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**Simulating stable isotope ratios in plumes of groundwater pollutants with
BIOSCREEN-AT-ISO**

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1 Abstract

2 BIOSCREEN is a well-known simple tool for evaluating the transport of dissolved
3 contaminants in groundwater, ideal for rapid screening and teaching. This work extends the
4 BIOSCREEN model for the calculation of stable isotope ratios in contaminants. A three-
5 dimensional exact solution of the reactive transport from a patch source, accounting for
6 fractionation by first-order decay and/or sorption, is used. The results match those from a
7 previously published isotope model but are much simpler to obtain. Two different isotopes
8 may be computed, and dual isotope plots can be viewed. The dual isotope assessment is a
9 rapidly emerging new approach for identifying process mechanisms in aquifers. Furthermore,
10 deviations of isotope ratios at specific reactive positions with respect to “bulk” ratios in the
11 whole compound can be simulated. This model is named BIOSCREEN-AT-ISO and will be
12 downloadable from the journal homepage.

13

14 Article Impact Statement

15 This BIOSCREEN-AT decision support system can compute compound- and position-
16 specific stable isotope ratios in groundwater pollutant plumes.

17

18 Keywords

19 Reactive transport, saturated zone, contaminated sites, natural attenuation, stable isotopes

20 **Introduction**

21 The BIOSCREEN model had been developed by the US EPA in 1996 (Newell et al. 1996) as a
22 user-friendly simulation tool for the evaluation of the transport of dissolved contaminants in
23 groundwater. Under the name of BIOSCREEN-AT, an improved version based on the exact
24 analytical solution for reactive transport from a patch source in 3 dimensions was later published
25 (Karanovic et al. 2007) and distributed as an MS EXCEL-based spreadsheet. Within the last 15
26 years, considerable progress has been made in the analysis of isotope ratios in dissolved
27 groundwater pollutants. Compound-specific isotope analysis (CSIA) of either ^{13}C , ^2H , or ^{15}N can
28 be made using isotope ratio monitoring by Mass Spectrometry (irm-MS) (Hofstetter and Berg
29 2007; Elsner 2010; Thullner et al. 2012). This method is able to realize multi-element analyses
30 using a small amount of sample and to determine isotope ratios of mixtures components using
31 Gas Chromatography (GC) or High Performance Liquid Chromatography (HPLC) coupling. The
32 main inconvenient of this method is that it only allows determining the average over the whole
33 molecule isotopic composition, missing the intramolecular distribution of heavy isotopes in the
34 studied compounds. In this context, different methods have been developed in order to perform
35 Position-Specific Isotope Analysis (PSIA). The isotope ratio measurement by ^{13}C Nuclear
36 Magnetic Resonance Spectrometry (irm- ^{13}C NMR) is a recently developed technique capable of
37 determining the isotopic composition of each carbon position of a large panel of molecules
38 (Caytan et al. 2007). In a previous study, irm- ^{13}C NMR has recently proven its interest in the
39 determination of origin of contaminants (Julien et al. 2016) and the study of their remediation
40 (Julien et al. 2015a+b).

41 Changes in isotope ratios during reactive transport are indicative of reactive processes: bond-
42 breaking processes can cause a large isotope fractionation at the position of the initial bond

43 cleavage, often leading to an enrichment of the remaining non-degraded pollutant.. Smaller
44 secondary isotope fractionation at sites adjacent to a reactive position can also occur. Also,
45 when the transformation products of pollutants are also components of the primary pollutants in
46 the contamination source, isotope ratio can be used to differentiate the origins of chemicals and
47 provide actual description of reactive processes. Thus, US EPA recommended the use of CSIA to
48 access biodegradation processes and to identify the source of organic groundwater contaminants
49 (Hunkeler et al. 2008). CSIA has been largely applied to study natural attenuation processes in
50 contaminated field investigation like discussed in three critical review articles (Meckenstock et
51 al. 2004; Schmidt et al. 2004; Elsner 2010). To our knowledge, PSIA has not been applied in
52 field investigation but it represents a promising trend of isotope fractionation pattern for the
53 study of natural attenuation processes in contaminated groundwater.

54 Equilibrium sorption can also create small to intermediate isotope fractionation at certain
55 positions of molecules, but unfortunately the effect also causes in most cases an enrichment of
56 the remaining pollutant (Kopinke et al. 2005; Höhener and Yu 2012), which could be wrongly
57 interpreted as an effect of degradation. In contrast, the physical dilution of compounds should *a*
58 *priori* not change isotope ratios (Elsner 2010). In combination, these isotope fractionations can
59 impact on the bulk (average over the whole molecule) isotope ratios observed, but position
60 specific fractionations are inevitably diluted out when only CSIA is exploited. PSIA, in contrast,
61 gives access to the individual values.

62 Because of the high information content of isotope ratios in contaminants in groundwater plumes,
63 they are often measured to obtain a better understanding of natural attenuation processes.
64 Moreover, fractionation factors for a large number of bond-breaking reactions and for
65 equilibrium sorption are available (Aelion et al. 2010; Höhener and Yu 2012).

66 Analytical or numerical models for compound-specific isotope ratios in aquifer pollutants have
67 been developed. Höhener and Atteia (2010) showed with analytical models on MAPLE
68 worksheets that only the exact analytical solution in BIOSCREEN-AT gives correct isotope
69 ratios at lateral plume margins. However, all current isotope models are quite demanding in
70 operational skills and partly also in CPU time and therefore have not been widely exploited.

71 The present work here combines the know-how of isotope evolution from the more complex
72 models with the well-known and user-friendly model BIOSCREEN-AT to propose a simple tool
73 predicting isotope ratios in groundwater as a function of time and space. The tool should compute
74 two different isotopes in each compound (e.g. ^{13}C and ^2H) in order to create the so-called dual-
75 isotope plots (Vogt et al. 2016). These plots are very sensitive to different reaction mechanisms.
76 The overall goal is that a user can rapidly deduce whether their combined data on concentration
77 and isotope ratios prove unambiguously the degradation and/or sorption of the target pollutant in
78 the studied aquifer.

79 **Analytical solution and its implementation**

80 The schematic representation of the pollution scenario in a homogeneous 3-dimensional aquifer
81 is shown in Figure 1. The aquifer is semi-infinite in the x direction, and infinite in the y and z
82 directions. Reactive transport is modeled with the advection-dispersion equation given for the x-
83 y-z space as in equation (1), under the following assumptions: groundwater flow is steady and
84 uni-directional along the x-axis; material properties are homogeneous; partitioning between
85 dissolved and sorbed phases is instantaneous and reversible; neither gas phases nor volatilization
86 from groundwater is modeled; the solute undergoes degradation following first-order kinetics, but
87 only in the dissolved phase (which is realistic for microorganisms which degrade dissolved
88 pollutants at low environmental concentrations).

$$89 \quad R_f \frac{\partial C}{\partial t} = v\alpha_x \frac{\partial^2 C}{\partial x^2} + v\alpha_y \frac{\partial^2 C}{\partial y^2} + v\alpha_z \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial x} - \lambda C \quad (1)$$

90 In Eq. (1), v is the unretarded groundwater flow velocity (m yr⁻¹), α_x is longitudinal dispersivity
 91 (m), α_y , and α_z are the transversal dispersivities in the y (horizontal), and z (vertical) direction
 92 (m), λ is a first-order degradation rate (yr⁻¹), and R_f is the retardation factor (see eq. (4)). We use
 93 the exact solution of eq. (1) from Cleary and Ungs (1978) which is equation (2):

$$94 \quad C_{i(x,y,z,t)} = C_{0,i} \Omega_{(\lambda i, x, y, z, t)} \quad (2)$$

95 with

$$96 \quad \Omega_{(\lambda i, x, y, z, t)} = \frac{x}{8\sqrt{\pi\alpha_x v'}} \exp\left(-\gamma\left(t - \frac{x}{v'}\right)\right) \int_0^t \frac{1}{\tau^{1.5}} \exp\left[-\frac{\lambda_i}{R_{f,i}} \tau - \frac{x^2}{4v'\alpha_x \tau}\right]$$

$$97 \quad \left\{ \operatorname{erfc}\left[\frac{y - 0.5Y}{2\sqrt{\alpha_y v' \tau}}\right] - \operatorname{erfc}\left[\frac{y + 0.5Y}{2\sqrt{\alpha_y v' \tau}}\right] \right\} \left\{ \operatorname{erfc}\left[\frac{z - Z}{2\sqrt{\alpha_y v' \tau}}\right] - \operatorname{erfc}\left[\frac{z + Z}{2\sqrt{\alpha_y v' \tau}}\right] \right\} d\tau$$

$$98 \quad \left\{ \operatorname{erfc}\left[\frac{y - 0.5Y}{2\sqrt{\alpha_y v' \tau}}\right] - \operatorname{erfc}\left[\frac{y + 0.5Y}{2\sqrt{\alpha_y v' \tau}}\right] \right\} \left\{ \operatorname{erfc}\left[\frac{z - Z}{2\sqrt{\alpha_y v' \tau}}\right] - \operatorname{erfc}\left[\frac{z + Z}{2\sqrt{\alpha_y v' \tau}}\right] \right\} d\tau$$

$$99 \quad \left\{ \operatorname{erfc}\left[\frac{y - 0.5Y}{2\sqrt{\alpha_y v' \tau}}\right] - \operatorname{erfc}\left[\frac{y + 0.5Y}{2\sqrt{\alpha_y v' \tau}}\right] \right\} \left\{ \operatorname{erfc}\left[\frac{z - Z}{2\sqrt{\alpha_y v' \tau}}\right] - \operatorname{erfc}\left[\frac{z + Z}{2\sqrt{\alpha_y v' \tau}}\right] \right\} d\tau$$

100 and where i stands for a specific isotope, γ is a first-order decay rate of the concentration in the
 101 source, $v' = v/R_{f,i}$, and $C_{0,i}$ is the (constant) concentration of isotope i in the source (mol L⁻¹).

102 The use of the exact solution fixes problems associated with the first BIOSCREEN model which
 103 was based on Domenico's analytical solution. This issue was broadly discussed in several
 104 publications (Guyonnet and Neville 2004; Srinivasan 2007; West et al. 2007).

105 For isotope modeling, we use the isotope approach (Hunkeler et al. 2009; Höhener and Atteia
 106 2010) where each isotope is modeled separately. Light (l) and heavy (h) isotopes are modeled
 107 using different λ caused by kinetic isotope fractionation during bond cleavage (fractionation
 108 factor α_{react}), and using different $R_{f,i}$ caused by equilibrium isotope effects by sorption
 109 (fractionation factor α_{sorption} , eqns. 3-5, Höhener and Yu 2012).

$$110 \quad {}^l\lambda = \lambda \quad (3a)$$

$$111 \quad {}^h\lambda = \lambda\alpha_{react} \quad (3a)$$

$$112 \quad {}^lR_f = 1 + \frac{\rho_b}{n} f_{OC} K_{OC} \quad (4a)$$

$$113 \quad {}^hR_f = 1 + \frac{\rho_b}{n} f_{OC} K_{OC} \alpha_{sorption} \quad (4b)$$

$$114 \quad {}^lC_0 = C_0 / (1 + R_0) \quad (5a)$$

$$115 \quad {}^hC_0 = C_0 R_0 / (1 + R_0) \quad (5b)$$

116 Here, ρ_b is the soil bulk density (kg L^{-1}), n is effective porosity, K_{OC} is the partitioning coefficient
 117 of the contaminant between organic carbon and water (L kg^{-1}), f_{OC} is the unitless fraction of
 118 organic carbon of the aquifer solids, and R_0 is the initial (constant) isotope ratio of the
 119 contaminant in the source. Equations 3 and 4 create different transport behavior of light and
 120 heavy isotopes, which finally lead to changes in the isotope ratios.

121 These isotope ratios in delta notation (in ‰) are finally obtained by equation (6):

$$122 \quad \delta_{(x,y,z,t)} = \left(\frac{\left[\frac{{}^hC_{(x,y,z,t)}}{{}^lC_{(x,y,z,t)}} \right]}{R_{standard}} - 1 \right) 1000 \quad (6)$$

123 where $R_{standard}$ is the isotope ratio of the international standard for the element of interest.

124 For the purpose of the assessment of degradation, equation (7), which computes the percent of
 125 degradation B (%) compared to overall concentration decrease in the contaminant, was
 126 incorporated into the model:

$$127 \quad B \text{ (\%)} = \left(1 - \left(\frac{\delta + 1000}{\delta_{source} + 1000} \right)^{1000 \epsilon_{reaction}} \right) \cdot 100 \quad (7)$$

128 B (%) is mainly caused by biotic reaction, but at some sites also abiotic reactions were found to
 129 fractionate isotopes. The equation 7 is only valid when the change in isotope ratios is uniquely

130 caused by reaction. In cases where sorption fractionates isotopes, the B (%) will be wrong. This is
131 illustrated in the spreadsheet because the model gives also the true B (%) obtained from modeling
132 a sorption-affected tracer and equation (8).

$$133 \quad B (\%)_{true} = 100 \left(1 - \frac{C_{compound} / C_{compound,source}}{C_{tracer} / C_{tracer,source}} \right) \quad (8)$$

134 Here, C_{tracer} is a simulated concentration of a sorbing tracer affected by R_f . The equations were
135 implemented on a spreadsheet (MS EXCEL, version 2010). The integration of the Ω factors of
136 equation (1) is made in 100 steps of $d\tau$. In order to test the exactness of the approach
137 implemented in EXCEL, the results were compared to numerical integrations made by MAPLE
138 (version 13, Waterloo Maple Inc, Waterloo, Canada) using the Maple worksheet from Höhener
139 and Atteia (2010) with the exact solution of Wexler (1992).

140 **Example calculations**

141 The presented example here is for methyl *tert*-butyl ether (MTBE). Fractionation factors of ^{13}C
142 and ^2H during aerobic degradation were chosen as similar to those found in laboratory
143 experiments (Rosell et al. 2007). MTBE has an intra-molecular variation in ^{13}C isotope ratio, with
144 the methyl group (in the NMR spectrum position 2 according to the chemical shift) being most
145 negative (Julien et al. 2016). Initial enzymatic attack will occur at this position, leading to the
146 largest isotope fractionation at this C atom. Two scenarios were modeled (see Table 1 for model
147 parameters). Scenario 1 presents an old plume in groundwater with low flow velocity, without
148 any sorption, whereas scenario 2 is a young plume in a faster flowing groundwater where
149 sorption occurs and sorption fractionates the pollutant in addition to the fractionation by
150 degradation. Both scenarios were modeled with the present model (BIOSCREEN-AT-ISO) and
151 the MAPLE model (Höhener and Atteia 2010). The results are shown in Figures 2 and 3.

152 Figures 2a and 3a show that concentrations along the plume centerline both match exactly the
153 concentrations modeled by the MAPLE worksheet, indicating that the integration of time in the
154 EXCEL model in 100 steps is sufficiently accurate compared to an independent numerical
155 integration both for short and long times (2 and 50 years). The other subsets in Figures 2 and 3
156 show that both models also yield identical results for isotope ratios of ^{13}C and of ^2H . The
157 modeled curves along the plume centerline indicate that the isotope data enable a clear distinction
158 between scenario 1, wherein only degradation fractionates, and scenario 2, wherein sorption also
159 contributes to fractionation. The increases of the ratios are enhanced in scenario 2, especially at
160 the forerunning plume front. The explanation for this is that only at the fore-running front of
161 young plumes, there are sorption sites unoccupied by the contaminant, and therefore fractionation
162 can occur when the contaminant sorbs to these sites. Near the source, or everywhere in old
163 plumes, sorption sites are already occupied by contaminant, and no fractionation occurs anymore.
164 This had previously been predicted (Kopinke et al. 2005). Figures 2c and 3c show that the slope
165 Λ in the dual isotope plots $\Delta\delta^2\text{H}$ vs $\Delta\delta^{13}\text{C}$ does not lie exactly on the approximation $\Lambda \approx$
166 $\varepsilon\text{H}/\varepsilon\text{C} \approx 15$ in both cases, and that the present model is a helpful tool to investigate why and how
167 such slopes change as a function of two fractionating processes and of dispersion. It had been
168 shown previously that dispersion must be taken into account for the interpretation of field isotope
169 data, even when dispersion itself does not create fractionation (Abe and Hunkeler 2006). Finally,
170 Figures 2b and 3b show in addition that, for the carbon isotope ratios, a position-specific isotope
171 measurement of $\delta^{13}\text{C}$ would enhance even more the discriminatory power of the isotope
172 approach, since the $\delta^{13}\text{C}$ in the reactive position 2 increases by up to 10‰, whereas the bulk $\delta^{13}\text{C}$
173 increases only by 2‰. Once progress is made in the purification of samples in order to perform

174 PSIA by NMR (Julien et al. 2015) in real-world groundwater, our model is operational for data
175 interpretation.

176 **Conclusions**

177 To sum up, the BIOSCREEN-AT-ISO model with stable isotopes is validated in this work and
178 can serve in future as a tool for isotope geochemists for the assessment of natural attenuation of
179 dissolved groundwater pollutants during reactive transport. The BIOSCREEN-AT format was
180 chosen because it gained popularity in the community of groundwater remediation and proved to
181 be useful for rapid assessment and teaching. The study of field processes using compound-
182 specific isotope analysis is recommended by US EPA which published guidelines for isotope data
183 interpretations (Hunkeler et al. 2008). Field data of concentrations and isotope ratios are easily
184 assessed with the model, and the contribution of biodegradation to natural attenuation can be
185 quantified at any point in the aquifer. The model predicts dual isotope evolutions in space and
186 time and reinforces interpretations of degradation mechanisms (Vogt et al. 2016). The model is
187 an ideal complement to more sophisticated numerical models: this analytical model is free of
188 numerical dispersion and can be used to validate results from numerical codes for homogeneous
189 cases. More sophisticated numerical approaches would need very time-consuming tailor-made
190 modeling and maybe development of codes, while the use of a spreadsheet model like
191 BIOSCREEN-AT-ISO can simulate in some hours a three-dimensional field case and can check
192 whether an investment in more complex models is worthwhile. The limitations of this model
193 compared to numerical approaches are: 1) it is only valid only in homogeneous systems; 2) only
194 for constant or experimentally decaying sources; 3) only for linear sorption isotherms; and 4)
195 only for stable isotopes of C, H, N, and O, but not for Cl which behaves differently (Hunkeler et

196 al. 2009). The BIOSCREEN-AT-ISO is a Microsoft EXCEL spreadsheet compatible with
197 versions 2010 or later and can be downloaded free of charge from the Journal website.

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202

203 **Supplementary Material**

204 The following supplementary material is available for this article: EXCEL Spreadsheets
205 containing the model and the example calculations of scenarios 1+ 2.

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Table 1: Aquifer and compound properties used for modeling isotope fractionation in the groundwater plumes with equation (1).

Aquifer Parameters	Notation	Unit	Value Scenario 1	Value Scenario 2
Groundwater flow velocity	v	m yr^{-1}	180	365
Longitudinal dispersivity	α_x	m	10	10
Transversal dispersivities	α_y	m	1	1
	α_z	m	0.1	0.1
Ratio of solids to water	r_{sw}	kg L^{-1}	5	5
Organic carbon content	f_{oc}	$\frac{\text{kg}_{oc}}{\text{kg}^{-1}}$	0	0.05
Source width and depth	Y	m	20	20
	Z	m	infinite	infinite
Compound parameters	MTBE			
Concentration of MTBE	C_0	mM	1	1
Org. carbon-water part. coefficient	K_{OC}	L kg_{oc}^{-1}	12	12
Retardation factor	R_f	(-)	1	5.8
Carbon enrichment factor for degradation for sorption	$\epsilon_{\text{react.-bulk}}^C$	(‰)	-2	-2
	$\epsilon_{\text{react.-pos1/2/3}}^C$	(‰)	0/-10/0	0/-10/0
	$\epsilon_{\text{sorption}}^C$	(‰)	na	-0.3
	$\epsilon_{\text{sorp.-pos1/2/3}}^C$	(‰)	na	0/0/-0.5
Hydrogen enrichment factor for degradation for sorption	$\epsilon_{\text{react.-bulk}}^H$	(‰)	-30	-30
	$\epsilon_{\text{sorption}}^H$	(‰)	na	-5
Initial isotope ratio	$\delta^{13}\text{C}_{0 \text{ bulk}}$	(‰)	-29	-29
	$\delta^{13}\text{C}_{0 \text{ pos1/2/3}}$	(‰)	-17/-40/-29	-17/-40/-29
	$\delta^2\text{H}_0$	(‰)	-95	-95
Degradation rate	λ	yr^{-1}	1.4	1.4
Source decay rate	γ	yr^{-1}	0	0

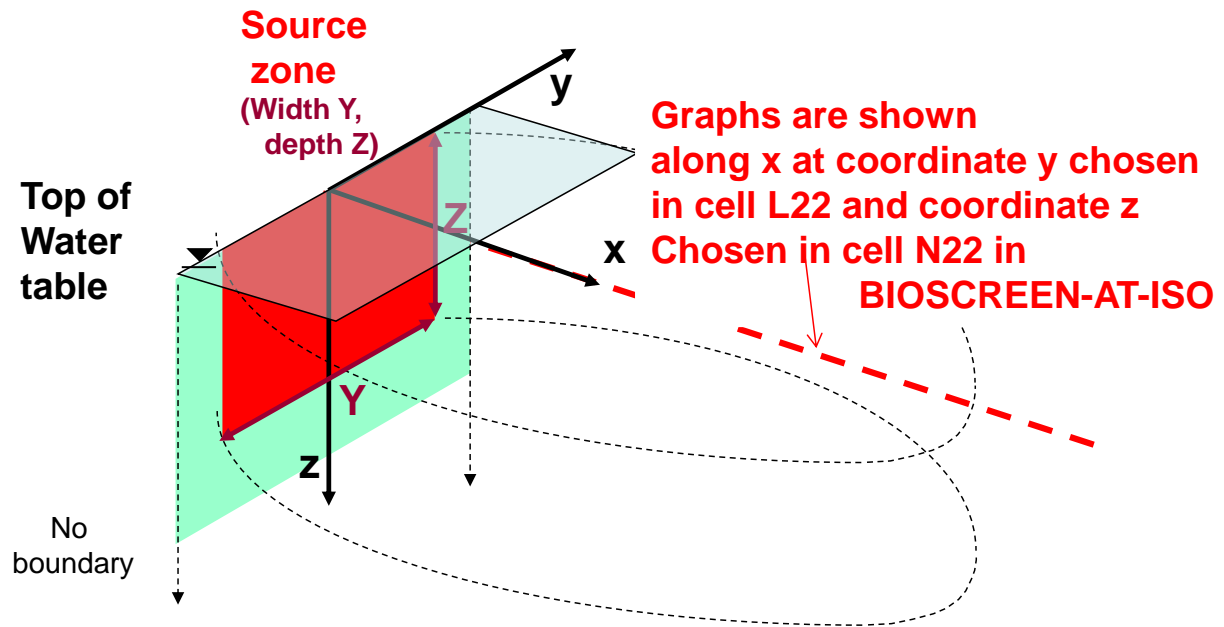
na: not applicable

FIGURE CAPTIONS

Fig. 1: Illustration of pollution scenario setting in x-y-z coordinate system in the modeled aquifer.

Fig. 2: Results from BIOSCREEN-AT-ISO (this work) compared to results from MAPLE models for the scenario 1: a) concentrations, b) isotope ratios, and c) dual isotope evolution, with linear regression of slope Λ .

Fig. 3: Results from BIOSCREEN-AT-ISO (this work) compared to results from MAPLE models for the scenario 2: a) concentrations, b) isotope ratios, and c) dual isotope evolution, with linear regression of slope Λ .

Figure 1:

Figures 2 and 3:

