KWR BTO 2019.004 | January 2019

Predicting organic micropollutant behavior for standardized public supply well field types, with TRANSATOMIC Lite



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Project manager Dr. Stefan Kools<sup>1</sup>

Client BTO

Quality Assurance Dr. ir. Gijsbert Cirkel<sup>1</sup>

Author(s) Prof. dr. Pieter J. Stuyfzand<sup>1,2</sup>

<sup>1</sup> KWR<sup>; 2</sup> Technical Univ. Delft

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More information Prof. dr. Pieter J. Stuyfzand T E pieter.stuyfzand@kwrwater.nl Postbus 1072 3430 BB Nieuwegein The Netherlands

T +31 (0)30 60 69 511 F +31 (0)30 60 61 165 E info@kwrwater.nl I www.kwrwater.nl



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### **BTO** Management samenvatting

# *Voorspelling gedrag organische microverontreinigingen voor 4 typen puttenvelden van drinkwaterbedrijven, met TRANSATOMIC Lite*

Auteur Prof. dr. P. J. (Pieter) Stuyfzand



#### Belang: (nieuwe) organische microverontreinigingen in waterwingebieden vergen een 'grondige' risico-analyse

Een gedegen risico-analyse van (nieuwe) organische microverontreinigingen (OMiVe) in grondwaterwingebieden dient rekening te houden met processen die de inputconcentratie verlagen tijdens de soms zeer lange reistijden in de ondergrond (van 1 maand tot honderden jaren) in uiteenlopende milieus (qua sorberend en reducerend vermogen). Het hanteren van DT<sub>50</sub>-waarden voor biodegradatie (in de bouwvoor of onder optimale condities) geeft een te optimistisch beeld van wat er in dikwijls zeer schone/arme aquifers mogelijk is.

#### Aanpak: Modellering 4 standaard puttenvelden

- definitie van 4 gestandaardiseerde, kwetsbare puttenveldtypen met representatieve hydro(geo)logische en hydro(geo)chemische kenmerken voor de Nederlandse (en Vlaamse) situatie;
- constructie van een reactief transportmodel voor elk van deze 4 typen; en
- toepassing van dit model op (tenminste) 5
   OMiVe, elk met een stapinput van 0 tot 100%, in elk van de 4 standaard puttenveldtypen. Vier

In dit rapport, wordt een nieuwe modelmatige methode gepresenteerd om het gedrag te voorspellen van (nieuwe) Organische MIcroVErontreinigingen (OMiVe) voor 4 gestandaardiseerde puttenveldtypen. Deze omvatten de meest voorkomende en meest kwetsbare grondwaterbronnen voor de drinkwatervoorziening in Nederland (en Vlaanderen). Doel is om hiermee het risico voor puttenvelden in kaart te brengen, a priori bij het toelatingsbeleid van nieuwe OMiVe en a posteriori bij de prioritering van de monitoring van in het milieu reeds voorkomende OMiVe.

van de 5 OMiVe zijn bekende stoffen, OMP-X is een fictieve OMiVe die zich volledig conservatief gedraagt (zonder afbraak, zonder sorptie). Het reactieve transportmodel (TRANSATOMIC Lite) is een beperkte, aangepaste variant van TRANSATOMIC (acronym: TRANS Aquifer Transport Of MIroContaminants).

#### Resultaat I: De 4 gestandaardiseerde puttenveldtypen

Elk van de 4 puttenveldtypen wint uit een zand of gravel aquifer. Type A onttrekt freatisch, (sub)oxisch grondwater, type A2 wint anoxisch semispannings-grondwater, type i onttrekt viabekkens-geïnfiltreerd rivierwater ((sub)oxisch uit ondiepe aquifer, anoxisch uit diepere aquifer), en type U wint oeverfiltraat (diep anoxisch op geringe diepte, anoxisch op grotere diepte). Voor elk type zijn kenmerkende systeemparameters gedefinieerd, zoals wel (A en A2) of geen (i en U) onverzadigde zone, wel (i en U) of geen (A en A2) voedende waterloop, reistijden in de onderscheiden compartimenten, wel (i en U) of geen (A en A2) verdunning, bodemeigenschappen en kwaliteit van het voedende water.

#### **Resultaat II: TRANSATOMIC Lite**

Dit in Excel spreadsheet geprogrammeerde model berekent concentratieveranderingen van OMiVe met analytische oplossingen, tijdens bodempassage en, in geval van type i en U, ook tijdens verblijf in een infiltratiebekken of riviersegment (voordat het water infiltreert). De verdisconteerde processen omvatten vervluchtiging, fotolyse, filtratie, advectie, verdunning door bijmenging van ander water, lineaire sorptie en eerste orde afbraak door biodegradatie, in een hydrologisch en hydrogeochemisch stationaire situatie.

Als OMiVe-inputsignaal geldt een stapfunctie van 0 tot 100% (na de stap blijft de concentratie 100%). De standaard modeloutput bestaat uit het concentratieverloop met de tijd in de winning (5 OMiVe), het concentratieverloop met de afstand wanneer de OMiVe is doorgebroken in de winning (1 OMiVe), en een tabel met kwantitatieve informatie over het gedrag van vele OMiVe (thans ~170) op enkele cruciale punten in de ondergrond.

Het transport wordt berekend langs 1 of meerdere stroombanen, parallel (uniform) of radiaal. Het concentratieverloop in de output van het puttenveld wordt berekend voor het freatische type met een gecombineerd Exponentieel Piston Model (EPM) of met een Multi-Stroombuis Model (MFM), voor het semispanningstype uitsluitend met MFM, en voor zowel het kunstmatige infiltratie type als het oevergrondwatertype met een tweeledig Lineair Stroombuis Model.

In het rapport worden alle analytische oplossingen voor de berekening van reistijden en reactief transport verduidelijkt.

#### **Resultaat III: Toepassing model**

Het model is toegepast op elk van de 4 puttenveldtypen. De 5 uitverkoren OMiVe bestonden in geval van de freatische en semispanningswinning uit OMP-X (fictieve conservatieve OMiVe), ASTCA (metaboliet herbicide florasulam), 1,2-DCP (1,2-dichloorpropaan; oplosmiddel), bentazon (herbicide), en MDchloridazon (metaboliet herbicide chloridazon). In geval van BAR en RBF waren het OMP-X, SMX (sulfamethoxazole; geneesmiddel), BAM (2,6dichloorbenzamide; metaboliet herbicide dichlobenil en fungicide fluopicolide), CHBr<sub>2</sub>Cl (dibroomchloormethaan; trihalomethaan) en acene (acenafteen; PAK). Onderstaande tabel biedt een compact overzicht van het voorspelde gedrag van deze 5 stoffen voor elk puttenveldtype.

		Puttenveld type									
Kenmerken	Α	A2	i	U							
	Freatisch	Semispanning	open infiltratie	oeverfiltratie							
Reistijd water	12-445 j	6-1300 j	40-1500 d	1000-4500 d							
	OMP-X [100]	OMP-X [100]	OMP-X [90]	OMP-X [90]							
Doorbraak %	Bentazon [100]	ASTCA [53]	SMX [74]	BAM [62]							
na max.	1,2-DCP [91]	1,2-DCP [22]	BAM [18]	SMX [0]							
reistijd water	MD-chloridazon [66]	Bentazon [14]	CHBr2CI [1.5]	CHBr2CI [0]							
	ASTCA [3]	MD-chloridazon [0.2]	Acene [0]	Acene [0]							

i en U: 10% bijmenging gebiedseigen grondwater zonder OMiVe

#### Implementatie: Waterbedrijven en derden

Met TRANSATOMIC Lite kan op eenvoudige wijze het gedrag voorspeld worden van elke OMiVe in elk van de 4 gestandaardiseerde puttenveldtypen. Dit is van grote waarde voor het in kaart brengen van risico's voor puttenvelden, omdat deze kennis het toelatingsbeleid van nieuwe OMiVe en de monitoringstrategie van overheid en waterleidingbedrijf ondersteunt.

Voor de algemene risico-inschatting van een OMiVe is modellering met de gestandaardiseerde puttenveldtypen de aangewezen vorm. Daarbij dienen de modelsettings niet veranderd te worden. Wanneer er echter behoefte is aan maatwerk voor een puttenveld, dan zijn de standaard settings heel eenvoudig te wijzigen.

De belangrijkste zwakke schakel in de modellering bestaat uit de stofeigenschappen en dan met name de halfwaardetijden (afbraakconstantes in diverse redoxmilieus).

#### Rapport

De resultaten van dit onderzoek zijn beschreven in KWR rapport BTO 2019.004: Predicting organic micropollutant behavior for standardized public supply well field types, with TRANSATOMIC Lite.

### Summary and conclusions

In this report, a new modeling approach is presented to predict the behavior of Organic MicroPollutants (OMPs) for 4 standard types of Public Supply Well Fields (PSWFs), which cover the most frequently occurring and most vulnerable groundwater resources for drinking water supply in the Netherlands (and Flanders). One of the aims of this approach is to forecast the behavior of new OMPs in the groundwater compartment. This compartment is often overlooked in the current environmental risk assessment methods, which are a priori or a posteriori applied when new organic chemicals appear on the market.

The 4 standard PSWF types consist of a phreatic, a semiconfined, a Basin Artificial Recharge (BAR) and River Bank Filtration (RBF) well field, each predefined with very representative, standard hydrogeological, hydrological and hydrogeochemical characteristics. The chosen OMP transport model is the Lite version of TRANSATOMIC (acronym: TRANS Aquifer Transport Of MicroContaminants), in which concentration changes are calculated with analytical solutions set in Excel spreadsheet. The processes addressed include volatilization, photolysis, filtration, advection, dispersion (+ diffusion), dilution by mixing with other water, linear sorption and first order decay (by either radioactive decay or biodegradation), in a hydrologically and hydrogeochemically stationary situation.

In order to keep the model simple and practical, the following is assumed: (i) a stepwise input from 0 to 100% (or any concentration >0) which happened e.g. 60 years ago; (ii) no dispersion, thus piston flow; (iii) downgradient of land surface or the basin / river bank, the OMPs do not participate in any volatilization, photochemical oxidation, dissolution or precipitation reaction, (iv) there is no storage in living biomass nor mobilization from dying biomass; (v) sorption is linear, fully reversible and immediate, and (vi) (bio)degradation follows first order decay, with the same constant for the dissolved and sorbed fraction. The standard model settings serve the purpose of comparison of OMP behavior under well defined settings. The model is nevertheless very versatile, meaning that most settings can be changed at will. This opens up the possibility to apply TRANSATOMIC Lite for PSWFs with quite different characteristics.

The model consists of 8 worksheets, in order: ReadMe (a brief introduction), OMP-data (a database with physico-chemical characteristics of 165 OMPs; to be expanded), Basin (changes in recharge basin or fluvial compartment due to volatilization, biodegradation and photolysis), Filtr (effects of filtration at water/sediment interface in recharge basin or river), Phreatic (changes in unsaturated and saturated zone), Semiconfined (changes in unsaturated and saturated zone), BAR (changes in shallow and deeper aquifer) and RBF (changes in shallow and deeper aquifer). The model calculates for each PSWF type the concentration changes along 1 (phreatic and semiconfined) or 2 (BAR and RBF) standard, very representative flowline(s), when the OMP has broken through in the well field along the respective flowline. Concentration changes in the well field's output over time are calculated for the phreatic well field with a combined Exponential Piston Model (EPM) or better with a Multi-Flowtube Model (MFM), for the semiconfined well field with an MFM exclusively, and for both the BAR and RBF systems with a dual Linear Flowtube Model.

In this report, the most relevant transport equations are specified. Also the equations for travel time and travel time distribution are given (Annex 1 and 2).

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# **1** Introduction

One of the tasks of the BTO research project 'Reconnaissance of future use, application and risks of (new) chemicals especially for drinking water supply', is to predict the behavior of (new) organic micropollutants (OMPs) in groundwater catchments for drinking water supply. The risk assessment needs to include the various processes that may reduce the input concentration of any OMP during the sometimes long transit times (from 1 month up to hundreds of years) in the subsurface from land surface or infiltrating river/basin towards a public supply well field (PSWF).

The approach consists of 3 essential parts:

- definition of 4 standard, vulnerable PSWF types with hydro(geo)logical and hydro(geo)chemical characteristics that are very representative for the Dutch (and Flemish) situation;
- construction of a reactive transport model for each of these 4 PSWF types; and
- application of this model to (at least) 5 OMPs, each with a stepwise input from 0 to 100% (or any constant input concentration), in each of the standard 4 PSWF types. A fictive OMP called 'OMP-X' behaves in a completely conservative way (as the water molecule; worst case scenario), whereas the 4 others are real OMPs that do not behave conservatively.

The chosen reactive transport model is TRANSATOMIC Lite, a restricted, adapted version of TRANSATOMIC (2 § 1.3).

## 2 The 4 selected public supply well field types

In the Netherlands, there are 5 main public supply well field (PSWF) types, A, B, i, K and U (together ABiKU), each of which further subdivided into 2 subtypes (X and X2), with X being more vulnerable to pollution than X2. The characteristics of these 10 PSWF types and their mean raw water quality are presented in Table 2.1.

For this study the following 4 most vulnerable and relevant PSWF types are selected: A (phreatic, sand/gravel aquifer), A2 (semiconfined, sand/gravel aquifer), i (basin artificial recharge of river water, sand aquifer), and U (river and lake bank filtration, sand & gravel aquifer). We thus exclude type K (slightly comparable to type A), B and B2 (not vulnerable to OMPs on the short term), i2 (very similar to i, but more exposed to low flows than i2), and U2 (less common, less vulnerable).

#### 2.1 Type A: phreatic, sand/gravel aquifer

This PSWF type is schematized by one single, centralized well with an aggregated pumping rate, averaged well screen depth, and a circular catchment area (Fig.2.1). The hydrogeological system consists, from top to base, of an unsaturated zone, an upper aquifer zone without well screens, the deeper aquifer zone with well screens, and an aquiclude.



FIG. 2.1. Schematic of a phreatic (left) and semiconfined public supply well field (PSWF; right), with circular groundwater catchment area, divide at distance rE, uniform recharge R, and 3 subterranean zones: an unsaturated zone (h), either the upper aquifer zone above the top of well screens (D1) or an aquitard (D1), and the pumped zone of the aquifer (D2). The well screen is fully penetrating the aquifer if phreatic and D1 = 0, or if semiconfined and D1 >0. Travel time sections along a flow path from site X at radial distance r refer to the whole unsaturated zone (tU, vertical parallel flow), the whole aquitard or the upper aquifer zone above the top of well screens (t1; vertical parallel flow), and the aquifer (t2, predominantly horizontal radial flow).

TABLE 2.1. Characteristics and average raw water quality of the 5 main ABIKU Public Supply Well Field types, with subdivision into more (X) and less (X2) vulnerable to contamination from either land surface or surface water (compilation of data from various sources, among others KIDAP database). A = phreatic, sand & gravel; B = (semi)confined, sand & gravel; i = basin artificial recharge of surface water, sand; K = limestone; U = river and lake bank filtration, sand & gravel. ASL = Above Sea Level.

TYPE		Α	A2	В	B2	i	i2	К	K2	U	U2
			A2	B1	B3			A1K	B3K	A1C	A2C
Types defined by Van Beek et			A3	B2	B4	Meuse	Rhine	A2K	B4K		B1C
al. 1987 (i and i2 excluded)		AI	A4			River	River				B2C
											B3C
Flow resistance Aquitard on top	day	<250	≥250	<2500	≥2500	0	0	<250	≥2500	<250	≥250
Groundwater age spectrum	а	<1-200	20-200	60-260	120- 25000	0.1-50	0.1-50	2-200	50-500	1-100	10-200
First year of operation		18	53	18	81	1976	1955	18	94	189	90
No. of active PSWFs (in 2008)	n	58	14	67	51	4	5	5	4	18	6
No. of closed PSWFs (in 2008)		52	2	5	4		3	1	7	15	5
Q (in 2004)	Mm³/a	2.8	2.2	3.9	3.7	23.6	18.7	3.6	1.4	2.7	1.6
Mean number of wells	n	1(	)	1	2	30	)3	1	5	7	
Land surface altitude	m ASL	19.8	14.3	14.6	13.1	12.3	6.6	76.8	56.1	4.4	0.7
Well screen top	m ASL	-9.0	-8.9	-52.1	-94.6	-3.3	3.0	59.6	24.6	-14.3	-14.9
Well screen base	m ASL	-42.9	-47.7	-102.1	-151.2	-30.5	-19.8	12.0	-30.1	-42.2	-69.4
Mean well screen depth \$	m ASL	-20.3	-21.9	-68.7	-113.4	-12.3	-4.6	43.7	6.4	-23.6	-33.1
рН	-	7.0	7.0	7.2	7.3	7.6	7.8	6.9	7.2	7.2	7.3
temp	°C	10.2	10.7	11.3	12.1	12.7	12.1	11.3	12.7	11.9	12.4
DOC	mg/L	1.7	5.1	2.8	2.5	2.7	2.2			2.8	4.0
CI	mg/L	26	30	24	25	43	88	24	41	84	129
SO4	mg/L	41	42	17	2	55	55	59	68	51	33
HCO3	mg/L	128	214	192	225	162	180	350	387	233	298
NO3	mg/L	6.3	0.6	0.2	0.0	4.7	4.3	39.8	0.0	2.4	0.0
Na		18	18	17	22	31	53	9	26	46	75
К	mg/L	2.5	2.4	2.6	3.5	5.3	5.1	2.2	3.0	4.6	4.8
Са	mg/L	54	81	62	61	67	78	139	129	91	96
Mg		6.3	7.0	6.2	6.8	7.9	10.4	11.0	16.8	10.5	13.7
Fe	mg/L	3.35	6.41	4.60	2.53	0.51	0.12	0.02	0.79	3.12	5.57
Mn	mg/L	0.25	0.27	0.20	0.09	0.09	0.05	0.001	0.03	0.54	0.61
NH4	mg/L	0.19	0.63	0.46	0.51	0.11	0.10	0.01	0.07	1.70	4.01
SiO2	mg/L	17	19	21	20	6	7	28	19	14	20
As		1.8	2.3	1.4	1.4	3.8	3.1	0.3	0.3	2.2	2.8
В	µg/L	19	16	26	74	49	61	12	32	72	73
Cu	µg/L	7.0	0.8	0.8	0.8	3.3	1.6	2.1	0.6	1.6	0.7
F	µg/L	77	75	87	96	295	120	153	168	149	172
I	μg/L	4.6	7.5	5	10.1	7.7	15	3.9	6.3	22.8	26
AOX	µg Cl/L	1.4	2	2	2	13.9	12.2	3.8	1	5.1	4.4
EOCI	µg Cl/L	<0.03	<0.02	0	0.15		0.25	0.03	0.16	0.23	<0.12
Tritium (1983)	Bq/L	21.3	25.0	9.1	8.2	53.2	102.0	23.0	19.3	64.9	50.2
226Ra (1983)	Bq/L	1.4	1.4	1.5	1.6	1.7	0.8	3.9	15.4	1.7	1.7
Thermotolerant Coli	kve/L	0.5	0.05	0.2	<0.01	5	4	1021	0.2	<0.01	<0.01
Sulfite Reducing Clostridia	kve/L	<0.01	0.02	0.03	<0.01	10	24			<0.01	

\$: calculated by taking: (2 x screen top + 1x screen base) / 3

The pumped aquifer is phreatic, the wells are partially penetrating (screen top 5-10 m below the dynamic water table, screen base down to aquiclude top).

Flow is assumed parallel, vertically downward in the unsaturated zone and in the unscreened upper part of the aquifer, but (sub)horizontal and radial in the screened, lower part of the aquifer. The well screen is assumed to penetrate a homogeneous, isotropic aquifer. Dispersion is excluded, resulting in plug (also called piston) flow.

The analytical solutions to calculate the travel times  $t_u$ ,  $t_1$  and  $t_2$  along all flowlines departing at radial distance r from the well (field) in the centre of the circular catchment area (Fig.2.1), are presented in Annex 1, partly based on Stuyfzand (2017).

Table 2.2 presents an overview of the most important standard model settings regarding the flow and redox system, characteristics of the porous medium, quality parameters of the infiltrating water, and hydrological parameters such as travel time and distance, recharge rate etc. Some of these data correspond with the data in Table 2.1. The travel time distribution (TTD) in the aquifer, for water leaving the aquitard or upper, unscreened part of the aquifer flowing towards the wells, is approached with both an exponential piston flow model (EPM) and Multi-flowline model (MFM, see Annex 1). This allows to depict the breakthrough curve (BTC) in the wells as function of time since introduction of the OMP.

TABLE 2.2. Standard model settings for PSWF type A (phreatic) and type A2 (semiconfined). More details in Fig.5.1 (Phreatic) and Fig.5.4 (Semiconfined), respectively.

			Α			A2	
	-	Unsat. zone	Aquifer top	Aquifer \$	Unsat. zone	Aquitard	Aquifer \$
	Flow system	vert. plug	vert. plug	radial plug	vert. plug	vert. plug	radial plug
System	Redox environment	(sub)oxic	(sub)oxic	(sub)oxic	(sub)oxic	anoxic	anoxic
	Dilution [%]	0	0	0	0	0	0
	n = porosity [-]	0.38	0.35	0.35	0.38	0.35	0.35
Porous	D = thickness	5	10	40	5	10	40
medium	θ = soil moisture	0.10			0.10		
	C <sub>ORG</sub> [% d.w.]	0.1	0.05	0.05	0.1	0.15	0.05
Inf	DOC [mg/L]	10	4	2	10	5	3
wator	рН	5.0	6.0	7.0	5.0	6.5	7.0
water	Temp [oC]	10.5	10.5	10.5	10.5	10.5	10.5
	R = Recharge [m/a]	0.3			0.3		
	t <sub>H2O</sub> = travel t. [a] #	2.04	11.67	32.35	2.04	69.44	36.51
Hydro-	Q <sub>OUT</sub> PSWF [m3/d]			7666			7666
logy	Median travel dist. [m] #	5	10	1219	5	10	1219
logy	time since step input [a]	60			60		
	KD aquifer [m2/d]		140	D			1400
	cv covering aquitard [d]		0			500	
	#: travel time and travel d	istance along fl	owline, within e	ach zone. In A	quifer \$, travel di	istance equals	0.7071 r <sub>⊨</sub>

( $r_{\rm E}$  = radial distance from groundwater divide to well field) \$ with fully penetrating well screens

#### 2.2 Type A2: semiconfined, sand/gravel aquifer

In many respects this PSWF type resembles type A. The main difference consists of the role of zone D1 in Fig.2.1. For A2 this zone is an aquitard with vertical hydraulic resistance ( $c_v$ ) of 500 d, for A it is the upper part of the aquifer above the top of well screens (with  $c_v = 0$ ). The hydrogeological system therefore consists, from top to base, of an unsaturated zone, an aquitard, an aquifer with fully penetrating well screens, and an aquiclude.

Table 2.2 gives an overview of the most important standard model settings for type A2. Important differences with type A consist of anoxic conditions in the pumped aquifer, aquifer transmissivity (KD), and travel times. Yet another difference is formed by the reaction of the groundwater table on pumping: In the phreatic case, a depression cone is formed, whereas in the semiconfined case a flat groundwater table is maintained by an intricate system of canals and ditches.

The analytical solutions to calculate the travel times  $t_u$ ,  $t_1$  and  $t_2$  along all flowlines departing at radial distance r from the well (field) in the centre of the circular catchment area (Fig.2.1), are presented in Annex 1, partly based on Stuyfzand (2017). The travel time distribution in the aquifer, for water leaving the aquitard and flowing towards the wells, is approached with a special multi-flowline model, because the EPM model does not work (see Annex 1). This allows to depict the breakthrough curve in the wells as function of time since introduction of the OMP.

#### 2.3 Type i: basin artificial recharge of river water, in a dune sand aquifer

A typical basin artificial recharge (BAR) type PSWF is depicted in Fig.2.2. There is normally no unsaturated zone below the recharge basin, and flow is quasi-uniform in a subhorizontal direction from basin banks to the recovery system, which is composed of wells in a row, drains or canals. In our schematic, we take rows of shallow and deep wells that pump from the (sub)oxic, upper and anoxic, deeper aquifer, respectively. The deep well is often separate from the shallow one, but not everywhere.

The infiltration water is pretreated near the intake (which closes when water quality exceeds the norms), transported by pipeline to the coastal dunes, infiltrated via a set of parallel basins or dune valleys, and recovered after 40-120 m of aquifer passage. Some ambient dune groundwater is also recovered, which is assumed to dilute the concentration of OMPs in the infiltration water if they reach the wells. For further details about BAR systems reference is made to Stuyfzand (1988, 2018).

The travel times in basin and aquifers have been estimated from multitracing studies (Stuyfzand 1986, 2011). For simplicity it is assumed that the flow velocity in the basins and in the aquifers is constant, both in time and space. Table 2.3 gives an overview of the most important standard model settings for type i.

#### 2.4 Type U: river bank filtration, in a fluvial sand aquifer

A typical River Bank Filtration (RBF) type PSWF is depicted in Fig.2.2. There normally is no unsaturated zone below the river bed, and flow is quasi-uniform in a subhorizontal direction from river banks to the recovery system, which is composed of wells in a row. The wells pump deeply anoxic river bank filtrate from the shallow parts of the semiconfined aquifer, which passed the Holocene clayey and peaty aquitard (especially during inundation of the endiked flood plain), and anoxic river bank filtrate from the deeper parts of the semiconfined aquifer, which infiltrated via the sandy, deeper parts of the river bed (the fairway for shipping).

Compared to BAR the infiltration water is in a more reduced state, there is no pretreatment and no possibility of intake stops, and the travel times are longer. Some ambient groundwater is also recovered, which is assumed to dilute the concentration of OMPs in the infiltration water if they reach the wells. For further details about RBF systems reference is made to Stuyfzand et. al. (2006) and Stuyfzand (2011).



FIG. 2.2. Schematic of a Basin Artificial Recharge (BAR) type (left) and River Bank Filtration (RBF) type public supply well field (PSWF; right), with quasi-uniform, subhorizontal flow and 2 aquifer zones with different redox conditions. The well screen is nearly fully penetrating the aquifer.

			i		U					
		Basin	Aquifer 1	Aquifer 2	River	Aquifer 1A	Aquifer 1B			
	Flow system	horiz. plug	subhor. plug	subhor. plug	horiz. plug	subhor. plug	subhor. plug			
Sustam	Redox envir.	oxic	(sub)oxic	anoxic	oxic	deeply anoxic	anoxic			
System	Dilution [%]	0	6	4	0	7	3			
	fraction in well output		0.8	0.2		0.2	0.8			
	n = porosity [-]	1.00	0.38	0.35	1.00	0.35	0.35			
Porous	D = thickness	1	12	38	10	10	40			
medium	org.C [% d.w.]		0.05	0.1		0.15	0.1			
	TOC [mg/L]	5.0	3.0	3.3	4.2	6	4			
Inf	DOC [mg/L]	4.0	3.0	3.3	3.5	6	4			
wator	рН	8.5	7.8	7.6	7.8	7.3	7.5			
water	Temp [oC]	12.1	12.1	12.1	12.5	11.9	11.9			
	R = Recharge [m/a]	66.1			10					
	t <sub>H2O</sub> = travel time [d]	5.1	80	1000	0	3000	2000			
Hydro-	Q <sub>OUT</sub> PSWF [m3/d]		511	99		73	92			
	Median travel dist. [m]	300	87	119	0	750	830			
logy	time since step input [a]	60			60					
	KD aquifer [m2/d]		70	4		150	00			
	cv covering aquitard [d]					3000				

TABLE 2.3. Standard model settings for PSWF i (basin artificial recharge with river water) and U (river bank filtration, Rhine River). Dilution with water not containing the OMP

The travel times in the aquifer have been estimated from multitracing studies and flow modeling (Seegers 2007; Stuyfzand 1985). For simplicity it is assumed that the flow velocity in the aquifer is constant, both in time and space. Table 2.3 gives an overview of the most important standard model settings for type U.

### **3 Reactive transport model TRANSATOMIC**

#### 3.1 The full fledged version

TRANSATOMIC (version 1.3) is the acronym for TRANS Aquifer Transport Of MIcroContaminants. With TRANSATOMIC concentration changes are calculated with analytical solutions set in Excel spreadsheet, for trace elements, radionuclides and organic micropollutants, during aquifer passage and, if applicable, also during detention in a spreading basin or fluvial compartment prior to infiltration (Stuyfzand 2012). The processes addressed include volatilization, photolysis, filtration, advection, dispersion (+ diffusion), dilution by mixing with other water, linear sorption and first order decay (by either radioactive decay or biodegradation), in a hydrologically and hydrogeochemically stationary situation.

The following input signals are included: step, pulse, peak, sinusoidal (Fig.3.1), and any shape (but then with dispersion simplified). The output consists of a concentration-time plot at a specific distance, or a concentration-distance plot at a specific time, or a table giving quantitative information on the behaviour of various micropollutants for a given set of conditions.

Transport is calculated on a flow tube basis, which can be parallel (uniform) or radial. By defining a representative number of flow tubes and also assigning their individual flux contribution (using the HRC), the system's mixed output can be calculated. Parts of the model have been validated against a finite element model comparable to PHREEQC (which is less user-friendly), while other parts have been successfully applied to various test data sets.

TRANSATOMIC.xlsx facilitates a tiered approach for studying aquifer transport behaviour. The first tier could be with a step input (0 to 100%) without dispersion for a single flowline (Fig.3.1), departing from a line source such as an AR basin, an RBF system or an infiltrating water course to a row of wells or a drain parallel to the banks. The second tier could be with a step input without dispersion for a single flowline ànd for the whole well field, with an unsaturated zone on top of an aquitard and an aquifer below (Fig.2.1). The third tier could be a pulse input with dispersion, in the line source setting as above. And the fourth could consist of a reconstructed generalized pesticide input curve, (simplified) dispersion ànd aquifer leaching resulting in a downward shift of the (sub)oxic zone.

The added value of TRANSATOMIC with its tiered approach is, that (i) in one Excel program a tool box is offered for several scenario's of varying complexity, (ii) these tools are really easy to use, and (iii) they generate in some cases direct answers for a multitude of dissolved species (e.g. a group of OMPs or Radionuclides).



FIG. 3.1. Schematic of the 4 main input signal types that can be addressed by TRANSATOMIC (Stuyfzand 2012).

#### 3.2 The lite version

The lite version is the one prepared for this project, by addressing the 4 PSWF types defined above, and by eliminating unused parts of TRANSATOMIC which deal with e.g. (i) effects of atmospheric inputs and evaporation of water from basins, (ii) peak, pulse and sinusoidal input signals, and (iii) behavior of main constituents, trace metals and radionuclides. It now consists of 8 worksheets, in order: ReadMe, OMP-data, OMPs basin, Filtr, Phreatic, Semiconfined, BAR and RBF. The latter 7 are briefly discussed in the sections below.

#### 3.3 OMP database

The OMP database is under continuous expansion, for storing those physico-chemical data that are considered essential for OMP transport behavior in surface water and in the underground. A fraction of this data base (containing 164 OMP in Sept. 2018) is shown in Fig.3.2. In the other 6 worksheets, the essential physico-chemical characteristics of the selected OMPs are automatically retrieved from this internal database via lookup functions.

The data can be subdivided into 2 groups (Fig.3.2). The first consists of data obtained under fixed, generally well defined conditions in the lab (columns 'Molar mass' up to and including 'pK<sub>A</sub>'), and listed in various databases of chemical molecules (and their activities against biological assays), such as Pubchem, Herts and Chemspider (see ReadMe for website links). The second group consists of data regarding half-lives (T½) that apply to field conditions which in general are less well defined, also realizing that the half-life concept forms a crude approximation of the actual (bio)degradation.

It is emphasized that data on half-lives strongly depend on the redox conditions, pH, temperature, EC, scale (e.g. column or pilot in the field or operational MAR system), by-pass possibilities, water saturation (fully unsaturated or unsaturated followed by saturated or fully saturated), recharge interruptions (with an effect on the microbiological population), OMP concentration level etc. In many cases no data exist, so that a conservative estimate has been selected ( $T_{2}^{\prime} = 10^{99}$ ).  $DT_{50}$  values, if available, reflect (bio)degradation rates in aerobic, arable soils in the unsaturated zone, and have been multiplied (in accordance with US-EPA; Greskowiak et al. 2017) with 9 to better represent the lower (bio)degradation rates in the poorer, saturated zone.

OMP in full	OMP	Туре	Molar	Solubility	Vapour	K-Henry	logKow	logKoc	logD	Koc	рКа	T1/2	2 [d]	T1/2	in aquifer	[d]
	abbrev.		Mass	in H2O	pressure	K <sub>H,V</sub>			at pH8	calc		photo	DT50	suboxic	anoxic	deeply
			g/mol	ng/L 20oC	Pa	Pa m3/mol				kg C/L		lysis	soil			anoxic
1,1,1-trichloroethane	1,1,1-TE	pesticide	133.4	4400	1.33E+04	1825	2.47	2.25		178	99.0	1333		273	560	3.5
1,2,4-triazole	1,2,4-triazo	metabolite	69.067	700	0.22	0.022	-0.58	1.95		89	99.0	1E+99	60.5	545	1E+99	1E+99
1,2,4-trimethylbenzene	1,2,4-trime	industrial	120.195	48.2		0	3.42			518	99.0	1E+99		1E+99	1E+99	1E+99
1,2-dichloorethylene	1,2-DEY	pesticide	98.96	4300	1.04E+04	560	2.55			150	99.0	1E+99		28	720	720
1,2-dichlorobenzene	1,2-DB	chlorinated	147	140		126	3.39	2.52		331	99.0	40		183	1E+99	10
1,2-dichloroethane	1,2-DE	chlorinated	99	8770		100	1.51	1.51		32	99.0	1E+99		180	720	1E+99
1,2-dichloropropane	1,2-DCP	chlorinated	113	2700		210	1.99	1.66		46	99.0	1E+99		1E+99	10958	5479
1,3,5-naphthalene trisulfonate	1,3,5-NTS	industrial	365.321			0			-6.62	0	99.0	1E+99		1E+99	569	1E+99
1,3,5-trichlorobenzene	1,3,5-TB	chlorinated	181.4			185	4.19	3.8		6310	99.0	1666667		135	365	1E+99
1,3,5-trimethylbenzene	1,3,5-trime	industrial	120.195	48.2		0	3.42			518	99.0	1E+99		1E+99	1E+99	1E+99
1,3,6-naphthalene trisulfonate	1,3,6-NTS	industrial	365.321			0			-6.62	0	99.0	1E+99		1E+99	1044	1E+99
1,3-dichlorobenzene	1,3-DB	chlorinated	147			240	3.38			839	99.0	1E+99		180	1E+99	7
1,3-dichloropropene	1,3-DPE	pesticide	110.98	2200		200		1.50		32	99.0	0.4	1.7	53	5.7	1E+99
1,4-dichlorobenzene	1,4-DB	chlorinated	147			240	3.39			853	99.0	1E+99		180	1E+99	6
1,4-dioxane	1,4-dioxan	industrial	88.106	283000		0	-0.27	0.595	-0.09	4	-3.9	1E+99		1E+99	36525	18263
1,5-naphthalene disulfonate	1,5-NDS	industrial	286.272			0			-3.43	0	99.0	1E+99		1E+99	1E+99	1E+99
17β-estradiol	estradiol	EDC	272.388	3.9		0	4.01			2065	99.0	1E+99		1E+99	1E+99	1E+99
2,3,3,3-tetrafluor-2-(heptafluorpro	FRD-902	industrial	347.08	207		4.06E-06		1.09		12	3.82	1E+99		1E+99	1E+99	1E+99
2,3,3,3-tetrafluor-2-(heptafluorpro	FRD-903	industrial	330.06			0					2.8	1E+99		1E+99	1E+99	1E+99
2,4-D	2,4-D	pesticide	221.033	24300	0.000019	0.000004	-0.82	1.57		37	3.4	1E+99	13.7	123	1E+99	1E+99
2,6-dichlorobenzamide	BAM	metabolite	190.027	10810	0.00002	0.000000	0.77	1.52		33	99.0	1E+99		35	660	1E+99
3-or 5-chlorotoluidine	3-or 5-chlo	chlorinated	141.6	2510	8.5	0.480	2.26	2.3		200	99.0	1E+99		1E+99	182500	1E+99
4-dimethylaminosulfoton	DMST	metabolite	214.28			0			0.85	7	11.68	1E+99		1E+99	1E+99	1E+99
4-tolyltriazole	5-TT	industrial	133.15	50		0	1.71			508	99.0	1E+99		1E+99	1E+99	1E+99
5-tolyltriazole	4-TT	industrial	133.15	50		0	1.71			508	99.0	1E+99		1E+99	1E+99	1E+99
acenaftene	acene	PAH	154.2			0	4.33	3.94		8710	99.0	1.31	12.3	102	408	1E+99
aldicarb-sulfoxide	aldicarb-so	metabolite	206.26	28000		0		1.00		10	99.0	1E+99	22	1E+99	1E+99	1E+99
amidotrizoic acid	amidoTA	X-ray contr	613.916	500000		0	1.37		-0.63	23	1.13	1E+99		1E+99	40	20
aminomethylphosphonic acid	AMPA	metabolite	111.04	1000000	0.00768	1.27E-10	-2.17	-0.36	-3.89	0	0.4	1E+99	32	46	46	1E+99

FIG. 3.2. Screen dump of upper part of the current OMP database in TRANSATOMIC. The yellow cells present data from various references with variable uncertainty. The  $T_2^{\prime}$  values in red or blue are missing data for which a worst case scenario is chosen or  $9xDT_{50}$ , respectively.

The various options to calculate or select  $K_{oc}$  values led to the following algorithm in the OMP database:

```
if log K_{oc} available, then K_{oc} = 10^{\log KOC}
elseif constants a and b available, then K_{oc} = 10^{b} \{10^{\log KOW}\}^{a}
elseif solubility S available, then K_{oc} = 10^{3.64} \text{ S}^{0.55}
elseif log D_{ow} available, then K_{oc} = 10^{\log DOW}
elseif only log K_{ow} available, then K_{oc} = 10^{\log KOW}
```

 $K_{oc}$  and T<sup>1</sup>/<sub>2</sub> values generally refer to a standard lab temperature ( $t_{REF}$  = 20-25°C) and should therefore be corrected when field temperature ( $t_{FIELD}$ ) is different. Lüers and Ten Hulscher (1996) observed a significant increase of  $K_{oc}$  by a factor of 1.7 ± 0.2 for 6 PAH, when temperature declined from 20 to 10°C. Assuming the relation to be similar to the Van 't Hoff equation and equally performing for other OMPs yields:

$$log\left(\frac{K_{OC,T_1}}{K_{OC,T_2}}\right) = log\left\{1913\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right\} \quad with \ T[K]$$
(3.1)

A decrease in ambient temperature yields a longer OMP half-life. This can be predicted by replacing, in the Arrhenius equation, the reaction rates  $r_{T1}$  and  $r_{T2}$  by  $T/_{2T2}$  and  $T/_{2T1}$  respectively:

$$log\left(\frac{T^{\frac{1}{2}T_{1}}}{T^{\frac{1}{2}T_{2}}}\right) = \frac{-E_{A}}{2.303 R} \left(\frac{1}{T_{2}} - \frac{1}{T_{1}}\right)$$
(3.2)

where:  $T_{2_{T1}}$ ,  $T_{2_{T2}}$  = half life at temperature  $T_1$  and  $T_2$  [K], respectively;  $E_A$  = activation energy, for biochemical reactions ~63 10<sup>3</sup> [J/mol]; R = molecular gas constant [8.314 J K<sup>-1</sup> mol<sup>-1</sup>].

Both temperature corrections are not made in the OMP data-base, but in the sheets Phreatic, Semiconfined, BAR and RBF, if the option to do so is activated in cells AG32:AG33 (phreatic or Semiconfined) or cells AC30:AC31 (BAR or RBF).

The definition of redox conditions or redox zones follows the scheme presented by Stuyfzand (1993, 2012b), which is in simplified form: (sub)oxic:  $NO_3 \ge 1 \text{ mg/L}$ , Fe = Mn < 0.1 mg/L; anoxic:  $O_2$  and  $NO_3 < 1 \text{ mg/L}$ , no  $SO_4$ -reduction; deeply anoxic: =  $O_2$  and  $NO_3 < 1 \text{ mg/L}$ , with  $SO_4$ -reduction and/or methanogenesis.

### 4 Calculation of water quality changes

#### 4.1 Changes in basins or a fluvial compartment

The volatilization, biodegradation and photolysis in recharge basins or a fluvial compartment are separately calculated in sheet 'OMPs Basin', while being calculated also as part of sheets 'BAR' and 'RBF'. In sheets BAR and RBF, these combined processes can be switched on and off in cell AC33.

Assuming simultaneous decay and first order decay rates for all 3 processes, we obtain:

$$C_t = C_0 e^{-(\lambda_V + \lambda_P + \lambda_B)t_{IN}}$$
(4.1)

With:

 $\lambda = \frac{\ln 2}{T^{\frac{1}{2}}}$ 

where:  $\lambda_{v}$ ,  $\lambda_{P}$ ,  $\lambda_{B}$  = decay constant of OMP during resp. volatilisation, photolysis and biodegradation, in general in aerobic environment [1/d];  $T_{2}' =$  half-life during resp. volatilisation, photolysis and biodegradation [d];  $t_{IN}$  = travel time in infiltrating water course [d];  $C_{0}$  = initial concentration [ $\mu$ g/L];  $C_{t}$  = concentration after  $t_{IN}$  days [ $\mu$ g/L].

Volatilisation is calculated using the approach of Southworth (1979), with correction for POC and DOC binding which hampers volatilization. Combination yields:

$$\lambda_{\rm V} = \frac{\kappa_{\rm G}\kappa_{\rm L}\kappa_{\rm H}}{D_{\rm IN}(K_{\rm H}k_{\rm G} + 8.314 {\rm Tk}_{\rm L})(1 + (f_B {\rm DOC} + {\rm POC})K_{\rm OC} 10^{-6})}$$
(4.3)

with:

$$k_{\rm G} = 273.15 \left( V_{\rm CUR} + V_{\rm WIND} \right) \sqrt{\frac{18}{M}}$$
 (4.4)

$$k_{\rm L} = 5.6424 \, V_{\rm CUR}^{0.969} \, D_{\rm IN}^{-0.673} \sqrt{\frac{32}{M}} \, e^{0.526(V_{\rm WIND} - 1.9)} \tag{4.5}$$

where:  $K_{H}$  = constant of Henry [Pa.m<sup>3</sup>/mol; conversion from dimensionless to this unit by multiplying with 1000 RT/M = 2.3542 10<sup>6</sup>/M at 10<sup>o</sup>C]; T = absolute temperature [K];  $D_{IN}$  = mean water depth of infiltrating water course [m]; M = Molecular weight of organic micropollutant [g/mol]; DOC, POC = Dissolved and Particulate Organic Carbon in surface water, respectively [mg C/L]; );  $f_{B}$  = fraction (~0.2) of the binding sites supplied by DOC that bind the OMP and prevent it to sorb to the aquifer [-];  $K_{OC}$  = distribution coefficient of OMP between organic carbon and water [L/kg C];  $V_{CUR}$ ,  $V_{WIND}$  = velocity of water current and wind, respectively [m/s].

Part of the input and output screen of sheet 'OMPs Basin' is shown in Fig.4.1. The input data consist of the desired OMPs, wind speed, flow velocity of the water, water temperature, concentration of OMPs (any unit), TOC and DOC (mg/L), basin depth and mean travel time in basin. These system values (in yellow) reflect the standard state of PSWF type i, but they can be changed.

Two plots are automatically constructed (Fig.4.2), showing the behavior of e.g. chloroform as function of water depth and detention time in basin, and the behavior of 3 OMPs as function of detention time in a basin with fixed depth.

(4.2)

Physic	o-chemic	al charac	teristics	of OMP			Input of system data								Model output						
OMP	OMP	Koc	K <sub>H,V</sub>	T½	2 (d)	GFW	v-Wind	v-Curr	temp	Conc.	TOC	DOC	Depth	t-H2O	۲ د	ŀ	X	λ. C <sub>t</sub>			
OWF	abbrev.	L/kg C	Pa m3/n	ub)oxic	photol	g/mol	m/s	m/s	oC	input	mg	g/I	m	d	۳L	►G	Λv	v	V+B	V+B+P	
1,1,1-trichloroethane	1,1,1-TE	178	1825	273	1333	133.4	5	0.05	17	100	5.2	4	1	5	0.77	506	0.77	2.1	2.1	2.1	
1,2-dichlorobenzene	1,2-DB	331	126	183	40	147.0	5	0.05	17	100	5.2	4	1	5	0.74	482	0.72	2.8	2.7	2.5	
1,3,5-trichlorobenzene	1,3,5-TB	6310	185	135	1.7E+06	181.4	5	0.05	17	100	5.2	4	1	5	0.66	434	0.64	4.0	3.9	3.9	
benzene	C6H6	83	557	10.5	673	78.1	5	0.05	17	100	5.2	4	1	5	1.01	662	1.01	0.7	0.5	0.5	
bromodichloromethane	CHBrCl	117	162	100	1.0E+99	163.8	5	0.05	17	100	5.2	4	1	5	0.70	457	0.68	3.3	3.2	3.2	
bromoform	CHBr3	275	44	60	1.0E+99	252.7	5	0.05	17	100	5.2	4	1	5	0.56	368	0.52	7.5	7.1	7.1	
chloroform	CHCI3	65	304	120	1.0E+99	119.4	5	0.05	17	100	5.2	4	1	5	0.82	535	0.81	1.8	1.7	1.7	
chloromethane	CH3CI	4	2430	28	1.0E+99	50.5	5	0.05	17	100	5.2	4	1	5	1.26	823	1.26	0.2	0.2	0.2	
dibromochloromethane	CHBr2C	182	88	80	1.0E+99	208.3	5	0.05	17	100	5.2	4	1	5	0.62	405	0.59	5.1	4.9	4.9	

FIG. 4.1. Screen dump of part of sheet 'OMP Basin' in TRANSATOMIC. Data input in yellow cells only (system data assumed equal, but can be different); the system values reflect the standard state of PSWF type i, but can be changed. The 3 right most columns give the calculated output concentration, i.e. the concentration ( $C_1$ ) after 5 days detention and removal by Volatilization (V), V + Biodegradation (B), and V+B+ Photolysis (P).



FIG. 4.2. Plots generated by TRANSATOMIC: Left = behavior of chloroform as function of water depth and detention time in basin; Right = behavior of 3 OMPs as function of detention time in basin with fixed depth. The OMPs to plot can be selected.  $CHCI_3$  = chloroform.

#### 4.2 Effects of filtration

The effects of filtration at the water/sediment interface in recharge basins or a river are separately calculated in sheet 'Filtr', while being calculated also as part of sheets 'BAR' and 'RBF'. In sheets BAR and RBF, the filtration process can be switched on and off in cell AC34.

Analytical results of OMPs in surface water generally refer to total concentrations (OMP<sub>TOT</sub>). OMPs are distributed over 3 main fractions: a free fraction ( $f_F$ ; uncomplexed, dissolved), a fraction bound to Dissolved Organic Carbon ( $f_{DOC}$ ; complexed, dissolved), and a fraction bound to Particulate Organic Carbon ( $f_{POC}$ ; siltbound). Within the filtration context, the focus is on  $f_{POC}$ , but for other processes (volatilization and sorption)  $f_{DOC}$  is important to quantify.

The OMP fraction that is removed by filtration ( $f_{POC}$ ) can be approximated only when data on TOC and DOC in the input (surface water) are available. In the following estimate of the 3 fractions discerned, Schwarzenbach et al. (1993) assumed that: (i) all sorption to suspended particles occurs to POC (POC = TOC - DOC), (ii) DOC-binding forces are similar to POC-binding forces; and (iii) DOC offers only a fraction  $f_B$  (equal to 0.17-0.3) of the binding sites supplied by POC (Brannon et al. 1991; Grathwohl 1990):

$OMP_{TOT} = OMP_{FREE} + OMP_{DOC} + OMP_{POC}$	(4.6)
$OMP_{FREE} = (1 - f_{DOC} - f_{POC}) OMP_{TOT}$	(4.6A)
$OMP_{DOC} = f_{DOC} OMP_{TOT}$	(4.6B)
$OMP_{POC} = f_{POC} OMP_{TOT}$	(4.6C)

$$f_{DOC} = \frac{f_B DOC K_{OC}}{10^6 + K_{OC}(f_B DOC + POC)}$$
[-] (4.7A)

$$f_{POC} = f_{SB,OMP} = \frac{OMP_{POC}}{OMP_{TOC}} = \frac{POC K_{OC}}{10^6 + K_{OC}(f_B DOC + POC)}$$
[-] (4.7B)

where: DOC = Dissolved Organic Carbon in surface water [mg/L];  $OMP_{TOT}$  = total concentration of Organic MicroPollutant [µg/L];  $OMP_{DISS}$  = concentration of dissolved OMP;  $f_B$  = fraction (~0.2) of the binding sites supplied by DOC, that bind the OMP and prevent it to sorb to the aquifer [-].

In Fig.4.3 the resulting distribution over free, dissolved and silt-bound is presented for 19 OMPs with diverging  $K_{oc}$  and with 3 DOC/POC ratio's. It is concluded that DOC and POC binding and filtration become important for OMPs with log  $K_{oc}$  >4.

			POC	1.0	mg/l	POC	3.0	mg/l	POC	1.0	mg/l
			DOC	3.0	mg/l	DOC	1.0	mg/l	DOC	30.0	mg/l
Compound	log Koc	X-DOC	% free	% DOC	% POC	% free	% DOC	% POC	% free	% DOC	% POC
			disso	olved	siltbound	disso	olved	siltbound	diss	olved	siltbound
indeno(1,2,3-cd)pyrene	6.77	0.2	9.6	33.9	56.5	5.0	5.9	89.0	2.4	83.7	13.9
chrysene	5.19	0.2	80.0	7.5	12.5	66.7	2.1	31.2	47.8	44.7	7.5
pentachlorobenzene	4.70	0.2	92.6	2.8	4.6	86.2	0.9	13.0	74.0	22.3	3.7
hexachlorobenzene	4.60	0.2	94.0	2.2	3.7	88.7	0.7	10.6	78.2	18.7	3.1
pentachlorophenol	4.52	0.2	95.0	1.9	3.1	90.4	0.6	9.0	81.2	16.1	2.7
dieldrin	4.08	0.2	98.1	0.7	1.2	96.3	0.2	3.5	92.2	6.7	1.1
phenantrene	4.08	0.2	98.1	0.7	1.2	96.3	0.2	3.5	92.2	6.7	1.1
1,2,4-trichlorobenzene	3.80	0.2	99.0	0.4	0.6	98.0	0.1	1.9	95.8	3.6	0.6
hexachlorobutadiene	3.70	0.2	99.2	0.3	0.5	98.4	0.1	1.5	96.6	2.9	0.5
tetrachlorobenzene	3.48	0.2	99.5	0.2	0.3	99.0	0.1	0.9	97.9	1.8	0.3
lindane	3.30	0.2	99.7	0.1	0.2	99.4	0.0	0.6	98.6	1.2	0.2
tetrachloroethylene	2.32	0.2	100.0	0.0	0.0	99.9	0.0	0.1	99.9	0.1	0.0
trichloroethylene	2.20	0.2	100.0	0.0	0.0	99.9	0.0	0.0	99.9	0.1	0.0
mecoprop	1.98	0.2	100.0	0.0	0.0	100.0	0.0	0.0	99.9	0.1	0.0
benzene	1.92	0.2	100.0	0.0	0.0	100.0	0.0	0.0	99.9	0.0	0.0
atrazine	1.85	0.2	100.0	0.0	0.0	100.0	0.0	0.0	100.0	0.0	0.0
carbendazim	1.56	0.2	100.0	0.0	0.0	100.0	0.0	0.0	100.0	0.0	0.0
bentazone	1.00	0.2	100.0	0.0	0.0	100.0	0.0	0.0	100.0	0.0	0.0

FIG. 4.3. Screen dump of sheet 'Filtr' in TRANSATOMIC, showing the effects of sorption of selected OMPs to DOC (Dissolved Organic Carbon) and POC (Particulate Organic Carbon). Sorption to POC leads to removal by filtration. The fraction that is not eliminated by filtration equals 1-%POC/100.

#### 4.3 Changes in the subsurface

#### Conditions

In order to keep the model simple and practical, we assume the following: (i) a stepwise input from 0 to 100% (or any concentration >0) which happened e.g. 60 years ago; (ii) no dispersion, thus plug flow; (iii) downgradient of land surface or the basin / river bank, the OMPs do not participate in any volatilization, photochemical oxidation, dissolution or precipitation reaction, (iv) there is no storage in living biomass nor mobilization from dying biomass; (v) sorption is linear, fully reversible and immediate, and (vi) (bio)degradation follows first order decay, with the same constant for the dissolved and sorbed fraction or with decay exclusively for the dissolved fraction (thus no decay for the sorbed fraction). The choice is to be inserted in cell AG34 (phreatic and semiconfined) or AC32 (BAR or RBF).

#### Retardation by sorption

Retardation of OMPs due to hydrophobic sorption is calculated using the classical approach of Karickhoff (1981) and Schwarzenbach et al. (1993) ( $\rightarrow$  § 10.3 in Appelo & Postma 2005), however with addition of the

effects of (i) DOC-binding according to Kan & Tomson (1990), and (ii) OMP ionization (dissociation) according to Schellenberg et al. (1984):

$$R_{OMP} = 1 + \frac{f_{G \to L} f_{OC} f_{ND} K_{OC}}{1 + f_B DOC \ 10^{-6} f_{ND} K_{OC}}$$
(4.8)

with:

$$f_{ND} = \frac{1}{1 + 10^{(pH - pK_A)}}$$
(4.9)  
$$f_{G \to L} = \frac{\rho_S (1 - n)}{n}$$
(4.10)

Where:  $K_{oc}$  = distribution coefficient of OMP between organic carbon and water [L/kg C];  $f_{G \rightarrow L}$  = conversion factor for kg/kg d.w. to kg/L soil [kg/L];  $f_{oc}$  = weight fraction of organic carbon in aquifer matrix [-];  $f_{ND}$  = OMP fraction Not Dissociated, thus nonionic and thereby sorbable [-];  $pK_A = -logK_A$ , with  $K_A = first$ dissociation constant of acid H-OMP;  $f_{B}$  = fraction (~0.2) of the binding sites supplied by DOC that bind the OMP and prevent it to sorb to the aquifer.

#### Retardation + (bio)degradation along a flowline

The OMP concentration is predicted for any point on a characteristic or representative flowline at time t since infiltration, as follows:

If t - R<sub>OMP</sub> t<sub>H2O</sub> >0: 
$$C_t = C_{IN} e^{-\lambda_B t_{H2O} R_{OMP}} = C_{IN} 2^{\frac{-t_{H2O} R_{OMP}}{T_{2}}}$$
 else C<sub>t</sub> = 0 (4.11)

where:  $\lambda_{B}$  = first order decay constant of OMP during (bio)degradation [1/d]; t<sub>H20</sub> = travel time of the water phase [d];  $T_{2}' =$  half life due to (bio)degradation = ln(2) /  $\lambda_{B}$  [d];  $R_{OMP}$  = retardation factor for OMP according to Eq.1.10; C<sub>IN</sub> = OMP concentration in infiltration water (if BAR or RBF: after losses in recharge basin or fluvial compartment, and after filtration; if phreatic or semiconfined PSWF: after filtration);  $C_t =$ OMP concentration in underground at time t since infiltration.

For a phreatic or semiconfined PSWF only one single characteristic flowline is defined, namely the one with the median total travel time (see Annex 1). The output concentration from each zone (Fig.2.1), calculated with Eq.4.11, forms the input concentration for the next zone until reaching the pumping well(s).

For a BAR or RBF system 2 representative flowlines are defined (Fig.2.2), a shallow and a deep one, both from a representative basin / river bank directly to the well(s).

#### Concentration in the output from a phreatic or semiconfined well (field)

The travel time distribution (TTD) in the mixed output from the well (field) is approached in 2 ways: with a combined Exponential Piston model (EPM) and with a Multi-Flowtube model (MFM).

The EPM model consist of a first part with vertical, parallel piston flow, in both the unsaturated zone and aquitard or aquifer zone 1, followed by (sub)horizontal, radial flow in aquifer zone 2 where full mixing occurs which can be described by an exponential TTD. This results in the following equation to predict the OMP concentration at time t since infiltration, in the well:

if 
$$t - (R_{U}t_{U} + R_{1}t_{1}) \leq 0$$
  
else:  
with:  
 $C_{IN,2} = \frac{C_{IN}}{\frac{R_{U}t_{U}}{2^{(T_{2}'_{U})}U} + \frac{R_{1}t_{1}}{(T_{2}'_{U})_{1}}} (1 - e^{\frac{-R(t - R_{U}t_{U} - R_{1}t_{1})}{D_{2}n_{2}R_{2}}})$ 
(4)

with:

Where:  $C_{IN,2}$  = average input concentration for saturated aquifer (zone 2) since abrupt pollutant breakthrough [%]; R = groundwater recharge [m/d];  $R_{u}$ ,  $R_{1}$ ,  $R_{2} =$  retardation factor for pollutant in unsaturated zone, the upper unscreened part of the aquifer or aquitard (zone 1) and aquifer (zone 2), respectively [-];  $(T_{2})_{2}$  = half-life of pollutant in aquifer (zone 2) [d].

 $(\Lambda 0)$ 

12)

In the EPM model, the travel time in the unsaturated zone and groundwater zone 1 is set equal to the calculated travel time for the standard flowline starting on site X at distance 0.7071  $r_{\epsilon}$  from the well (field).

The MFM model is defined by taking 11 flowlines from ground level to the well (field), covering the whole spectrum of radial distances, from a total of ~100 flowlines for which the travel times in the unsaturated zone and both groundwater zones now have been calculated for each flowline individually. This results in more accuracy but also some more work. Details on both models are given in Annex 1, and a comparison of the results with both TTD models is presented in Annex 2.

#### Concentration in the output from a BAR or RBF system

The output concentration is calculated based on the volumetric contribution of the shallow and deep flowline (each with a linear TTD, which transforms them into a flowline bundle), and the permanent admixing of ambient groundwater with OMP concentration = 0. As a result we obtain:

If t - R<sub>OMP</sub> t<sub>H20</sub> >0: 
$$C_t = C_{IN} (f_A \ 2^{-(\frac{t_{H20}R_{OMP}}{T^{\frac{1}{2}}})_{\Sigma A}} + f_B \ 2^{-(\frac{t_{H20}R_{OMP}}{T^{\frac{1}{2}}})_{\Sigma B}})$$
 else C<sub>t</sub> = 0 (4.13)

with:

$$2^{-(\frac{t_{H2O}R_{OMP}}{T_{12}'})_{\Sigma A}} = \sum_{\% P=0}^{\% P=100} \frac{2^{-(\frac{t_{H2O}R_{OMP}}{T_{12}'})_A}}{N}$$

Where:  $f_A$ ,  $f_B$  = volumetric fraction of water from the shallow and deeper aquifer, respectively, in the abstracted water [-]; ()<sub>ΣA</sub>, ()<sub>ΣB</sub> = the average ratio for the shallow and deeper aquifer, respectively [-];  $C_{IN}$  = OMP concentration in the infiltrating water, after changes in the recharge basin or fluvial compartment (if included) and after filtration losses (if included); %P = percentile in TTD; N = number of steps in the TTD, set at 11 (thus %P = 0, 10, ....90, 100).

Eq.4.13 (for the shallow flowline bundle) also holds for the deeper flowline bundle. The linear TTD is such that the travel time for each of 11 flowlines becomes:

$$t_P = \frac{50 + \%P}{100} t_{50} \tag{4.15}$$

This results in the standard TTD setting for each flowline bundle, as defined in cells AP61:AZ61 (shallow) and BA61:BK61 (deep). These settings can be changed if a different TTD is desired, offering in total 20 points for its definition.

(4.14)

### 5 Model input and output

#### 5.1 For a standard phreatic PSWF

The model settings for a standard Dutch phreatic PSWF are shown in Fig.5.1. The yellow cells can be changed, the white (uncolored) ones result from calculations or contain text. Of course, the yellow cells should *NOT* be changed if the tool is serving the general purpose of predicting the behavior of (new) organic micropollutants (OMPs) in the standardized phreatic PSWF type.

Other model input consists of the OMPs for which we wish to predict the behavior. This needs to be done in: (i) column C of sheets OMPs Phreatic, OMPs Semiconfined, OMPs BAR and OMPs RBF. Even the whole OMP database can be filled in, or several OMPs can be selected with filter in column A (the selection is to defined in column Y of sheet OMP-data); (ii) cells AL8:AP8 (phreatic and semiconfined) or AH8:AL8 (BAR and RBF) to obtain concentration plots versus time for 5 OMPs; and (iii) BB18 (phreatic and semiconfined) or AX11 (BAR and RBF) to produce a concentration plot versus distance for 1 OMP.

Acnost	Barameter	Unsaturated	Aquifer	Aquifer
Aspeci	Faiailletei	Zone	Zone 1	Zone 2
	Scenario	Phreatic	aquifer, partial pe	enetration
System	Flow system	vertical p	iston flow	Radial to <b>PSWF</b>
	Redox system: 1 = (sub)oxic; 2 = anoxic; 3 = deeply anoxic	1	1	1
	porosity (n)	0.38	0.35	0.35
	soil moisture content θ [m3/m3]	0.10		
Porous	density solids ρ <sub>s</sub> [kg/L]	2.65	2.65	2.65
medium	f <sub>oc</sub> = fraction organic carbon	0.001	0.0005	0.0005
	D = thickness of zone [m]	5	10	40
	thickness full capillary fringe [m]	0.4		
	DOC after infiltration [mg/L]	10	4	2
Infiltration	TOC prior to infiltration [mg/L]	10		
wator	DOC/TOC prior to infiltration [-]	1.0		
water	рН	5.0	6.0	7.0
	Temperature [oC]		10.5	
	Recharge R [m/a]	0.3		
	travel time H <sub>2</sub> O along flowline, in zone [d]	782	4133	11814
	Q <sub>OUT</sub> well (field) [m3/h]			319.4
Hydrology	Median distance of site to well [m] ##		1219	
riyurology	time since stepwise input increase [a]	60	60	60
	KD aquifer [m2/d]			1400
	Vertical resistance aquitard cv [d]		0	
	Role of zone 1: 1 = aquitard, 2 = unscreened aquifer top		2	
	Temp. correction K <sub>oc</sub> : 0 = No, 1 = Yes	1		
Special	Temp correction T <sup>1</sup> / <sub>2</sub> : 0 = No, 1 = Yes	0		
model	Biodegradation sorbed phase: 0 = No, 1 = Yes (as in water)	1		
settings	Fixed or calc. thickness $D_U \& D_1$ : 1 = fixed, 2 = calc.	2		
	Thickness of zone at site X [m]	5.30	9.70	
##:	Standard setting in cell Ai45 = 0.7071 r <sub>E</sub>			

FIG. 5.1. Input screen of sheet 'Phreatic', displaying the main system parameters and special model settings. The values shown refer to the settings for a standard Dutch, Phreatic, Public Supply Well Field. It is very essential that the 'Role of zone 1' be fixed at 2 (otherwise changing to the semiconfined case). Time since stepwise input increase = time elapsed since pollutant(s) were introduced in input.

			oxic unsaturated zone					(sub)oxic aquifer top (zone 1)					(sub)oxic aquifer zone 2					Total						
Se -	OMP	OMP in full	ОМР	K <sub>oc</sub>	nK.		T1/2 [d]			Front	PV <sub>c</sub> [n]	C <sub>IN</sub>	if PV <sub>C</sub> ≥1		Front	PV <sub>c</sub> [n]	CIN	if PV <sub>C</sub> ≥ı		Front	PV <sub>c</sub> [n]	C <sub>IN</sub>	if PV <sub>C</sub> ≥ı	tEQ
Sel	abbrev.		type	calc	prog	suboxic	anoxic	deeply	R <sub>OMP</sub>	[m] after	bottom	CIN	COUT	R <sub>OMP</sub>	[m] after	bottom	CIN	Cout	R <sub>OMP</sub>	[m] after	pumping	CIN	COUT	PV <sub>c</sub> =1
Sel	e							anoxic		60.00 a	unsat.	%	%		60.00 a	suboxic	%	%		60.00 a	well(s)	%	%	year
0	1,1,1-TE	1,1,1-trichloroethane	pesticide	294.1	99.0	273	560	4	2.3	>5.3	12.3	100.00	1.10	1.7	>15	2.5	1.10	0.00	1.7	1069.7	0.7	0.00	0.00	80.1
2	1,2,4-triazo	1,2,4-triazole	metabolit	147.2	99.0	545	1.E+99	1.E+99	1.6	>5.3	17.1	100.00	19.62	1.4	>15	3.2	19.62	0.02	1.4	1204.7	1.0	0.02	0.00	63.0
0	1,2,4-trime	1,2,4-trimethylbenzene	industrial	856.8	99.0	1.E+99	1.E+99	1.E+99	4.7	>5.3	6.0	100.00	100.00	3.1	>15	1.3	100.00	100.00	3.1	797.0	0.4	100.00	100.00	145.7
0	1,2-DEY	1,2-dichloorethylene	pesticide	248.0	99.0	28	720	720	2.1	>5.3	13.5	100.00	0.00	1.6	>15	2.6	0.00	0.00	1.6	1107.0	0.8	0.00	0.00	74.7
0	1,2-DB	1,2-dichlorobenzene	chlorinat	547.7	99.0	183	1.E+99	10	3.4	>5.3	8.3	100.00	0.00	2.3	>15	1.8	0.00	0.00	2.3	916.4	0.5	0.00	0.00	109.7
0	1,2-DE	1,2-dichloroethane	chlorinate	53.5	99.0	180	720	1.E+99	1.2	>5.3	22.8	100.00	2.45	1.1	>15	3.9	2.45	0.00	1.1	>1234	1.2	0.00	0.00	52.0
0	1,2-DCP	1,2-dichloropropane	chlorinat	75.6	99.0	1.E+99	10958	5479	1.3	>5.3	21.1	100.00	100.00	1.2	>15	3.7	100.00	100.00	1.2	>1234	1.1	100.00	100.00	54.6
0	1,2,4-TB	1,2,4-trichlorobenzene	chlorinat	1.0E+04	99.0	135	365	1.E+99	45.2	3.3	0.6	100.00	0.00	26.5	3.3	0.2	0.00	0.00	26.6	3.3	0.0	0.00	0.00	1255.8
0	1,3,5-NTS	1,3,5-naphthalene trisulfona	industrial	0.0	99.0	1.E+99	569	1.E+99	1.0	>5.3	28.0	100.00	100.00	1.0	>15	4.5	100.00	100.00	1.0	>1234	1.3	100.00	100.00	45.8
0	1,3,5-TB	1,3,5-trichlorobenzene	chlorinat	1.0E+04	99.0	135	365	1.E+99	45.2	3.3	0.6	100.00	0.00	26.5	3.3	0.2	0.00	0.00	26.6	3.3	0.0	0.00	0.00	1255.8
0	1,3,5-trime	1,3,5-trimethylbenzene	industrial	856.8	99.0	1.E+99	1.E+99	1.E+99	4.7	>5.3	6.0	100.00	100.00	3.1	>15	1.3	100.00	100.00	3.1	797.0	0.4	100.00	100.00	145.7
0	1,3,6-NTS	1,3,6-naphthalene trisulfona	industrial	0.0	99.0	1.E+99	1044	1.E+99	1.0	>5.3	28.0	100.00	100.00	1.0	>15	4.5	100.00	100.00	1.0	>1234	1.3	100.00	100.00	45.8
0	1,3-DB	1,3-dichlorobenzene	chlorinat	1387.3	99.0	180	1.E+99	7	7.0	>5.3	4.0	100.00	0.00	4.4	13.9	0.9	0.00	0.00	4.4	13.9	0.0	0.00	0.00	207.5
0	1,3-DPE	1,3-dichloropropene	pesticide	52.1	99.0	53	6	1.E+99	1.2	>5.3	22.9	100.00	0.00	1.1	>15	3.9	0.00	0.00	1.1	>1234	1.2	0.00	0.00	51.9
0	1,4-DB	1,4-dichlorobenzene	chlorinat	1410.4	99.0	180	1.E+99	6	7	>5.3	4.0	100.00	0.00	4.5	13.7	0.9	0.00	0.00	4	13.7	0.0	0.00	0.00	210.2
1	1,4-dioxan	1,4-dioxane	industria	6.5	-3.9	1.E+99	36525	18263	1.0	>5.3	28.0	100.00	100.00	1.0	>15	4.5	100.00	100.00	1.0	>1234	1.3	100.00	100.00	45.8

FIG. 5.2. Fragment of sheet 'Phreatic', showing OMP input and predicted concentration at 3 points along the flowline starting at median radial distance ( $r = 0.7071 r_{e}$ ): upon leaving the unsaturated zone, unscreened upper aquifer (zone 1) and aquifer (in the well), respectively.





FIG. 5.3. Standard plots generated by TRANSATOMIC: Concentration versus time for the whole Phreatic PSWF (applying EPM model), and concentration versus distance for the flowline when OMP has broken through in the well (field). Dispersion ignored.

ASTCA is a metabolite of herbicide Florasulam.

The distance of the start point of the standard flowline to the well (field) is automatically calculated in cell Ai45 by taking 0.7071  $r_{e}$  ( $r_{e}$  = distance of groundwater divide to well(s); Fig.1.1). This equals the median flowline distance at which 50% of the abstracted water volume has a shorter or longer travel distance (0.7071 =  $\sqrt{1/2}$ ). In the standard setting, travel times along the fixed (or chosen) flowline in each of the 3 compartments are automatically calculated. Also the local thickness of the unsaturated zone (at the start point of the flowline) and zone 1 is automatically calculated, if cell AG35 = 2 (otherwise the values on row 17 are taken).

The model output of sheet Phreatic consists of: (i) tabular information for all OMPs in columns K-AC (Fig.5.2); concentration plots versus time for 5 OMPs (Fig.5.3 top); and (iii) a concentration plot versus distance along the standard flowline for 1 OMP (Fig.5.3 base). In the tabular output (Fig.5.2), results of calculation consist of the OMP retardation factor  $R_{OMP}$ , the front position after 60 years, the contaminant pore volumes (PV<sub>c</sub>), the input concentration (C<sub>IN</sub>), output concentration when PV<sub>c</sub> >1 (C<sub>OUT</sub>), and the time

needed for breakthrough in the well ( $t_{EQ}$ ). The output of the first part of the flowline is the input for the second, and the output of the second is the water abstracted by the well.

The concentration plots versus time for 5 OMPs in the well field's output were made by application of the EPM model for the travel time distribution (TTD). See Annex 2 for a comparison between the results with EPM and MFM. MFM is slightly more accurate than EPM for a phreatic PSWF.

#### 5.2 Model input and output for a standard semiconfined PSWF

The explanations given above for the standard phreatic PSWF are largely valid for the semiconfined PSWF as well. The model settings for a standard Dutch semiconfined PSWF are shown in Fig.5.4.

The model output of sheet Semiconfined consists of: (i) tabular information for all OMPs in columns K-AC (Fig.5.5); concentration plots versus time for 5 OMPs (Fig.5.6 top); and (iii) a concentration plot versus distance along the standard flowline for 1 OMP (Fig.5.6 base).

The concentration plots versus time for 5 OMPs in the well field's output were made by application of the MFM model for the travel time distribution (TTD). See Annex 2 for a comparison between the results with EPM and MFM. MFM is much more accurate than EPM for a semiconfined PSWF.

Acnost	Barameter	Unsaturated	Aquitard	Aquifer
Aspeci	Faialletei	Zone	Zone 1	Zone 2
	Scenario	S	emiconfined aquit	fer
System	Flow system	vertical p	iston flow	Radial to PSWF
	Redox system: 1 = (sub)oxic; 2 = anoxic; 3 = deeply anoxic	1	2	2
	porosity (n)	0.38	0.35	0.35
	soil moisture content θ [m3/m3]	0.10		
Porous	density solids ρ <sub>s</sub> [kg/L]	2.65	2.65	2.65
medium	f <sub>oc</sub> = fraction organic carbon	0.001	0.0015	0.0005
	D = thickness of zone [m]	5	10	40
	thickness full capillary fringe [m]	0.4		
	DOC after infiltration [mg/L]	10	5	3
Infiltration	TOC prior to infiltration [mg/L]	10		
water	DOC/TOC prior to infiltration [-]	1.0		
water	pH	5.0	6.5	7.0
	Temperature [oC]		10.5	
	Recharge R [m/a]	0.3		
	travel time H <sub>2</sub> O along flowline, in zone [d]	745	58420	44372
	Q <sub>OUT</sub> well (field) [m3/h]			319.4
Hydrology	Median distance of site X to well [m] ##		1775	
nyurology	time since stepwise input increase [a]	60	60	60
	KD aquifer [m2/d]			1400
	Vertical resistance aquitard cv [d]		500	
	Role of zone 1: 1 = aquitard, 2 = unscreened aquifer top		1	
	Temp. correction $K_{OC}$ : 0 = No, 1 = Yes	1		
Special	Temp correction $T\frac{1}{2}$ : 0 = No, 1 = Yes	0		
model	Biodegradation sorbed phase: 0 = No, 1 = Yes (as in water)	1		
settings	Fixed or calc. thickness $D_U \& D_1$ : 1 = fixed, 2 = calc.	1		
	Thickness of zone at site X [m]	5.00	10.00	

FIG. 5.4 Input screen of sheet 'Semiconfined', displaying the main system parameters and special model settings. The values shown refer to the settings for a standard Dutch, semiconfined, Public Supply Well Field. It is very essential that the 'Role of zone 1' be fixed at 1 (otherwise changing to the phreatic case). Time since stepwise input increase = time elapsed since pollutant(s) were introduced in input.

	Physico-chemical characteristic of Organic MicroPollutants (OMPs)									oxic unsaturated zone					anoxic	aquitard (a	zone 1)		anoxic aquifer (zone 2)					Total
Se -	OMP	OMP in full	ОМР	κ <sub>oc</sub>	nK.		T1/2 [d]			Front	PV <sub>c</sub> [n]	C <sub>IN</sub>	if PV <sub>C</sub> ≥ı		Front	PV <sub>c</sub> [n]	C <sub>IN</sub>	if PV <sub>C</sub> ≥1		Front	PV <sub>c</sub> [n]	CIN	if PV <sub>C</sub> ≥1	tEG
Sele	abbrev.		type	calc	pria	suboxic	anoxic	deeply	ROMP	[m] after	bottom	CIN	Cout	R <sub>OMP</sub>	[m] after	bottom	CIN	COUT	R <sub>OMP</sub>	[m] after	pumping	CIN	COUT	PV <sub>c</sub> =1
Sele								anoxic		60.00 a	unsat.	%	%		60.00 a	suboxic	%	%		60.00 a	well(s)	%	%	year
0	1,1,1-TE	1,1,1-trichloroethane	pesticide	294.1	99.0	273	560	4	2.3	>5.0	13.0	100.00	1.36	3.2	1.8	0.1	1.36	0.00	1.7	1.8	0.0	0.00	0.00	721.2
2	1,2,4-triazo	1,2,4-triazole	metabolit	147.2	99.0	545	1.E+99	1.E+99	1.6	>5.0	18.0	100.00	21.19	2.1	2.7	0.2	21.19	21.19	1.4	2.7	0.0	21.19	21.19	502.5
0	1,2,4-trime	1,2,4-trimethylbenzene	industria	856.8	99.0	1.E+99	1.E+99	1.E+99	4.7	>5.0	6.3	100.00	100.00	7.3	0.8	0.1	100.00	100.00	3.1	0.8	0.0	100.00	100.00	1557.8
0	1,2-DEY	1,2-dichloorethylene	pesticide	248.0	99.0	28	720	720	2.1	>5.0	14.2	100.00	0.00	2.8	2.0	0.1	0.00	0.00	1.6	2.0	0.0	0.00	0.00	652.6
0	1,2-DB	1,2-dichlorobenzene	chlorinat	547.7	99.0	183	1.E+99	10	3.4	>5.0	8.7	100.00	0.01	5.0	1.1	0.1	0.01	0.01	2.3	1.1	0.0	0.01	0.01	1098.3
0	1,2-DE	1,2-dichloroethane	chlorinat	53.5	99.0	180	720	1.E+99	1.2	>5.0	23.9	100.00	2.92	1.4	4.0	0.3	2.92	0.00	1.1	4.0	0.0	0.00	0.00	363.1
0	1,2-DCP	1,2-dichloropropane	chlorinat	75.6	99.0	1.E+99	10958	5479	1.3	>5.0	22.2	100.00	100.00	1.6	3.6	0.2	100.00	0.32	1.2	3.6	0.0	0.32	0.01	396.0
0	1,2,4-TB	1,2,4-trichlorobenzene	chlorinat	1.0E+04	99.0	135	365	1.E+99	45.2	3.3	0.7	100.00	0.00	77.2	3.3	0.2	0.00	0.00	26.5	3.3	0.0	0.00	0.00	15669.7
0	1,3,5-NTS	1,3,5-naphthalene trisulfon	industria	0.0	99.0	1.E+99	569	1.E+99	1.0	>5.0	29.4	100.00	100.00	1.0	5.6	0.4	100.00	0.00	1.0	5.6	0.0	0.00	0.00	283.5
0	1,3,5-TB	1,3,5-trichlorobenzene	chlorinat	1.0E+04	99.0	135	365	1.E+99	45.2	3.3	0.7	100.00	0.00	77.2	3.3	0.2	0.00	0.00	26.5	3.3	0.0	0.00	0.00	15669.7
0	1,3,5-trime	1,3,5-trimethylbenzene	industria	856.8	99.0	1.E+99	1.E+99	1.E+99	4.7	>5.0	6.3	100.00	100.00	7.3	0.8	0.1	100.00	100.00	3.1	0.8	0.0	100.00	100.00	1557.8
0	1,3,6-NTS	1,3,6-naphthalene trisulfon	industria	0.0	99.0	1.E+99	1044	1.E+99	1.0	>5.0	29.4	100.00	100.00	1.0	5.6	0.4	100.00	0.00	1.0	5.6	0.0	0.00	0.00	283.5
0	1,3-DB	1,3-dichlorobenzene	chlorinat	1387.3	99.0	180	1.E+99	7	7.0	>5.0	4.2	100.00	0.00	11.2	0.5	0.0	0.00	0.00	4.4	0.5	0.0	0.00	0.00	2345.8
0	1,3-DPE	1,3-dichloropropene	pesticide	52.1	99.0	53	6	1.E+99	1.2	>5.0	24.0	100.00	0.00	1.4	4.0	0.3	0.00	0.00	1.1	4.0	0.0	0.00	0.00	361.0
0	1,4-DB	1,4-dichlorobenzene	chlorinat	1410.4	99.0	180	1.E+99	6	7	>5.0	4.2	100.00	0.00	11.4	0.5	0.0	0.00	0.00	4	0.5	0.0	0.00	0.00	2380.2
1	1,4-dioxan	1,4-dioxane	industria	6.5	-3.9	1.E+99	36525	18263	1.0	>5.0	29.4	100.00	100.00	1.0	5.6	0.4	100.00	33.00	1.0	5.6	0.0	33.00	14.22	283.5

FIG. 5.5. Fragment of sheet 'Semiconfined', showing OMP input and predicted concentration at 3 points along the flowline starting at median radial distance ( $r = 0.7071 r_{e}$ ): upon leaving the unsaturated zone, aquitard and aquifer (in the well), respectively. NB: After 60 years no OMP reached the aquifer along this flowline ( $PV_{c} = 0$ ). Only after 283.5 years the first OMPs such as 1,4-dioxane can reach the well.



#### 5.3 Model input and output for a standard BAR type PSWF

The explanations given above for the standard phreatic PSWF are largely valid for the Basin Artificial Recharge type PSWF as well. The model settings for a standard Dutch BAR system are shown in Fig.5.7. Note that the travel time is one of the input parameters (not calculated as for type A and A2). The model output of sheet BAR consists of: (i) tabular information for all OMPs in columns K-Y (Fig.5.8); concentration plots versus time for 5 OMPs (Fig.5.9 top); and (iii) a concentration plot versus distance along the standard flowline for 1 OMP (Fig.5.9 base).

The distance of the startpoint of both standard flowlines to the well (field) and the total travel time of the water are fixed, but can be changed, as are all yellow cells.

In the tabular output (Fig.1.14), results of calculation consist of the retardation factor R, the front position after 60 years, the contaminant pore volumes (PV<sub>c</sub>), the input concentration (C<sub>IN</sub>; including changes in the recharge basins (if AC33 =1) and effects of filtration (if AC34 = 1), output concentration when PV<sub>c</sub> >1 (C<sub>OUT</sub>), the time needed for breakthrough of the shallow (t<sub>EQ-up</sub>) and deeper flowline (t<sub>EQ-lo</sub>) in the well, and the mixed output concentration of the BAR system (including effects of dilution with ambient groundwater).

		Challow	Deemen	Missimm					
Aspect	Parameter	Aquifor	Aquifor	in wolls					
	Secondaria -	BAP in duno sand							
0	Scenario								
System	Flow system	(SUD)	n flow						
	Redox system: 1 = (sub)oxic; 2 = anoxic; 3 = deeply anoxic	1	2	1+2					
	porosity (n)	0.38	0.35						
Porous	rho solids [kg/L]	2.65	2.65						
medium	f <sub>oc</sub> = fraction organic carbon	0.0005	0.001						
	D = thickness of zone [m]	12	38	50					
	DOC after infiltration [mg/L]	3	3.3	3.1					
Infiltration	TOC prior to infiltration [mg/L]	4.7							
minu auon	DOC/TOC prior to infiltration [-]	0.85							
water	pH	7.80	7.60	7.76					
	Temperature [oC]	12.1							
	Recovery rate Q <sub>OUT</sub> [m3/d]			51200					
	travel time H2O in zone [d]	80	1000						
	v-H2O [m/d]	1.09	0.12						
Ibudaalaanu	flow path length [m]	87	119						
Hydrology	time since step input [a]	60	60						
	contribution inf. water to recovery system	0.74	0.16	0.90					
	contribution ambient groundwater to recovery	0.06	0.04	0.10					
	Settings for recharge basin	5	See cells CF7:CM	7					
	Temp. correction K <sub>oc</sub> : 0 = No, 1 = Yes	1							
Special	Temp correction T <sup>1</sup> / <sub>2</sub> : 0 = No, 1 = Yes	0							
model	Biodegradation sorbed phase: 0 = No, 1 = Yes (as in water)	1							
settings	Changes in recharge basins included: 0 = No, 1 = Yes	1							
U U	Filtration at basin / river bank included: 0 = No. 1 = Yes	1							

FIG. 5.7 Input screen of sheet 'BAR', displaying the main system parameters and special model settings. The values shown refer to the settings for a standard Dutch, Basin Artificial Recharge system.

				BAR	(sub)oxic	zone		BAR anoxic zone						Wells							
Sel 🖵	OND		0110	Koc	рK <sub>A</sub>		T1/2 [d]			Front	PVc		if PPV ≥1		Front	PVc		if PV <sub>c</sub> ≥1	t <sub>EQ-up</sub>	t <sub>EQ-lo</sub>	Mixed
Selec	OMP	OMP in full	OMP	calc		suboxic	anoxic	deeply	ROMP	[m] after	Upper	CIN	COUT	ROMP	[m] after	Lower	CIN	COUT	PV <sub>c</sub> =1	PV <sub>c</sub> =1	Court
Selec	abbrev.		type					anoxic		60.00 a	n	%	%		60.00 a	n	%	%	year	year	%
0	1,1,1-TE	1,1,1-trichloroethane	pesticide	177.8	99.0	273	560	4	1.4	>87	197.9	2.07	1.6E+00	1.9	>119	11.7	2.07	6.0E-01	0.30	5.1	1.25
2	1,2,4-triazo	1,2,4-triazole	metabolit	89.0	99.0	545	1.E+99	1.E+99	1.2	>87	229.8	96.28	8.5E+01	1.4	>119	15.2	96.28	9.6E+01	0.26	3.9	78.51
0	1,2,4-trimet	1,2,4-trimethylbenzene	industrial	518.0	99.0	1.E+99	1.E+99	1.E+99	2.1	>87	129.2	99.96	1.0E+02	3.5	>119	6.2	99.96	1.0E+02	0.46	9.7	89.97
0	1,2-DEY	1,2-dichloorethylene	pesticide	150.0	99.0	28	720	720	1.3	>87	206.9	1.02	7.4E-02	1.7	>119	12.6	1.02	3.9E-01	0.29	4.8	0.12
0	1,2-DB	1,2-dichlorobenzene	chlorinate	331.1	99.0	183	1.E+99	10	1.7	>87	159.7	2.51	1.5E+00	2.63	>119	8.3	2.51	2.5E+00	0.38	7.2	1.50
0	1,2-DE	1,2-dichloroethane	chlorinate	32.4	99.0	180	720	1.E+99	1.1	>87	256.0	1.29	9.3E-01	1.2	>119	18.9	1.29	4.9E-01	0.23	3.2	0.76
0	1,2-DCP	1,2-dichloropropane	chlorinate	45.7	99.0	1.E+99	10958	5479	1.1	>87	249.3	1.60	1.6E+00	1.2	>119	17.9	1.60	1.5E+00	0.24	3.4	1.43
0	1,2,4-TB	1,2,4-trichlorobenzene	chlorinate	6309.6	99.0	135	365	1.E+99	14.6	>87	18.8	3.90	9.7E-03	31.9	81.69	0.7	3.90	5.8E-01	3.20	87.4	0.10
0	1,3,5-NTS	1,3,5-naphthalene trisulfonate	industrial	0.0	99.0	1.E+99	569	1.E+99	1.0	>87	273.9	100.00	1.0E+02	1.0	>119	21.9	100.00	3.0E+01	0.22	2.7	78.73
0	1,3,5-TB	1,3,5-trichlorobenzene	chlorinate	6309.6	99.0	135	365	1.E+99	14.6	>87	18.8	3.90	9.7E-03	31.9	81.69	0.7	3.90	5.8E-01	3.20	87.4	0.10
0	1,3,5-trimet	1,3,5-trimethylbenzene	industrial	518.0	99.0	1.E+99	1.E+99	1.E+99	2.1	>87	129.2	99.96	1.0E+02	3.5	>119	6.2	99.96	1.0E+02	0.46	9.7	89.97
0	1,3,6-NTS	1,3,6-naphthalene trisulfonate	industrial	0.0	99.0	1.E+99	1044	1.E+99	1.0	>87	273.9	100.00	1.0E+02	1.0	>119	21.9	100.00	5.1E+01	0.22	2.7	82.24
0	1,3-DB	1,3-dichlorobenzene	chlorinate	838.7	99.0	180	1.E+99	7	2.8	>87	97.4	2.61	1.1E+00	5.1	>119	4.3	2.61	2.6E+00	0.62	14.0	1.23
0	1,3-DPE	1,3-dichloropropene	pesticide	31.5	99.0	53	6	1.E+99	1.1	>87	256.5	0.00	7.5E-05	1.2	>119	19.0	0.00	3.5E-57	0.23	3.2	0.00
0	1,4-DB	1,4-dichlorobenzene	chlorinate	852.7	99.0	180	1.E+99	6	2.8	>87	96.4	2.61	1.1E+00	5.2	>119	4.2	2.61	2.6E+00	0.62	14.2	1.22
1	1.4-dioxane	1.4-dioxane	industrial	3.9	-3.9	1.E+99	36525	18263	1.0	>87	273.9	100.00	1.0E+02	1.0	>119	21.9	100.00	9.8E+01	0.22	2.7	89.70

FIG. 5.8. Fragment of sheet 'BAR', showing OMP input and predicted concentration at 3 points: at the endpoint of the shallow and deep flowline in the (sub)oxic and anoxic zone (in the well), and in the mixed output of the recovery system (including the admixed ambient groundwater.





FIG. 5.9. Standard plots generated by TRANSATOMIC: Concentration versus time for the whole BAR recovery system, and concentration versus distance for the 2 flowlines when breakthrough of OMP completed. Changes in basin and filtration included in input concentration. No dispersion.

#### 5.4 Model input and output for a standard RBF type PSWF

The explanations given above for the standard phreatic PSWF are largely valid for the River Bank Filtration type PSWF as well. Note that the travel time is one of the input parameters (not calculated as for type A and A2). The model settings for a standard Dutch RBF system are shown in Fig.5.10.

The model output of sheet RBF consists of: (i) tabular information for all OMPs in columns K-Y (Fig.5.11); concentration plots versus time for 5 OMPs (Fig.5.12 top); and (iii) a concentration plot versus distance along the standard flowline for 1 OMP (Fig.5.12 base).

The distance of the startpoint of both standard flowlines to the well (field) and the total travel time of the water are fixed, but can be changed, as are all yellow cells.

In the tabular output (Fig.5.11), results of calculation consist of the retardation factor R, the front position after 60 years, the contaminant pore volumes ( $PV_c$ ), the input concentration ( $C_{IN}$ ; including effects of filtration (if AC34 = 1), output concentration when  $PV_c > 1$  ( $C_{OUT}$ ), the time needed for breakthrough of the shallow ( $t_{EQ-Up}$ ) and deeper flowline ( $t_{EQ+lp}$ ) in the well, and the mixed output concentration of the RBF system (including effects of dilution with ambient groundwater).

Acrost	Boromotor	Shallow	Deeper	Mixing					
Aspect	Faialletei	Aquifer	Aquifer	in wells					
	Scenario		RBF in fluvial plai	n					
System	Flow system	(sub)horizontal, uniform flow							
	Redox system: 1 = (sub)oxic; 2 = anoxic; 3 = deeply anoxic	3	2	3 + 2					
	porosity (n)	0.35	0.35						
Porous	rho solids [kg/L]	2.65	2.65						
medium	f <sub>oc</sub> = fraction organic carbon	0.0005	0.001						
	D = thickness of zone [m]	10	40	50					
	DOC after infiltration [mg/L]	6	4.0	5.6					
Infiltration	TOC prior to infiltration [mg/L]	4.2							
minuation	DOC/TOC prior to infiltration [-]	0.85							
water	рН	7.30	7.50	7.34					
	Temperature [oC]	11.9							
	Recovery rate Q <sub>OUT</sub> [m3/d]			7392					
	travel time H2O in zone [d]	3000	2000						
	v-H2O [m/d]	0.25	0.42						
Hydrology	flow path length [m]	750	830						
nyurology	time since step input [a]	60	60						
	contribution inf. water to recovery system	0.74	0.16	0.90					
	contribution ambient groundwater to recovery	0.06	0.04	0.10					
	Settings for river segment	5	See cells CF7:CM	7					
	Temp. correction K <sub>oc</sub> : 0 = No, 1 = Yes	1							
Special	Temp correction T <sup>1</sup> / <sub>2</sub> : 0 = No, 1 = Yes	0							
model	Biodegradation sorbed phase: 0 = No, 1 = Yes (as in water)	1							
settings	Changes in river segment included: 0 = No, 1 = Yes	0							
	Filtration at basin / river bank included: 0 = No, 1 = Yes	1							

FIG. 5.10 Input screen of sheet 'RBF', displaying the main system parameters and special model settings. The values shown refer to the settings for a standard Dutch, River Bank Filtration system.

				RBF dee	eply anox	ic zone		RBF anoxic zone						Wells							
Sel 🕞	OND		01410	Koc	pK₄		T1/2 [d]			Front	PVc		if PPV≥1		Front	PVc		if PV <sub>c</sub> ≥1	t <sub>EQ-up</sub>	t <sub>EQ-lo</sub>	Mixed
Selec	OMP	OMP in full	OMP	calc		suboxic	anoxic	deeply	ROMP	[m] after	Upper	CIN	Cout	R <sub>OMP</sub>	[m] after	Lower	CIN	Cout	PV <sub>c</sub> =1	PV <sub>c</sub> =1	Cout
Selec	abbrev.		type					anoxic		60.00 a	n	%	%		60.00 a	n	%	%	year	year	%
0	1,1,1-TE	1,1,1-trichloroethane	pesticide	272.5	99.0	273	560	4	1.7	>750	4.4	99.98	0.0E+00	2.3	>830	4.7	99.98	8.4E+00	13.72	12.8	1.35
2	1,2,4-triazol	1,2,4-triazole	metabolit	136.4	99.0	545	1.E+99	1.E+99	1.3	>750	5.5	99.99	1.0E+02	1.7	>830	6.6	99.99	1.0E+02	10.97	9.1	89.99
0	1,2,4-trimet	1,2,4-trimethylbenzene	industrial	793.9	99.0	1.E+99	1.E+99	1.E+99	3.0	>750	2.5	99.95	1.0E+02	4.9	>830	2.2	99.95	1.0E+02	24.24	26.9	89.96
0	1,2-DEY	1,2-dichloorethylene	pesticide	229.8	99.0	28	720	720	1.6	>750	4.7	99.99	1.1E+00	2.1	>830	5.1	99.99	1.5E+01	12.86	11.7	3.14
0	1,2-DB	1,2-dichlorobenzene	chlorinat	507.5	99.0	183	1.E+99	10	2.2	>750	3.2	99.97	0.0E+00	3.50	>830	3.1	99.97	1.0E+02	18.46	19.1	15.99
0	1,2-DE	1,2-dichloroethane	chlorinat	49.6	99.0	180	720	1.E+99	1.1	>750	6.5	100.00	1.0E+02	1.2	>830	8.8	100.00	1.5E+01	9.22	6.8	76.33
0	1,2-DCP	1,2-dichloropropane	chlorinat	70.1	99.0	1.E+99	10958	5479	1.2	>750	6.2	100.00	6.4E+01	1.3	>830	8.1	100.00	8.8E+01	9.63	7.4	61.52
0	1,2,4-TB	1,2,4-trichlorobenzene	chlorinat	9670.2	99.0	135	365	1.E+99	24.5	223.4	0.3	99.41	9.9E+01	48.2	188.59	0.2	99.41	2.2E+00	201.42	264.1	73.92
0	1,3,5-NTS	1,3,5-naphthalene trisulfonate	industrial	0.0	99.0	1.E+99	569	1.E+99	1.0	>750	7.3	100.00	1.0E+02	1.0	>830	11.0	100.00	8.7E+00	8.21	5.5	75.40
0	1,3,5-TB	1,3,5-trichlorobenzene	chlorinat	9670.2	99.0	135	365	1.E+99	24.5	223.4	0.3	99.41	9.9E+01	48.2	188.59	0.2	99.41	2.2E+00	201.42	264.1	73.92
0	1,3,5-trimet	1,3,5-trimethylbenzene	industrial	793.9	99.0	1.E+99	1.E+99	1.E+99	3.0	>750	2.5	99.95	1.0E+02	4.9	>830	2.2	99.95	1.0E+02	24.24	26.9	89.96
0	1,3,6-NTS	1,3,6-naphthalene trisulfonate	industrial	0.0	99.0	1.E+99	1044	1.E+99	1.0	>750	7.3	100.00	1.0E+02	1.0	>830	11.0	100.00	2.7E+01	8.21	5.5	78.24
0	1,3-DB	1,3-dichlorobenzene	chlorinat	1285.4	99.0	180	1.E+99	7	4.2	>750	1.8	99.92	0.0E+00	7.3	>830	1.5	99.92	1.0E+02	34.15	40.1	15.99
0	1,3-DPE	1,3-dichloropropene	pesticide	48.3	99.0	53	6	1.E+99	1.1	>750	6.5	100.00	1.0E+02	1.2	>830	8.9	100.00	0.0E+00	9.19	6.8	74.00
0	1,4-DB	1,4-dichlorobenzene	chlorinat	1306.9	99.0	180	1.E+99	6	4.2	>750	1.7	99.92	0.0E+00	7.4	>830	1.5	99.92	1.0E+02	34.59	40.7	15.99
1	1,4-dioxane	1,4-dioxane	industrial	6.0	-3.9	1.E+99	36525	18263	1.0	>750	7.3	100.00	8.9E+01	1.0	>830	11.0	100.00	9.6E+01	8.21	5.5	81.44
0	1.5-NDS	1 5-nanhthalene disulfonate	industrial	0.0	99.0	1 F+99	1 E+99	1 F+99	10	>750	73	100 00	1 0E+02	10	>830	11.0	100 00	1 0E+02	8 21	5.5	90.00

FIG. 5.11. Fragment of sheet 'RBF', showing OMP input and predicted concentration at 3 points: at the endpoint of the shallow and deep flowline in the deeply anoxic and anoxic zone (in the well), and in the mixed output of the recovery system (including the admixed ambient groundwater.





FIG. 5.12. Standard plots generated by TRANSATOMIC: Concentration versus time for the whole RBF recovery system, and concentration versus distance for the 2 flowlines when breakthrough of OMP completed. Changes in river not included and effects of filtration included in input concentration. No dispersion.

### 6 Discussion

#### Pesticide inputs from the plough layer

In case of phreatic or semiconfined PSWFs, pesticide applications within the groundwater catchment area form a particular, major OMP input source. Modelling of pesticide leaching from arable soil horizons (the plough layer) down to about 1 meter depth, is very complex. Various models have been developed for evaluating the environmental fate of plant protection products (<u>www.pesticidemodels.eu</u>, <u>http://www.pearl.pesticidemodels.eu</u>/), and for registration of plant protection products on a European and national level. CLM Onderzoek en Advies developed the Environmental Yardstick (Milieumeetlat in Dutch; <u>www.Milieumeetlat.nl</u>) to inform all stakeholders (farmers, industry, environmental agencies, advisors) about the potential environmental effects of specific pesticides with the aim to reduce undesired impacts on biota, soil, groundwater and surface water in the Netherlands.

A crucial aspect is the risk assessment of pesticide leaching, which CLM is currently tackling with a simplified version of the (Geo)PEARL model developed by Tiktak et al. (2003). This model predicts pesticide leaching from the plough layer down to about 1 meter depth, and stops there. TRANSATOMIC Lite starts here, so that many processes acting at the soil atmosphere interface and in the upper soil, such as volatilization, photochemical degradation and plant interception and uptake do not need to be addressed at all. CLM is very interested in expanding their Environmental Yardstick with TRANSATOMIC to predict pesticide fate in the deeper unsaturated zone and groundwater compartment (Hoftijzer et al. (2018).

#### The database of OMP physico-chemical characteristics

It is of paramount importance to continue filling up the OMP database with new OMPs and field-based data on (bio)degradation under well defined conditions regarding temperature, redox environment, pH, travel time etc. The number of relevant studies is rapidly expanding, which requires regular maintenance of the database. In addition, more information should be given in the database about the source of the data, source of field studies, OMP synonyms, OMP applications, removal rates in (waste) water treatment plants, etc. Automatic coupling to an institute-wide database is recommended.

#### Future work

TRANSATOMIC Lite could be expanded to include the following:

- input signals other than the step input (such as peak, pulse and sine). A very recent application
  of TRANSATOMIC Lite with a peak /pulse input signal for a basin recharge system was developed
  by Stuyfzand (2018), in order to predict the poison concentration in recovered water after a
  fictive terroristic drone dropping in dunes with artificial recharge;
- main constituents, radionuclides and trace elements with speciation, and pathogens; and
- other PSWF types, e.g. a phreatic limestone aquifer.

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#### The transit time distribution of a well (field)

The transit time distribution (TTD), also called hydrological response curve (HRC), is defined as the cumulative frequency distribution of travel times, in our case from land surface or open water course to a well (field). This TTD is of great value to predict concentration trends in the well (field) since the pollutant has been applied. An example of the HRC is shown in Figure A.2.

The purpose is to predict or simulate the behaviour of OMPs within a phreatic (very vulnerable) and semi-confined (moderately vulnerable) groundwater catchment area, given a 100% input from the plough zone, as a step input for either a specific site at radial distance  $r_x$  or for the whole catchment area. The well field is schematized into one single centralized well, with an aggregated pumping rate, mean well screen depth, a concentric catchment area, and an underground composed of 4 layers. We discern 2 situations (Fig.1.1): a phreatic aquifer and a semiconfined aquifer leaky at its top. The layer sequence is as follows, from top to bottom: an unsaturated zone, the top zone of the aquifer above the well screens (phreatic case) or an aquitard (semiconfined case), the pumped aquifer, and an aquiclude. Flow is assumed vertical and parallel in both the unsaturated zone and upper aquifer or aquitard zone 1, but horizontal and radial in the pumped aquifer zone 2.

A simplified hydraulic model provides the total travel time from land surface to the well (field), by adding up the travel time in each of the 3 discerned zones (Fig.1.1).

#### The phreatic case:

In the phreatic case, the total travel time from land surface at site X to the well (field) is the sum of the travel time in the unsaturated zone  $(t_0)$ , aquifer or aquitard zone 1  $(t_1)$ , and aquifer zone 2  $(t_2)$ , each being a function of r (Fig.1.1):

$$t_{TOT} = t_U + t_1 + t_2 \tag{A.1}$$

$$t_{II} = \frac{(h_r - c_F)\theta + n_U c_F}{2} \tag{A.2}$$

$$t_1 = \frac{(D_1 - h_r)n_1}{r} \tag{A.3}$$

$$t_{2} = \frac{n_{2}D_{2}}{R} \ln \frac{1}{1 - \left(\frac{r}{r_{E}}\right)^{2}} = \frac{n_{2}D_{2}}{R} \ln \left[\frac{Q}{Q - \pi Rr^{2}}\right]$$
(A.4)

with:

$$h_r = h_E + \frac{Q \ln(\frac{r_E}{r})}{2 \pi K D_2} \tag{A.5}$$

Where: Q = pumping rate of well (field)  $[m^3/d]$ ;  $t_{TOT}$  = total travel time from ground level at site X to well screen [d];  $t_U$ ,  $t_1$ ,  $t_2$  = travel time in unsaturated zone, aquifer or aquitard zone 1 and aquifer zone 2, respectively [d];  $n_U$ ,  $n_1$ ,  $n_2$  = effective porosity of unsaturated zone, aquitard or aquifer zone 1 and aquifer zone 2, respectively [volume fraction];  $h_r$ ,  $h_E$  = thickness of unsaturated zone (incl. full-capillary fringe) at distance r and  $r_E$ , respectively [m];  $D_1$ ,  $D_2$  = mean total thickness of aquifer or aquitard zone 1 and aquifer zone 2, respectively, prior to pumping [m]; R = mean multi-annual groundwater recharge rate [m/d]; r,  $r_E$  = radial distance to well (field), from site X within and any site on the groundwater divide, respectively [m];  $\theta$  = mean multi-annual moisture content of unsaturated zone [volume fraction];  $c_F$  = thickness full-capillary fringe [m];

For details on equations A.2 – A.4, see Stuyfzand (2015). The right hand part of Eq.A.4 is obtained from its left hand part by combination with the following equation based on the water balance:

$$r_E = \sqrt{\frac{Q}{\pi R}} \tag{A.6}$$

The thickness of the unsaturated zone ( $h_r$ ) is calculated with Thiem's equation for the position of the groundwater table in a confined aquifer. According to Bear (1979) this equation also holds for a phreatic aquifer, if the drawdown is small relative to  $D_1+D_2$ .

Inserting  $(r_x/r_E)^2 = 0.01P_x$  in Eq.A.4, with  $P_x =$  percentile X [0-99.999), yields:

$$t_2 = \frac{n_2 D_2}{R} \ln[\frac{1}{1 - 0.01 P_X}] \tag{A.7}$$

This equation can be directly used, after adding  $t_u$  and  $t_1$  to calculate the TTD with EPM. The approximate depth of entrance in the well screen ( $d_x$  in m – top of aquifer) for a ring of flowlines depends on r as follows:

$$d_X = D_2 \left(\frac{r}{r_p}\right)^2 \tag{A.8}$$

The following equation holds for a conservative pollutant ( $R_{OMP} = 1$ ,  $T_{2}' = 10^{99}$ ) from a fully penetrating well in a homogeneous, isotropic aquifer (such as in Figure 1.1), with initial concentration in the aquifer (and in both the unsaturated zone and aquitard) being zero:

$$C_t = C_{IN} (1 - e^{\frac{-R(t - t_U - t_1)}{D_2 n_2}}) \qquad \text{if } t - t_u - t_1 > 0, \qquad \text{else } C_t = 0 \qquad (A.9)$$

where:  $C_{IN}$  = average (constant) input concentration for unsaturated zone since start of application at t =0 [%];  $C_t$  = concentration in output of well in zone 2 after time t since start; t = time since start of pollutant application (entrance into system) [d].

#### The semiconfined case:

In the semiconfined case, the total travel time from land surface to the well (field) is the sum of the travel time in the unsaturated zone  $(t_u)$ , aquitard  $(t_1)$  and aquifer  $(t_2)$ . An average constant value needs to be taken for the thickness of the unsaturated zone (h) and aquitard  $(D_1)$ , for the sake of simplicity. The lack of drawdown of the groundwater table in the aquitard, even in the vicinity of the well (field), can indeed be explained by an intricate system of influent ditches and canals.

De Glee (1930) presented an analytical solution of the drawdown of the piezometric head in the aquifer, for this scenario. Peters (1985) used his solution to calculate the travel time in both the aquitard  $(t_1)$  and aquifer  $(t_2)$ . We thereby obtain the following set of solutions:

$$t_{TOT} = t_U + t_1 + t_2 \tag{A.10}$$

$$t_U = \frac{(h - c_F)\theta + n_U c_F}{R} \tag{A.11}$$

$$t_1 = f \frac{2\pi\lambda^2 D_1}{QK_0(\frac{r}{\lambda})} \tag{A.12}$$

$$t_2 = \frac{2\pi\lambda^2 n_2 D_2}{Q} \int_0^{r/\lambda} \frac{dr}{K_1(r)}$$
(A.13)

$$\int_{0}^{r/\lambda} \frac{dr}{\kappa_{1}(r)} \approx 1.0872 \left(\frac{r}{\lambda}\right)^{3} - 1.7689 \left(\frac{r}{\lambda}\right)^{2} + 1.5842 \left(\frac{r}{\lambda}\right)^{1} - 0.2544$$
(A.14)

Where:  $t_1$  = travel time in water-saturated aquitard [d]; h = mean constant thickness of unsaturated zone [m];  $D_1$  = mean total thickness of aquitard (saturated) [m];  $\lambda = \sqrt{(K_2D_2c_v)}$  = leakage factor [m];  $c_v$  = mean resistance of aquitard to vertical flow [d];  $K_0(x)$  = modified Bessel function of the second kind and zero order (= besselk(x,0) function in Excel);  $K_1(r)$  = modified Bessel function of the second kind and first order (= besselk(x,1) function in Excel); f = fraction of aquitard contacted, to account for gaps in aquitard [-].

The approximation of the integral in Eq.A.13 by Eq.A.14 is based on its plot against  $r/\lambda$  as provided by Peters (1985). The steady state position of the circular groundwater divide ( $r_{\rm f}$ ) is roughly approximated by taking 3 times the leakage factor (as usual):

$$r_E = 3\lambda = 3\sqrt{K_2 D_2 c_V} \tag{A.15}$$

#### The travel time distribution

INDUT Donal

The travel time distribution (TTD) in the mixed output from the well (field) is approached in 2 ways: with a combined Exponential Piston Model (EPM) and with a Multi-Flowtube Model (MFM), as explained in § 1.7. The difficult part resides in aquifer zone 2, where we use Eq.A.7 for the phreatic case. The semiconfined case as presented above, cannot be approached, however, by a simple equation similar to Eq.A.7. As stated by Bear (1979), the ratio  $Q_r/Q_0$  indicates for every distance r the portion of the well's discharge ( $Q_0$ ) flowing through the aquifer, so that we take:

$$P_r = 100 \frac{Q_r}{Q_0} = 100 \left[1 - \left(\frac{r}{\lambda}\right) K_1\left(\frac{r}{\lambda}\right)\right]$$
(A.16)

In a separate sheet called 'TTD', the results of the MFM model for both the phreatic and semiconfined PSWF are shown, with independent system input (which in the example of Fig.A.1 equals the standard settings).

OUTP	UT Panel															
	P (%)	0.001	0.01	0.1	0.5	1	10	20	30	40	50	60	70	80	90	100
Phrea	tic															##
r	m	5	17	55	122	172	545	771	944	1090	1219	1335	1442	1542	1635	1723
φ	m ASL	12.0	13.0	14.0	14.7	15.0	16.0	16.3	16.5	16.6	16.7	16.8	16.8	16.9	17.0	17.0
tυ	year	5.3	4.8	4.3	4.0	3.8	3.3	3.2	3.1	3.0	3.0	2.9	2.9	2.9	2.8	2.8
t <sub>1</sub>	year	5.8	7.0	8.2	9.0	9.3	10.5	10.8	11.1	11.2	11.3	11.4	11.5	11.6	11.6	11.7
t <sub>2</sub>	year	0.000	0.005	0.05	0.23	0.47	4.9	10.4	16.6	23.8	32.3	42.8	56.2	75.1	107.5	429.8
t <sub>TOT</sub>	year	11.1	11.8	12.5	13.2	13.6	18.7	24.4	30.8	38.0	46.6	57.1	70.6	89.5	121.9	444.3
Semic	onfined															
r	m	1.5	5.5	20	32	118	262	429	584	742	911	1099	1316	1586	1973	2510
Δφ <sub>2</sub>	m	-5.6	-4.5	-3.3	-2.9	-1.8	-1.2	-0.8	-0.6	-0.4	-0.3	-0.2	-0.2	-0.1	-0.1	0.0
tυ	year	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8
t <sub>1</sub>	year	<3	3.1	4.2	5.0	9.5	11.8	17.2	23.2	30.6	40.5	54.8	76.6	115	213	452
t <sub>2</sub>	year	<0.1	<0.1	<0.1	<0.1	0.4	4.9	11.7	17.0	23.3	33.4	52.3	88.6	166	379	856
t <sub>TOT</sub>	year	4.3	5.9	7.0	7.8	12.7	19.5	31.7	43.0	56.7	76.7	109.8	168.0	284	595	1311

##: 99.99% for phreatic, 1.1369 \* 87.95% = 99.99% for semiconfined (100% set at  $r_E = 3$  \* labda (labda = leakage factor)

INFUL	NFUT Fallel														
Zone		base	top	D	n	KD	<b>C</b> 1	λ	Q	٢ <sub>E</sub>	[m]	R	CF	θ	φε
		m ASL		m		m2/d	m2/d d		m3/h	phreat semicon		m/a	m		m ASL
U	Unsaturated	17	22.0	5.0	0.38							0.30	0.4	0.15	17.00
1 #	Zone 1 Aquitard	7	17	10.0	0.35	0	500	837		1724	2510				
1\$	Zone 1 Aquifer	7	17	10.0	0.35	0	0		319.4	1724	2510				
2	Zone 2 Aquifer	-33	7	40.0	0.35	1400	0								

#: if semiconfined aquifer; \$: if phreatic aquifer, aquifer zone above top of well screens.

FIG. A.1. Below: input panel with input in yellow cells only, for calculating the travel time of water in the 3 discerned zones of a phreatic and semiconfined PSWF, the total travel time, drawdown of the water table / hydraulic head, and radial distance to well field. Above: the results of calculation.



FIG. A.2. Left: Travel time distribution (TTD) for the standard phreatic and semiconfined PSWFs, based on output panel of Fig.A.1. Right: Total travel time along the standard flowline of the standard phreatic and semiconfined PSWFs.

# Annex 2. Comparison of OMP breakthrough via EPM and MFM travel time distribution models

#### For the phreatic PSWF

The calculated breakthrough curve (BTCs) of 5 OMPs, for the standard phreatic PSWF, via the combined Exponential Piston model (EPM) and the Multi-Flowline Model (MFM) are shown in Fig.A.3. These plots are produced in sector CP57:DL223 of sheet 'OMPs Phreatic'. The EPM results of 5 OMPs are produced standard, the MFM results are produced standard for 1 OMP, thus requiring to 'copy paste special as numbers' the results of CM62:CM223 to the equally labelled column in sector CU62:CV223.



It is not surprising that both models yield very similar results, because the underlying equations are very similar. The main differences consist of a higher fraction of water with a very short travel time and consequently a lower fraction of water with a very long travel time, for MFM compared to EPM. This is explained by the fact that with EPM the median travel time in the unsaturated zone and aquifer zone 1 is calculated, whereas MFM is taking the individual travel time in the unsaturated zone and aquifer zone 1 for 11 flowlines with well distributed distances within the groundwater catchment area to the well field.

#### For the semiconfined PSWF

The calculated BTC of 5 OMPs, for the standard semiconfined PSWF via the EPM and MFM model are shown in Fig.A.4. These plots are produced as indicated for the phreatic PSWFs.

It is not surprising that both models yield dissimilar results, because the hydrogeological setting and the underlying equations are quite different. The main differences consist of a much earlier breakthrough of all OMPs, a higher breakthrough level for certain OMPs and a less steep BTC.

The MFM model is judged much more reliable than the less laborious EPM model, and therefore highly recommended.





FIG. A.4. Calculated Breakthrough Curves of 5 OMPs for the standard semiconfined PSWF, via the combined Exponential Piston Model (EPM) and the Multi-Flowline Model (MFM). MFM is by far superior to EPM.