



Chlorinated solvents source identification by nonlinear optimization method

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Abstract In this work, chloride ions were used as conservative tracers and supplemented with conservative amounts of chloroethenes (PCE, TCE, Cis-DCE, 1,1-DCE), chloroethanes (1,1,1-TCA, 1,1-DCA), and the carbon isotope ratios of certain compounds, the most representative on the sites studied, which is a novelty compared to the optimization methods developed in the scientific literature so far. A location of the potential missing sources is then proposed in view

of the balances of the calculated mixing fractions. A test of the influence of measurement errors on the results shows that the uncertainties in the calculation of the mixture fractions are less than 11%, indicating that the source identification method developed is a robust tool for identifying sources of chlorinated solvents in groundwater.

Keywords Chlorinated solvents · Mixing models · Nonlinear optimization · Conservative tracers · Compound-specific isotope ratios

Highlights

- An unknown source of contaminants was detected by nonlinear optimization method.
- The effect of measurement errors on a source identification is negligible.
- The uncertainties on the calculated mixing fractions are less than 11 %.

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Introduction

Sources of groundwater pollution can have diffuse origins (phytosanitary products from agriculture, runoff from cities, highways, and industrial areas) (Allen et al., 2014; Azzellino et al., 2019; Balderacchi et al., 2013; Knapp, 2005; Meinardi et al., 1995), or punctual origins through leaks from tanks/pipes, infiltration of products at landfills, or accidental spills (Blessing et al., 2009; Christ et al., 2010; Guilbeault et al., 2005; Lerner et al., 2003; Luciano et al., 2018; McGuire et al., 2006; Rivett et al., 2014; Yang & Lee, 2012). In all cases, when groundwater pollution is detected, the sources must be identified so that adequate treatment or monitoring measures can be applied (Atteia et al., 2013, 2017; Chen et al., 2010; Höhener et al., 1998; Jousse et al., 2020; McGuire et al., 2006; Verardo et al., 2021; Wiedemeier et al., 1995). In industrial

areas, there can be several sources of contamination linked to different activities. In this context, historical data on the use of chemicals and the monitoring of incidents, acquired either by the public services or by the companies using these products, are often insufficient to provide answers on the locations of the sources and the contaminant fluxes that come out of it. It is therefore necessary to develop techniques which allow distinguishing all the pollutants' sources and determining for each of these sources their contribution proportions. This would permit to discriminate the level of the responsibility shares in the management of the pollution (Aronovsky, 2000; Marrayott et al., 2000; Morrison, 2000; Murphy & Morrison, 2007; Sauer & Uhler, 1994; Stout et al., 1998).

After carrying out historical studies to locate potential sources of pollutants, the first approach is often to spatially characterize the pollution by identifying the chemical fingerprints of the water in piezometers of the study area. Yang and Lee (2012) have shown that the use of chemical fingerprints of several volatile organic compounds (VOCs), combined with a good seasonal analysis, allows reliable source identification. However, depending on several physico-chemical parameters, certain processes can modify the pollutants' chemistry and make the use of chemical fingerprints alone insufficient to identify sources and estimate their contributions (Atmadja & Bagtzoglou, 2001a, b; Newell & Connor, 1998; Sun et al., 2006). To overcome this, other approaches mainly use the power of compound specific isotope analysis (CSIA) which makes it possible to further constrain the models or to discriminate the origin of sources according to isotope ratios (Blessing et al., 2009; Hunkeler et al., 2004; Kaown et al., 2014; Mansuy et al., 1997; Schmidt et al., 2004; Smallwood et al., 2002; Walker et al., 2005).

To locate a source of groundwater pollution, inverse modeling is often used by adjoining advection–dispersion equations and by exploiting the concentration data measured at piezometers. In the case of heterogeneous aquifers, source identification approaches combine inverse modeling with geostatistical and probabilistic methods (Bagtzoglou et al., 1991; Hwang et al., 2020; Liu & Wilson, 1995; Michalak & Kitanidis, 2004; Neupauer & Wilson, 2001, 2005; Snodgrass & Kitanidis, 1997; Wilson & Liu, 1994). The major limitations of these approaches are the fact that (i) they assume sources appearing simultaneously and (ii) sometimes require (for Bayesian models) an a priori knowledge

of potential locations. In contrast to probabilistic approaches, there are deterministic approaches which are based on optimization methods (multiple regressions, minimization of a linear or nonlinear function) coupled with inverse modeling including advection–dispersion equations (Essouayed et al., 2020; Gorelick et al., 1983; Liu & Ball, 1999; Mahar & Datta, 1997, 2001; Samarskaia, 1995; Skaggs & Kabala, 1994; Wagner, 1992).

In this work, the last type of approach is adopted, and the problem of identifying sources and calculating their contributions is formulated as a nonlinear optimization problem (Aral & Guan, 1996; Aral et al., 2001; Datta et al., 1989; Gorelick et al., 1983; Mahar & Datta, 2001), which variables to be determined are the mixing fractions coming from the piezometers located upstream to the considered piezometer. When trying to determine the proportion of two sources, it is possible to avoid advection–dispersion modeling by simply assuming that a sample is a mixture of different types of water. This will not make it possible to identify the source location or emitted mass fluxes, but to determine whether the known sources can produce the concerned water sample.

In the first part of this manuscript, the chemical calculation and optimization methods are presented with an argumentative development on the choice of the calculation parameters. The second part shows the study site and the analyzed data (hydrogeological, geochemical, studied contaminants) for application of the developed method. The third part shows the results obtained by the mixing calculations and the comparative balances of the calculated and measured concentrations. Finally, a summary and a discussion on the robustness of the developed method are proposed.

Case study

Studied site and potential pollutant sources

The study area is located on Quaternary silts lying on the Senonian chalk aquifer with a thickness of about 65 m. The impermeable substratum includes marls of the Middle and Lower Turonian. The sector is an industrial area housing an old airfield, an automobile production plant, various activity areas (welding, metalwork), and a landfill where various wastes were buried in the past

(Fig. 1). The analysis of the concentrations of chlorinated solvents in all the piezometers shows the presence of the following compounds: tetrachloroethene (PCE), trichloroethene (TCE), cis-1,2-dichloroethene (cis-DCE), 1,1,1-trichloroethane (1,1,1-TCA), 1,1-dichloroethene (1,1-DCE), and 1,1-dichloroethane (1,1-DCA).

On the hydrogeological level, piezometric maps of the study area based on synchronous measurements show water flows generally oriented from southwest to northeast with an average hydraulic gradient of 1.2‰.

Geochemical data were obtained through sampling campaigns in accordance with French standard FD X 31–615 of December 2000 relating to sampling of groundwater in a borehole. The piezometers were always purged, and the physicochemical parameters, electrical conductivity, pH, dissolved oxygen, and redox, were monitored until stabilization before sampling. The samples taken from the site were collected in 20-mL vacuum clear glass vials, hermetically

sealed with magnetic caps topped with septa (silicone/PTFE, 1.3 mm thick, 18 mm diameter). Standards, consisting of different chloroethanes and chloroethenes sought, at known concentrations were inserted into the sequence of samples. The measurements of the concentrations of the chlorinated solvents were carried out using a gas phase chromatograph coupled to a quadrupole mass spectrometer (GC-qMS, type: 8860 GC System, Agilent; 5977B GC/MSD, Agilent). The carbon isotope ratios of chlorinated solvents were measured with a gas chromatograph coupled to an isotope ratio mass spectrometer (GC-IRMS). A type SPME fiber (Carboxen/PDMS 85 μm) was used. It was exposed to the samples for 15 min at a temperature of 60 °C, before it was introduced into the injector at 280 °C. The GC program is 35 °C for 5 min and then a gradient of 30 C/min up to 200 °C for 4 min. The detection is carried out in FID and in IrMS in CO2 detection.

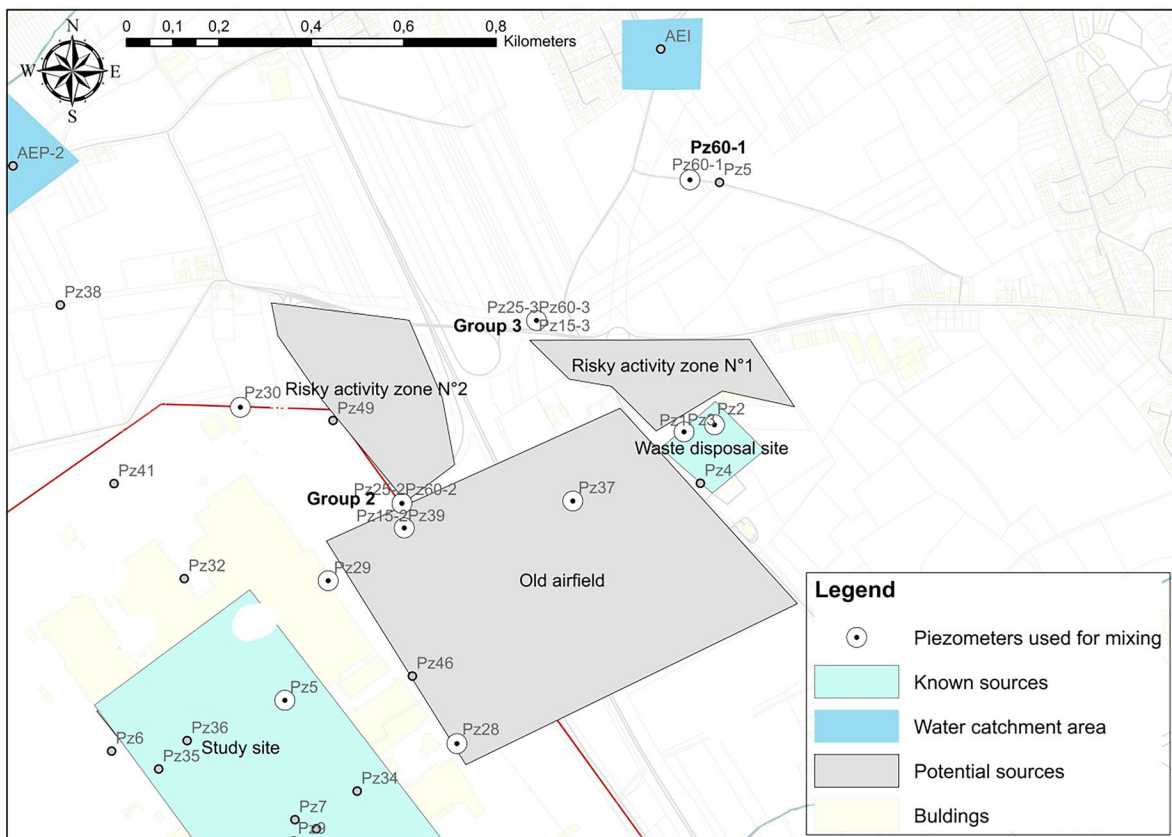


Fig. 1 Map of the studied area showing the piezometers and the potential sources of VOCs (named “risky activity zone” N°1, 2, and the old airfield)

Points used to calculate mixing

Three piezometers' downstream of the site were considered for the mixing calculations. The first point, Pz60-1 (Fig. 1), was chosen because of its proximity to an industrial water supply borehole on which it was necessary to calculate the contributions of the different sources of pollution. The second point, group 3, was considered because of the presence of chloroethanes at high concentrations. Finally, the third calculation point is the landfill (waste disposal site), because of its position downstream of the studied site and the presence of high concentrations of VOCs.

The configurations studied are presented in Table 1.

Methodology

Considering a point in the study area, the aim is to determine the proportions of groundwater coming from fixed points upstream. To reach this goal, the concentration data for several chemical elements quantified at these points in the groundwater are used. Then, the values of mixing fractions that minimize the differences between the simulated concentrations and those actually observed are determined by the solver.

Conservative sums of chlorinated compounds

The geochemical conditions of the groundwater showed mostly a dissolved oxygen level between 1 and 10 mg L⁻¹ and a redox potential that varies between 100 and 220 mV, except at one source zone (close to pz7) where the presence of co-contaminants such as BTEX can make the conditions locally anaerobic. The optimization parameters for the calculation are defined so that they are conservative quantities

under those conditions (Palau et al., 2016; Scheutz et al., 2011). In particular, when 1,1-DCA is produced by anaerobic degradation in the source or nearby anaerobic area and is transported to the groundwater where conditions are aerobic, it no longer degrades and is then a tracer of 1,1,1-TCA pollution. Moreover, there are no other pathways for the production of 1,1-DCA from other chlorinated solvents that could interfere with the 1,1-DCA from the source area (Palau et al., 2016).

On the other hand, the sums of 1,1,1-TCA + 1,1-DCE on one side and PCE + TCE + Cis-DCE on the other are preserved under aerobic conditions. Indeed, the degradation of 1,1-DCE or Cis-DCE (producing vinyl chloride) only takes place under highly anaerobic conditions (Palau et al., 2016).

Therefore, the following “conservative” quantities can be defined for the organic substances:

- 1,1-DCA
- 1,1,1-TCA + 1,1-DCE
- PCE + TCE + Cis-DCE

Major ion tracer

Chloride ions were added as parameters of the mixing calculation method due to their nonreactive and essentially conservative properties (Datta & Tyagi, 1996; Olmez & Hayes, 1990; Olmez et al., 1994; Schemel et al., 2006). The geochemical background (GB) for chloride is fixed at 9 mg L⁻¹ as it corresponds to average values outside the contaminated area. As the concentrations of chlorinated solvents are very small compared to the background Cl, their degradation will not interfere with Cl concentrations. The background value of VOCs is considered to be equal to zero.

Table 1 Studied configurations for the mixing calculation (for group 3 which is a multi-layer well, several sub-configurations were studied according to depth)

	Downstream piezometer	Upstream piezometers
Mixture reaching Pz60-1	Pz 60-1	Group 3 – Pz37–Pz2
Mixture reaching landfill	Pz2- Pz1 average	Pz39, Pz29, Pz5, Pz28
Mixture reaching Group3	Pz15-3	Pz15-2 – Pz30–Pz39
	Pz25-3	Pz25-2 – Pz30–Pz39
	Pz60-3	Pz60-2 – Pz30–Pz39
	Group3 (mean)	Group 2 (mean) – Pz30–Pz39

Isotope ratios

Chlorinated solvent pollution in industrial areas often involves several sources of the same compound (Aral et al., 2001; Wycisk, 2003). The use of the isotope ratios as an additional parameter of the mixing calculation can eventually make the method more robust by taking into account the isotopic signatures when they are distinct. Indeed, the values of the isotope ratios of a compound vary according to the synthesis process used (Beneteau et al., 1999; Jendrzewski et al., 2001; Shouakar-Stash et al., 2003; Van Warmerdam et al., 1995).

To take into account the fact that the isotope ratio of a parent substance like 1,1,1-TCA changes during hydrolysis, the parameter to be considered will be the total amount of carbon 13 of 1,1,1-TCA + 1,1-DCE, as ¹³C bounded to organic substance is conservative. The total carbon concentration C_{ij} of a compound i at a point j is given by the following Eq. (1):

$$C_{ij} = C_{ij}^{13C} + C_{ij}^{12C} \tag{1}$$

where C_{ij}^{13C} et C_{ij}^{12C} are, respectively, the 12 and 13 carbon concentrations of a compound i at point j .

The isotope ratio R_{ij}^{13C} of a compound i at a point j corresponds to the concentration ratio of the two isotopes given by:

$$R_{ij}^{13C} = \frac{C_{ij}^{13C}}{C_{ij}^{12C}} \tag{2}$$

By convention and in order to allow inter-laboratory comparisons, the isotopic ratio is expressed with delta notation:

$$\delta_{ij}^{13C} = \left(\frac{R_{ij}^{13C}}{R_{std}} - 1 \right) \tag{3}$$

where R_{std} is the isotope ratio of the standard. Its value is 0.011237 for carbon (Coplen et al., 2006).

Equations (1), (2), and (3), allow calculating ¹³C concentrations with the following equation:

$$C_{ij}^{13C} = C_{ij} \frac{\left(1 + \delta_{ij}^{13C} \right) R_{std}}{1 + \left(1 + \delta_{ij}^{13C} \right) R_{std}} \tag{4}$$

Finally, the ¹³C concentration of the sum 1,1,1-TCA + 1,1-DCE is given by Eq. 5:

$$^{13}C_{\sum(1,1,1-TCA+1,1-DCE)} = ^{13}C_{1,1,1-TCA} \chi_{1,1,1-TCA} + ^{13}C_{1,1-DCE} \chi_{1,1-DCE} \tag{5}$$

where χ is the aqueous molar fraction of the compound.

Optimization constraints

The variables of the optimization problem are subject to the laws of conservation of mass and are constrained by the observed concentration data.

Fractions and sum of the mixing fractions

Each mixing fraction for each point must lie between 0 and 1.

$$0 \leq X_j \leq 1 \tag{6}$$

For the sum of the mixing fractions, two options are possible:

- Option 1: It is considered that all the water arriving at the downstream point comes from the upstream points considered. Therefore, the sum of the mixing fractions at the n upstream points must be equal to 1.

$$\sum_{j=1}^n X_j = 1 \tag{7}$$

- Option 2: It is considered that only a part of the water arriving at the downstream point comes from upstream points not considered in the calculation, the rest coming from an unknown source. The sum of the mixing fractions at the n upstream points must then be less than 1.

$$\sum_{j=1}^n X_j < 1 \tag{8}$$

Option 2 was adopted in this study because of the complexity of the flows in the chalk aquifer. Indeed, there are sometimes zones of preferential flows which are not always compatible with the general directions of the flows obtained from the global piezometric maps.

Calculated concentrations

The concentration at the downstream point \overline{C}_i^{down} for each i specie or species group is calculated according to:

$$\overline{C}_i^{down} = \sum_{j=1}^n C_{i,j}^{up} X_j \quad (9)$$

where $C_{i,n}^{up}$ are the measured concentrations at the upstream point, X_j is the mixing fraction at each j upstream point, and n is the total number of considered upstream points.

The value of the calculated concentration \overline{C}_i^{down} for species i must not significantly exceed the measured one C_i^{down} :

$$\overline{C}_i^{down} \leq C_i^{down} \quad (10)$$

Description of the solver used

The Excel solver is used to solve the optimization problem. It makes it possible to find a set of optimal solutions for a given objective function. The solver acts on all the mixing fractions indirectly related to the objective function which respects defined constraints. The solver has 3 methods of resolution: (1) GRG nonlinear method for simple nonlinear problems (Lasdon et al., 1978; Murtagh & Saunders, 1978; Smith & Lasdon, 1992), (2) the Simplex PL for linear problems, and (3) the evolutionary method for complex problems (Grosan & Abraham, 2008; Van Hentenryck et al., 1997). The evolutionary method was chosen because the problem is nonlinear with several variables and parameters. Indeed, the evolutionary method treats each parameter (species or group of species) as an objective function and minimizes the difference between the measured and the calculated concentration. The advantage of this method of resolution is that the result is less sensitive to the initial values of the variables.

The objective function Φ to be minimized is expressed as follows:

$$\Phi = \sum_{i=1}^m dff_i \quad (11)$$

where m represents the total number of species, or group of species, considered and dff_i defined as:

$$\left\{ \begin{array}{l} dff_i = \frac{|C_i^{down} - \overline{C}_i^{down}|}{C_i^{down} + \overline{C}_i^{down}}, \text{ if } \overline{C}_i^{down} < C_i^{down} \\ dff_i = 5 * \frac{|C_i^{down} - \overline{C}_i^{down}|}{C_i^{down} + \overline{C}_i^{down}}, \text{ if } \overline{C}_i^{down} \geq C_i^{down} \end{array} \right. \quad (12)$$

The weight of 5 put on the lower part of Eq. (12) is an arbitrary penalty due to the analytical uncertainties. Indeed, it is possible that the estimated concentrations are higher than those measured due to analytical errors, though such a case is less probable.

Figure 2 illustrates the optimization method.

In order to increase the robustness of the method, average values of 3 sampling campaigns were considered for the calculations.

Validation of the mixing model

To validate the mixing model, a synthetic dataset with fixed mixing fractions was created with the BIOCHLOR-ISO analytical model (Höhener, 2016). The BIOCHLOR-ISO model assumes transport in a homogeneous medium with advection + dispersion + degradation, using the exact analytical solution of Cleary and Ungs (1978) for the degradation chain of chloroethenes.

Figure 3 illustrates the BIOCHLOR-ISO validation model and compares its results with those of the mixing calculation by nonlinear optimization model.

As shown in the table of mixing fractions and the concentration graphs of Fig. 3, the results simulated by the mixing calculation are the same as the data from the BIOCHLOR synthetic case. This illustrates that dispersion really acts as mixing.

Results

Results of the investigations carried out on the studied site

The geochemical conditions of the groundwater showed mostly a dissolved oxygen level between 1 and 10 mg L⁻¹ and a redox potential that varies between 100 and 220 mV, except at one source zone (close to

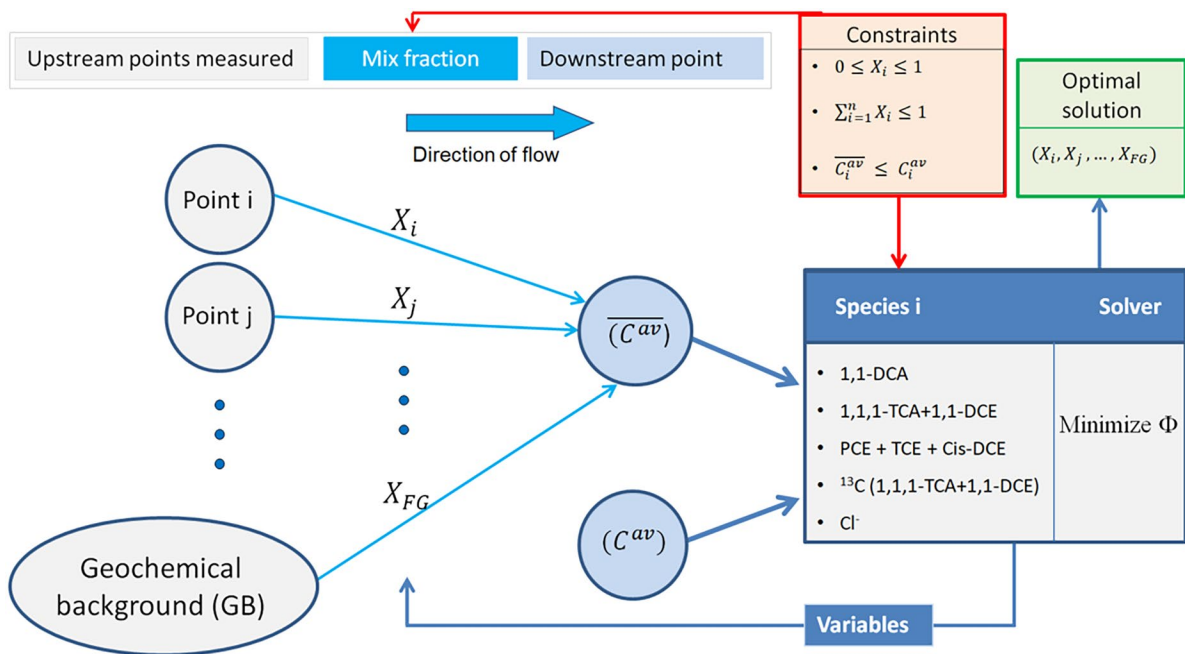


Fig. 2 Illustration of the used optimization strategy. For the evaluation of the solver, the initial values of the mixing fractions to be optimized are taken equal to 1 (i.e., 100%)

pz7) where the presence of co-contaminants such as BTEX can make the conditions locally anaerobic. Data on concentrations, isotope ratios of chlorinated compounds, and concentrations of the tracer (chloride ions) are provided in the supporting information.

Mixing results at Pz60-1 downgradient several potential sources of pollutants

The piezometer Pz60-1 is located downstream of several sources of pollution. The upstream piezometers considered are also downstream of the potential sources. The optimization results at Pz60-1 (Fig. 4) show differences in the range of 10 to 20% for the estimated and measured groundwater composition at group 3 and Pz37, respectively. A mixing fraction of 0.58 by unpolluted water was observed.

The optimized results show a 23% deficit on the 1,1,1-TCA+1,1-DCE sum compared to the measured concentration. This concentration deficit is accompanied by a 14% deficit on the carbon 13 concentration of the sum 1,1,1-TCA+1,1-DCE. The other parameters fitted quite well except for the chloride (deficit of 21%). Source detection is “yes” because the concentration predicted by the model is lower than the measured concentration

(± 15%, to take into account concentration measurement errors). Thus, the “yes” means that the concentrations of the waters of the piezometer considered do not come solely from the concentrations recorded in the piezometers upstream, which consequently suggest a missing source of the considered conservative sum.

Mixing results at group 3: a group of multi-level piezometers with varying concentrations

When piezometers have different depths with varying concentration data, it is necessary to take in to account the possible flowpaths. At group 3, three configurations according to depths (15 m, 25 m, and 60 m) were therefore studied. The mixing results are summarized in Table 2.

If the pollutants measured at the points of calculation are considered as a mixing of surface water table (i.e., between 15 and 18 m deep), the results essentially show a dilution by unpolluted water and an estimated mixing fraction of 0.19 for group 2. If, on the contrary, the pollutants measured are considered as a mixture of the deep part of the water table (from 25 to 60 m deep), the mixing fraction of group 2 decreases very slightly, but

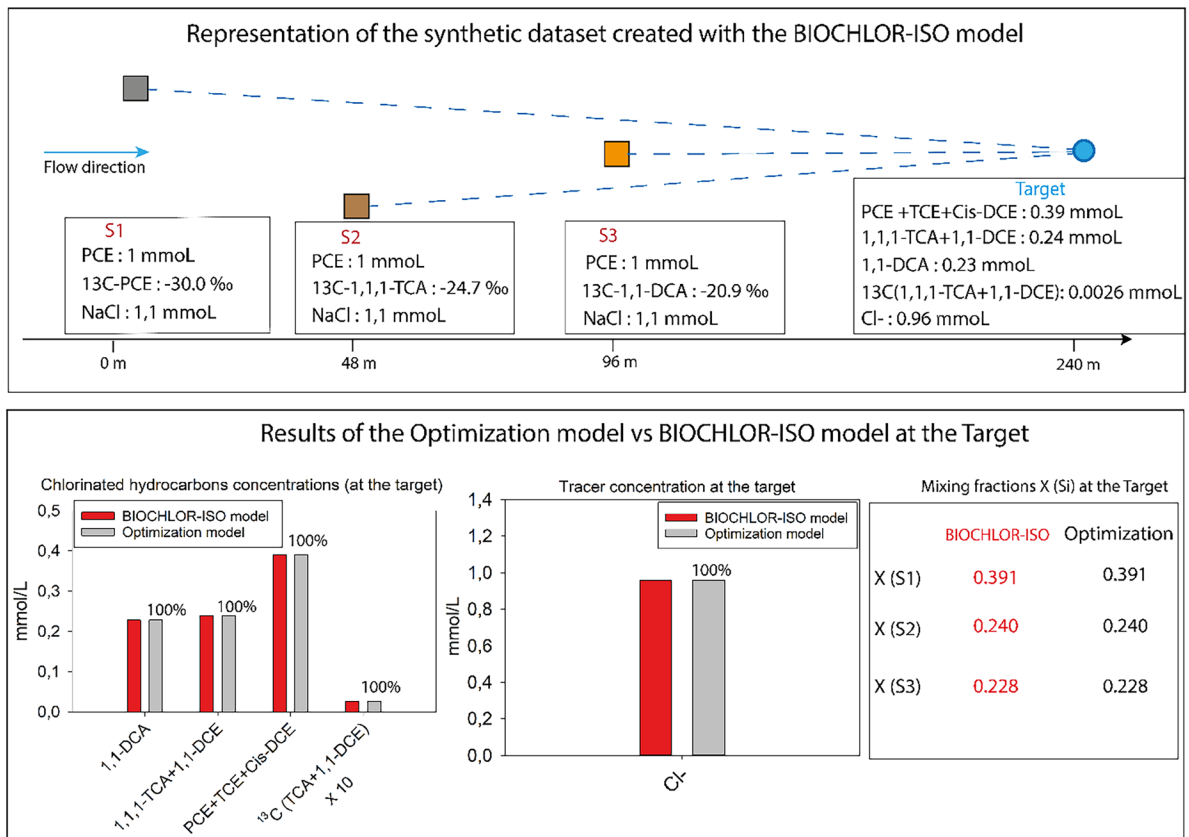


Fig. 3 Validation of the mixing calculation by nonlinear optimization model by a set of known data. The model parameters are as follows: the longitudinal dispersion coefficient

(0.2 m), lateral dispersion coefficient (0.1 m), the flow velocity (36.5 m year^{-1}), and the total simulation duration (20 years)

the geochemical background decreases sharply as to indicate a missing fraction of water. Finally, if the average concentration from all depths is considered, a fraction of 0.21 for group 3, a dilution of 0.57, and a significant difference between the calculated and measured concentrations of VOCs are highlighted (Fig. 5).

Mixing reaching the landfill

As said before, the landfill itself is a potential source of pollutant and in addition is located downstream from an identified source. The mixing results at the landfill by considering upgradient piezometers Pz28, Pz29, and Pz39 show a very close water composition compared to measured concentrations at the landfill except for the chloride ion (Fig. 6). This finding suggests the presence of a source of chloride at the landfill, or

between the considered upstream piezometers and the landfill, i.e., on the perimeter of the old airfield.

Effect of measurement errors on the mixing results

In order to test the robustness of the calculation method, an error ϵ is introduced into the measured concentrations as shown:

$$C_i^{\text{down}'} = C_i^{\text{down}} + \epsilon C_i^{\text{down}} \quad (13)$$

where $C_i^{\text{down}'}$ is the measured concentration with error and ϵ is the measurement error. In this study we chose to apply $\epsilon = 0.20$. Then the optimization is re-run with the new downgradient concentrations, leading to a difference in mixing fractions with the original case Δf . Table 3 shows the deviations Δf of the mixing fractions obtained with the error from that of the “error-free” case.

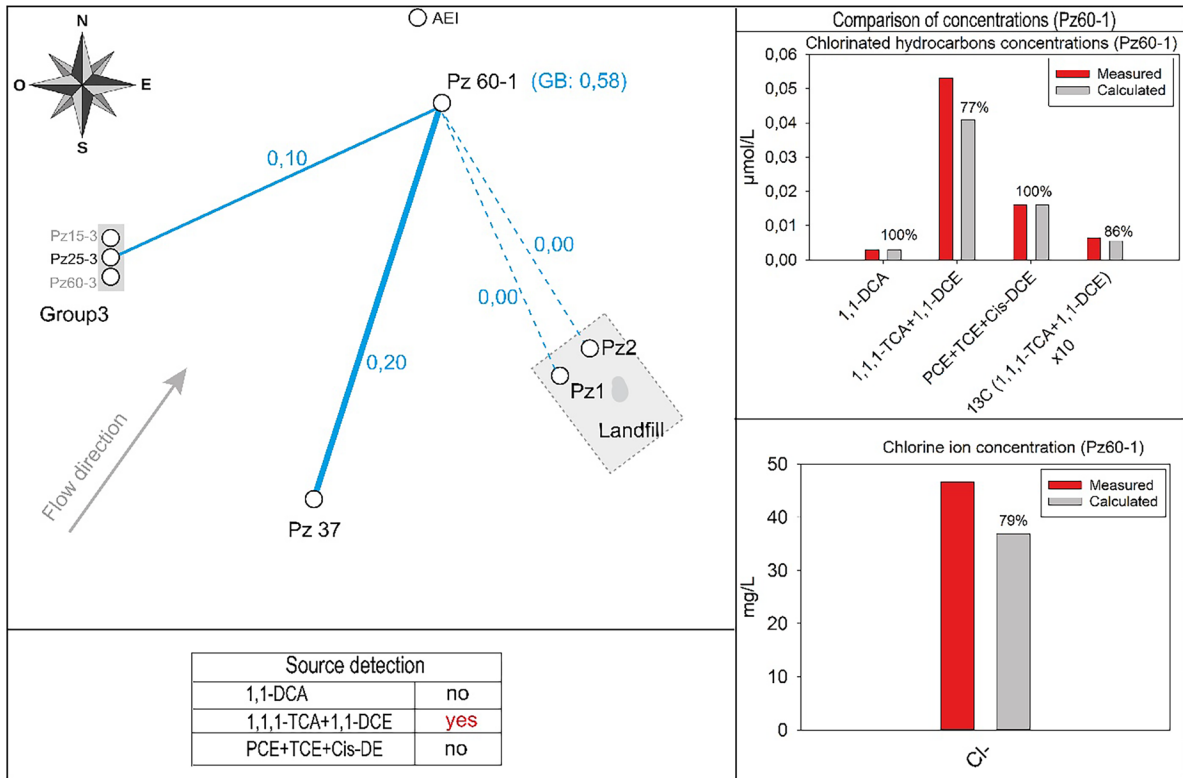


Fig. 4 Mixing fractions for the Pz60-1 well. Upgradient wells are group 3, Pz37, Pz1, and Pz2

Discussion

The case studied

The developed method allows the detection of an unidentified VOCs source while taking into consideration the possibility of the existence of degradation. If the measured isotopic ratios of a compound are significantly different between piezometers, the

method allows valuing this information and providing a better estimation of the mixing fractions. This is the case here with the mixing at Pz60-1 where the concentration of ¹³C-(1.1.1-TCA + 1.1-DCE) at Pz60-1 is 14% higher than the calculated value. The mixing calculations allowed us to understand that the water at Pz60-1 is a mixture of water coming from group 3 and Pz37 with a significant dilution by unpolluted water (Fig. 7).

Table 2 Summary of the fractions of water reaching group 3 according to the depths considered on the multi-level piezometers involved: at 15 m depth (scenario 1), at 25 m depth (scenario 2), and at 60 m depth (scenario 3), averaging all depths (scenario 4)

Different scenarios according to depths	Pz 30 (18 m)	Group 2 (15 m; 25 m; 60 m)	Pz 39 (18 m)	Geochemical background (GB)
Scenario 1 (15 m)	0.05	0.19 (15 m)	0.00	0.76
Scenario 2 (25 m)	0.00	0.15 (25 m)	0.06	0.24
Scenario 3 (60 m)	0.01	0.17 (60 m)	0.14	0.22
Scenario 4 (mean)	0.00	0.21 (mean)	0.00	0.57

The geochemical background (GB) represents the fraction of groundwater uncontaminated by chlorinated solvents

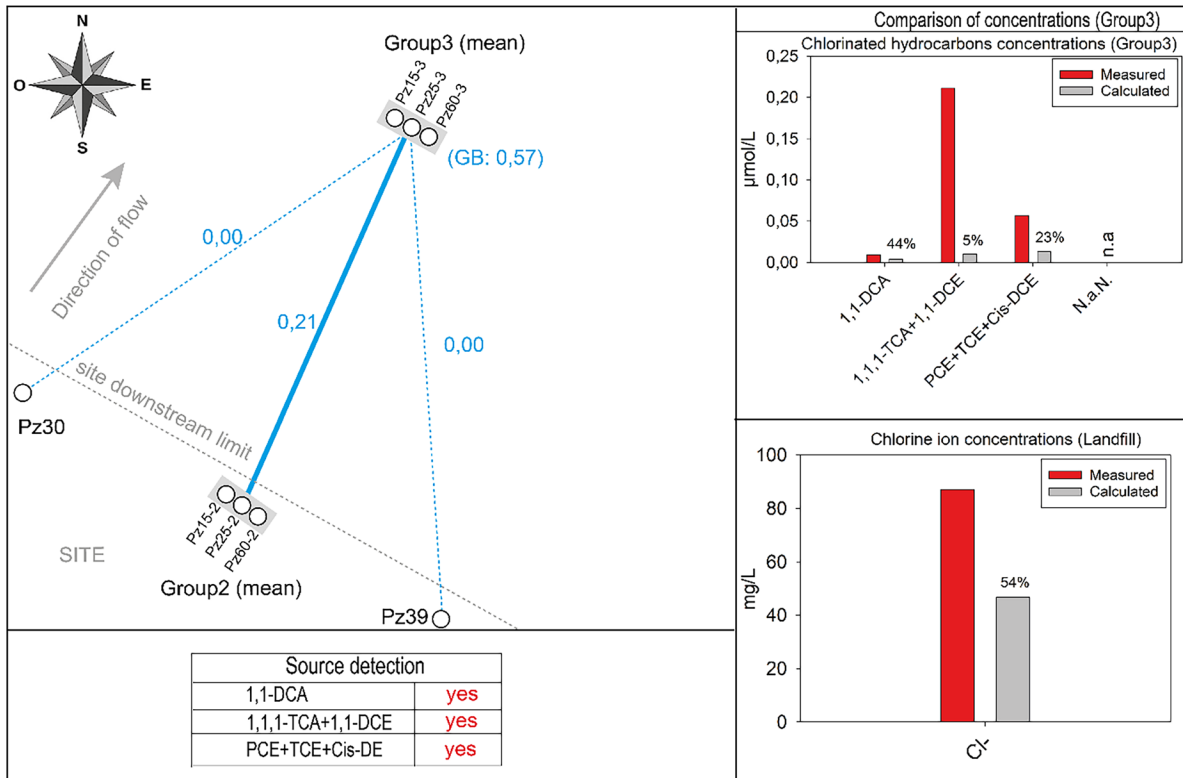


Fig. 5 Mixing fractions for the group 3 wells. Upgradient wells are Pz30, Pz39, and the group 2

At group 3, the concentration budget indicates a significant difference between calculated and measured VOCs concentrations, with only a 0.21 water fraction coming from group 2. This strongly suggests the contribution of an unidentified VOCs source.

In contrast, at the landfill, the mixing is very similar to the measured VOCs concentrations. However, the mixture suggests that a chloride source is missing. Given the known history of various wastes buried at the landfill, the missing chloride source could actually be from the degradation of pollution at the same landfill.

In summary, the studied method allows analyzing several aspects of the pollution transport and would be very useful for the investigations to locate sources of VOCs pollution in the groundwater.

Applicability of the method

The potential of the method developed for the identification of source of groundwater contaminants is

tested by its application on a complex industrial site with several sources of pollution. Two of these source areas are known and three other potential source areas co-exist. Groundwater flow direction, ions, and contaminant concentrations were used for this study. Assessments were made to determine the effect of measurement errors of concentrations on the calculated mixing fractions and on the results of the identification of sources.

The method is applicable when the studied site has a significant network of piezometers distributed in space, having data of concentrations of ions and contaminants. This is generally the case for sites with a history of pollution with VOCs. This method therefore applies to this type of site and is particularly suitable for cases of multi-pollution belonging to different companies. The incorporation of isotopic ratios of contaminants can only be done when these data exist for all the points considered in the calculation. It makes the identification method more robust, especially when the isotopic signatures of

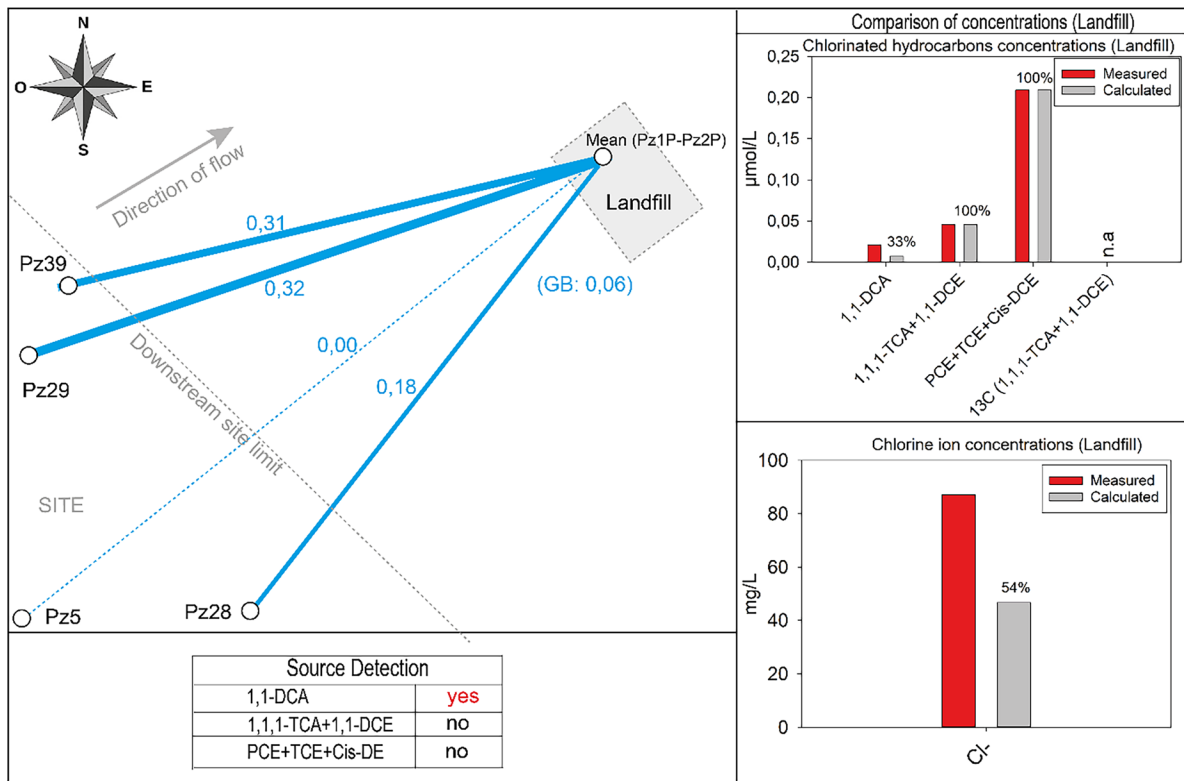


Fig. 6 Mixing fractions for the landfill (mean Pz1P-Pz2P). Upgradient wells are Pz39, Pz29, Pz5, and Pz28

the different sources are very distinct. A characterization of the groundwater flow direction remains however necessary to properly define the groups of piezometers to be considered in the calculations.

Robustness and limits of the method

Analysis of the effect of concentration measurement errors on the results shows that (1) measurement

Table 3 The deviations Δf of the mixing fractions, induced by an error ϵ of 20% on the measured concentrations

Δf /piezometer	Mixing for Pz60-1		Mixing for group3		Mixing for landfill	
	Piezometer	Δf value	Piezometer	Δf value	Piezometer	Δf value
Δf (GB)	Pz2-P	0.00	Pz30	0.00	Pz39	0.09
	Pz1-P	0.00	Pz39	-0.01	Pz29	-0.06
	Pz37	-0.05	Group2 (mean)	-0.04	Pz5	0.00
	Group3 (25 m)	-0.01	n.a	n.a	Pz28	-0.03
Source identification	Detection	Effect of ϵ	Detection	Effect of ϵ	Detection	Effect of ϵ
1.1-DCA	No	None	Yes	None	Yes	None
PCE+TCE+ Cis-DCE	Yes	None	Yes	None	No	None
1.1.1-TCA+1.1-DCE	No	None	Yes	None	No	None

One observes that in all cases the deviation is less than or equal to 0.11 and that the results on the identification of sources are not impacted by the measurement error

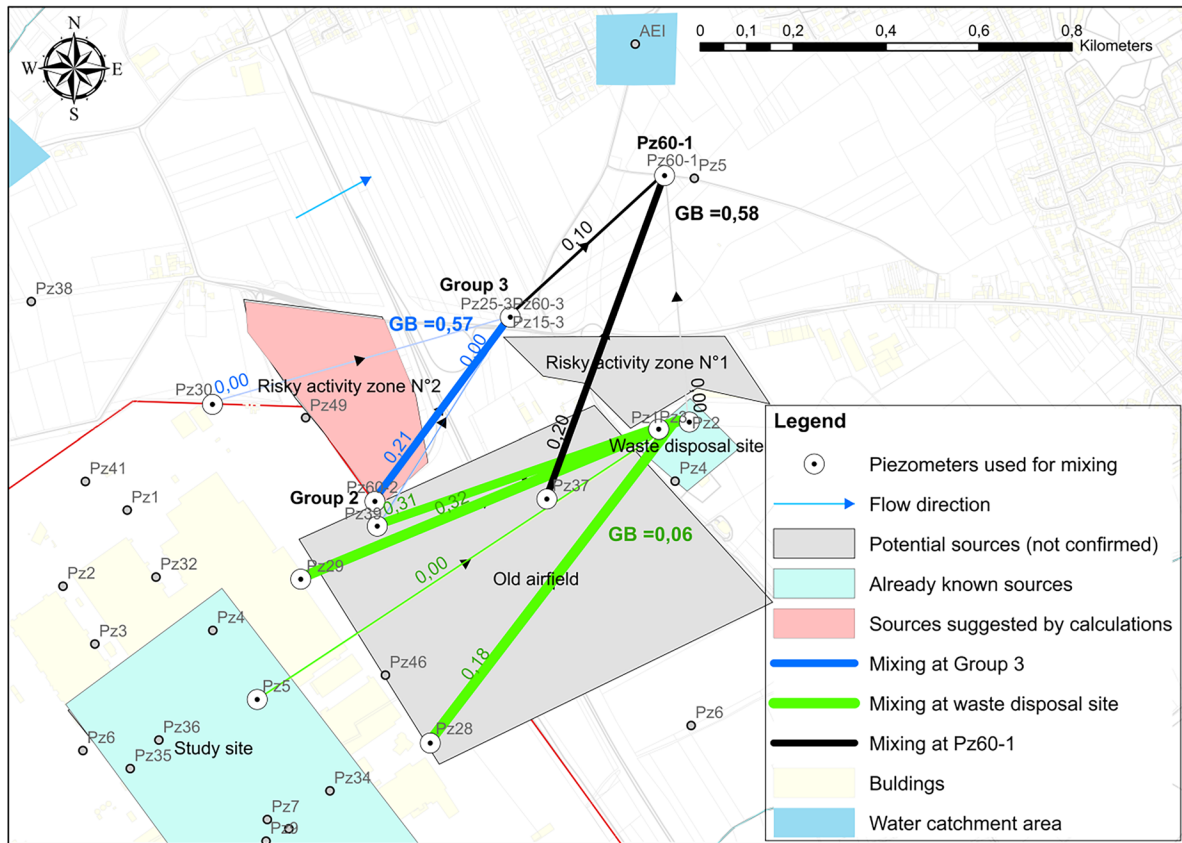


Fig. 7 Mixing fraction obtained by optimization at Pz60-1 (in black), group 3 (in blue), and at the landfill (in green)

errors on contaminant concentrations reduce the accuracy of the calculated mixing fractions. The error on the mixing fractions remains below 0.11 for an error of 0.20 on the measured concentrations. (2) The identification of unknown sources is not significantly influenced by the measurement errors on the concentrations.

The problem of source identification and calculation of mixing fractions is treated in this study as a nonlinear optimization problem with constraints on calculated concentrations and mixing fractions. Consequently, the solutions obtained are not necessarily optimal. In addition, there is a problem of uniqueness of the solutions and therefore an uncertainty related to that (Sun, 2013; Tikhonov & Arsenin, 1977). However, the solutions remain globally close if one adopts the evolutionary resolution method (Grosan & Abraham, 2008). Another limitation is that the approach does not take into account the temporal variation of concentrations. Indeed, if concentrations vary in the source zone,

these variations are not transmitted instantaneously to the downstream point and thus, the estimated mixing fractions will be erroneous.

Conclusion

A nonlinear optimization method for highlighting the contribution of an unknown source has been proposed in this work. In this optimization method, the water fractions from the upstream piezometers are treated as variables defined between 0 and 1. The parameters of the optimization problem are conservative sums of VOCs, tracers, and carbon isotope ratios of some VOCs. The use of conservative sums involves parent and daughter products in degradation chains and handles the problem of mass loss by degradation. The developed optimization method thus makes it possible to estimate the fractions of mixtures of each of the

upstream points and to highlight a possible excess of mass at the considered calculation point. An industrial area comprising several known and potential sources of VOCs is used to demonstrate the operation and the robustness of the method. The analysis of the effect of the measurement errors of the concentrations on the results shows that the source identification results are not significantly impacted by those errors. The calculation method can therefore be used to identify sources of contaminants using only data observed on the existing piezometric network. Once the source areas have been identified, techniques for precise delimitation of the sources can then be used in a more efficient and economical manner.

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Data availability All data generated or analyzed during this study are included in this published article and its supplementary information files.

Declarations

Consent for publication All authors agreed with the content and gave explicit consent to submit and they have obtained consent from the responsible authorities at the institute/organization where the work was carried out.

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