNT and nitrotoluene (NT) were found in both the upper and the lower aquifers. In all contaminated wells, TNT was present but not all wells contained DNT and NT. TNT accounted for 70-80% of the total P-NACs abundance, 2,4-DNT for 15-25% and 2,6-DNT up to 10%. NTs were only found in trace concentrations (2%, Tables 2 and 3). The P-NACs were predominantly present in the wells towards the Tejo Estuary along a direction perpendicular to the main groundwater flow, forming zones containing different levels

of contamination. Regarding TNT, the contamination in both aquifers can be divided into three areas (Fig. 4): i) the 'hot-spot' (25,000-33,000 µg/L), ii) the zone to the northwest of SPEL (100-300 µg/L, ~1% of the concentration in the 'hot-spot'), and iii) the zone to the north and east of SPEL (1.5-3.5 µg/L, ~0.1% of the concentration in the 'hot-spot'). The samples from the two ponds (upper aquifer) were free of P-NACs. The three most contaminated wells at the 'hot-spot' (one well in the upper and two wells in the lower aquifer) are located in or slightly downstream of the location of the (presumed) former discharge pools, where SPEL disposed its P-NACs production waste-waters.

[TABLES 2 AND 3]

[FIGURE 3]

[FIGURE 4]

The C-isotopic compositions of TNT and DNT were determined in the 'hot-spot' samples (Tables 2 and 3). The $\delta^{13}C$ values of TNT (-27‰) and 2,4-DNT (-29‰) remained constant along the flow path. The $\delta^{13}C$ of 2,6-DNT were also constant (-28.4 to -29‰) with the exception of well 564, which showed a slightly heavier isotopic signature (-25‰). The initial $\delta^{13}C$ compositions of the P-NACs synthesized by SPEL are not known.

[FIGURE 5]

5. Discussion

The composition of major ions and tritium levels in groundwater show that the upper and lower aquifers are distinct groundwater bodies, with different groundwater residence times (Fig. 3). However, P-NACs were present in very high concentrations in both aquifers (Table 3), which suggests a hydraulic connection although tritium concentrations and chemical data would suggest two separated aquifers. The P-NACs waste waters deposited in the permeable pits have infiltrated directly into the upper unconfined aquifer, but not into the lower aquifer, whose recharge area is far upstream (see section 2.2). Thus, the presence of P-NACs in the lower aquifer indicates water leakage from the upper aquifer. Moreover, the P-NACs formed three areas of distinct P-NACs concentration levels (see Fig. 4). The most contaminated area ('hot-spot') was also distinct in its water chemistry to the other contaminated and non-contaminated wells. The very low pH (<3.8) at the 'hot-spot' can be

explained by the sulphuric and nitric acids used at SPEL in the production of explosives as is further reflected in the high nitrate and sulphate concentrations.

The P-NACs zoning may have resulted from the heterogeneous artificial groundwater flow conditions induced by pumping. The extensive pumping from the lower aquifer leads to the development of a groundwater divide north of the 'hot-spot' from where groundwater flows either east- or westwards. Such pumping disturbed the natural groundwater flow conditions considerably, which could explain why P-NACs were mainly present along the transverse direction to the natural groundwater flow, rather than along it.

Another hypothesis for the zoning of P-NACs would be the existence of several P-NACs point sources. This would mean that more than two pits were operated by SPEL to dispose production waste waters, leading to spatially isolated sources of groundwater contamination. However, since the precise location, size and number of the former pits remain unknown, this scenario can not be verified.

5.1 Extent of the P-NACs contamination

Despite the long groundwater residence times as well as the relatively high porosities of sandstones and calcarenitic rocks in the aquifers (Domenico and Schwarz, 1998), the P-NACs do not form a clearly defined plume. The sharp decrease of P-NAC concentrations with distance to SPEL in both aquifers (Tables 2 and 3), must be related to dispersion and sorption. P-NACs can be removed from the aqueous phase by sorption to clay-surfaces (Haderlein et al., 2000), which would greatly diminish the aqueous P-NACs concentration downstream of the source. Thus, studies to further assess the P-NACs evolution at SPEL should characterize the sorption capacity of the present clays in order to assess P-NACs retardation more closely.

Another explanation for the low P-NACs extension is the re-infiltration of contaminated groundwater at the 'hot-spot'. Two of the three wells (560 and 564) in the 'hot-spot' area are by far the most intensively pumped wells. The intensive water use for irrigation and industrial purposes (i.e. sand washing) causes local infiltration of contaminated water to the upper aquifer. Such water 'recycling' might generate a P-NACs 'loop' in an almost closed-system within the upper aquifer, thus strongly limiting the contamination to the 'hot-spot' and preventing P-NACs to be transported beyond the source area.

5.2 Age of the P-NACs contamination and interaction between the upper and the lower aquifer

The lower aquifer is nearly devoid of ^{3}H, which implies that its groundwater recharged mainly prior to 1955 (see chapter 3.2). Hence, the fact that P-NACs are present in the lower aquifer indicates that the contaminants must have leached to the lower aquifer more than 55 years ago, i.e. shortly after the beginning of the SPEL operation in 1949.

Nevertheless, the ^{3}H concentration in the lower aquifer can also be explained by continuous infiltration of water from the upper to the lower aquifer, throughout the period of explosives production at SPEL (1949-1998). Since the two aquifers show distinct ^{3}H concentrations at the 'hot-spot', such continuous mixing over 50 years would have occurred in a manner that the ^{3}H-void water of the lower aquifer would not be masked by the ^{3}H-containing water from the upper aquifer. In the 'hot-spot' area, the upper aquifer had ^{3}H levels of 2.5 TU, and the lower aquifer 0.3-0.1 TU (i.e. ^{3}H is virtually absent). This means the groundwater of the upper aquifer would be diluted by a factor of at least 8 to 25 to reach the ^{3}H concentrations in the lower aquifer. That would be today's scenario. However, at the beginning of SPEL's activity in 1949, the ^{3}H concentration in the upper aquifer must have been magnitudes higher than today's 2.5 TU (see atmospheric input curve in IAEA (2001), and the decrease of the atmospheric ^{3}H concentration occurred at higher rates than the ^{3}H decay. Thus, if the groundwater mixing occurred earlier, the dilution of the groundwater of the upper aquifer would have been significantly larger to reach the virtually ^{3}H-void levels of the groundwater of the lower aquifer, which recharged prior to 1955.

Although such continuous mixing scenario might in principle explain the virtually absent ^{3}H concentrations in the lower aquifer, it can hardly explain the high P-NACs concentrations in the lower aquifer, which are in the same range or even higher than those in the upper aquifer. Thus, these considerations based on the present ^{3}H levels strongly suggest that P-NACs contamination of the lower aquifer occurred early in the SPEL operation when the explosive production began.

5.3 Persistence of TNT and DNT

The δ^{13}C values of TNT remained almost constant with increasing groundwater residence time (i.e. along a presumed groundwater flow path), implying that no significant TNT transformation has taken place. 2,4-DNT and 2,6-DNT were isotopically lighter than TNT, and could in principle be interpreted as metabolites of TNT. However, since TNT isotope signatures give no evidence of transformation, it is more likely that DNTs are by-products from the TNT synthesis and that they must have been already isotopically lighter in the SPEL waste

waters.

With increasing water age, the $\delta^{13}C$ of DNTs remained also constant. The constant C-isotopic signature under aerobic conditions excludes any transformation of DNT because transformation would cause DNT to become isotopically enriched (Hofstetter et al., 2008), i.e. exhibit increasing isotopic signatures along the groundwater flow. Thus, the slight differences in the C-isotopic compositions seems to be solely related to the initial $\delta^{13}C$ signatures of TNT and DNT present in the production wastes of SPEL, in which the disposed P-NACs may have had varying isotopic signatures over time.

The combined use of the ^3H-^3He water dating technique and CSIA thus indicates that the P-NACs have not been degraded over a time span of half a century under the aerobic conditions present in the aquifers at SPEL. If such oxic conditions remain, the TNT and DNT contamination is expected to persist for time spans of many decades to centuries.

6 Conclusions

The studied aquifers were delineated based on their water chemistry and tritium contents. Moreover, the evolution of the P-NACs contamination in both aquifers could be assessed by carbon-CSIA. To our knowledge this study is the first to apply carbon-CSIA on TNT and DNT in natural groundwater samples to assess the evolution of a P-NACs contamination at the field scale. With a few samples, we were able to constrain the P-NACs contamination of the lower aquifer to have occurred right at the beginning of the SPEL operation. Our study showed that more than 50 years after the beginning of the explosives production, the spilled P-NACs have not been transformed and will probably persist under the current aerobic conditions. We further suggest that the relatively sharp decrease of the P-NAC concentrations downstream from SPEL are related to the extensive water pumping and/or to sorption to clays.

Acknowledgements

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Figures
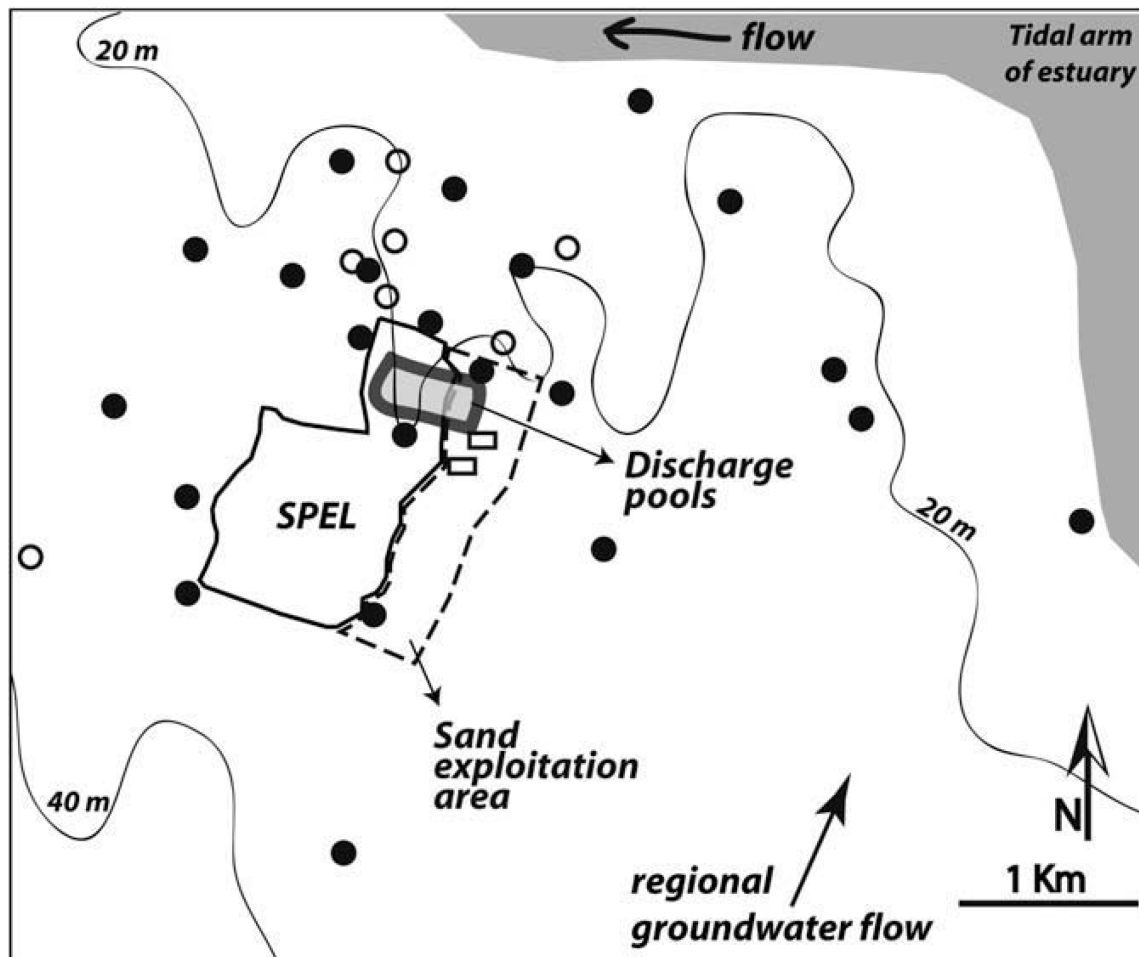
Figure 1: Map of the studied site: depicted are the SPEL area (full line polygon), the presumed area of the discharge pits (small full line polygon) where waste waters from the TNT and DNT production were disposed. Locations of the groundwater sampling points are depicted as circles (upper aquifer) and black dots (lower aquifer). The dashed polygon indicated the present-day sand exploitation area.
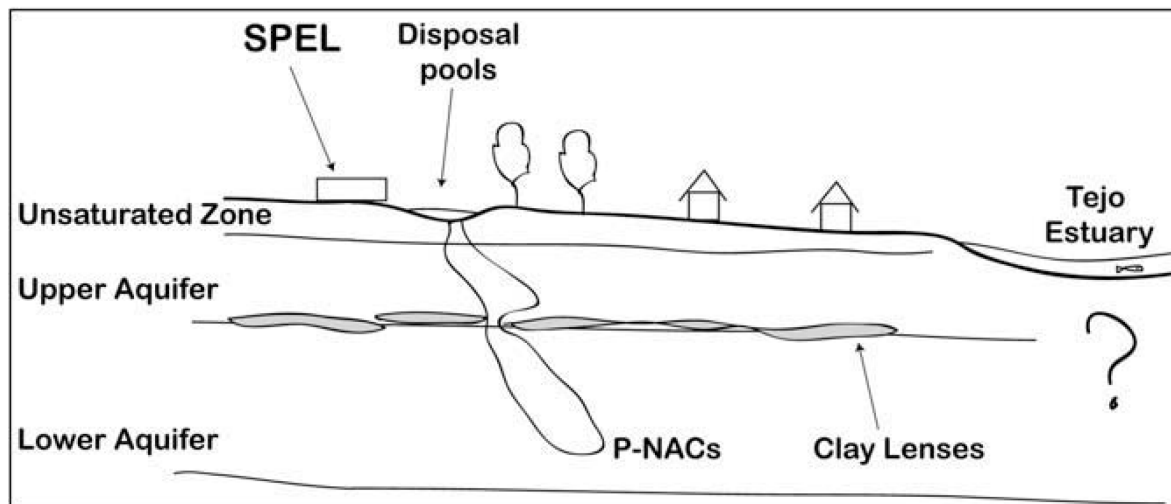
Figure 2: Schematic geological profile of the SPEL site (not to scale).
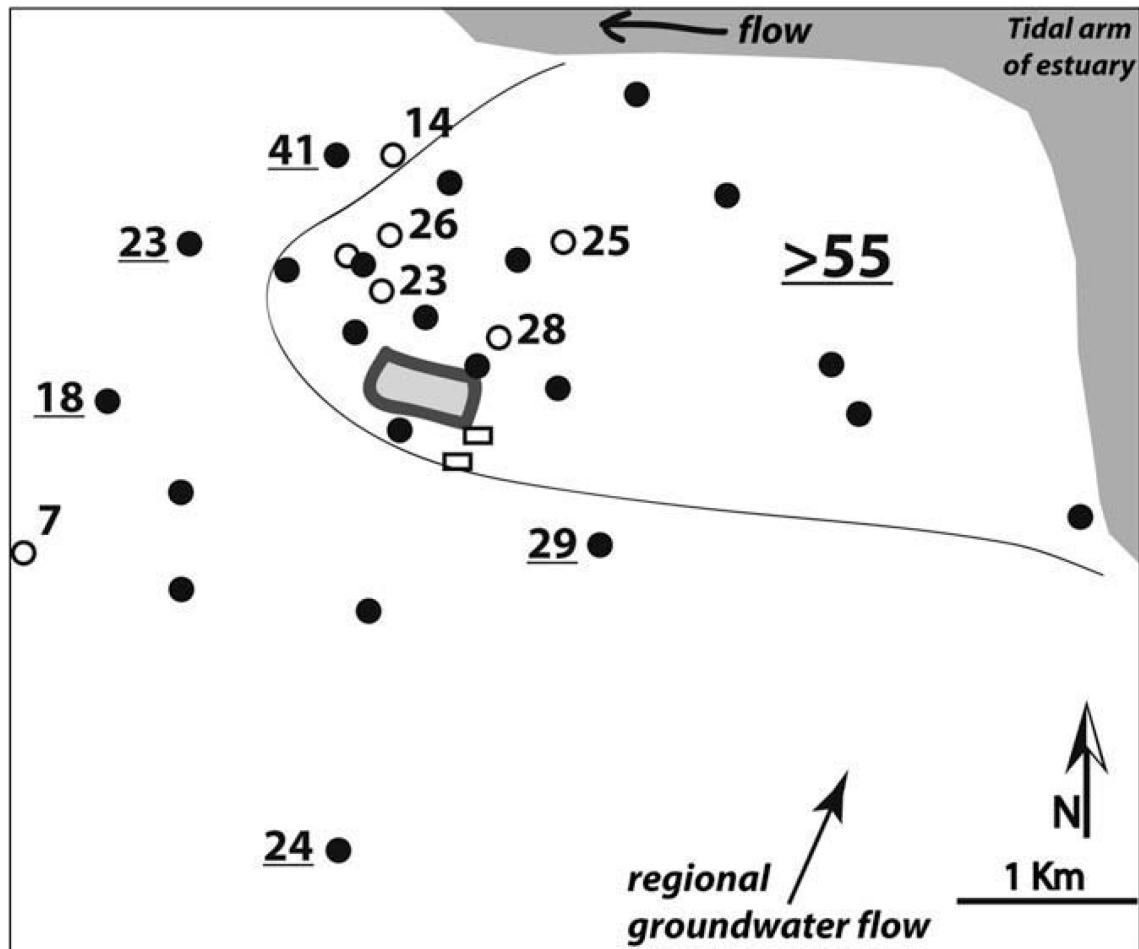
Figure 3: Groundwater ages (in years) determined in groundwater samples of the SPEL site. Upper aquifer: circles with groundwater ages given in normal font. Lower aquifer: dots with groundwater ages given in underlined font. The curved line refers to water ages in the lower aquifer beyond which (towards the Tejo Estuary) groundwater residence times are >55 years.
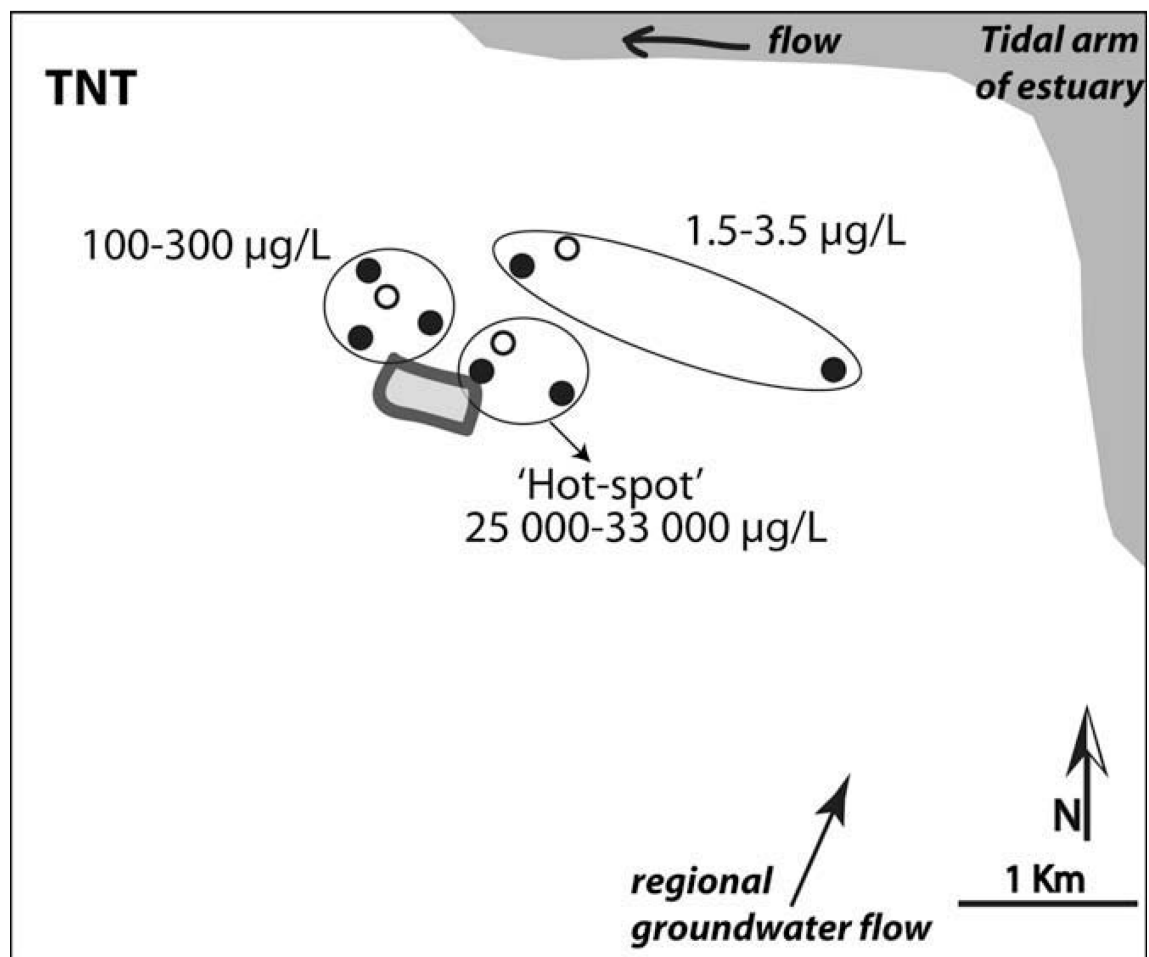
Figure 4: Concentration ranges of TNT in groundwater at the SPEL site. Only contaminated wells are shown. Depicted are the three zones exhibiting different levels of contamination.
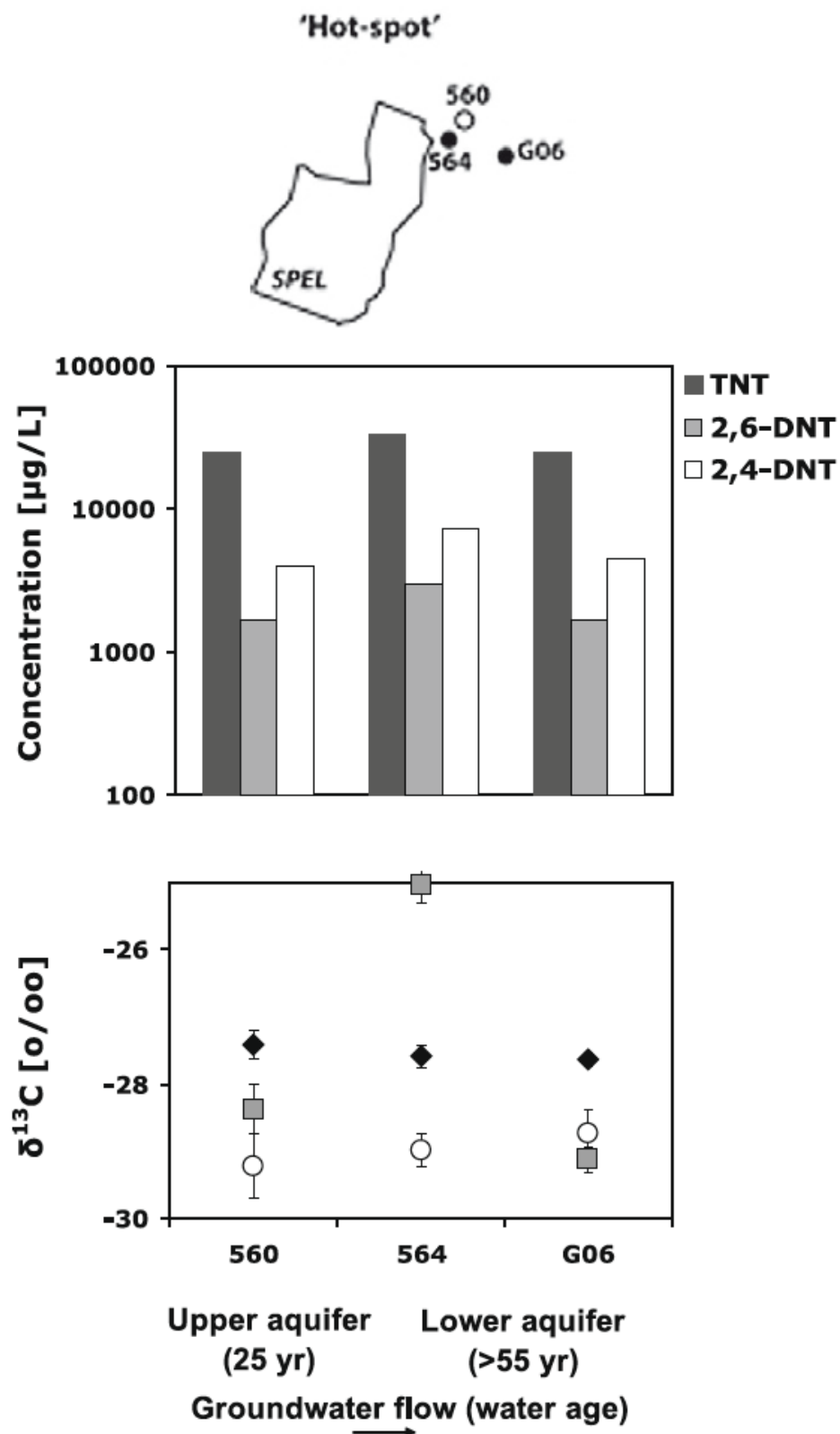
Figure 5: Carbon isotopic signatures (δ^{13}C) and concentrations of TNT and DNT in groundwater samples from the 'hot-spot' (locations are indicated in the right panel). Corresponding groundwater ages and the groundwater flow direction (i.e. increasing water age) is indicated at the bottom of the left panels.

Table 1. Field parameters and chemical components in groundwater samples collected from the upper and lower aquifers at the SPEL site. The three samples from the 'hot-spot' area where TNT and DNTs reach highest concentrations are highlighted in bold font. T = temperature, EC = electrical conductivity and n.d. = not determined.

| Well	T	EC	pH	O_2	Cl^-	NO_3^-	NO_2^-	SO_4^{-2}	Na^+	Mg^{+2}	K^+	Ca^{+2}	NH_4^+	DOC	TOC	Fe	Mn
	(ºC)	(µS/cm)	(-)	(mg/L)	(mg/L)	(mg N/L)	(µg N/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(µg N/L)	(mg C/L)	(mg C/L)	(µg/L)	(µg/L)
Upper Aquifer																	
560	20	1790	3.71	2.4	**82**	**44**	**6.1**	**1320**	**76**	**75**	**20**	**270**	**<5**	**28**	**29**	**20**	**20**
569	19	543	5.30	3.3	82	16	<2	48	50	19	8	29	7.1	2.3	2.8	280	580
QL	19	360	5.58	4.6	58	8	<2	24	35	11	5	8	<5	1.3	1.4	290	480
Eva	23	643	5.67	5.0	62	19	<2	103	38	10	39	40	<5	2.4	3.0	480	1210
Irene	19	920	6.26	3.9	121	41	<2	64	78	22	21	47	<5	1.9	2.5	3940	790
173	20	524	5.87	5.9	67	16	<2	39	34	23	6	99	<5	1.5	1.3	7.3	20
Lrj.	19	530	6.30	4.0	64	5	<2	57	41	22	5	27	<5	1.2	1.5	1810	85
Pond 1	29	495	8.43	10.0	36	<0.25	<2	92	36	17	3	38	<5	4.3	4.4	3280	140
Pond 2	27	340	7.81	5.8	57	4	<2	40	40	9	7	4	<5	2.2	2.6	1180	91
Lower Aquifer																	
G06	**19**	**2140**	**3.74**	**1.3**	**82**	**51**	**4.8**	**1210**	**84**	**79**	**20**	**76**	**960**	**35**	**37**	**13**	**20**
564	**21**	**4470**	**3.33**	**4.2**	**86**	**98**	**13.0**	**3810**	**120**	**210**	**36**	**23**	**n.d.**	**57**	**57**	**4570**	**21300**
PS1	19	318	7.90	7.8	40	1	<2	9	20	4	3	23	10	0.9	1.1	3.2	8.8
PS3	20	442	6.90	5.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	450	140
FR12	19	465	7.02	6.7	63	1	<2	8	28	6	4	40	<5	1.1	1.0	3.2	2.6
JK16	19	480	7.31	7.9	55	3	2.9	18	29	7	4	35	<5	1.5	1.3	1.7	1.8
FR10Q	19	502	6.90	6.3	42	2	<2	9	21	4	3	11	5.4	0.8	0.8	1.6	0.2
AC1	20	402	7.50	5.8	60	1	<2	8	26	6	3	12	6.4	0.9	0.7	7.5	1.9
AC4	19	306	7.66	6.0	32	<0.25	<2	4	21	5	1	34	<5	0.6	0.6	840	48
PS4	19	442	7.58	6.6	51	2	<2	13	31	6	3	48	<5	0.7	0.9	1160	67
PS2	19	313	7.50	8.3	40	1	<2	5	24	3	3	31	<5	0.6	0.9	930	230
FR5	19	364	6.81	6.2	44	1	<2	9	26	5	2	43	<5	0.8	1.1	710	42
JK13	18	394	9.80	-	48	1	<2	13	23	4	4	23	<5	1.0	1.1	2.5	0.3
JK14	19	456	7.05	6.4	65	2	<2	7	36	6	2	44	<5	0.8	1.0	240	14
Cond.	19	315	6.61	7.0	47	4	<2	6	29	5	2	20	<5	0.9	1.7	2840	1100
FR3	19	710	7.03	5.1	104	6	<2	21	57	14	4	62	<5	1.0	1.3	890	230
FR6	18	260	6.41	7.0	54	1	<2	6	31	5	3	7	<5	0.7	0.8	<1	7470
FR10	19	430	6.50	6.1	70	8	<2	19	46	9	5	19	<5	0.7	0.7	2770	150
JK15	19	331	6.90	6.2	60	1	<2	5	33	5	3	28	<5	0.6	0.8	5480	2550
JK24	19	376	6.90	6.5	59	1	<2	6	31	5	2	41	<5	0.7	0.7	630	53
JK25	19.5	319	7.00	5.3	67	1	<2	7	37	8	4	16	<5	0.7	1.0	280	16
FR4	19	395	7.00	6.1	81	2	<2	11	43	6	4	27	<5	0.8	0.8	5690	2280

Table 2. 'Hot-spot' samples: concentrations of tritium and corresponding water ages, as well as concentrations and carbon isotopic signatures of TNT, DNTs and NTs.

Well	^{3}H	Water Age	2,4,6-TNT		2,4-DNT		2,6-DNT		2-NT	4-NT
	(TU)	(yr±0.4)	(μg/L)	$\delta^{13}C\pm\sigma$ (‰)	(μg/L)	$\delta^{13}\pm\sigma$ (‰)	(μg/L)	$\delta^{13}C\pm\sigma$ (‰)	(μg/L)	(μg/L)
560	2.5	28	25100	-27.4±0.2	3950	-29.2±0.4	1670	-28.4±0.5	190	38
G06	0.1	>55	24800	-27.6±0.1	4470	-28.7±0.2	1670	-29.1±0.4	350	45
564	0.1	>55	33100	-27.6±0.2	7250	-29.0±0.3	2980	-25.0±0.3	580	125

Table 3. Non-'hot-spot' samples: concentrations of tritium and corresponding water ages, as well as concentrations of TNT and 2,6-DNT.

Well	^{3}H	Water Age	2,4,6-TNT	2,6-DNT
	(TU)	(yr±0.4)	(µg/L)	(µg/L)
Upper Aquifer				
569	1.9	23	280	7
QL	1.2	26	<1	<0.1
Eva	2.3	14	<1	<0.1
Irene	1.5	3	<1	<0.1
173	1.3	25	3	1
Ljr.	2.6	7	<1	<0.1
Pond 1	-	-	<1	<0.1
Pond 2	-	-	<1	<0.1
Lower Aquifer				
PS1	0.1	>55	1.5	<0.1
PS3	-	-	280	1
FR12	0.1	>55	95	<0.1
Jk16	0.3	>55	206	4.4
FR10Q	0.1	>55	<1	<0.1
AC1	0.1	>55	<1	<0.1
AC4	0.1	>55	<1	<0.1
PS4	0.3	>55	<1	<0.1
PS2	0.3	>55	<1	<0.1
FR5	0.4	>55	<1	<0.1
JK13	0.1	>55	<1	<0.1
JK14	0.2	41	<1	<0.1
Cond.	1.8	29	<1	<0.1
FR3	1.5	18	<1	<0.1
FR6	3.6	24	<1	<0.1
FR10	2.2	23	<1	<0.1
JK15	-	-	<1	<0.1
JK24	-	-	<1	<0.1
JK25	-	-	<1	<0.1
FR4	-	-	<1	<0.1