## BEHAVIOR OF PHARMACEUTICALS AND OTHER EMERGING POLLUTANTS IN VARIOUS ARTIFICIAL RECHARGE SYSTEMS IN THE NETHERLANDS

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## ABSTRACT

Basin recharge and deep well recharge systems contribute ca 15% to the annual total of drinking water (1,250 Mm<sup>3</sup>/a) produced in the Netherlands. With 2 snapshot surveys in summer 2005 and 2006, of 10 monitoring transects of 2-4 observation wells in 3 basin artificial recharge (BAR) and 2 deep well injection (DWI) systems, insight has been gained in the behavior of 140 organic micropollutants (<0.001 – 5  $\mu$ g/L). 80 of these are pharmaceuticals and other emerging pollutants (PEPs) and 60 regulated organic pollutants (ROPs).

Most PEPs (71%) and ROPs (60%) were everywhere below the limit of quantification. Concentrations of detected pharmaceuticals and X-ray contrast agents were low (0.01-0.2  $\mu$ g/L). They showed significant (bio)degradation (>90%) during aquifer passage regarding phenazone, iohexol, iomeprol and iopamidol in suboxic environment, and of sulfamethoxazole and amidotrizoic acid in anoxic environment. Carbamazepine, MCPP, bentazone, tertiary octylphenole, iso-nonylphenole, PFOA, PFOS, TCEP, 1,4-dioxane and diglyme showed a very persistent behavior, both in young, suboxic infiltrates and in 1-36 years old, anoxic infiltrates. Phenazone and iopamidol showed a persistent behavior only in anoxic environment.

Uncertainty levels in half lives (as a relative measure of decay rates) of organic micropollutants in BAR and DWI systems with low input levels, as deduced from a snapshot survey, are related to (a) analytical noise, (b) uncertainties in (reconstructed) input concentration, travel time of the water and sorption (retardation factor), and (c) variations in temperature and redox environment. For iopamidol in suboxic environment the uncertainties result in a range of half lives down to half and up to twice the expected mean value (58 days).

## **KEYWORDS**

Artificial recharge, coastal dunes, pharmaceuticals, emerging pollutants, degradation rate, redox environment, uncertainty analysis

## INTRODUCTION

Emerging pollutants are defined as pollutants that are currently not included in routine monitoring programmes nor in regulation, but which deserve attention due to their suspected (eco)toxicity, potential health effects, public perception and detection in various environmental compartments. Pharmaceuticals and other emerging pollutants (together PEPs) have been detected in low concentrations (0.001 -10  $\mu$ g/L) internationally, in decreasing order, in (treated) sewage effluents, surface waters, surface waters pretreated for artificial recharge (AR), river bank filtrate (RBF), the recovered infiltrates after AR, and drinking water (Ternes & Hirsch 2000; Drewes et al. 2002; Zühlke et al. 2004). This has been demonstrated also in the Netherlands (Noy et al. 2003).

Gradually insight is gained in the occurrence and behavior of various PEPs in RBF and AR groundwater flow systems, as a function of the redox environment and travel time, especially in Germany (Massmann et al., 2006). No such information was available, however, on PEPs in AR systems in the Netherlands, which contribute 15% to the annual total of drinking water supply of 1,250  $\text{Mm}^3$ /a. This study aims at filling up this knowledge gap in order to (a) predict concentrations in the recovered water also on the long term; and if needed (b) optimize the existing drinking water production systems utilizing AR, by either changing the redox environment and travel time or intensifying the pre- or post-treatment.

## MATERIAL AND METHODS

Three dune areas with artificial recharge were investigated on the occurrence and their elimination capacity of PEPs (Fig.1): one close to Castricum (operated by Provincial Waterworks North-Holland), one south of Zandvoort (operated by Waternet supplying drinking water to the city of Amsterdam) and one north of The Hague (operated by Duinwatermaatschappij Zuid-Holland).

Eight rows of observation wells, in between different recharge basins and recovery wells or drains (Fig.2-a), and 2 rows of observation wells in between an injection and recovery well (Fig.2-b) were sampled to determine in 2 snap-shot surveys (summer 2005 and 2006) the spatial distribution of ca 80 PEPs, 60 regulated organic pollutants (ROPs: pesticides, volatile organohalogens and volatile benzenes), DOC (Dissolved Organic Carbon) and inorganic chemistry along well defined flow paths in diverging redox systems. Most observation wells (screen length 0.5-1 m) have a long monitoring record (10-40 years) on water levels, macroparameters and various pollutants (not PEPs), thus supplying background information on groundwater flow and hydrogeochemical processes. For some PEPs a 2-5 years input record was available, of the water after pretreatment and/or of the Rhine and Meuse Rivers at national monitoring points.



#### FIGURE 1. Site map showing all basin aquifer recharge systems in the Netherlands, incl. the 3 studied recharge areas (numbered 1,4 and 6 on map) and their water intake (resp. E+B, B, A+D). Intake A abandoned in 1978. Red lines = transport mains from pretreatment plant near intake to AR area.

Monitoring wells were selected that were installed >4 years ago and are regularly pumped, thus avoiding problems due to PVC interaction. Samples were taken after evacuation of >3 times the volume of well screen (length 1 m) plus riser (diameter 2.5 cm), using a rotary peristaltic pump. Ultraclean bottles were used for PEPs. The samples for main cations, Si, P and TEs were filtrated in the field over 0.45  $\mu$ m and subsequently acidified. On site, the samples were immediately cooled down to 4°C and kept in the dark. Temperature, EC and pH were measured on site, main constituents by routine methods, main cations, Si, P and TEs by ICP-MS and ICP-AES.

The following PEPs were analysed within 1 week in an extract of each sample that was obtained within 1-2 days after sampling: pharmaceuticals and X-ray contrast fluids by Solid Phase Extraction (SPE) HPLC-MS-MS, nitrosoamines, alkylphenols, perfluoro compounds, various individual industrial compounds, hormones and Endocrine Disruptive Compounds (EDCs) by Liquid Liquid Extraction (LLE) with ethylacetate and detection by LC-GC-MS, volatile organics by purge and trap isolation and GC-MS detection, diglyme by SPE-GC-MS.





Travel times in the aquifer (in our observation wells ranging from 1 day to 40 years) were determined by history matching of Cl,  $SO_4$ , <sup>3</sup>H and temperature (retardation factor 1.8-2) in both the input and observation wells, and by hydrological

calculations using piezometric levels and well known hydraulic conductivities. The redox environment was assessed by data on  ${\rm O_2,~NO_3^{-},~SO_4^{2-},~Fe^{2+},~Mn^{2+}}$  and  ${\rm NH_4^+}$  , using the classification system indicated in Fig.2 (Stuyfzand, 1993, 2005).

#### TABLE 1. The 10 monitoring transects of observation wells with important background information.

Transect No.	Recharge Type \$	AR start	Source water	No. wells	distance [m]	depth [m+ MSL]	travel time	redox envir #	Geol. Forma- tion @
CASTRICUM (PVM)									
1	BAR	1957	$R^1, R/Y^2$	5	1-64	1/-3	2-56 d	SO	D
2	BAR	1957	R <sup>1</sup> , R/Y <sup>2</sup>	4	34-340	-34/-52	3.>36 y	A	E
3	DW	1989	R <sup>1</sup> , R/Y <sup>2</sup>	3	10-73	-67 / -97	18-103 d	SO-A	En
ZANDVOORT (Waternet)									
4	BAR	1957	R <sup>3</sup>	2	4-96	5/-3	2-49 d	SO	D
4A	BAR	1957	R <sup>3</sup>	2	4-96	-8/-14	75-351 d	A	NS
5	BAR	1957	R <sup>3</sup>	4	3-57	5/4	8-57 d	SO	D
6	BAR	1957	R <sup>3</sup>	5	95-500	-2/-20	3.5.>26 y	A	NS
THE HAGUE (DZH)									
7	BAR	1956	R <sup>4</sup> , R/M <sup>2</sup> , M <sup>6</sup>	4	3-37	-2	20-48 d	SO	D
8	BAR	1956	R*, R/M*, M*	3	2-100	-16/-54	1.7-11.4 y	(D)A	NS/E/U
9	DW	1989	M <sup>7</sup>	3	23-120	-31/-34	21-112 d	SO-A	E/U
	Transect No. 1 2 3 wet) 4 4 4 A 5 6 7 7 8 9	Transect Recharge Type \$ 1 BAR 2 BAR 3 DW 4 BAR 4A BAR 5 BAR 6 BAR 7 BAR 8 BAR 9 DW	Transect No.         Recharge Type \$         AR start           1         BAR         1957           2         BAR         1957           3         DVM         1989           ret)         1         BAR         1957           4         BAR         1957           5         BAR         1957           6         BAR         1957           7         BAR         1956           8         BAR         1956           9         DVM         1989	Transect No.         Recharge Type \$         AR start         Source water           1         BAR         1957         R <sup>1</sup> , R/Y <sup>2</sup> 2         BAR         1957         R <sup>1</sup> , R/Y <sup>2</sup> 3         DVM         1989         R <sup>1</sup> , R/Y <sup>2</sup> 4         BAR         1957         R <sup>3</sup> 44         BAR         1957         R <sup>3</sup> 5         BAR         1957         R <sup>3</sup> 6         BAR         1957         R <sup>3</sup> 7         BAR         1956         R <sup>4</sup> , R/M <sup>5</sup> , M <sup>6</sup> 8         BAR         1956         R <sup>5</sup> , R/M <sup>6</sup> , M <sup>6</sup> 9         DVM         1989         M <sup>7</sup>	Transect No.         Recharge Type \$         AR start         Source water         No. wells           1         BAR         1957         R <sup>1</sup> , R/Y <sup>2</sup> 5           2         BAR         1957         R <sup>1</sup> , R/Y <sup>2</sup> 5           2         BAR         1957         R <sup>1</sup> , R/Y <sup>2</sup> 4           3         DWI         1989         R <sup>1</sup> , R/Y <sup>2</sup> 3           ret)	Transect No.         Recharge Type \$         AR start         Source water         No.         distance [m]           1         BAR         1957         R <sup>1</sup> , R/Y <sup>2</sup> 5         1.64           2         BAR         1957         R <sup>1</sup> , R/Y <sup>2</sup> 5         1.64           3         DVM         1989         R <sup>1</sup> , R/Y <sup>2</sup> 3         10.73           et/         Her         1957         R <sup>3</sup> 2         4.96           4         BAR         1957         R <sup>3</sup> 2         4.96           4A         BAR         1957         R <sup>3</sup> 2         4.96           5         BAR         1957         R <sup>3</sup> 4         3.57           6         BAR         1957         R <sup>3</sup> 4         3.57           6         BAR         1957         R <sup>3</sup> 4         3.57           7         BAR         1956         R <sup>4</sup> , R/M <sup>6</sup> , M <sup>6</sup> 3.37         3         2.100           9         DVM         1989         M <sup>7</sup> 3         23.120	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

\$: BAR = Basin Aquifer Recharge; DWI = Deep Well hjection
\$: BAR = Basin Aquifer Recharge; DWI = Deep Well hjection
1 = Rhine River III 1981, filtrated and since 1974 also cosgulated
2 = Mix of Rhine River and Lake Yssel since 1981, both cosgulated, Y also with activated carbon filtration since 1989
3 = Rhine River, cosgulated since 1974.
4 = Rhine River since 1976, cosgulated; 5 = Mix of Rhine and Mause Rivers 1976-1978, both cosgulated;
6 = Meuse River since 1978, cosgulated; 7 = Meuse River valer, twice cosgulated, since 1986 also activated carbon filtration;
#: SO = (Sub)(Dxic; A = Anoxic; DA = Deep Anoxic; (D)A = (Deep) Anoxic
@: D = Holocene dune sand; NS = Holocene North Sea deposits; E = Eemian Formation (marine, Pleistocene);
U = Urk and Sterksel Formation (fluvial, Pleistocene); En = Enschede Formation (fluvial, Pleistocene)

## HYDROGEOLOGICAL AND GEOCHEMICAL SETTING

Relevant background information on the 10 transects is given in Table 1. There are 4 shallow transects in the upper phreatic aquifer (1, 4, 5, 7), which is recharged via basins and composed of Holocene coastal dune sands on top of North Sea sand deposited in a beach and shallow marine environment. These sands are mostly suboxic, calcareous, poor in organic carbon (ca. 0.01-0.1%), medium grained, well sorted and relatively homogeneous. Travel times and distances are relatively short (<100 d, <100 m).

The 4 deep transects (2, 4A, 6, 8) reach basin infiltrate in anoxic, calcareous, pyritiferous, semiconfined aquifer layers below the upper aquifer. These layers consist of Pleistocene coarse grained, marine and fluvial sands (2, 8) or heterogeneous, fine grained, silty North Sea sands deposited during the Holocene in a tidal or estuarine environment (4A, 6). Travel times and distances are relatively long (75 d - >36 y, 100-500 m). The deep transects 2 and 8 consist of dispersed monitoring wells projected on an imaginary cross section, the others are based on a row of observation wells perpendicular to a basin's bank.

Both transects of a deep well injection system (3, 9) address a deep, semiconfined, coarse sandy, Pleistocene aquifer which is calcareous, pyritiferous and low in organic carbon (0.05-0.11%). The system is suboxic close to the injection well and turns anoxic at a distance of 20-40 m. Travel times and distances are relatively short (<112 d, <120 m).

A typical cross section with the position of monitoring wells and redox zonation, is presented for basin aquifer recharge systems and deep well injection systems in Fig.2.

## PRESENTATION OF ANALYTICAL RESULTS

The analytical results for all detected and quantified PEPs and ROPs during the 2 snapshots are given in Table 2. The results refer to the snapshots in 2005 and 2006, each of which totalling 30 samples (4-5 input, 25-26 monitoring wells). In total 23 out of 80 PEPs and 24 out of 60 ROPs have been detected and quantified during at least one of both snapshots.

Differences in detection frequency and concentration levels of the PEPs and ROPs, between the snapshot of 2005 and 2006, are mainly caused by: (a) differences in analytical program; (b) small differences in the analytical methods applied, also leading to different limits of quantification (LOQs; samples of 2005 by OMEGAM in Amsterdam, those of 2006 by TZW in Karlsruhe); (c) a different selection of sampled wells (21 wells identical, 9 wells different); and (d) fluctuating input levels.

Nevertheless quite comparable results have been obtained for the pharmaceuticals, X-ray contrast agents, diglyme and MTBE. Bisphenol-A is the only exception, with significantly higher concentrations in 2006, probably due to a better isolation and quantification with the method applied in 2006.

Somewhat lower frequencies of detection in 2006 (Table 2) are related to more focus on relatively 'old' infiltration waters by addressing 9 more observation wells in transects 2, 6 and 8. A more detailed picture of the number of detections in 2006 is given in Fig.3, where young (n=20) and old dune infiltrates (n = 10) are distinguished. The young group is further subdivided into the categories influent, suboxic, anoxic and deep anoxic (for redox criteria see subtitle of Fig.2).

It can already be concluded from Fig.3 that the following pollutants, with frequent detection in old infiltrates, are very persistent and mobile, and had a higher input in the past (>3 years ago): MCPP, bentazone, tertiary octylphenole, iso-nonylphenole, PFOA, TCEP, 1,4-dioxane and diglyme. Also persistent but with possibly a lower input in the past (>3 years ago) or less mobile/persistent than the previous pollutants are: carbendazim, iopamidol, PFOS and carbamazepine.

TABLE 2. Detected Pharmaceuticals and other emerging pollutants (PEPs) and regulated organic micropollutants (pesticides, volatile organohalogens, benzenes), with their Limit of Quantification (LOQ), frequency of detection (No. > LOQ; max = 30), and maximum concentration levels. Cell colouring: black = No.  $\geq$  10, Max  $\geq$  0.1 µg/L; red = No.  $\geq$  10, Max < 0.1 µg/L; blue = No. < 10, Max  $\geq$  0.1 µg/L; white = No. < 10, Max < 0.1 µg/L.

Туре	PEP		2005			2006	
	or	LOQ	No.	Max	LOQ	No.	Max
	organic micropollutant	µg/L	> LOQ	μg/L	µg/L	> LOQ	µg/L
ca	carbamazepine	0.01	26	0.10	0.03	20	0.14
<u>ع</u>	phenazone	0.01	10	0.20			
Ш	primidone	0.02	3	0.07			
Чd	sulfamethoxasole	0.01	18	0.04	0.03	0	
	amidotrizoic acid	0.01	25	0.20	0.01	16	0.25
st	inhexol	0.01	4	0.08	0.01	5	0.04
s at	iomenrol	0.01	5	0.07	0.01	6	0.08
	ionamidol	0.01	30	0.20	0.01	21	0.14
а С С	ionromide	0.01	6	0.10	0.01	7	0.09
-ra	ioxadine acid	0.01	1	0.01	0.01	1	0.01
×	iovitalamine acid	0.01	2	0.01	0.01		0101
	Riceboool 0	0.01			0.00	40	0.46
60	Displication-A	0.05	U		0.000	6	0.97
2	ice Nerdeborel				0.03	10	0.01
ш					0.025	40	0.00
	ren-oktypnenoi				0.005	19	0.09
	1,4-Dioxane				0.1	13	4.8
	diglyme	0.01	29	0.39	0.1	23	0.74
ŝ	methyl-tert-butyl-ether (MTBE)	0.02	30	0.86	0.05	17	0.86
<u>io</u> r	Perfluorooctanoic acid (PFOA)				0.001	27	0.017
/ar	Perfluorooctanosulfonate (PFOS)				0.001	24	0.039
-	Triglyme				0.1	9	0.57
	Tris(chloroethyl)phosphate (TCEP)				0.025	21	0.34
	n-nitrosomorpholine (NMOR)	0.003	0		0.001	1	0.001
\$	Atrazine				0.01	3	0.01
de	Carbendazim				0.01	14	0.06
tici	Dimethanamide				0.01	3	0.01
8	Bentazone				0.05	7	0.55
Р	MCPP				0.05	4	0.25
su	trichloromethane	0.02	19	0.37			
ge	bromodichloromethane	0.02	2	0.15			
hal	dibromochloromethane	0.02	1	0.12			
2	tribromomethane	0.02	4	0.10			
gal	1,2-dichloroethane	0.02	4	0.28			
ъ	cis-1.2-dichloroethylene	0.02	4	0.29			
ile	trans-1,2-dichloroethylene	0.02	2	0.05			
lat	trichloroethylene	0.02	2	0.06			
ş	1.2-dichloropropane	0.02	3	0.06			
	benzene	0.02	1	0.03	0.1	0	
enzenes	methydbenzene	0.02	12	0.50	0.1		
	1.2 dimethylbenzene	0.02	2	0.40			
	1.3 and 1.4 dimethylbenzene	0.02	44	0.13			
	1.2.4.trimethylbenzene	0.02	r.	0.36			
	1 3 5 trimethylbenzene	0.02	3	0.30			
	ethylbenzene	0.02	3	0.13			
-	ieo propythepzepe	0.02	3	0.20			
	n propylbalzale	0.02	1	0.09			
	ablerabergana	0.02	2	0.10			
	chiorobenzene	0.02	1	0.02			



FIGURE 3. Detection frequencies of the 19 most important PEPs plus 5 pesticides in 2006, in young dune infiltrates (4 inputs + 16 monitoring wells; water age < 1 year) and old dune infiltrates (10 monitoring wells, water age 3-40 years). The young dune infiltrate is further subdivided into influent (max. 4), suboxic (max. 9), anoxic (max. 5) and deep anoxic (max. 2). The old dune infiltrates are anoxic.

# BEHAVIOR IN YOUNG INFILTRATES, IN SUBOXIC AND ANOXIC ENVIRONMENT

Young infiltrates are defined here as those with a travel time <1 year. The behavior of PEPs in these groundwaters can only be deduced from snapshot surveys when their input signal is known, and when retardation by sorption and effects of filtration of suspended matter can be ignored or accounted for.

The PEPs with a well known input record are indicated in Table 3. In general, pharmaceuticals and X-ray contrast agents appear to be much less variable in the input than pollutants like MTBE and diglyme. The physicochemical properties of most PEPs (Table 3) justify the assumption that sorption to suspended matter and to the aquifer matrix can be neglected in most cases. Carbamazepine is an exception, showing a calculated retardation coefficient for dune sand R = 2.2. Its sorption to suspended and dissolved organic material can be neglected however.

The behavior of carbamazepine, amidotrizoic acid and iopamidol is shown in Fig.4, for both the suboxic and anoxic transects with a travel time <1 year. In the anoxic

transects the position of the redox barrier is indicated, where suboxic infiltrate (upgradient) is reduced to anoxic infiltrate. At this point the graphs can be misleading: the changes between 2 points on both sides of this barrier probably take place exclusively on one side. The patterns for carbamazepine are mainly dictated by fluctuations in the input indicating that degradation is insignificant. This is confirmed by the persistence in anoxic old infiltrate (see below) and observations by Massmann et al. (2006). Amidotrizoic acid and iopamidol show a contrasting redox dependent behavior: the first is clearly only degraded in anoxic environment, and the latter mainly in suboxic environment.



FIGURE 4. Left: concentration profile along the shallow, suboxic transects 1 (Castricum ICAS), 4 (Zandvoort Basin 6), 5 (Zandvoort, Basin 12) and 7 (The Hague, Pond 13.1), for summer 2005 and 2006. *Right: concentration profile along the deep, anoxic transects 3* (Castricum DWAT), 4A (Zandvoort Basin 6), and 9 (The Hague, Waalsdorp), for summer 2005 and 2006.

The behavior of other PEPs and 3 pesticides is summarized in Table 3. It can be concluded that phenazone is rapidly degraded in suboxic conditions and very slowly in anoxic environment. This matches the conclusions of Massmann et al. (2006). lohexol, iomeprol and iopromide show such a fast degradation in suboxic environment, that their behavior in anoxic environments, which in our study are preceded by suboxic conditions, could not be determined here. Grünheid & Jekel (2006) noticed that iopromide hardly degraded in anoxic environment.

TABLE 3. Preliminary conclusions regarding the behavior of PEPs and 3 pesticides in all studied transects. In yellow: pollutants with much higher loads in the remote past (1980s).

DED		loak	nka	Input	Removal process				T½ [d] †	
	FLF	TOGINO A	μια	signal#	Basin##	Filtration	Sorption	Biodegr	(Sub)oxic	Anoxic
U	Carbamazepine	2.45		1	?	no	R=2.2 \$	<10	9999	>7300
ha	Phenazone	0.38		?	?	no	no	0-100	2	>> 730
д	Sulfamethoxazole	0.89	6	1	?	no	no	0-70	9999	30
	Amidotrizoic acid	1.37		1	45	no	no	0-70	9999	25 - 55
X-ray	lohexol	-3.05		1	0-40	no	no	>90	<1 - <7	no data
	iomeprol	low		1	0-20	no	no	>90	<0.5 - <6	no data
	lopamidol	-2.42		1	30	no	no	0-90	25 - 85	140 - 9999
	lopromide	-2.05		2	20-40	no	no	>90	0.7 - <7	no data
	1,4-Dioxane	-0.27		?	prob	no	no		9999	9999
/ar	Diglyme	-0.36		3	?	no	no	<20	9999	9999
_	MTBE	1.07		3	prob	no	no	0-70	9999?	9999?
Pest	Bentazone	-0.46	2.9	4	?	no	no	<20	?	>2200
	Carbendazim	1.56		?	?	no	no	0-90	9999	25
	MCPP	0.1	3.8	4	?	no	no	<20	?	>2200

# : 1-3 = well known since 2004; 1 = low variability; 2 = moderate variability; 3 = high variability; 4 = well known since 1988, low variability ##: removal by volatilization or photolysis [%]; prob = probable but not quantified \$ = in dune sand

†: 9999 = >365 days probably, hard to quantify

Sulfamethoxazole and carbendazim are both slowly/hardly degraded in suboxic environment and much more rapidly in environment. anoxic Grünheid & Jekel (2006) demonstrated this for sulfamethoxazole as well.

The elimination rate of iopamidol in suboxic environment seems to depend on the concentration level of nitrate (Fig.5): the higher nitrate the higher the



FIGURE 5. Mean removal of iopamidol as a function of mean nitrate concentration, at the shallow, suboxic transects 1 (Castricum ICAS), 4 (Zandvoort Basin 6), 5 (Zandvoort, Basin 12) and 7 (The Hague, Pond 13.1), for summer 2005 and 2006

elimination rate. Probably nitrate is a surrogate here for the oxidation capacity of water (in this environment being  $4O_2 + 5 NO_3$  in me/L)

## BEHAVIOR IN OLD INFILTRATES, IN ANOXIC ENVIRONMENT

Old infiltrates are defined here as those with a travel time >1 year. All 14 pollutants listed in Table 3 have been present in the source and infiltration waters for more than at least 5 years. Their exact input signal is largely unknown, although the earliest data on bentazone, MCPP and diglyme data back from the late 1980s. Obviously the input levels of bentazone and 1,4-dioxane were much higher in the 1980s than today (Fig.6). Other pollutants that are present in older, anoxic infiltrate, are MCPP (mecoprop), diglyme, MTBE and carbamazepine. Their presence demonstrates their resistance against (bio)degradation.





### QUANTIFYING DEGRADATION RATES

The rate of (bio)degradation of a pollutant is commonly and conveniently defined by a single parameter, the half life (T,) under the assumption of first order decay. Taking R  $t_{H2O}$  as the residence time of the pollutant in the aquifer system then yields:

$$T = 0.3 R t_{H2O} / \log (C_0 / C_t)$$
 [d] (EQ 1)

With:

- C<sub>0</sub> = input concentration at t = 0 [ug/L]
- C<sub>t</sub> = concentration after t days [ug/L]
- T<sup>1</sup>/<sub>2</sub> = (ln2) / ' = where ' = decay constant of pollutant [1/d]
- t<sub>H2O</sub> = residence (travel) time of the water since infiltration [d]
- R = Retardation factor of the pollutant due to sorption to the aquifer matrix [-]
- The factor R can be estimated by:

R=1+
$$\rho_{\rm S}$$
 (1-n) f<sub>ND</sub> K<sub>D</sub>/n [-] (EQ 2)

With:

- $\rho_{\rm S}$  = density porous medium, solids [kg/L]
- n = effective porosity [-]
- $f_{ND}$  = non-dissociated fraction = 1 / {1 + 10^(pH pK\_A)}
- $pK_A = -\log K_A$ , with  $K_A$  being the 1<sup>st</sup> acid dissociation constant of the pollutant
- K<sub>D</sub> = distribution coefficient of pollutant, soil/water (L/kg) often to be calculated as follows Appelo & Postma, 2005):

$$K_{\rm D} = f_{\rm OC} \, 10^{\rm B} \, K_{\rm OW}^{\rm A} \qquad [\rm L/kg] \qquad (EQ 3)$$

Where:

- f<sub>OC</sub> = fraction of bulk organic carbon in aquifer matrix [-]
- K<sub>OW</sub> = octanol water distribution coefficient [-]
- A, B = constants depending on pollutant (type), listed in literature.

## UNCERTAINTY ANALYSIS FOR IOPAMIDOL IN SUBOXIC ENVIRONMENT

The nearly exponential decline of iopamidol concentration levels with increasing travel time (Fig.4, left) suggest that the half life concept is valid enough. A closer inspection of Fig.4 and the apparent relation of iopamidol removal with the oxidation capacity of water ( $NO_{3}$ , Fig.6) reveal, however, that the removal rate of oxidants by bulk organic matter in the aquifer is more important in determining the degradation rate than the initial amount of iopamidol. Although this does disrupt the validity of the half life concept, it does not invalidate calculated half lives as long as they are considered as relative measures for comparison.

When we accept T as a valuable parameter, then it is worthwhile to make a kind of uncertainty analysis.

In this analysis we try to quantify the combined effects of estimated errors in the 4 terms in Eq.1: R,  $t_{H2O}$ ,  $C_0$  and  $C_t$  ( $C_0 > C_t$ ), by taking:

 $(T)_{MIN} = 0.3 R_{MIN} (t_{H2O})_{MIN} / \log \{(C_0)_{MAX} / (C_t)_{MIN}\}$  [d] (EQ 4)

$$(T)_{MAX} = 0.3 R_{MAX} (t_{H2O})_{MAX} / \log \{(C_0)_{MIN} / (C_t)_{MAX}\}$$
 [d] (EQ 5)

We estimate the errors in the individual terms as follows:

- R: if R = 1 then 0%, else if R = 1-10 then +/- 10%, else if R 10-100 then +/- 20% etc.
- $t_{\rm H2O}$ : if based on history matching of environmental tracers then +/- 15%, otherwise if calculated with a hydrological model well validated on water balances, piezometric levels and high quality KD and effective porosity values, then +/- 30%
- $C_0$  and  $C_t$  dealing with relative analytical errors only: if C > 4\*LOQ then +/- 10%, else +/- 20%

When we apply these estimates to Eqs.4 and 5 we obtain, with the mean T values for iopamidol in 6 transects with travel times < 100 days in 2005 (Table 4), minimum values that are about half the value calculated using Eq.1 (mean T), and maximum values that double that value (see Table 4).

Not included in this uncertainty analysis are the effects of temporal and spatial changes in redox environment and temperature of the infiltration water. These effects can be very large.

lopamidol, suboxic	T½ Min	T½ Mean	T½ Max
Basin Recharge pan 13	28	48	94
Basin Recharge G6	30	45	73
Basin Recharge G12	48	85	194
Basin Recharge Castricum 8	30	53	120
Deep Well Injection Waalsdorp	20	36	81
Deep Well Injection dWat	26	82	205
Mean Range / Values	30	58	128
Max Range / Values	20	58	205

## TABLE 4. Range of calculated half lives for iopamidol in suboxic environment along 6 transects in 2005.

## CONCLUSIONS

Two snapshot surveys of 10 monitoring transects of observation wells in 3 basin artificial recharge (BAR) and 2 deep well injection (DWI) systems yielded insight in

the behavior of 140 organic micropollutants ( $<0.001 - 5 \mu g/L$ ). These consist of 80 pharmaceuticals and other emerging pollutants (PEPs) and 60 regulated organic pollutants (ROPs). At this stage our interpretation is still in progress, which means that various results presented here are preliminary.

Most PEPs (71%) and ROPs (60%) were everywhere below the limit of quantification. This low score is partly explained by a very effective sanitation of the Rhine and Meuse fluvial basins, and by a thorough pretreatment of the infiltration waters (consisting of coagulation, rapid sand filtration and in several cases activated carbon filtration).

Concentrations of detected pharmaceuticals and X-ray contrast agents were low  $(0.01-0.2 \ \mu g/L)$ . Various of these pollutants showed significant (bio)degradation (>90%) during aquifer passage, in either suboxic or anoxic environment or both. Others were not removed at all, not even after 36 years. These findings again demonstrate a strong influence of redox conditions on removal rates (cq persistency) of many organic micropollutants, in addition to others mapped for artificial recharge and river bank filtration systems in the Netherlands by Stuyfzand (1998).

All together, artificial recharge significantly contributes to water quality improvements, also regarding PEPs and ROPs. Even better achievements of aquifer passage can be realized, however, by increasing the travel times and forcing the infiltrates to flow through first suboxic and then anoxic environments, for instance by installing the recovery system in a deeper anoxic aquifer.

Further research should focus on the relation between the oxidation capacity and temperature of water and the removal of organic pollutants in suboxic and anoxic environments.

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