TECHNISCHE UNIVERSITÄT DARMSTADT

INCOME Water Care

Improved Management of Contaminated Aquifers by Integration of Source Tracking, Monitoring Tools and Decision Strategies

Action A.4.4:

Contaminant fingerprinting methods

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Remarks

This report is a result of the INCOME Action A.4.4: Contaminant fingerprinting methods. It summarizes the work for the development of passive samplers for the detection of low average contaminant concentrations in groundwater, the optimization of the analytical techniques in the laboratory, and presents and analyzes the field data obtained.

Content

1. Introduction

This project was intended to address a specific problem that had occurred in the Ljubljana alluvial aquifer. It was observed, that at random peak concentrations of contaminants, especially chlorinated solvents, were detected in the groundwater threatening the water works supplying drinking water for Ljubljana. The polluters could not be identified and due to the high groundwater flow-velocities (up to 20 – 30 m/d) concentrations in general quickly decreased below legal limits on the order of weeks.

The problem of such rapid changes in contaminant concentrations is that peak concentrations or the temporal occurrence of contaminants might be missed as time intervals between regular groundwater sampling campaigns are typically in the range of several months. Therefore it was suggested to install passive samplers into groundwater monitoring wells over extended periods of time and that allow the calculation of average contaminant concentrations during the sampling period (several months). With this, a mass based evaluation of contaminations is possible rather than a concentration based approach. By analyzing the passive samplers in terms of sorbed mass, the occurrence of a contamination event can be detected at the specific location even after concentrations declined. In addition, by analyzing the isotopic signature of the contaminants in several passive samplers the likely pathway of the contaminant plume can be backtracked.

The underlying assumption is, that the molecular isotopic signature of environmental contaminants varies, depending on the original supplier or production process, and can therefore be used to trace their sources, serving as an ideal tool in 'environmental forensics'. In addition, the occurrence of an isotopic fractionation during abiotic and biotic degradation of organic contaminants can proof degradation processes and furthermore might allow the quantification of degradation progress.

A major drawback in applying this method are the facts, that (i) concentrations of the contaminants in groundwater might be too low to get reliable isotope measurements, (ii) determination of the isotopic composition of only one element of the contaminant (i.e. $^{12}C/^{13}C$) often leads to ambiguous results, and (iii) a spacial (horizontal and vertical) resolution of plumes cannot be achieved by conventional water sampling methods resulting in averaged concentrations and isotope values.

In this project these limitations were tackled by (i) passive sampling methods with sampling intervals of several months resulting in a contaminant mass accumulation in the passive samplers, (ii) analyzing carbon isotopes as well as chlorine isotopes applying a newly developed method, and (iii) installing several passive sampling devices in distinct depths in one well to achieve a high vertical resolution of contaminant concentrations and isotope signatures.

The main goals of the project were

- To develop a passive sampling system suitable to collect substantial contaminant masses even at low groundwater contaminant concentrations.

- To characterize collected contaminants isotopically in terms of carbon and chlorine isotopes.
- To generate an isotopic database of relevant contaminants for the Ljubljana aquifer.
- To delineate the existing distribution of contaminants in the aquifer by isotopic methods.

The use of a contaminants isotopic signature can also complement numerical backtracking methods for the delineation of source zones in the future, adding a second line of evidence. However, the feasibility of the applied isotope methods is dependent the occurrence of contaminants in the aquifer in a µg/l range, to at least for some limited time, as it was observed during peak events before.

2. Background

Carbon has two stable isotopes, ^{12}C with a natural abundance of ~ 99% and ^{13}C with a natural abundance of ~ 1 %. The ratio of the two isotopes in carbon containing molecules, such as PCE or TCE, is expressed in permil (‰) using the delta-notation ($\delta^{13}C$). The isotope ratio is normalized to an international standard (Vienna Pee Dee Belemnite) that has, by definition, a $\delta^{13}C$ value of 0 ‰. Positive $\delta^{13}C$ values indicate a sample heavier than the standard (relatively more ^{13}C), negative $\delta^{13}C$ values indicate a sample lighter than the standard (relatively less ^{13}C). $\delta^{13}C$ values can be determined using a sector field mass spectrometer coupled to a gaschromatograph for separation of contaminant mixtures (GC-IRMS). This is a widely applied technique that is in routine operation in many laboratories. The typical error range of such measurements is < 0,5 ‰.

In principal also chlorine isotopes can be used to characterize chlorinated solvents. However, in practice chlorine isotope analysis is rarely used although several methods are available. Chlorine has a number of isotopes, of which only two stable isotopes occur naturally: ^{35}Cl with a natural abundance of ~ 76% and ^{37}Cl with a natural abundance of ~ 24%. Unlike carbon isotope analysis, chlorine isotope analysis by traditional methods cannot be carried out without upstream, labor-intensive, offline pretreatments to convert chlorinated compounds into a molecule containing a single chlorine atom, such as methyl chloride (CH_3Cl) or cesium chloride (CsCl). After conversion into methyl chloride, the chlorine isotope ratio is determined using dual-inlet isotope ratio mass spectrometry (DI-IRMS). In the case of conversion into cesium chloride, which involves multi-step, wet processing, thermal ionization mass spectrometry (TIMS) is used to determine the chlorine stable isotope ratio. The degree of chlorine isotope fractionation is normally determined by relating the chlorine isotope ratio of a sample to that of Standard Mean Ocean Chloride (SMOC).

If a sample contains multiple chlorinated compounds, for DI-IRMS and TIMS, separation of the compounds is required before further pretreatment. These complex

sample preparation processes are disadvantages of conventional chlorine isotope methods although high-precision isotopic analysis is achievable with these techniques.

2.1 Application of stable isotopes in environmental studies

For the evaluation of sites that are contaminated with chlorinated solvents, stable isotopes can be typically used in two ways:

Source identification: For this it is assumed, that the isotopic signature of a chlorinated solvent is indicative for a distinct production process of a distinct producer. In the case of more than one potential groundwater polluter, that may have used chlorinated solvents from different producers, the isotopes can then be used to identify the polluter. For this, the isotopic signature of the solvent in the groundwater is compared to the ones used by the potential polluters.

In Fig. 1 isotopic data for carbon ($\delta^{13}C$) and chlorine ($\delta^{37}Cl$) for chlorinated solvents of four different producers are plotted. It was shown, that e.g. $\delta^{13}C$ values for TCE ranged from -32 ‰ to -28 ‰, and for PCE from -37 ‰ to -23 ‰. These variations are much larger than the error range of the analytical methods. The figure also illustrates, that by adding a second isotope (chlorine) the solvents from the different producers can be better distinguished.

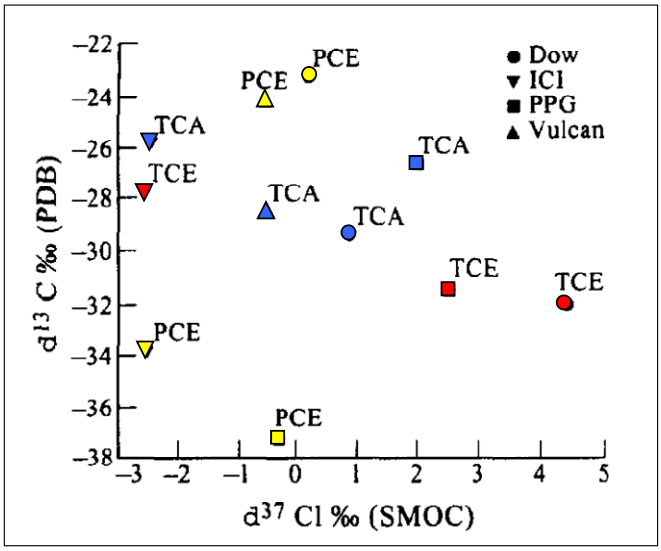

Fig. 1: Variations of the isotopic signatures of carbon ($\delta^{13}C$) and chlorine ($\delta^{37}Cl$) of Trichlorethylene (TCE), Perchloethylene (PCE) and Trichlorethane (TCA) from different producers (van Warmerdam et al. (1995).

Proof and quantification of degradation processes: A bond containing a lighter isotope (e.g. ^{12}C) has in general a slightly lower bond strength compared to a bond containing a heavier isotope (e.g. ^{13}C). In biological as well as in abiotic degradation reactions preferably bonds are broken that contain lighter isotopes, resulting in

isotopic fractionation. The isotopic signature of the remaining, not yet degraded molecules is therefore heavier compared to its initial composition. At the same time the product is isotopically lighter than the original compound. Assuming complete degradation to a product, at least the carbon isotopic composition of the product is identical to the initial isotopic composition of the initial compound. In Figure 2 this is shown for the microbial degradation of PCE to ethene (Yang and McCarty, 1998). This is more complicated in the case of chlorine, as the chlorine atom leaves the molecule during degradation while the carbon atom remains in the molecule.

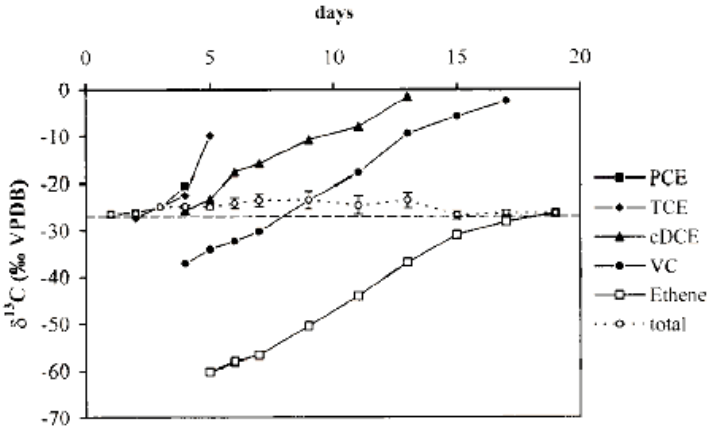

Fig. 2: Comlete microbial degradation of PCE to ethen and associated carbon isotopic effects. Each product is isotopically lighter as the respective precursor. The final product ethene hast he same carbon isotopic composition compared to PCE at 100% conversion (Yang and McCarty (1998).

The isotopic evolution of educt and product during the degradation process follows a physical law that can be described using the Rayleigh equation. The kinetic isotope fractionation factor α can be defined using the following set of equations:

$$R_t/R_0 = (\delta_t + 1000)(\delta_0 + 1000)$$

$$R_t/R_0 = (C_t/C_0)^{(\alpha-1)} = f^{(\alpha-1)}$$

$$\ln R_t/R_0 = (\alpha - 1) \times \ln(C_t/C_0)$$

where δ_t is the isotope ratio R (e.g. $^{37}Cl/^{35}Cl$) at time t, δ_0 is the initial isotope ratio of the substrate (R_0), and C_t/C_0 is the fraction f of substrate remaining at time t. The fractionation factor a can therefore be obtained by plotting $ln(R_t/R_0)$ over $ln(C_t/C_0)$ for a certain experimental time t. The slope of a linear regression through the data points then expresses α as (α – 1) according to the last equation.

Is the fractionation factor and the initial isotopic composition of a compound known, the progress of the degradation reaction can be calculated by measuring the isotopic composition of the educt at any time of the degradation reaction.

Stable isotope compositions are usually expressed as per mil (‰) deviations from an international standard in the conventional δ notation, according to Eqn. (1):

$$\delta = \left(\left({}^{R_{\text{sample}}}/_{R_{\text{standard}}} \right) - 1 \right) \times 1000 \quad (‰) \qquad (1)$$

where R_{sample} and $R_{standard}$ are the ratios of the heavy isotope to the light isotope in the sample and in the reference, respectively.

2.2 Stable carbon isotope analysis

Analysis of stable carbon isotopes ($\delta^{13}C$) is nowadays a routine laboratory method using sectorfield mass spectroscopy. Stable carbon isotope measurements were performed using a Hewlett- Packard gas chromatograph (HP 6890) equipped with an FID and a Micromass Isoprime isotope ratio mass spectrometer (GC-IRMS). The GC was equipped with an Alltech AT-Q capillary column (30 m┐ 0.32 mm ID). For the carbon isotope measurements, the GC and the IRMS were connected via a combustion unit set to 940 °C and a reduction oven set to 600 °C. Carbon isotope ratios are expressed as per mil (x) deviations from the Vienna Pee Dee Belemnite (V-PDB) standard in the conventional δ notation.

2.2 Stable chlorine isotope analysis

The method for the analysis of chlorine isotopes using Quadrupole GC-MS was developed by us in 2007 (Sakaguchi et al. (2007). The background of the method is described in brief in the following:

For chlorine isotopes, SMOC is commonly used as a reference, although no international standard for chlorine isotopic analysis has yet been defined. In order to determine chlorine isotope ratios, chlorine in a sample as well as in a reference are usually chemically converted into a molecule containing one chlorine atom, such as CH_3Cl for analysis with DI-IRMS, or CsCl for analysis with TIMS. Chlorine isotope ratios (R) are then determined by comparing the peak signal intensities of two molecular ions: one containing the heavy chlorine isotope (^{37}Cl) and the other containing the light chlorine isotope (^{35}Cl).

The chlorine isotope ratio of a chlorinated compound can, in principle, also be determined by conventional GC/MS by analyzing the peak intensities of selected molecular and fragment ions of the chlorinated compound without chemical

conversion into CH_3Cl or CsCl. When, for instance, PCE is analyzed by quadrupole GC/MS, four peak groups related to molecular ions and fragment ions can be observed (Fig. 3). The masses of the ions in these peak groups represent different chlorine isotopic compositions, e.g. the peak group related to the PCE molecule represents the PCE molecular ions with ^{35}Cl atoms only (m/z 164), with ^{35}Cl and ^{37}Cl atoms (m/z 166, 168 and 170), and with ^{37}Cl atoms only (m/z 172).

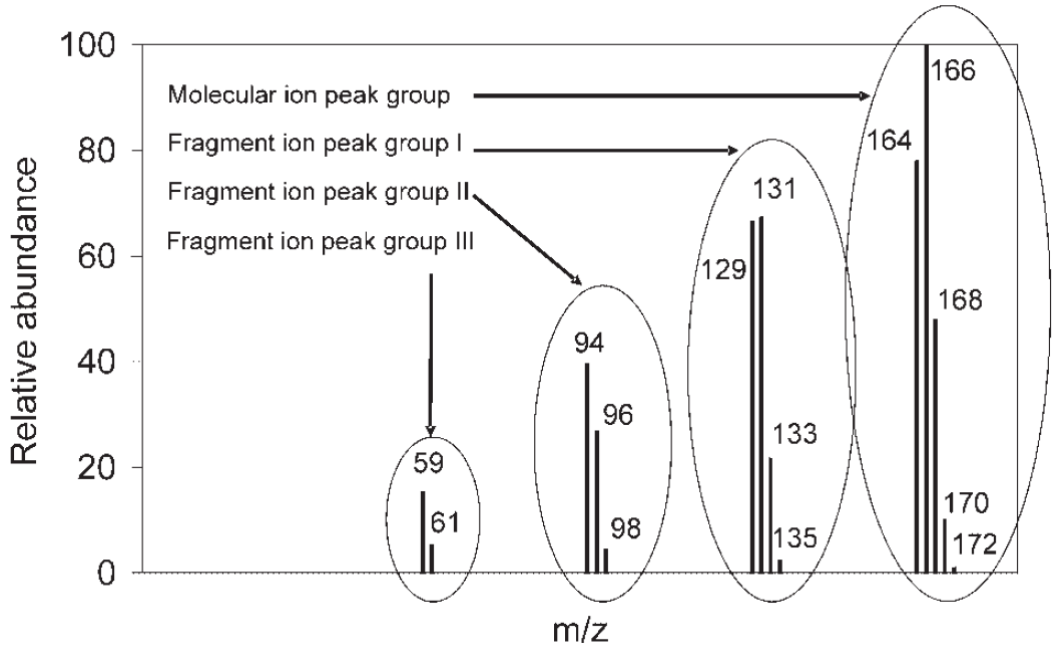

Fig. 3: Characteristic PCE mass spectrum showing the four peak groups related to the fragmentation of PCE.

Analyzing the peak signal intensities of all or selected ions in the peak groups should therefore enable a determination of the chlorine isotopic ratio of the bulk PCE. When, as for chlorine, an element A has two isotopes, a principal isotope a_0 and an isotope a_1, their abundances can be expressed as Xa_0 and Xa_1, respectively. As a molecule can contain several (n) elements A (A_n), the peak intensities of the molecular ions can be obtained by expanding the following binomial theorem:

$$(Xa_0 + Xa_1)^n = (Xa_0)^n + n(Xa_0)^{n-1}(Xa_1) + n(n-1)(Xa_0)^{n-2}(Xa_1)^2 \Big/ 2! + \cdots \qquad (2)$$

The first term on the right-hand side indicates the peak intensity of the molecular ion made up of the principal isotopes (a_0) only. The second term shows the intensity of the molecular ion containing one a1 isotope and n – 1 principal isotopes, and so on.

Focusing on the two major ions in each peak group in Fig. 3, i.e.:

$$R_m : {}^{12}C_2^{35}Cl_3^{37}Cl^+ (m/z\,166) \text{ and } {}^{12}C_2^{35}Cl_4^+ (m/z\,164) : \text{Molecular ion peak group}$$

$$R_1 : {}^{12}C_2^{35}Cl_2^{37}Cl^+ (m/z\,131) \text{ and } {}^{12}C_2^{35}Cl_3^+ (m/z\,129) : \text{Fragment ion peak group 1}$$

$$R_2 : {}^{12}C_2^{35}Cl^{37}Cl^+ (m/z\,96) \text{ and } {}^{12}C_2^{35}Cl_2^+ (m/z\,94) : \text{Fragment ion peak group 2}$$

$$R_3 : {}^{12}C_2^{37}Cl^+ (m/z\,61) \text{ and } {}^{12}C_2^{35}Cl^+ (m/z\,59) : \text{Fragment ion peak group 3}$$

The calculation of the isotopic ratio of the bulk PCE can be shown as follows. According to Eqn. (2), the peak intensities of $^{12}C_2{}^{35}Cl_3{}^{37}Cl^+$ and $^{12}C_2{}^{35}Cl_4{}^+$ representing the molecular ion peak group, can then be expressed with the following equations:

$$^{12}C_2{}^{35}Cl_3{}^{37}Cl^+ = (X_{^{12}C})^2 \times 4(X_{^{35}Cl})^3(X_{^{37}Cl}) \qquad (3)$$

$$^{12}C_2{}^{35}Cl_4^+ = (X_{^{12}C})^2 \times (X_{^{35}Cl})^4 \qquad (4)$$

where $X^{12}C$, $X^{35}Cl$ and $X^{37}Cl$ indicate the isotopic abundances of ^{12}C, ^{35}Cl and ^{37}Cl, respectively. Thus, the chlorine isotope ratio R_m is determined with the peak intensities of these two molecular ions with the following equation:

$$R_m = \frac{X_{^{37}Cl}}{X_{^{35}Cl}} = \frac{^{166}I/4}{^{164}I} = \frac{(X_{^{12}C})^2 \times 4(X_{^{35}Cl})^3(X_{^{37}Cl})/4}{(X_{^{12}C})^2(X_{^{35}Cl})^4} \qquad (5)$$

where ^{166}I and ^{164}I indicate the peak intensities of masses 166 and 164, respectively. Likewise, R_1, R_2, and R_3 can be determined with the two strongest peaks in the fragment on peak groups 1, 2 and 3 using the following equations:

$$R_1 = \frac{X_{^{37}Cl}}{X_{^{35}Cl}} = \frac{^{131}I/3}{^{129}I} = \frac{(X_{^{12}C})^2 \times 3(X_{^{35}Cl})^2 (X_{^{37}Cl})/3}{(X_{^{12}C})^2 (X_{^{35}Cl})^3} \quad (6)$$

$$R_2 = \frac{X_{^{37}Cl}}{X_{^{35}Cl}} = \frac{^{96}I/2}{^{94}I} = \frac{(X_{^{12}C})^2 \times 2(X_{^{35}Cl})(X_{^{37}Cl})/2}{(X_{^{12}C})^2 (X_{^{35}Cl})^2} \quad (7)$$

$$R_3 = \frac{X_{^{37}Cl}}{X_{^{35}Cl}} = \frac{^{61}I}{^{59}I} = \frac{(X_{^{12}C})^2 (X_{^{37}Cl})}{(X_{^{12}C})^2 (X_{^{35}Cl})} \quad (8)$$

Theoretically, isotope ratios R_m, R_1, R_2 and R_3 should be equivalent. A series of preliminary experimental results showed, however, that a certain level of isotopic fractionation occurs in the ion source during fragmentation of the ions. Therefore, to determine the chlorine isotope ratio of bulk PCE (R_{PCE}), all four isotope ratios, namely, R_m, R_1, R_2 and R_3, need to be taken into account. The degree of contribution of each R to R_{PCE} is defined by the relative intensity of the strongest peak in each peak group.

The chlorine isotope ratio of bulk PCE (R_{PCE}) can now be determined using eight peaks:

$$\begin{aligned} R_{PCE} = & \frac{^{166}I}{^{166}I + ^{129}I + ^{94}I + ^{59}I} \times R_m \\ & + \frac{^{129}I}{^{166}I + ^{129}I + ^{94}I + ^{59}I} \times R_1 \\ & + \frac{^{94}I}{^{166}I + ^{129}I + ^{94}I + ^{59}I} \times R_2 \\ & + \frac{^{59}I}{^{166}I + ^{129}I + ^{94}I + ^{59}I} \times R_3 \end{aligned} \quad (9)$$

Note that, theoretically, 15 peaks with different mass/ charge ratios (m/z values) exist in the molecular ion peak group (Fig. 1), because PCE molecular ions consist of four chlorine atoms and two carbon atoms and both chlorine and carbon have two stable isotopes. The five 'visible' peaks represent PCE molecular ions containing two light stable carbon isotopes (^{12}C). The remaining 10 peaks represent PCE molecular ions that contain one or two heavy stable carbon isotopes (^{13}C). The natural abundance of ^{13}C is only about 1% and the likelihood of one or two C atoms in one PCE molecule

being ^{13}C is very small. Therefore, these 10 peaks may not be clearly identified on a mass spectrum. In addition, some of these 10 peaks that are located close to the larger five peaks are usually incorporated into the larger peaks. For instance, PCE molecular ions $^{13}C_2{}^{35}Cl_4{}^+$ and $^{12}C_2{}^{35}Cl_3{}^{37}Cl^+$ have the mass/charge ratio of 166 and relative abundances of 0.009 and 100, respectively. Conventional quadruple GC/MS cannot separate these two peaks whose exact masses are 165.88 and 165.87. The signal intensity of m/z 166, therefore, actually represents not only the intensity of $^{12}C_2{}^{35}Cl_3{}^{37}Cl^+$ but also that of $^{13}C_2{}^{35}Cl_4{}^+$.

When determining the chlorine isotope ratio of bulk PCE using Eqn. (9), in total, four unnecessary peaks associated with ^{13}C are unavoidably integrated with these eight target peaks, which are actually necessary for the calculation. However, the relative abundances of these four peaks are much smaller (between 0.009 and 0.012) than those of the eight target peaks (between 32 and 100). In order to determine the degree of the influence of these four peaks, we have analyzed a PCE standard repeatedly and determined the chlorine isotope ratio of the standard using Eqn. (9). The experimental value of the chlorine isotope ratio of this PCE standard was 0.32171 +/- 0.00014 (1σ, n=10). Based on the experimental values, we estimated the chlorine isotope ratios of the PCE without the four unnecessary inseparable peaks. The difference in chlorine isotope ratio of the PCE determined with and without the four unnecessary peaks was 0.00005. We are therefore justified in neglecting the effect of these four peaks on the calculated chlorine isotope ratio of PCE.

The above equations can be easily expanded to include all possible mass fragments, as indicated in Fig. 1. In principle, there are no differences in the chlorine isotope ratios calculated using either the two major mass fragments of each peak group or all mass fragments. On the contrary, including fragments with lower abundances, as is characteristic for those fragments containing multiple ^{37}Cl atoms, required a larger sample size to precisely determine the intensity of these peaks. Therefore, all calculations are based on the two major fragments of each peak group, as shown in Figure 3 and Table 1.

Table 1. Selected masses for determining the component specific stable chlorine isotopic compositions using the SIM mode of the quadrupole GC/MS system

PCE	TCE
166	132
164	130
131	97
129	95
96	62
94	60
61	
59	

In principle the method can also be expanded to all chlorinated compounds (e.g. TCE) with a similar set of equations as described above.

3. Laboratory Activities

Laboratory activities focused on (i) the selection of appropriate passive sampling device membranes, (ii) the selection of appropriate sorbents, and (iii) on the optimization of the analytical procedures to determine chlorine isotope ratios.

3.1 Selection of an appropriate sampling device membrane

A suitable membrane for the construction of the passive sampling devices should allow high diffusive fluxes to increase the mass of contaminants captured by the sampling device over time. This is especially important due to the very low concentrations of chlorinated compounds in most of the wells in the Ljubljana aquifer. Therefore, instead of using ceramic tubes as originally proposed, but that are limited in contaminant uptake fluxes by the small pores (5 nm), silicon tubes were used at a later stage of the project that have significantly higher uptake rates. Diffusion rates in silicone were found to be orders of magnitude faster compared to the ceramic having a pore size of 5nm. The silicone tubes can be easily closed at the ends by inserting a glass plug (Fig. 4).

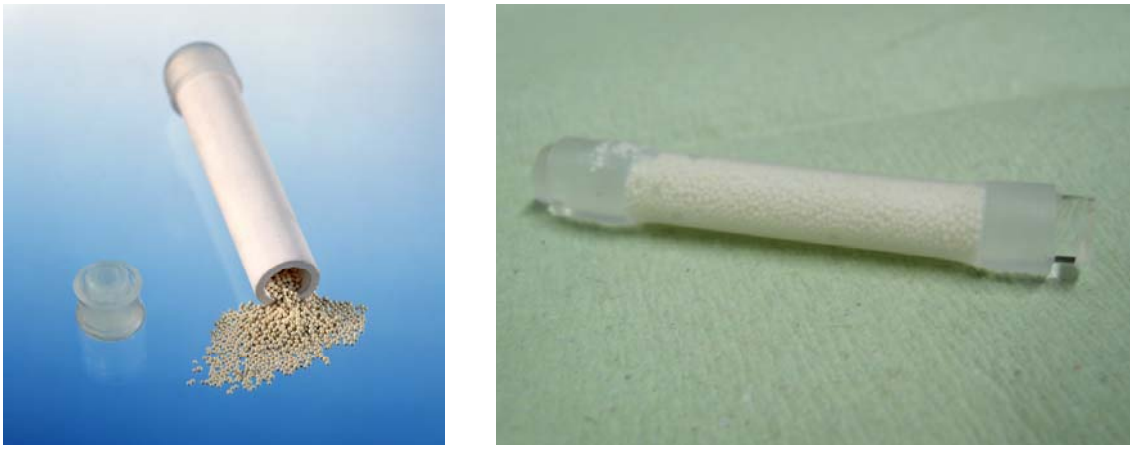

Fig. 4: Two alternative passive sampling devices. Left: Porous ceramic tubes with pore diameters of 5 nm. Right: Silicon tubes. Both filled with adsorber resins.

With this, theoretically groundwater concentrations of less than 1 µg/l are sufficient to generate reliable isotopic signatures for sampling times of less than 3 month. This could be shown in defined laboratory sorption experiments in which the silicon passive sampling devices were stored in water with an aqueous PCE concentration of 10 µg/l and analyzed in frequent intervals. Already after one day of contact, peak areas for mass 165, indicative for PCE, were in the million range (Fig. 5).

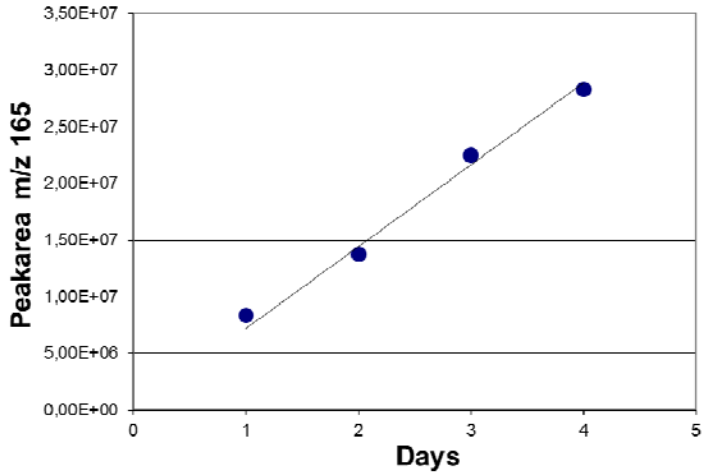

Fig. 5: Uptake experiment of PCE in silicon passive sampling devices. PCE aqueous concentrations 10µg/l..

Based on these results, the silicon tube based passive sampling devices were chosen as the preferred system.

3.2 Selection of appropriate adsorbent

Two different adsorbents to be filled into the silicone tubes were tested, (i) Dowex Optipore L470, and IRA Amberlite, an ion exchange resin. With both adsorbents batch experiments were performed to establish sorption isotherms for Trichloroethylene (TCE) and Perchloroethylene (PCE).

It was found, that Dowex Optipore L470 as well as IRA Amberlite have very high distribution coefficients indicating that they can maintain a concentration gradient for the contaminants from the groundwater into the passive samplers over extended periods of time. Both were therefore found to be suited as adsorbent materials. However, important for the later chemical analysis is also the desorption behavior of the compounds from the adsorbent. For this it was found, that recovery of the contaminants from IRA Amberlite is significantly higher compared to Dowex Optipore L470, qualifying IRA Amberlite as the material of choice.

The resulting passive sampling devices were stored in water in sealed headspace glas vials for storage and shipping (Fig. 6).

Fig. 6: Passive sampling devices stored in water in sealed headspace glas vials for storage and shipping.

3.3 Selection of an appropriate desorption method

Key step for the final chemical analyses is the desorption of the contaminants from the adsorber. Desorption should be as efficient as possible and conservative with respect to isotope fractionation. Several desorption methods were tested including (i) desorption by extraction with different solvents, (ii) direct temperature desorption in a purge and trap device.

Extraction by solvents was found to be efficient but resulted in an dilution of contaminants in the solvent, raising the detection limit. Therefore the direct desorption in a purge and trap device was favored as the total contaminant mass is directly injected into the GS-MS system. However, the adsorbent has to be dried before the desorption step to prevent an overload of the trap and finally the GC due to the desorbed water. The direct temperature desorption method was therefore optimized by testing different pre-drying methods for the adsorber resins. The qualified final method is to dry the resins in a two-step process. In a first step, a dry nitrogen flow at ambient temperature is directed over the resins to evaporate excess water on the outside surface of the resins. Then, the resins are further dried using a freeze dryer in which the samples are cooled down to a low temperature accompanied by the application of a vacuum. Adsorbents are filled then into standard 20ml headspace vials and directly desorbed in the automated purge and trap desorber at a maximum temperature of 150°C. With this, an easy and efficient desorption method is available that allows to inject the total sorbed mass into the GS-MS system, resulting in a very low detection limit. The analytical system, a Purge and Trap system directly coupled to the GC-MS is shown in Figure 7.

Fig. 7: Purge and Trap (left) coupled to GC-MS (right) via heated transfer lines.

In addition, as the silicon tube has also a sorption capacity for the contaminants it was tested whether the silicone tube could be desorbed directly in the pure and trap system. The advantage is also that no water phase is introduced into the purge and trap system as the silicon is hydrophobic, repelling water, and therefore no extra drying step has to be performed. The desorption of the silicone tube directly was found to be a suitable alternative and will be performed in parallel to the resin desorption

3.4 Optimization of the GC-MS method

The final quantification and isotope characterization step is achieved using GC-MS directly coupled to the purge and trap system for chlorine isotopes, and GC-IRMS for carbon isotopes. The GC-MS method is run in the selected ion mode to specifically detect the relevant masses for isotope determination. For GC-IRMS, the contaminants are converted into CO_2 in a combustion furnace and then analyzed using dedicated cups for the different CO_2 masses.

For chlorine isotopes and the GC-MS method it was found, that the isotope signal shows a slight dependency on the mass injected, i.e. a slight change in the isotope signal is observed with increasing peak areas. This is shown for PCE (mass 166) and TCE (mass 130) (Fig. 8 and 9).

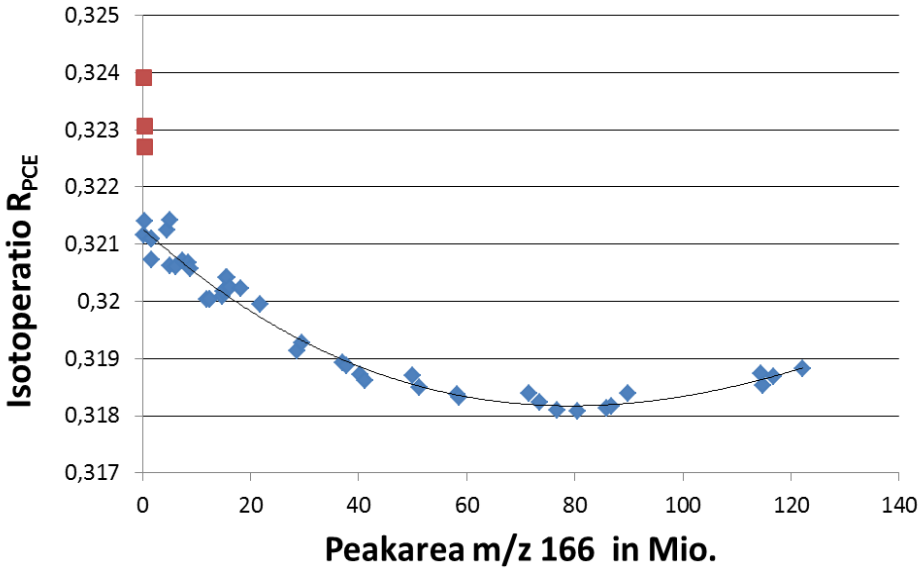

Fig. 8: Dependency of chlorine isotope ratio of PCE on mass injected based on the peak area of mass 166.

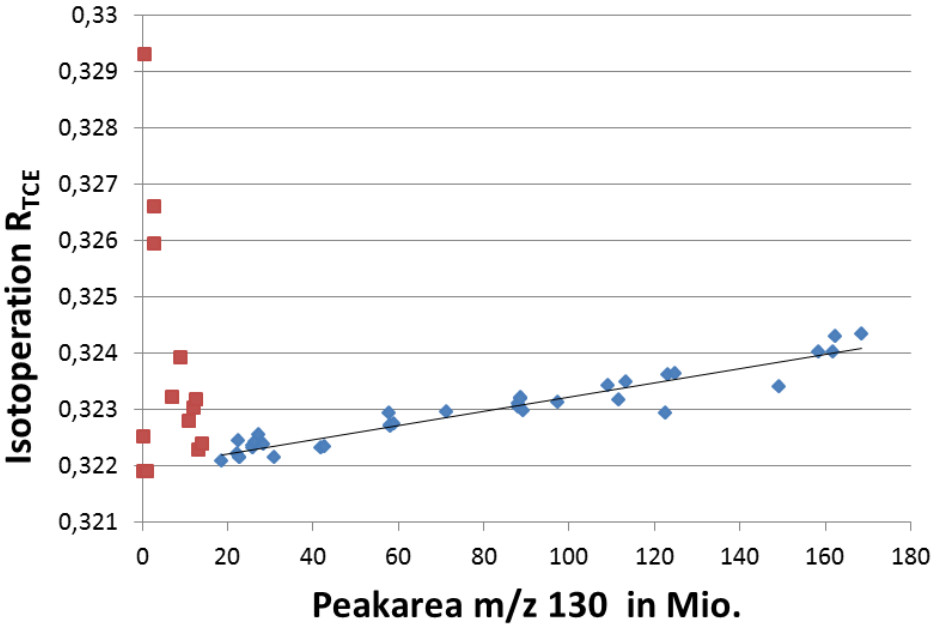

Fig. 9: Dependency of chlorine isotope ratio of TCE on mass injected based on the peak area of mass 130.

Due to these results correction functions were established to account for the mass dependency of the isotope signals. The red data points in both figures were not included into the regressions (solid lines) as for low peak areas a large data scatter was observed.

In the case of PCE a second order polynomial equation was used to correct the measured isotope ratios for the peak area dependency (eq.10), while in the case of TCE a linear equation was sufficient for correction (eq. 11):

$$y = 5E\text{-}07x^2 - 8E\text{-}05x + 0{,}3212 \quad (10)$$

$$y = 1E\text{-}05x + 0{,}322 \quad (11)$$

With these equations, isotope ratios were corrected and converted to the conventional δ-notation. This is shown as an example for PCE with a normalized chlorine isotopic composition ($\delta^{37}Cl$) of 0‰ in Fig. 10. It can be clearly seen, that deviations of measured values from the reference are getting larger for smaller peak areas. For peak areas larger than 20 Million counts, corrected values in general deviate less than 0,5 ‰ (+/-) from the reference. This is an excellent precision, comparable to the standard deviation reported for carbon isotope measurements using a sector field mass-spectrometer.

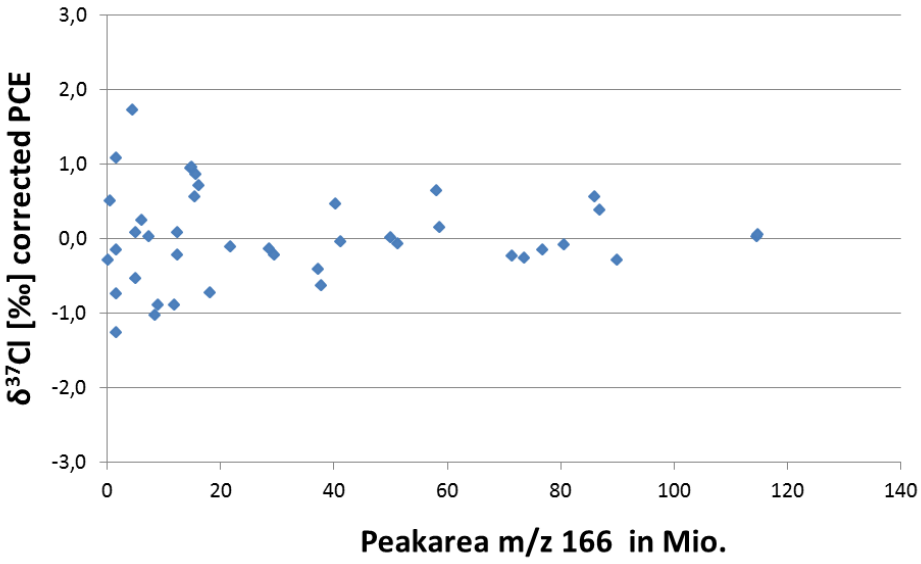

Fig. 10: Corrected isotope values for injections of different PCE masses, converted into the conventional δ-notation.

From these experiments it was also concluded, that peak areas for a reliable determination of chlorine isotopes should be at least 20 million (for PCE and the major mass 166). In further experiments it was shown, that for peak areas above 120 million, deviations again increase (data not shown). This indicates that to produce reliable results peak areas should fall within the range between 20 million and 120

million. For the field samples this means, that at least duplicate samples have to be taken to determine the mass sorbed on the resins in a first step and then tailor the amount to be desorbed for the second sample. However, this is easily achieved by splitting either the resin into subsamples, or by cutting the silicone tube into various fragments that can then be desorbed, establishing a tailored contaminant mass due to the reliable and reproducible range of the GC-MS system. The standard deviation for multiple samples injected by the direct thermal desorption using the purge and trap system followed by GC-MS analyses was within 1 permil, indicating the reliability of the method.

4. Field Activities

The installation of the passive samplers for multi-level sampling at the various piezometers was done as follows: the individual samplers were attached on pre-selected different intervals to a thin but robust carrier line including a stainless steel bottom weight of approx. 150g. After finishing the before described set-up and attaching it securely to the well-head, the whole construction was lowered down into the screened section of the respective piezometer. The time interval between installation and retrieval was at least 2 months - due to the fast uptake rates the passive samplers should have accumulated enough contaminant mass to determine the isotope of the target components.

Several field campaigns were performed during the project time. Samplers were installed by staff of the Technical University of Darmstadt or send to the Slovenian partners in regular intervals for replacement of installed samplers. Retrieved samplers were send to our laboratory in at the Technical University of Darmstadt sealed in glass vials with crimp tops and Teflon coated rubber septa filled with DI water for further analyses. Samples were stored in the fridge until analysis.

4.1 Analyses of passive samplers

In the first phase of the project, passive samplers based on ceramics tubes were installed in several observation wells, however, due to very low concentrations only traces of TCE and PCE could be detected in the passive samplers. As a consequence, neither carbon isotopes, nor chlorine isotopes could be determined in these samples. That indicates, that no peak concentrations passed the samplers during the installation time, however, it also indicated that the applied technique was inappropriate for the very low concentrations of contaminants in the Ljubljana alluvial aquifer

Thereafter it was decided to change the passive sampling system to the silicone tubes that allow higher mass fluxes at the same aqueous concentrations, compared to the ceramics tubes. As a drawback, the calculation of averaged concentrations is not possible as the silicone is not the bottleneck for contaminant uptake, as it is the case for the ceramics membrane.

With this system, several further sampling campaigns in late 2010 and 2011 were conducted. In the following Tables, sampled wells, sampling times, and sampling depths in the wells are summarized. In addition, red colors indicate samples that allowed at least the determination of chlorine isotopes for PCE, in some cases also for TCE:

BRP - 1B	08.11.2010	36 m
BRP - 1B	08.11.2010	41 m
BRP - 1B	08.11.2010	46 m
BRP - 1B	08.11.2010	51 m
BRP - 1A	08.11.2010	67 m
BRP - 1A	08.11.2010	76 m
BRP - 1A	08.11.2010	85 m
BRP - 1A	08.11.2010	94 m

Vodovodna	15.04.2011	30 m
Vodovodna	15.04.2011	35 m
Vodovodna	15.04.2011	40 m
Vodovodna	15.04.2011	45 m
Vodovodna	15.04.2011	48 m
Vodovodna	15.04.2011	52 m

LP Obrije	**15.04.2011**	**15 m**
LP Obrije	**15.04.2011**	**18 m**
LP Obrije	**15.04.2011**	**21 m**
LP Obrije	**15.04.2011**	**24 m**
LP Obrije	**15.04.2011**	**27 m**
LP Obrije	**15.04.2011**	**30 m**
LP Obrije	**15.04.2011**	**33 m**
LP Obrije	**15.04.2011**	**36 m**
LP Obrije	**15.04.2011**	**42 m**
LP Obrije	**15.04.2011**	**45 m**

LP Obrije	**15.04.2011**	**48 m**
LP Obrije	**15.04.2011**	**51 m**
LP Obrije	**15.04.2011**	**54 m**
LP Obrije	**15.04.2011**	**57 m**
LP Obrije	**15.04.2011**	**63 m**
LP Obrije	15.04.2011	66 m

BRP - 1C	**15.04.2011**	**23 m**
BRP - 1C	**15.04.2011**	**28 m**
BRP - 1B	**15.04.2011**	**36 m**
BRP - 1B	**15.04.2011**	**41 m**
BRP - 1B	**15.04.2011**	**46 m**
BRP - 1B	**15.04.2011**	**51 m**
BRP - 1A	**15.04.2011**	**67 m**
BRP - 1A	**15.04.2011**	**76 m**
BRP - 1A	**15.04.2011**	**85 m**
BRP - 1A	**15.04.2011**	**94 m**

LP Stozice	15.04.2011	20m
LP Stozice	15.04.2011	22,5m
LP Stozice	15.04.2011	25 m
LP Stozice	15.04.2011	30 m
LP Stozice	15.04.2011	35 m
LP Stozice	15.04.2011	40 m
LP Stozice	15.04.2011	60 m

SM-1/2A (P4)	26.08.2011	62m
SM-1/2A (P4)	26.08.2011	65 m
SM-1/2A (P4)	26.08.2011	68 m
SM-1/2A (P4)	26.08.2011	71 m
SM-1/2A (P4)	26.08.2011	74 m
SM-1/2A (P4)	26.08.2011	77 m

SM-1/2B (P3)	26.08.2011	47 m
SM-1/2B (P3)	26.08.2011	50 m
SM-1/2B (P3)	26.08.2011	53 m
SM-1/2B (P3)	26.08.2011	56 m

SM-1/2c (P2)	26.08.2011	33 m
SM-1/2c (P2)	26.08.2011	36 m
SM-1/2c (P2)	26.08.2011	38,5 m

SPS-3	30.09.2011	17 m
SPS-3	30.09.2011	20 m
SPS-3	30.09.2011	23 m
SPS-3	30.09.2011	26 m
SPS-3	30.09.2011	29 m
SPS-3	30.09.2011	32 m
SPS-3	30.09.2011	35 m
SPS-3	30.09.2011	38 m

It can be seen, that also for the silicone samplers, only in a fraction of the samples PCE and TCE were collected in amounts sufficient for chlorine isotope analyses. In none of the samples, carbon isotopes could be determined, due to the substantially higher detection limit of the method.

However, results of the analyses of the passive samplers were reproducible and showed some interesting features especially for the chlorine isotope analyses. As an example, for the well LP Obrije in total 17 samples that were installed at depths between 15 and 66 m and were analyzed for chlorine isotopes. In all samples PCE was detected with highest PCE masses on the passive samplers in a depth between 15 and 22 m. No TCE was detected. PCE chlorine isotopes could be determined in 15 samples but showed no significant differences over the whole water column sampled (Fig. 11). This may indicate, that the contamination is due to a single source, however, the contamination was also found to be spread out over a substantial vertical depth in the aquifer. In addition, the quite constant isotopic signature of the PCE suggests that no degradation reactions are occurring in the aquifer as these would result in an isotopic fractionation. One outlier in a depth of 55m showing slightly lower isotope ratios might be due to the small sampled mass, at the detection limit for the isotope method.

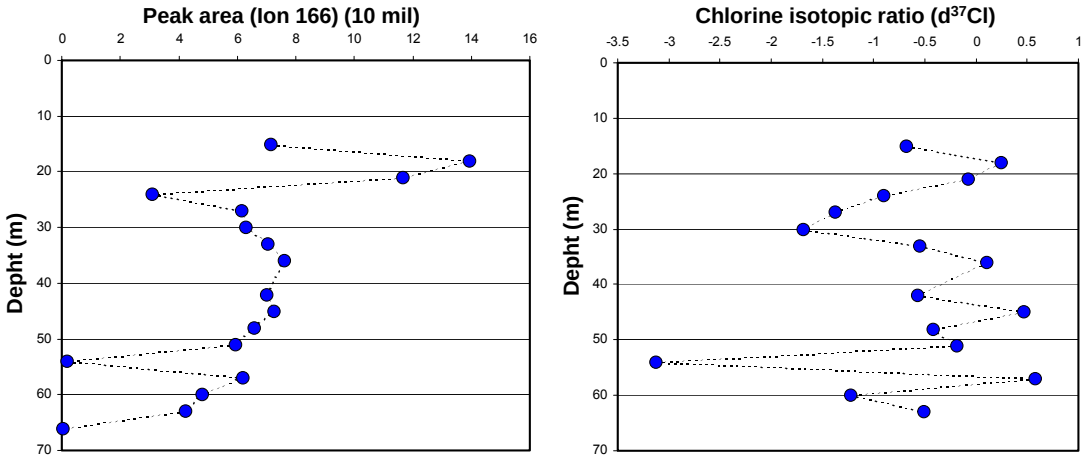

Fig. 11: Well Obrijesamoled on 15.04.2011 and PCE. Extracted masses (left, corresponding to relative concentrations) and chlorine isotope ratios, (right).

Fig. 12 shows another example for the third sampling campaign in well BRP. Here, PCE as well as TCE could be analyzed. Both compounds showed an increasing mass in the passive samplers with depths, indicating higher contaminant concentrations in the lower part of the aquifer (up to 100 m depth). Due to low TCE masses, TCE isotopes could only be analysed in the lower part, however, no trend was observed. For PCE, isotope ratios seem to decrease with depth.

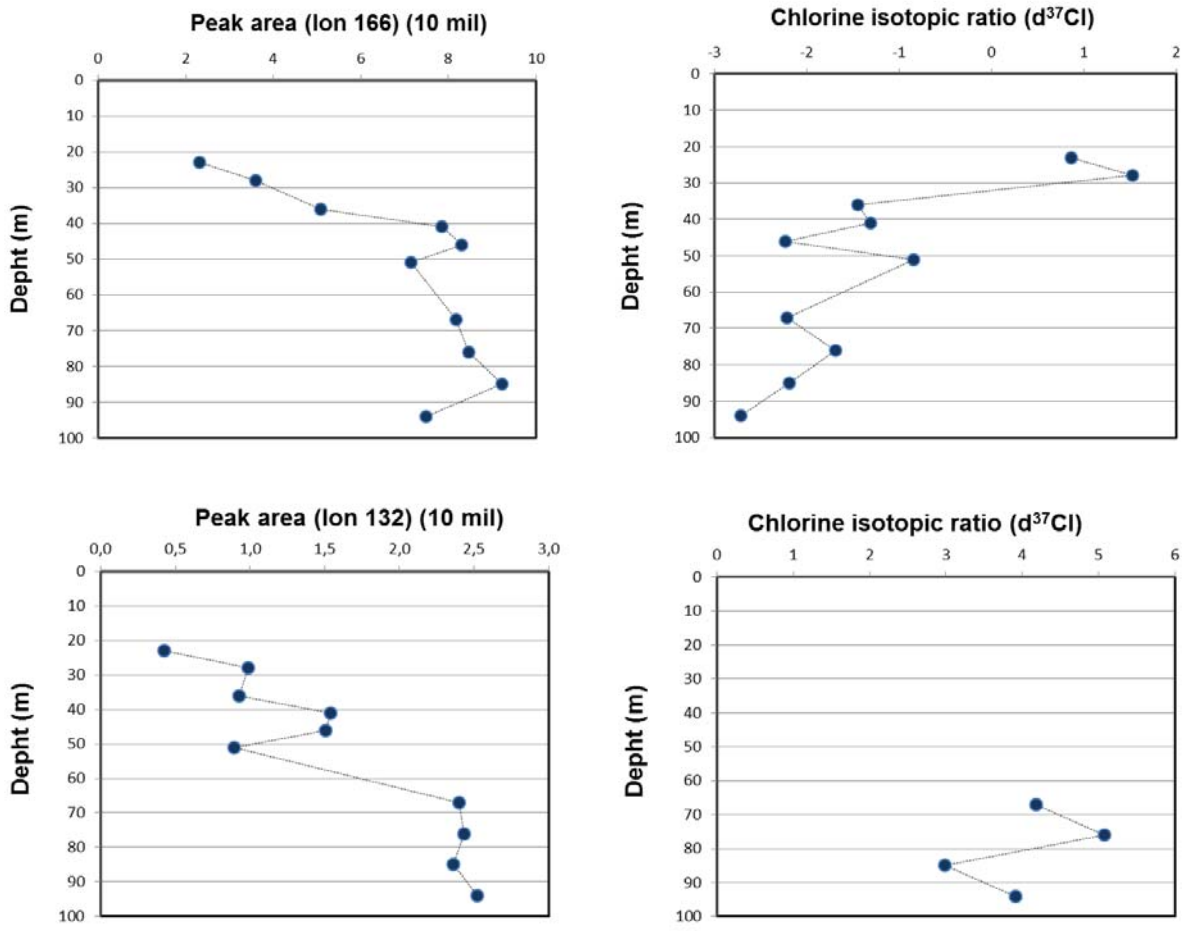

Fig. 12: Well BRP, sampled at 15.04.2011. Extracted masses (left, corresponding to relative concentrations) and chlorine isotope ratios, (right) for PCE (upper graphs) and TCE (lower gaphs).

This might indicate a slight degradation of PCE in the upper part of the aquifer, as this would result in an isotope fractionation with an enrichment of the heavier isotopes in the remaining PCE. Also the higher isotope ratios of TCE compared to PCE in the lower part of the aquifer would indicate some degradation of the PCE to TCE. However, the data base is still not large enough for definite statements.

5. Discussion

The results obtained in this project are somewhat ambiguous. Recalling the initial project targets it has to be stated, that targets could only be partly reached. In the following this is illustrated for the specific targets.

Target 1:

- To develop a passive sampling system suitable to collect substantial contaminant masses even at low groundwater contaminant concentrations.

The target of the development of a suitable passive sampling system for low groundwater concentrations was reached. For this the original system based on ceramic dosimeters was altered and the ceramic tube replaced by a silicon tube. This material allows much faster diffusional uptake of contaminants and proved to be effective even at contaminant concentrations of about 1 µg/l. Required sampling times are estimated to be in the range of a few weeks, to be on the safe side. Due to the fast diffusional uptake rates, the determination of an average concentration is not possible with this system, as contaminants are depleted around the silicone tube altering uptake rates independent on the overall groundwater concentrations. However, this was not the main purpose of the passive sampler development.

Target 2:

- To characterize collected contaminants isotopically in terms of carbon and chlorine isotopes.

In all samples, contaminant masses collected were too low to determine stable carbon isotopes. This is due to the higher detection limit of the isotope ratio mass spectrometer used for the analysis of the carbon isotopes compared to the quadrupol GC-MS used for the determination of chlorine isotopes. Consequently, in some samples PCE and TCE were detected using the GC-MS and also for some samples chlorine isotopes could be determined. Due to the limited number of contaminants detected, in principal only PCE and TCE could be detected, and the limited chlorine isotope measurements that were possible, no general contaminant characterization based on carbon and chlorine isotopes was possible. It is also obvious, that a two-dimensional isotope analysis was not possible, due to the lack of carbon data.

Target 3:

- To generate an isotopic database of relevant contaminants for the Ljubljana aquifer.

It was not possible to generate an isotopic data base of the relevant contaminants as only a very limited number of contaminants were detected with the applied methods and also only very limited samples allowed a isotopic characterization of the contaminants. With this, the target could clearly not reached.

Target 4:

- To delineate the existing distribution of contaminants in the aquifer by isotopic methods.

This target is closely connected to target 3. Therefore also this target could not be reached, as concentrations in general were too low to delineate plums by isotopic methods.

Looking at the targets and considering the fact that some of the targets could not be reached some further interpretation is needed. Main starting point of the project was the observation, that at random peak concentrations of contaminants, especially chlorinated solvents, were detected in the groundwater of the Ljubljana aquifer. That led to the assumption, that contaminated areas exist that might have an impact on overall groundwater quality. Assuming this, a better knowledge of the contamination pattern would be highly desirable, for precautionary measures as well as for identification of polluters.

The investigations performed in this study showed, however, that at least for the time of sampling and the selected sampling locations no significant overall contamination of the aquifer was present and also no peak concentration due to an additional contaminant input occurred. Therefore the passive samplers and isotope methods were not suitable to characterize the contamination status of the aquifer. The missing of the project targets does therefore not question the potential of the applied methods, but proved to be inappropriate for the situation encountered in the field. It has to be noted, that applying more tailored methods for contaminant detection and quantification that are not based on stable isotopes, additional contaminants could have been found in the groundwater of the Ljubljana aquifer.

The results of this study showed, that the current contamination pattern of the groundwater in the study area indicates a diffuse pollution of the aquifer with chlorinated solvents in low concentrations. This is very typical for the industrialized European countries were chlorinated solvents have been applied for several decades. In addition, due to the chemical and physical properties of this group of contaminants, they are prone to spread by atmospheric processes and can then be washed out and infiltrated into the subsurface by precipitation.

6. Literature

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