



**HAL**  
open science

## **Chlorinated solvents source identification by nonlinear optimization method**

Valeureux Illy, Gregory Cohen, Elicia Verardo, Patrick Höhener, Nathalie Guiserix,  
Olivier Atteia

► **To cite this version:**

Valeureux Illy, Gregory Cohen, Elicia Verardo, Patrick Höhener, Nathalie Guiserix, et al.. Chlorinated solvents source identification by nonlinear optimization method. *Environmental Monitoring and Assessment*, 2023, 195 (4), pp.531. <10.1007/s10661-023-11107-x>. <hal-04071563>

**HAL Id: hal-04071563**

**<https://amu.hal.science/hal-04071563v1>**

Submitted on 29 Jan 2024

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

1 **Chlorinated solvents source identification by non-linear optimization**  
2 **method.**

3 Valeureux D. Illy<sup>a,b,\*</sup>, Gregory J. V. Cohen<sup>a</sup>, Elicia Verardo<sup>a</sup>, Patrick Höhener<sup>c</sup>, Nathalie  
4 Guiserix<sup>b</sup>, Olivier Atteia<sup>a</sup>

5 <sup>a</sup> EA 4592, Géoressources et Environnement, Bordeaux INP, Université Bordeaux Montaigne,  
6 1 Avenue Dr Schweitzer, 33400 Talence, France

7 <sup>b</sup> Renault SAS, 1 Allée du Golf, Guyancourt 78 280, France

8 <sup>c</sup> Laboratoire de Chimie Environnementale-UMR 7376, Aix-Marseille Université-CNRS, 3  
9 place Victor Hugo - Case 29, 13331 Marseille Cedex 3

10 \*Author for correspondence: valeureux.illy@gmail.com

11 Tel: +33 6 37 74 19 51

12 Fax : +33 5 57 12 10 01

13

## 14 **1. Highlights**

- 15 • An unknown source of contaminants was detected by non-linear optimization method.
- 16 • The effect of measurement errors on a source identification are negligible.
- 17 • The uncertainties on the calculated mixing fractions are less than 11 %.

18

## 19 **2. Abstract**

20 In this work, chloride ions were used as conservative tracers and supplemented with  
21 conservative amounts of chloroethenes (PCE, TCE, Cis-DCE, 1,1-DCE), chloroethanes  
22 (1,1,1-TCA, 1,1-DCA) and the carbon isotope ratios of certain compounds, the most  
23 representative on the sites studied, which is a novelty compared to the optimization methods  
24 developed in the scientific literature so far. A location of the potential missing sources is then  
25 proposed in view of the balances of the calculated mixing fractions. A test of the influence of  
26 measurement errors on the results shows that the uncertainties in the calculation of the  
27 mixture fractions are less than 11%, indicating that the source identification method  
28 developed is a robust tool for identifying sources of chlorinated solvents in groundwater.

29

30 **3. Keywords:** Chlorinated solvents, Mixing models, non-linear optimization, Conservative  
31 tracers, Compound-specific isotope ratios

32

## 33 **4. Introduction**

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

42 [et al. 2006](#); [Chen et al. 2010](#); [Atteia et al. 2017, 2013](#); [Jousse et al. 2020](#); [Verardo et al. 2021](#)).  
43 In industrial areas, there can be several sources of contamination linked to different activities.  
44 In this context, historical data on the use of chemicals and the monitoring of incidents,  
45 acquired either by the public services or by the companies using these products, are often  
46 insufficient to provide answers on the locations of the sources and the contaminant fluxes that  
47 come out of it. It is therefore necessary to develop techniques which allow distinguishing all  
48 the pollutants sources and determining for each of these sources their contribution  
49 proportions. This would permit to discriminate the level of the responsibility shares in the  
50 management of the pollution ([Aronovsky 2000](#); [Marryott et al. 2000](#); [Morrison 2000](#); [Murphy  
51 and Morrison 2007](#); [Sauer and Uhler 1994](#); [Stout et al. 1998](#)).

52 After carrying out historical studies to locate potential sources of pollutants, the first approach  
53 is often to spatially characterize the pollution by identifying the chemical fingerprints of the  
54 water in piezometers of the study area. [Yang and Lee \(2012\)](#) have shown that the use of  
55 chemical fingerprints of several Volatile Organic Compounds (VOCs), combined with a good  
56 seasonal analysis, allow reliable source identification. However, depending on several  
57 physico-chemical parameters, certain processes can modify the pollutants chemistry and  
58 make the use of chemical fingerprints alone insufficient to identify sources and estimate their  
59 contributions ([Atmadja and Bagtzoglou 2001a](#); [Newell and Connor 1998](#); [Sun et al. 2006](#)). To  
60 overcome this, other approaches mainly use the power of Compound Specific Isotope  
61 Analysis (CSIA) which makes it possible to further constrain the models or to discriminate  
62 the origin of sources according to isotope ratios ([Blessing et al. 2009](#); [Hunkeler et al. 2004](#);  
63 [Kaown et al. 2014](#); [Mansuy et al. 1997](#); [Schmidt et al. 2004](#); [Smallwood et al. 2002](#); [Walker et  
64 al. 2005](#)).

65 To locate a source of groundwater pollution, inverse modeling is often used by adjoining  
66 advection-dispersion equations, and by exploiting the concentration data measured at  
67 piezometers. In the case of heterogeneous aquifers, source identification approaches combine  
68 inverse modeling with geostatistical and probabilistic methods ([Bagtzoglou et al. 1991](#);  
69 [Hwang et al. 2020](#); [Liu and Wilson 1995](#); [Michalak and Kitanidis 2004](#); [Neupauer and Wilson  
70 2005, 2001](#); [Snodgrass and Kitanidis 1997](#); [Wilson and Liu 1994](#)). The major limitations of  
71 these approaches are the fact that (i) they assume sources appearing simultaneously, and (ii)  
72 sometimes require (for Bayesian models) an a priori knowledge of potential locations. In  
73 contrast to probabilistic approaches, there are deterministic approaches which are based on

74 optimization methods (multiple regressions, minimization of a linear or non-linear function)  
75 coupled with inverse modeling including advection-dispersion equations (Essouayed et al.  
76 2020; Gorelick et al. 1983; Liu and Ball 1999; Mahar and Datta 2001, 1997; Samarskaia  
77 1995; Skaggs and Kabala 1994; Wagner 1992).

78 In this work, the last type of approach is adopted and the problem of identifying sources and  
79 calculating their contributions is formulated as a nonlinear optimization problem (Aral et al.  
80 2001; Aral and Guan 1996; Datta et al. 1989; Gorelick et al. 1983; Mahar and Datta 2001),  
81 which variables to be determined are the mixing fractions coming from the piezometers  
82 located upstream to the considered piezometer. When trying to determine the proportion of  
83 two sources, it is possible to avoid advection-dispersion modeling by simply assuming that a  
84 sample is a mixture of different types of water. This will not make it possible to identify the  
85 source location or emitted mass fluxes, but to determine whether the known sources can  
86 produce the concerned water sample.

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

## 94 **5. Case study**

### 95 **5.1. Studied site and potential pollutant sources**

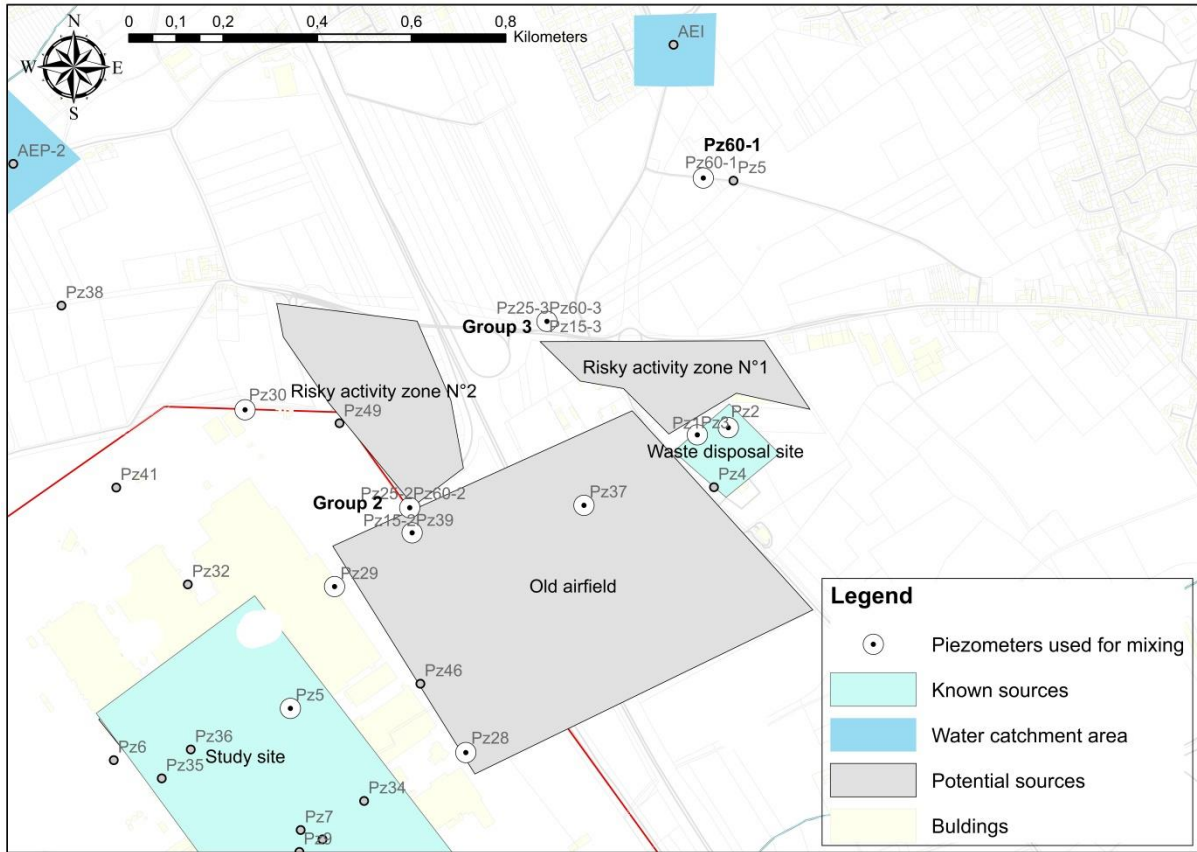
96 The study area is located on Quaternary silts lying on the Senonian chalks aquifer with a  
97 thickness of about 65 m. The impermeable substratum includes marls of the Middle and  
98 Lower Turonian. The sector is an industrial area housing an old airfield, an automobile  
99 production plant, various activity areas (welding, metalwork, ...), and a landfill where various  
100 wastes were buried in the past (Figure 1). The analysis of the concentrations of chlorinated  
101 solvents in all the piezometers shows the presence of the following compounds:  
102 Tetrachloroethene (PCE), Trichloroethene (TCE), cis-1,2-Dichloroethene (cis-DCE), 1,1,1-  
103 Trichloroethane (1,1,1-TCA), 1,1-Dichloroethene (1,1-DCE) and 1,1-Dichloroethane (1,1-  
104 DCA).

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

108 Geochemical data were obtained through sampling campaigns in accordance with French  
109 standard FD X 31-615 of December 2000 relating to sampling of groundwater in a borehole.  
110 The piezometers were always purged, and the physicochemical parameters: electrical  
111 conductivity, pH, dissolved oxygen and redox were monitored until stabilization before  
112 sampling. The samples taken from the site were collected in 20 mL vacuum clear glass vials,  
113 hermetically sealed with magnetic caps topped with septa (Silicone/PTFE, 1.3 mm thick, 18  
114 mm diameter ). Standards, consisting of different chloroethanes and chloroethenes sought, at  
115 known concentrations were inserted into the sequence of samples. The measurements of the  
116 concentrations of the chlorinated solvents were carried out using a gas phase chromatograph  
117 coupled to a quadrupole mass spectrometer (GC-qMS, type: 8860 GC System, Agilent;  
118 5977B GC/MSD, Agilent). The carbon isotope ratios of chlorinated solvents were measured  
119 with a Gas Chromatograph coupled to an Isotope Ratio Mass Spectrometer (GC-IRMS). A  
120 type SPME fiber (Carboxen/PDMS 85 µm) was used. It was exposed to the samples for 15  
121 min at a temperature of 60°C, before it was introduced into the injector at 280°C. The GC  
122 program is 35°C for 5 min then a gradient of 30°C/min up to 200°C for 4 minutes. The  
123 detection is carried out in FID and in IrMS in CO<sub>2</sub> detection.

## 124 5.2. Points used to calculate mixing

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



132

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

135 The configurations studied are presented in Table 1 below.

136 Table 1 : Studied configurations for the mixing calculation (for group 3 which is a multi-layer well,  
 137 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)	Group2 (mean) – Pz30 –Pz39

138

139

## 140 **6. Methodology**

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

### 146 **6.1. Conservative sums of chlorinated compounds**

147 The geochemical conditions of the groundwater showed mostly a dissolved oxygen level  
148 between 1 and 10 mg L<sup>-1</sup> and a redox potential that varies between 100 and 220 mV, except at  
149 one source zone (close to pz7) where the presence of co-contaminants such as BTEX can  
150 make the conditions locally anaerobic. The optimization parameters for the calculation are  
151 defined so that they are conservative quantities under those conditions (Palau et al. 2016;  
152 Scheutz et al. 2011). In particular, when 1,1-DCA is produced by anaerobic degradation in the  
153 source or nearby anaerobic area and is transported to the groundwater where conditions are  
154 aerobic, it no longer degrades and is then a tracer of 1,1,1-TCA pollution. Moreover, there are  
155 no other pathways for the production of 1,1-DCA from other chlorinated solvents that could  
156 interfere with the 1,1-DCA from the source area (Palau et al. 2016).

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

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

- 162 - 1,1-DCA
- 163 - 1,1,1-TCA + 1,1-DCE
- 164 - PCE + TCE + Cis-DCE

### 165 **6.2. Major ion tracer**

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

### 173 6.3. Isotope ratios

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

180 To take into account the fact that the isotope ratio of a parent substance like 1,1,1-TCA  
181 changes during hydrolysis, the parameter to be considered will be the total amount of carbon  
182 13 of 1,1,1-TCA+1,1-DCE, as <sup>13</sup>C bounded to organic substance is conservative. The total  
183 carbon concentration  $C_{i,j}$  of a compound  $i$  at a point  $j$  is given by the following equation (1):

$$184 \quad C_{i,j} = C_{i,j}^{13C} + C_{i,j}^{12C}, \quad (1)$$

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

187 The isotope ratio  $R_{i,j}^{\frac{13C}{12C}}$  of a compound  $i$  at a point  $j$ , corresponds to the concentration ratio of  
188 the two isotopes given by:

$$189 \quad R_{i,j}^{\frac{13C}{12C}} = \frac{C_{i,j}^{13C}}{C_{i,j}^{12C}} \quad (2)$$

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

192 
$$\delta_{i,j}^{\frac{13C}{12C}} = \left( \frac{R_{i,j}^{\frac{13C}{12C}}}{R_{std}} - 1 \right), \quad (3)$$

193 where  $R_{std}$  is the isotope ratio of the standard. Its value is 0.011237 for carbon (Coplen et al.  
194 2006).

195 Equations (1), (2) and (3), allow calculating  $^{13}C$  concentrations with the following equation:

196 
$$C_{i,j}^{13C} = C_{i,j} \frac{\left(1 + \delta_{i,j}^{\frac{13C}{12C}}\right) R_{std}}{1 + \left(1 + \delta_{i,j}^{\frac{13C}{12C}}\right) R_{std}} \quad (4)$$

197 Finally, the  $^{13}C$  concentration of the sum 1,1,1-TCA + 1,1-DCE is given by equation 5:

198 
$$^{13}C_{\Sigma(1,1,1-TCA+1,1-DCE)} = ^{13}C_{1,1,1-TCA} \chi_{1,1,1-TCA} + ^{13}C_{1,1-DCE} \chi_{1,1-DCE} \quad (5)$$

199 where  $\chi$  is the aqueous molar fraction of the compound.

## 200 6.4. Optimization constraints

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

### 203 6.4.1. Fractions and sum of the mixing fractions

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

205 
$$0 \leq X_j \leq 1 \quad (6)$$

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

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

210 
$$\sum_{j=1}^n X_j = 1 \quad (7)$$

211 - Option 2: It is considered that only a part of the water arriving at the downstream point  
212 comes from upstream points not considered in the calculation, the rest coming from an

213 unknown source. The sum of the mixing fractions at the  $n$  upstream points must then  
214 be less than 1.

$$215 \quad \sum_{j=1}^n X_j < 1 \quad (8)$$

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

#### 220 6.4.2. Calculated concentrations

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

$$223 \quad \overline{C_i^{down}} = \sum_{j=1}^n C_{i,j}^{up} X_j \quad (9)$$

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

226 The value of the calculated concentration  $\overline{C_i^{down}}$  for species  $i$  must not significantly exceed  
227 that of  $C_i^{down}$ :

$$228 \quad \overline{C_i^{down}} \leq C_i^{down} \quad (10)$$

#### 229 6.5. Description of the solver used

230 The Excel solver is used to solve the optimization problem. It makes it possible to find a set of  
231 optimal solutions for a given objective function. The solver acts on all the mixing fractions  
232 indirectly related to the objective function which respects defined constraints. The solver has  
233 3 methods of resolution: (1) GRG nonlinear method for simple nonlinear problems ([Lasdon et](#)  
234 [al. 1978](#); [Murtagh and Saunders 1978](#); [Smith and Lasdon 1992](#)), (2) the Simplex PL for linear  
235 problems and (3) the Evolutionary method for complex problems ([Grosan and Abraham 2008](#);  
236 [Van Hentenryck et al. 1997](#)). The evolutionary method was chosen because the problem is  
237 nonlinear with several variables and parameters. Indeed, the Evolutionary method treats each  
238 parameter (species or group of species) as an objective function and minimizes the difference

239 between the measured and the calculated concentration. The advantage of this method of  
 240 resolution is that the result is less sensitive to the initial values of the variables.

241 The objective function  $\Phi$  to be minimized is expressed as follows:

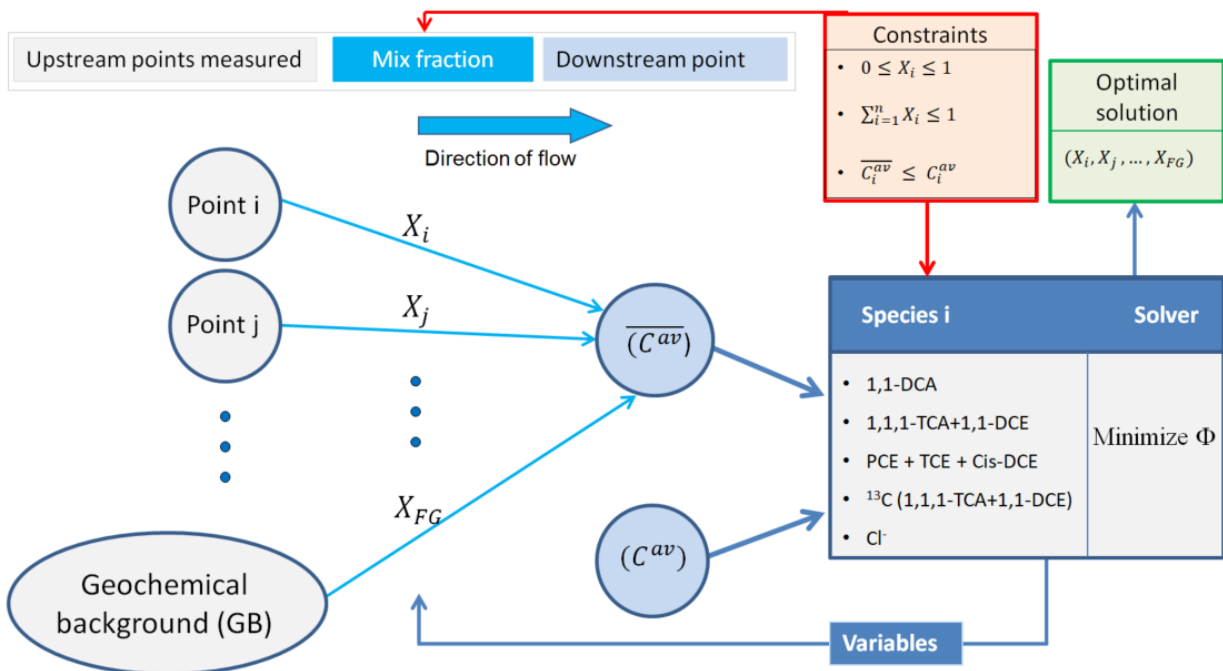
$$242 \quad \Phi = \sum_{i=1}^m \text{dff}_i, \quad (11)$$

243 where  $m$  represents the total number of species, or group of species, considered and  $\text{dff}_i$   
 244 defined as:

$$245 \quad \begin{cases} \text{dff}_i = \frac{|C_i^{\text{down}} - \overline{C_i^{\text{down}}}|}{C_i^{\text{down}} + \overline{C_i^{\text{down}}}}, & \text{if } \overline{C_i^{\text{down}}} < C_i^{\text{down}} \\ \text{dff}_i = 5 * \frac{|C_i^{\text{down}} - \overline{C_i^{\text{down}}}|}{C_i^{\text{down}} + \overline{C_i^{\text{down}}}}, & \text{if } \overline{C_i^{\text{down}}} \geq C_i^{\text{down}} \end{cases} \quad (12)$$

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

249 Figure 2 illustrates the optimization method.



250

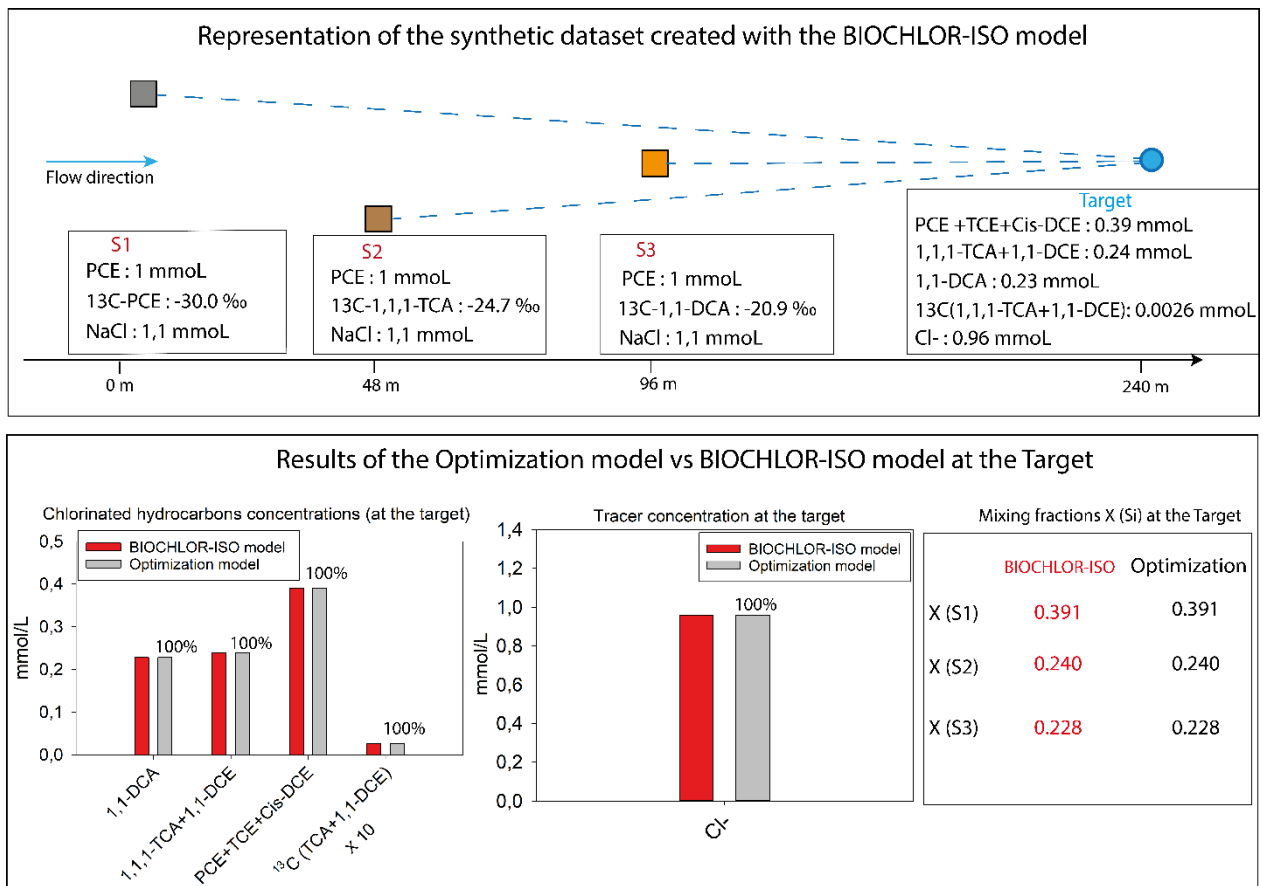
251 Figure 2 : Illustration of the used optimization strategy. For the evaluation of the solver, the initial  
 252 values of the mixing fractions to be optimized are taken equal to 1 (i.e. 100%).

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

255 **6.6. Validation of the mixing model**

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

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



262  
 263 Figure 3 : Validation of the mixing calculation by non-linear optimization model by a set of known  
 264 data. The model parameters are as follows: the longitudinal dispersion coefficient (0.2 m), lateral  
 265 dispersion coefficient (0.1 m), the flow velocity (36.5 m year<sup>-1</sup>), the total simulation duration (20  
 266 years).

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

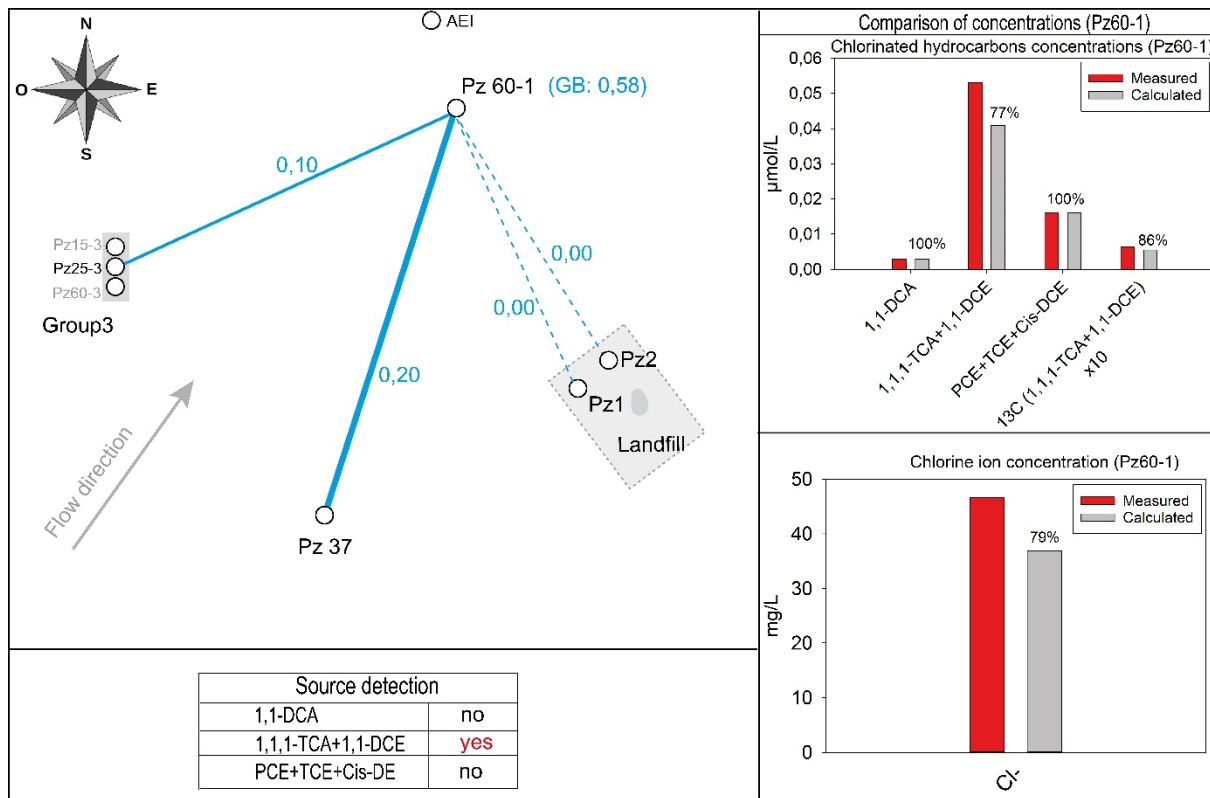
## 270 **7. Results**

### 271 **7.1. Results of the investigations carried out on the studied site**

272 The geochemical conditions of the groundwater showed mostly a dissolved oxygen level  
273 between 1 and 10 mg L<sup>-1</sup> and a redox potential that varies between 100 and 220 mV, except at  
274 one source zone (close to pz7) where the presence of co-contaminants such as BTEX can  
275 make the conditions locally anaerobic. Data on concentrations, isotope ratios of chlorinated  
276 compounds and concentrations of the tracer (chloride ions) are provided in the supporting  
277 information.

### 278 **7.2. Mixing results at Pz60-1. downgradient several potential sources of pollutants**

279 The piezometer Pz60-1 is located downstream of several sources of pollution. The upstream  
280 piezometers considered are also downstream of the potential sources. The optimization results  
281 at Pz60-1 (Figure 4) show differences in the range of 10 to 20% for the estimated and  
282 measured groundwater composition at Group-3 and Pz37. respectively. A mixing fraction of  
283 0.58 by unpolluted water was observed.



284

285 Figure 4 : Mixing fractions for the Pz60-1 well. Upgradient wells are: Group 3, Pz37, Pz1 and Pz2

286

287 The optimized results show a 23 % deficit on the 1.1.1-TCA+1.1-DCE sum compared to the  
 288 measured concentration. This concentration deficit is accompanied by a 14% deficit on the  
 289 carbon-13 concentration of the sum 1.1.1-TCA + 1.1-DCE. The other parameters fitted quite  
 290 well except for the chloride (deficit of 21 %). Source detection is “yes” because the  
 291 concentration predicted by the model is lower than the measured concentration ( $\pm 15\%$ , to take  
 292 into account concentration measurement errors). Thus, the “yes” means that the  
 293 concentrations of the waters of the piezometer considered do not come solely from the  
 294 concentrations recorded in the piezometers upstream; which consequently suggest a missing  
 295 source of the considered conservative sum.

296 **7.3. Mixing results at Group 3. a group of multi-level piezometers with varying**  
 297 **concentrations**

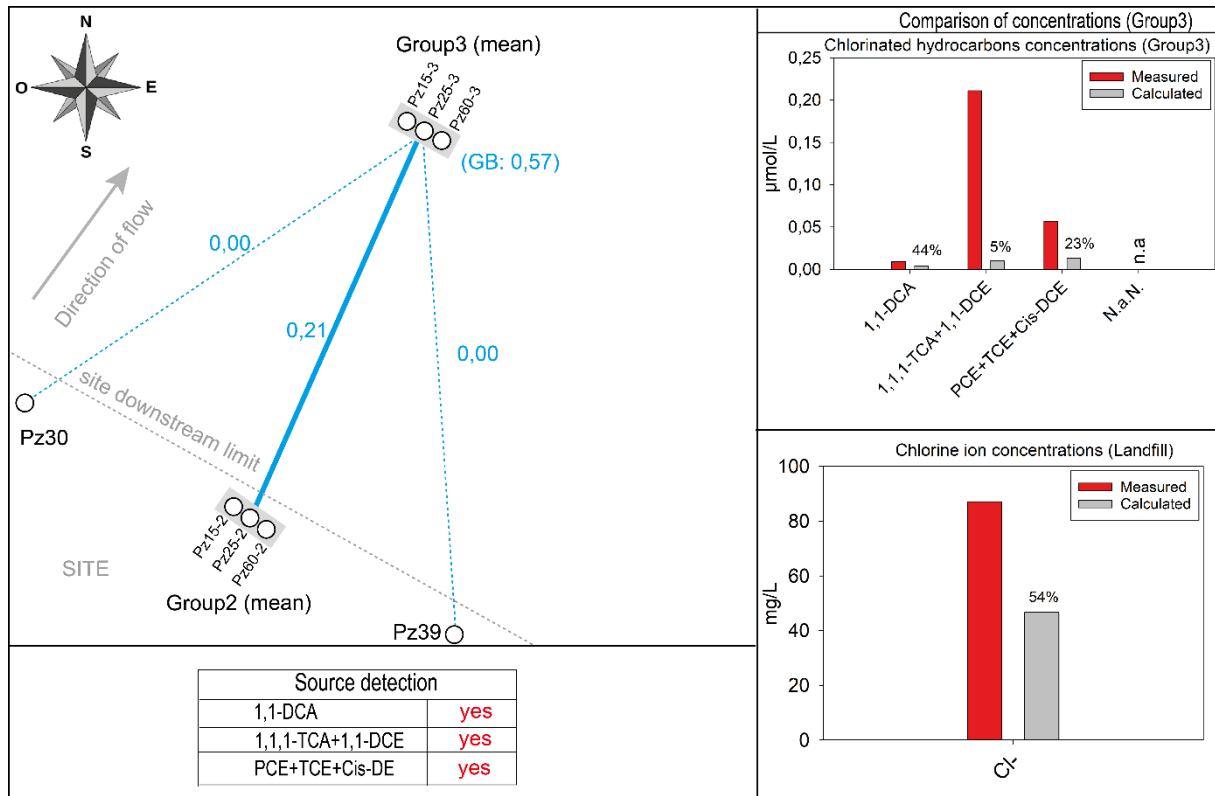
298 When piezometers have different depths with varying concentration data, it is necessary to  
 299 take in to account the possible flowpaths. At Group 3, three configurations according to

300 depths (15 m, 25 m, and 60 m) were therefore studied. The mixing results are summarized in  
 301 Table 2.

302 Table 2 : Summary of the fractions of water reaching Group 3 according to the depths considered on  
 303 the multilevel piezometers involved: at 15 m depth (scenario 1), at 25 m depth (scenario 2), at 60 m  
 304 depth (scenario 3), averaging all depths (scenario 4). The geochemical background (GB) represents the  
 305 fraction of groundwater uncontaminated by chlorinated solvents.

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

306 If the pollutants measured at the points of calculation are considered as a mixing of surface  
 307 water table (i.e., between 15 and 18 m deep), the results essentially show a dilution by  
 308 unpolluted water and an estimated mixing fraction of 0.19 for Group 2. If, on the contrary, the  
 309 pollutants measured is considered as a mixture of the deep part of the water table (from 25 to  
 310 60 m deep), the mixing fraction of Group 2 decreases very slightly but the geochemical  
 311 background decreases sharply as to indicate a missing fraction of water. Finally, if the average  
 312 concentration from all depths is considered, a fraction of 0.21 for Group 3 a dilution of 0.57  
 313 and a significant difference between the calculated and measured concentrations of VOCs are  
 314 highlighted (Figure 5).

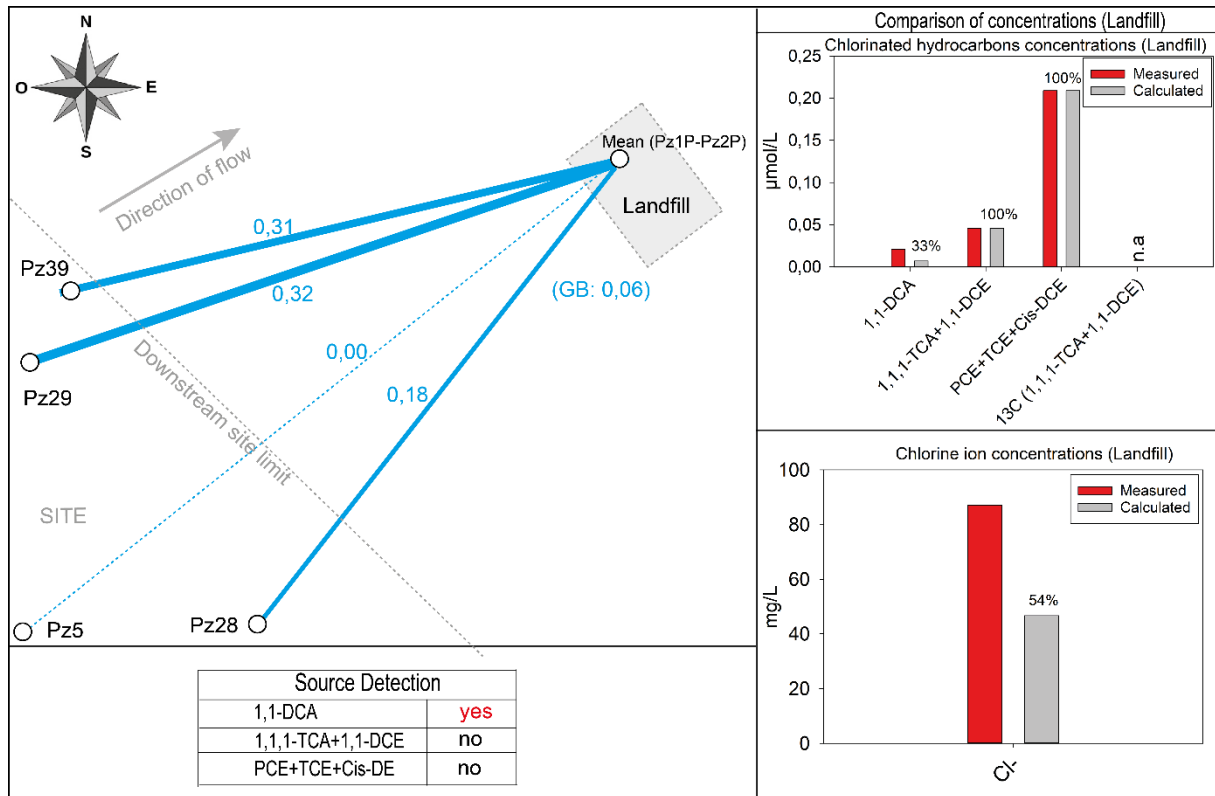


315

316 Figure 5 : Mixing fractions for the group 3 wells. Upgradient wells are: Pz30, Pz39 and the Group 2.

317 **7.4. Mixing reaching the landfill**

318 As said before, the landfill itself is a potential source of pollutant and in addition is located  
 319 downstream from an identified source. The mixing results at the landfill by considering  
 320 upgradient piezometers Pz28, Pz29, and Pz39, show a very close water composition compared  
 321 to measured concentrations at the landfill except for the chloride ion (Figure 6). This finding  
 322 suggests the presence of a source of chloride at the landfill, or between the considered  
 323 upstream piezometers and the landfill, i.e. on the perimeter of the old airfield.



324

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

327 **7.5. Effect of measurement errors on the mixing results**

328 In order to test the robustness of the calculation method, an error  $\varepsilon$  is introduced into the  
 329 measured concentrations as shown:

330 
$$C_i^{down'} = C_i^{down} + \varepsilon C_i^{down} . \quad (12)$$

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

336

337

338

339 Table 3 : The deviations  $\Delta f$  of the mixing fractions, induced by an error  $\epsilon$  of 20 % on the measured  
 340 concentrations

$\Delta f$ / piezometer	Mixing for Pz60-1		Mixing for group3		Mixing for Landfill	
	Piezometer	$\Delta f$ value	Piezometer	$\Delta f$ value	Piezometer	$\Delta f$ value
	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 (25m)	-0.01	n.a	n.a	Pz28	-0.03
$\Delta f$ (GB)	n.a	-0.06	n.a	-0.11	n.a	0.06
Source identification	Detection	Effect of $\epsilon$	Detection	Effect of $\epsilon$	Detection	Effect of $\epsilon$
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

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

## 343 8. Discussion

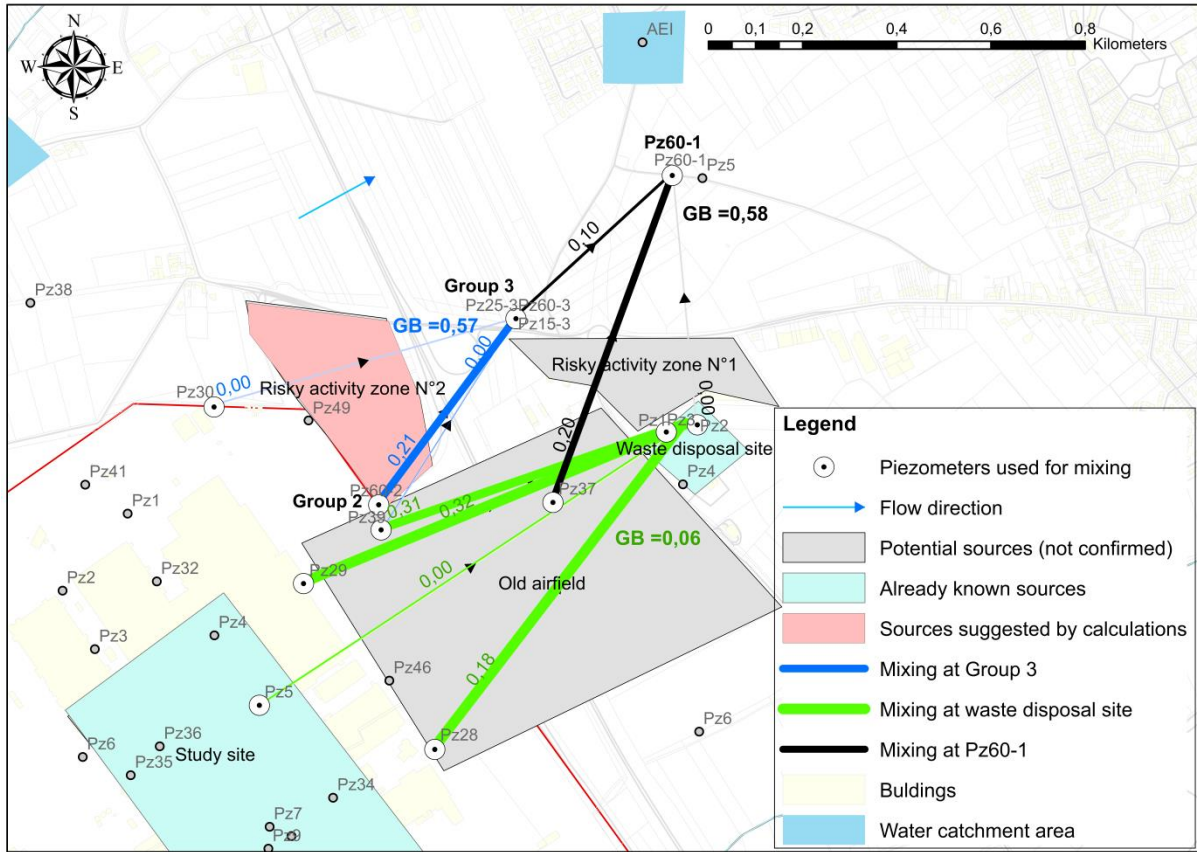
### 344 8.1. The case studied

345 The developed method allows the detection of an unidentified VOCs source while taking into  
 346 consideration the possibility of the existence of degradation. If the measured isotopic ratios of  
 347 a compound are significantly different between piezometers, the method allows valuing this  
 348 information and providing a better estimation of the mixing fractions. This is the case here  
 349 with the mixing at Pz60-1 where the concentration of  $^{13}\text{C}$ -(1.1.1-TCA+1.1-DCE) at Pz60-1 is  
 350 14% higher than the calculated value. The mixing calculations allowed us to understand that  
 351 the water at Pz60-1 is a mixture of water coming from Group 3 and Pz37 with a significant  
 352 dilution by unpolluted water (Figure 7).

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

356 In contrast, at the landfill, the mixing is very similar to the measured VOCs concentrations.  
 357 However, the mixture suggests that a chloride source is missing. Given the known history of

358 various wastes buried at the landfill, the missing chloride source could actually be from the  
 359 degradation of pollution at the same landfill.



360  
 361 Figure 7 : Mixing fraction obtained by optimization at Pz60-1 (in black), group 3 (in blue) and the  
 362 landfill (in green)

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

## 366 8.2. Applicability of the method

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

373 The method is applicable when the studied site has a significant network of piezometers  
374 distributed in space, having data of concentrations of ions and contaminants. This is generally  
375 the case for sites with a history of pollution with VOCs. This method therefore applies to this  
376 type of site and is particularly suitable for cases of multi-pollution belonging to different  
377 companies. The incorporation of isotopic ratios of contaminants can only be done when these  
378 data exist for all the points considered in the calculation. It makes the identification method  
379 more robust, especially when the isotopic signatures of the different sources are very distinct.  
380 A characterization of the groundwater flow direction remains however necessary to properly  
381 define the groups of piezometers to be considered in the calculations.

### 382 8.3. Robustness and limits of the method

383 Analysis of the effect of concentration measurement errors on the results shows that: (1)  
384 measurement errors on contaminant concentrations reduce the accuracy of the calculated  
385 mixing fractions. The error on the mixing fractions remains below 0.11 for an error of 0.20 on  
386 the measured concentrations. (2) The identification of unknown sources is not significantly  
387 influenced by the measurement errors on the concentrations.

388 The problem of source identification and calculation of mixing fractions is treated in this  
389 study as a nonlinear optimization problem with constraints on calculated concentrations and  
390 mixing fractions. Consequently, the solutions obtained are not necessarily optimal. In  
391 addition, there is a problem of uniqueness of the solutions and therefore an uncertainty related  
392 to that ([Sun 2013](#); [Tikhonov and Arsenin 1977](#)). However, the solutions remain globally close  
393 if one adopts the Evolutionary resolution method ([Grosan and Abraham 2008](#)). Another  
394 limitation is that the approach does not take into account the temporal variation of  
395 concentrations. Indeed, if concentrations vary in the source zone, these variations are not  
396 transmitted instantaneously to the downstream point and thus, the estimated mixing fractions  
397 will be erroneous.

## 398 9. Conclusion

399 A nonlinear optimization method for highlighting the contribution of an unknown source has  
400 been proposed in this work. In this optimization method, the water fractions from the  
401 upstream piezometers are treated as variables defined between 0 and 1. The parameters of the  
402 optimization problem are conservative sums of VOCs, tracers and carbon isotope ratios of  
403 some VOCs. The use of conservative sums involves parent and daughter products in

404 degradation chains and handles the problem of mass loss by degradation. The developed  
405 optimization method thus makes it possible to estimate the fractions of mixtures of each of the  
406 upstream points and to highlight a possible excess of mass at the considered calculation point.  
407 An industrial area comprising several known and potential sources of VOCs is used to  
408 demonstrate the operation and the robustness of the method. The analysis of the effect of the  
409 measurement errors of the concentrations on the results shows that the source identification  
410 results are not significantly impacted by those errors. The calculation method can therefore be  
411 used to identify sources of contaminants using only data observed on the existing piezometric  
412 network. Once the source areas have been identified, techniques for precise delimitation of the  
413 sources can then be used in a more efficient and economical manner.

414

#### 415 **Author contributions**

416 Valeureux D. Illy: Conceptualization, Writing.

417 Gregory Cohen: Review & editing.

418 Elicia Verardo: Conceptualization.

419 Patrick Höhener: Supervision, Conceptualization, Review.

420 Nathalie Guiserix: Funding acquisition.

421 Olivier Attéia: Supervision, Conceptualization, Review.

422

#### 423 **Data availability**

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

426

#### 427 **Declarations**

#### 428 **Consent for publication**

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

### 432 **Competing interests**

433 This article is published as part of a doctoral thesis funded by the RENAULT GROUP and the  
434 French ANRT.

435

### 436 **References**

437 Allen. D.J.. Darling. W.G.. Davies. J.. Newell. A.J.. Goody. D.C.. Collins. A.L.. 2014.  
438 Groundwater conceptual models: implications for evaluating diffuse pollution  
439 mitigation measures. *Q. J. Eng. Geol. Hydrogeol.* **47**. 65–80.

440 Aral. M.M.. Guan. J.. 1996. Genetic algorithms in search of groundwater pollution sources. In  
441 'Advances in Groundwater Pollution Control and Remediation'. Springer. pp. 347–  
442 369.

443 Aral. M.M.. Guan. J.. Maslia. M.L.. 2001. Identification of Contaminant Source Location and  
444 Release History in Aquifers. *J. Hydrol. Eng.* **6**. 225–234.  
445 [https://doi.org/10.1061/\(ASCE\)1084-0699\(2001\)6:3\(225\)](https://doi.org/10.1061/(ASCE)1084-0699(2001)6:3(225))

446 Aronovsky. R.G.. 2000. Liability theories in contaminated groundwater litigation. *Environ.*  
447 *Forensics* **1**. 97–116.

448 Atmadja. J.. Bagtzoglou. A.C.. 2001a. Pollution source identification in heterogeneous porous  
449 media. *Water Resour. Res.* **37**. 2113–2125.

450 Atmadja. J.. Bagtzoglou. A.C.. 2001b. State of the art report on mathematical methods for  
451 groundwater pollution source identification. *Environ. Forensics* **2**. 205–214.

452 Atteia. O.. Estrada. E.D.C.. Bertin. H.. 2013. Soil flushing: a review of the origin of efficiency  
453 variability. *Rev. Environ. Sci. Biotechnol.* **12**. 379–389.

454 Atteia. O.. Jousse. F.. Cohen. G.. Höhener. P.. 2017. Comparison of residual NAPL source  
455 removal techniques in 3D metric scale experiments. *J. Contam. Hydrol.* **202**. 23–32.

- 456 Azzellino. A.. Colombo. L.. Lombi. S.. Marchesi. V.. Piana. A.. Andrea. M.. Alberti. L..  
457 2019. Groundwater diffuse pollution in functional urban areas: The need to define  
458 anthropogenic diffuse pollution background levels. *Sci. Total Environ.* **656**. 1207–  
459 1222.
- 460 Bagtzoglou. A.C.. Tompson. A.F.. Dougherty. D.E.. 1991. Probabilistic simulation for  
461 reliable solute source identification in heterogeneous porous media. In 'Water  
462 Resources Engineering Risk Assessment'. Springer. pp. 189–201.
- 463 Balderacchi. M.. Benoit. P.. Cambier. P.. Eklo. O.M.. Gargini. A.. Gemitzi. A.. Gurel. M..  
464 Kløve. B.. Nakic. Z.. Predaa. E.. Ruzicic. S.. Wachniew. P.. Trevisan. M.. 2013.  
465 Groundwater Pollution and Quality Monitoring Approaches at the European Level.  
466 *Crit. Rev. Environ. Sci. Technol.* **43**. 323–408.  
467 <https://doi.org/10.1080/10643389.2011.604259>
- 468 Beneteau. K.M.. Aravena. R.. Frapce. S.K.. 1999. Isotopic characterization of chlorinated  
469 solventsD laboratory and ®eld results. *Org. Geochem.* 15.
- 470 Blessing. M.. Schmidt. T.C.. Dinkel. R.. Haderlein. S.B.. 2009. Delineation of multiple  
471 chlorinated ethene sources in an industrialized area□ A forensic field study using  
472 compound-specific isotope analysis. *Environ. Sci. Technol.* **43**. 2701–2707.
- 473 Chen. K.-F.. Kao. C.-M.. Chen. C.-W.. Surampalli. R.Y.. Lee. M.-S.. 2010. Control of  
474 petroleum-hydrocarbon contaminated groundwater by intrinsic and enhanced  
475 bioremediation. *J. Environ. Sci.* **22**. 864–871.
- 476 Christ. J.A.. Ramsburg. C.A.. Pennell. K.D.. Abriola. L.M.. 2010. Predicting DNAPL mass  
477 discharge from pool-dominated source zones. *J. Contam. Hydrol.* **114**. 18–34.
- 478 Cleary. R.W.. Unger. M.J.. 1978. Analytical models for groundwater pollution and hydrology.  
479 Water Resources Program. Department of Civil Engineering. Princeton University.
- 480 Coplen. T.B.. Brand. W.A.. Gehre. M.. Gröning. M.. Meijer. H.A.. Toman. B.. Verkouteren.  
481 R.M.. 2006. New guidelines for  $\delta^{13}\text{C}$  measurements. *Anal. Chem.* **78**. 2439–2441.
- 482 Datta. B.. Beegle. J.E.. Kavvas. M.L.. Orlob. G.T.. 1989. Development of an expert-system  
483 embedding pattern-recognition techniques for pollution-source identification. Report

484 for 30 September 1987-29 November 1989. California Univ., Davis, CA (USA). Dept.  
485 of Civil Engineering.

486 Datta, P.S., Tyagi, S.K., 1996. Major ion chemistry of groundwater in Delhi area: chemical  
487 weathering processes and groundwater flow regime. *J.-Geol. Soc. India* **47**. 179–188.

488 Essouayed, E., Verardo, E., Pryet, A., Chassagne, R.L., Atteia, O., 2020. An iterative strategy  
489 for contaminant source localisation using GLMA optimization and Data Worth on two  
490 synthetic 2D Aquifers. *J. Contam. Hydrol.* **228**. 103554.

491 Gorelick, S.M., Evans, B., Remson, I., 1983. Identifying sources of groundwater pollution:  
492 An optimization approach. *Water Resour. Res.* **19**. 779–790.

493 Grosan, C., Abraham, A., 2008. A New Approach for Solving Nonlinear Equations Systems.  
494 *IEEE Trans. Syst. Man Cybern. - Part Syst. Hum.* **38**. 698–714.  
495 <https://doi.org/10.1109/TSMCA.2008.918599>

496 Guilbeault, M.A., Parker, B.L., Cherry, J.A., 2005. Mass and flux distributions from DNAPL  
497 zones in sandy aquifers. *Groundwater* **43**. 70–86.

498 Höhener, P., Hunkeler, D., Hess, A., Bregnard, T., Zeyer, J., 1998. Methodology for the  
499 evaluation of engineered in situ bioremediation: lessons from a case study. *J.*  
500 *Microbiol. Methods* **32**. 179–192.

501 Hunkeler, D., Chollet, N., Pittet, X., Aravena, R., Cherry, J.A., Parker, B.L., 2004. Effect of  
502 source variability and transport processes on carbon isotope ratios of TCE and PCE in  
503 two sandy aquifers. *J. Contam. Hydrol.* **74**. 265–282.  
504 <https://doi.org/10.1016/j.jconhyd.2004.03.003>

505 Hwang, H.-T., Jeon, S.-W., Kaown, D., Lee, S.-S., Sudicky, E.A., Steinmoeller, D.T., Lee,  
506 K.-K., 2020. Backward Probability Model for Identifying Multiple Contaminant  
507 Source Zones Under Transient Variably Saturated Flow Conditions. *Water Resour.*  
508 *Res.* **56**. e2019WR025400. <https://doi.org/10.1029/2019WR025400>

509 Jendrzewski, N., Eggenkamp, H.G.M., Coleman, M.L., 2001. Characterisation of  
510 chlorinated hydrocarbons from chlorine and carbon isotopic compositions: scope of  
511 application to environmental problems. *Appl. Geochem.* **16**. 1021–1031.

- 512 Jousse. F.. Höhener. P.. Cohen. G.. Atteia. O.. 2020. Comparing the Efficiency of Oxidation.  
513 Sparging. Surfactant Flushing. and Thermal Treatment at Different Scales (Batch.  
514 Column. Metric Pilot). In 'Environmental Soil Remediation and Rehabilitation'.  
515 Springer. pp. 211–238.
- 516 Kaown. D.. Shouakar-Stash. O.. Yang. J.. Hyun. Y.. Lee. K.-K.. 2014. Identification of  
517 multiple sources of groundwater contamination by dual isotopes. *Groundwater* **52**.  
518 875–885.
- 519 Knapp. M.F.. 2005. Diffuse pollution threats to groundwater: a UK water company  
520 perspective. *Q. J. Eng. Geol. Hydrogeol.* **38**. 39–51.
- 521 Lerner. D.N.. Kueper. B.H.. Wealthall. G.P.. Smith. J.W.N.. Leharne. S.A.. 2003. An  
522 illustrated handbook of DNAPL transport and fate in the subsurface.
- 523 Liu. C.. Ball. W.P.. 1999. Application of inverse methods to contaminant source identification  
524 from aquitard diffusion profiles at Dover AFB. Delaware. *Water Resour. Res.* **35**.  
525 1975–1985.
- 526 Liu. J.. Wilson. J.L.. 1995. Modeling travel time and source location probabilities in two-  
527 dimensional heterogeneous aquifer. In 'Proc. 5th WERC Technology Development  
528 Conference'. pp. 59–76.
- 529 Luciano. A.. Mancini. G.. Torretta. V.. Viotti. P.. 2018. An empirical model for the evaluation  
530 of the dissolution rate from a DNAPL-contaminated area. *Environ. Sci. Pollut. Res.*  
531 **25**. 33992–34004.
- 532 Mahar. P.S.. Datta. B.. 2001. Optimal Identification of Ground-Water Pollution Sources and  
533 Parameter Estimation. *J. Water Resour. Plan. Manag.* **127**. 20–29.  
534 [https://doi.org/10.1061/\(ASCE\)0733-9496\(2001\)127:1\(20\)](https://doi.org/10.1061/(ASCE)0733-9496(2001)127:1(20))
- 535 Mahar. P.S.. Datta. B.. 1997. Optimal monitoring network and ground-water–pollution source  
536 identification. *J. Water Resour. Plan. Manag.* **123**. 199–207.
- 537 Mansuy. L.. Philp. R.P.. Allen. J.. 1997. Source Identification of Oil Spills Based on the  
538 Isotopic Composition of Individual Components in Weathered Oil Samples. *Environ.*  
539 *Sci. Technol.* **31**. 3417–3425. <https://doi.org/10.1021/es970068n>

540 Marryott. R.A.. Sabadell. G.P.. Ahlfeld. D.P.. Harris. R.H.. Pinder. G.F.. 2000. Allocating  
541 remedial costs at superfund sites with commingled groundwater contaminant plumes.  
542 *Environ. Forensics* **1**. 47–54.

543 McGuire. T.M.. McDade. J.M.. Newell. C.J.. 2006. Performance of DNAPL source depletion  
544 technologies at 59 chlorinated solvent-impacted sites. *Groundw. Monit. Remediat.* **26**.  
545 73–84.

546 Meinardi. C.R.. Beusen. A.H.W.. Bollen. M.J.S.. Klepper. O.. Willems. W.J.. 1995.  
547 Vulnerability to diffuse pollution and average nitrate contamination of European soils  
548 and groundwater. *Water Sci. Technol.* **31**. 159–165.

549 Michalak. A.M.. Kitanidis. P.K.. 2004. Application of geostatistical inverse modeling to  
550 contaminant source identification at Dover AFB, Delaware. *J. Hydraul. Res.* **42**. 9–18.

551 Morrison. R.D.. 2000. Application of forensic techniques for age dating and source  
552 identification in environmental litigation. *Environ. Forensics* **1**. 131–153.

553 Murphy. B.L.. Morrison. R.D.. 2007. Applications of environmental forensics. Elsevier.  
554 Amsterdam.

555 Neupauer. R.M.. Wilson. J.L.. 2005. Backward probability model using multiple observations  
556 of contamination to identify groundwater contamination sources at the Massachusetts  
557 Military Reservation. *Water Resour. Res.* **41**.

558 Neupauer. R.M.. Wilson. J.L.. 2001. Adjoint-derived location and travel time probabilities for  
559 a multidimensional groundwater system. *Water Resour. Res.* **37**. 1657–1668.

560 Newell. C.J.. Connor. J.A.. 1998. Characteristics of dissolved petroleum hydrocarbon plumes.  
561 results from four studies. *Rapp. Tech. Am. Pet. Inst. Wash. DC*.

562 Olmez. I.. Beal. J.W.. Villaume. J.F.. 1994. A new approach to understanding multiple-source  
563 groundwater contamination: factor analysis and chemical mass balances. *Water Res.*  
564 **28**. 1095–1101.

565 Olmez. I.. Hayes. M.J.. 1990. Identifying sources of groundwater pollution using trace  
566 element signatures. In 'Nuclear Analytical Methods in the Life Sciences'. Springer. pp.  
567 355–361.

- 568 Palau. J.. Jamin. P.. Badin. A.. Vanhecke. N.. Haerens. B.. Brouyère. S.. Hunkeler. D.. 2016.  
569 Use of dual carbon–chlorine isotope analysis to assess the degradation pathways of 1,  
570 1, 1-trichloroethane in groundwater. *Water Res.* **92**. 235–243.
- 571 Rivett. M.O.. Dearden. R.A.. Wealthall. G.P.. 2014. Architecture, persistence and dissolution  
572 of a 20 to 45 year old trichloroethene DNAPL source zone. *J. Contam. Hydrol.* **170**.  
573 95–115.
- 574 Samarskaia. E.. 1995. Groundwater contamination modeling and inverse problems of source  
575 reconstruction. *Syst. Anal. Model. Simul.* **18**. 143–147.
- 576 Sauer. T.C.. Uhler. A.D.. 1994. Pollutant source identification and allocation: advances in  
577 hydrocarbon fingerprinting. *Remediat. J.* **5**. 25–50.
- 578 Schemel. L.E.. Cox. M.H.. Runkel. R.L.. Kimball. B.A.. 2006. Multiple injected and natural  
579 conservative tracers quantify mixing in a stream confluence affected by acid mine  
580 drainage near Silverton, Colorado. *Hydrol. Process. Int. J.* **20**. 2727–2743.
- 581 Scheutz. C.. Durant. N.D.. Hansen. M.H.. Bjerg. P.L.. 2011. Natural and enhanced anaerobic  
582 degradation of 1, 1, 1-trichloroethane and its degradation products in the subsurface—a  
583 critical review. *Water Res.* **45**. 2701–2723.
- 584 Schmidt. T.C.. Zwank. L.. Elsner. M.. Berg. M.. Meckenstock. R.U.. Haderlein. S.B.. 2004.  
585 Compound-specific stable isotope analysis of organic contaminants in natural  
586 environments: a critical review of the state of the art, prospects, and future challenges.  
587 *Anal. Bioanal. Chem.* **378**. 283–300.
- 588 Shouakar-Stash. O.. Frapè. S.K.. Drimmie. R.J.. 2003. Stable hydrogen, carbon and chlorine  
589 isotope measurements of selected chlorinated organic solvents. *J. Contam. Hydrol.* **60**.  
590 211–228.
- 591 Skaggs. T.H.. Kabala. Z.J.. 1994. Recovering the release history of a groundwater  
592 contaminant. *Water Resour. Res.* **30**. 71–79. <https://doi.org/10.1029/93WR02656>
- 593 Smallwood. B.J.. Paul Philp. R.. Allen. J.D.. 2002. Stable carbon isotopic composition of  
594 gasolines determined by isotope ratio monitoring gas chromatography mass

595 spectrometry. *Org. Geochem.* **33**. 149–159. <https://doi.org/10.1016/S0146->  
596 6380(01)00142-5

597 Snodgrass. M.F.. Kitanidis. P.K.. 1997. A geostatistical approach to contaminant source  
598 identification. *Water Resour. Res.* **33**. 537–546.

599 Stout. S.A.. Uhler. A.D.. Naymik. T.G.. McCarthy. K.J.. 1998. Peer Reviewed:  
600 Environmental Forensics Unraveling Site Liability. *Environ. Sci. Technol.* **32**. 260A-  
601 264A.

602 Sun. A.Y.. Painter. S.L.. Wittmeyer. G.W.. 2006. A robust approach for iterative contaminant  
603 source location and release history recovery. *J. Contam. Hydrol.* **88**. 181–196.  
604 <https://doi.org/10.1016/j.jconhyd.2006.06.006>

605 Sun. N.-Z.. 2013. *Inverse Problems in Groundwater Modeling*. Springer Science & Business  
606 Media.

607 Tikhonov. A.N.. Arsenin. V.Y.. 1977. *Solutions of ill-posed problems*. VH Winston & Sons.  
608 Washington, DC: John Wiley & Sons. New York.

609 Van Warmerdam. E.M.. Frapce. S.K.. Aravena. R.. Drimmie. R.J.. Flatt. H.. Cherry. J.A..  
610 1995. Stable chlorine and carbon isotope measurements of selected chlorinated  
611 organic solvents. *Appl. Geochem.* **10**. 547–552.

612 Verardo. E.. Atteia. O.. Rouvreau. L.. Siade. A.. Prommer. H.. 2021. Identifying remedial  
613 solutions through optimal bioremediation design under real-world field conditions. *J.*  
614 *Contam. Hydrol.* **237**. 103751.

615 Wagner. B.J.. 1992. Simultaneous parameter estimation and contaminant source  
616 characterization for coupled groundwater flow and contaminant transport modelling. *J.*  
617 *Hydrol.* **135**. 275–303. [https://doi.org/10.1016/0022-1694\(92\)90092-A](https://doi.org/10.1016/0022-1694(92)90092-A)

618 Walker. S.E.. Dickhut. R.M.. Chisholm-Brause. C.. Sylva. S.. Reddy. C.M.. 2005. Molecular  
619 and isotopic identification of PAH sources in a highly industrialized urban estuary.  
620 *Org. Geochem.* **36**. 619–632.

621 Wiedemeier. T.H.. Wilson. J.T.. Kampbell. D.H.. Miller. R.N.. Hansen. J.E.. 1995. Technical  
622 Protocol for Implementing Intrinsic Remediation with Long-Term Monitoring for

623           Natural Attenuation of Fuel Contamination Dissolved in Groundwater. Volume II.  
624           PARSONS ENGINEERING SCIENCE INC DENVER CO.

625   Wilson. J.L.. Liu. J.. 1994. Backward tracking to find the source of pollution. *Water Manage*  
626           *Risk Remed* **1**. 181–199.

627   Wycisk. P.. 2003. Groundwater pollution and remediation options for multi-source  
628           contaminated aquifers (Bitterfeld/Wolfen. Germany). *Toxicol. Lett.* **140–141**. 343–  
629           351. [https://doi.org/10.1016/S0378-4274\(03\)00031-6](https://doi.org/10.1016/S0378-4274(03)00031-6)

630   Yang. J.-H.. Lee. K.-K.. 2012. Locating plume sources of multiple chlorinated contaminants  
631           in groundwater by analyzing seasonal hydrological responses in an industrial complex.  
632           Wonju. Korea. *Geosci. J.* **16**. 301–311.

633