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### ► To cite this version:

Patrick Höhener, Zhi M Li, Maxime Julien, Pierrick Nun, Richard J. Robins, et al.. Simulating compound-specific isotope ratios in plumes of groundwater pollutants with BIOSCREEN-AT-ISO. Groundwater, 2017, 55 (2), pp.261-267. 10.1111/gwat.12472 . hal-01491099

**HAL Id: hal-01491099**

**<https://amu.hal.science/hal-01491099>**

Submitted on 2 May 2018

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

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**Revised version, GW20160413-0085**

**Conflict of interest:** None.

## Abstract

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

## Article Impact Statement

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

## Keywords

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

## Introduction

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

Changes in isotope ratios during reactive transport are indicative of reactive processes: bond-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).

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

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

## **Analytical solution and its implementation**

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

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

In Eq. (1),  $v$  is the unretarded groundwater flow velocity ( $\text{m yr}^{-1}$ ),  $\alpha_x$  is longitudinal dispersivity ( $\text{m}$ ),  $\alpha_y$ , and  $\alpha_z$  are the transversal dispersivities in the  $y$  (horizontal), and  $z$  (vertical) direction ( $\text{m}$ ),  $\lambda$  is a first-order degradation rate ( $\text{yr}^{-1}$ ), and  $R_f$  is the retardation factor (see eq. (4)). We use the exact solution of eq. (1) from Cleary and Ungs (1978) which is equation (2):

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

with

$$\Omega_{(\lambda i, x, y, z, t)} = \frac{x}{8\sqrt{\pi\alpha_x v'}} \exp\left(-\gamma\left(t - \frac{x}{v'}\right)\right) \int_0^t \frac{1}{\tau^{1.5}} \exp\left[-\frac{\lambda_i}{R_{f,i}} \tau - \frac{x^2}{4v'\alpha_x \tau}\right] \left\{ \operatorname{erfc}\left[\frac{y - 0.5Y}{2\sqrt{\alpha_y v' \tau}}\right] - \operatorname{erfc}\left[\frac{y + 0.5Y}{2\sqrt{\alpha_y v' \tau}}\right] \right\} \left\{ \operatorname{erfc}\left[\frac{z - Z}{2\sqrt{\alpha_z v' \tau}}\right] - \operatorname{erfc}\left[\frac{z + Z}{2\sqrt{\alpha_z v' \tau}}\right] \right\} d\tau$$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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



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

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

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

### Example calculations

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

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

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

## Conclusions

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

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

## **Acknowledgments**

This work was funded by the French National Research Agency ANR, project ISOTO-POL funded by the program CESA (N° 009 01). M. Julien thanks the ANR for funding his PhD bursary through this project. We thank three unknown reviewers for their helpful comments.

## **Supplementary Material**

The following supplementary material is available for this article: EXCEL Spreadsheets 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	$v$	$\text{m yr}^{-1}$	180	365
Longitudinal dispersivity	$\alpha_x$	m	10	10
Transversal dispersivities	$\alpha_y$ $\alpha_z$	m m	1 0.1	1 0.1
Ratio of solids to water	$r_{sw}$	$\text{kg L}^{-1}$	5	5
Organic carbon content	$f_{oc}$	$\text{kg oc kg}^{-1}$	0	0.05
Source width and depth	$Y$ $Z$	m m	20 infinite	20 infinite
<b>Compound parameters</b>	<b>MTBE</b>			
Concentration of MTBE	$C_0$	mM	1	1
Org. carbon-water part. coefficient	$K_{OC}$	$\text{L kg}_{oc}^{-1}$	12	12
Retardation factor	$R_f$	(-)	1	5.8
Carbon enrichment factor for degradation	$\varepsilon_{\text{react.-bulk}}^C$	(‰)	-2	- 2
	$\varepsilon_{\text{react.-pos1/2/3}}^C$	(‰)	0/-10/0	0/-10/0
for sorption	$\varepsilon_{\text{sorption}}^C$	(‰)	na	- 0.3
	$\varepsilon_{\text{sorp.-pos1/2/3}}^C$	(‰)	na	0/0/-0.5
Hydrogen enrichment factor for degradation	$\varepsilon_{\text{react.-bulk}}^H$	(‰)	-30	- 30
for sorption	$\varepsilon_{\text{sorption}}^H$	(‰)	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	$\lambda$	$\text{yr}^{-1}$	1.4	1.4
Source decay rate	$\gamma$	$\text{yr}^{-1}$	0	0

na: not applicable

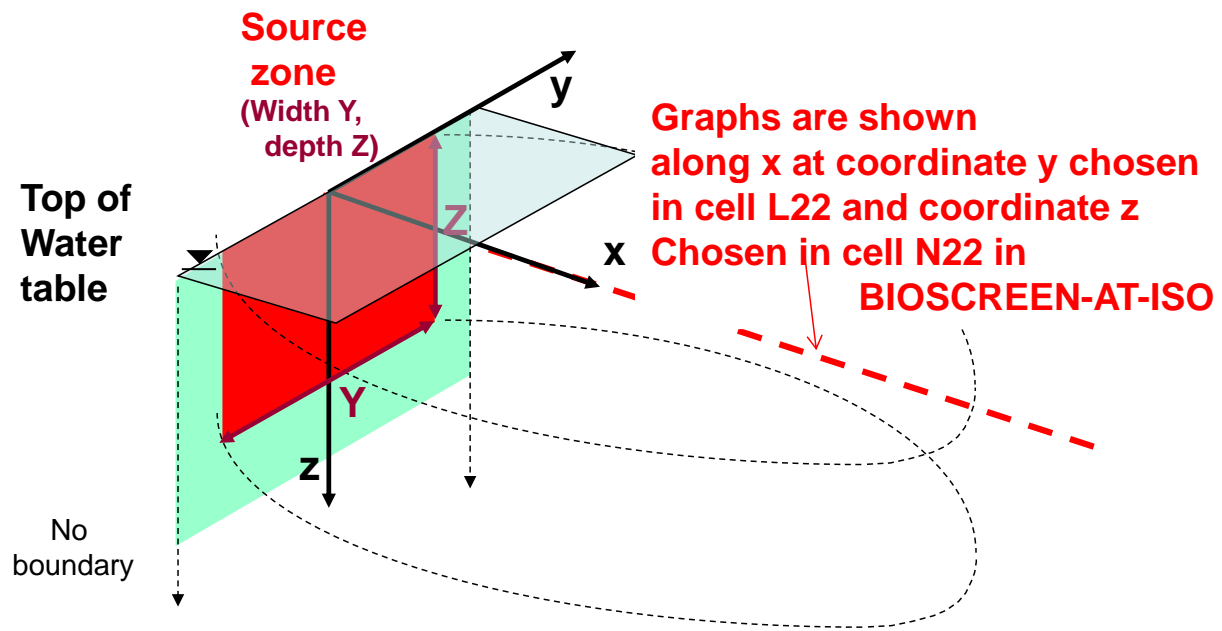
## FIGURE CAPTIONS

**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  $\Lambda$ .

**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  $\Lambda$ .



**Figure 1:**

## Figures 2 and 3:

