Quality of Groundwater, Proceedings of an International Symposium, Noordwijkerhout, The Netherlands, 23—27 March 1981, W. van Duijvenbooden, P. Glasbergen and H. van Lelyveld (Eds.), *Studies in Environmental Science*, Volume 17

THE BEHAVIOUR OF ORGANIC MICROPOLLUTANTS DURING PASSAGE THROUGH THE SOIL

G.J. PIET, C.H.F. MORRA and H.A.M. DE KRUIJF
National Institute for Water Supply, Voorburg, The Netherlands
L.J. SCHULTINK and J.G.H.M. SMEENK, respectively,
Provincial Water Works North-Holland and Municipal Water Works of Amsterdam

ABSTRACT

A study is described which is set up to increase insight in the effects of soil of the dunes on the removal and modification of organic compounds present in water of the river Rhine during dune-infiltration as a treatment step in drinking water production. The results presented in this report are based on a first orientation by field studies. An overview is given of the investigations which form a part of the project.

The first analytical results of field studies relate mainly to the behaviour of low boiling aromates, nitro aromates, chloro-nitro aromates and several organo-chlorine compounds. A kind of zone-formation of some compounds during passage in the soil is observed and specific chemicals are indicated which show a tendency to break through.

INTRODUCTION

A diversity of organic compounds has been released today by human activities. The project that is described below is being carried out to increase insight in removal and modification of organic compounds during passage in soil and to indicate potentially harmful compounds that occur regularly in water of the river Rhine and in spite of soil passage may occur in drinking water derived from that source.

Artificial recharge of groundwater for the drinking water supply is applied in the dunes of North- and South-Holland.

One of the most important aspects in assessing the suitability of drinking water supply systems which use dune- or bank infiltrated surface water, is the degree of removal of compounds which are harmful for human health. Particularly synthetic organic micropollutants that are present at high levels in heavily contaminated Rhine water are of concern.

Knowledge of the behaviour of these compounds during infiltration is rather scarce. The existing information is mainly limited to data of sumparameters such as pesticides, polynuclear aromatic hydrocarbons and total extractable organic chlorine etc. (1,2).

Only recently more advanced analytical techniques are used to get information about the identity and character of the micropollutants (3,4). There are indications that a considerable decrease of some important chemical groups or classes of organic compounds such as aromatic amines, nitro aromates, fenols, total extractable organic chlorine takes place during infiltration dependant on the character of the soil and its conditions. Some organo-chlorine compounds with low molecular weight and some chlorinated ethers evidently are less effectively removed.

At some locations in The Netherlands where bankinfiltration of water of the Rhine is used prolonged investigations indicate that odorous compounds progressively penetrate into the soil and affect the raw water sources for the drinking water supply(5).

The question has to be answered whether after prolonged infiltration micropollutants will break through and to what extent the soil itself will be polluted in the course of time.

EXPERIMENTAL

1. Studies at the Leiduin infiltration area of the Municipal Waterworks Amsterdam

a. The semi technical modelstudy takes place in special sand reservoirs placed above the ground, where surface water similar to that used for dune infiltration, is introduced. The organic substances are concentrated at the sample locations by passing continuously a known quantity of water through a small tube (i.d. 1 cm) that is filled with 5 ml XAD (4 and 8) with a volumetric velocity of 5 ml/min. The tubes are replaced every 24 hours, and eluted with diethylether and acetone. The eluates are compiled to 14-day samples and stored at -20^{o}C. The analyses take place with high resolution gas-chromatography-massspectrometry and liquid-liquid chromatography.

Identical XAD samples will not only be used for identification and characterization of organic substances but also for mutagenicity tests according to Ames.

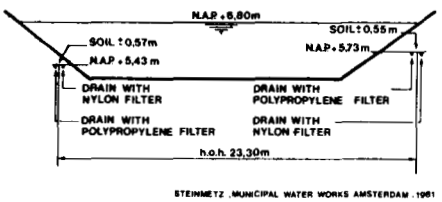
The soil will be examinated too for organic pollutants at several depths before and after the infiltration studies. A number of pertinent soil parameters will also be determined.

b. The field study consists of investigations of water passing through peatlayers and of water passing mainly through sand layers. The residence times at the sample locations are respectively 18, 38 and 50 days. At another location the behaviour of organic compounds is studied in the first 50 cm of the soil with a residence time of 1 hour (see a modified diagram in Fig. 1).

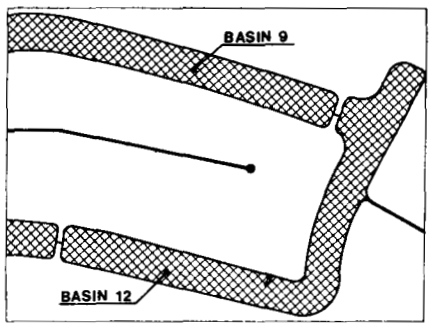
2. Studies at the infiltration area of the Provincial Water Works of North-Holland

A second study is performed in North-Holland. The same type of water is used at that place for artificial recharge. A scheme of the infiltration basins and the situation of the sampling wells of basin 9 is pictured in figure 2 and 3.
The soil of the infiltration terrain consists of fine-grained dune sand mixed with

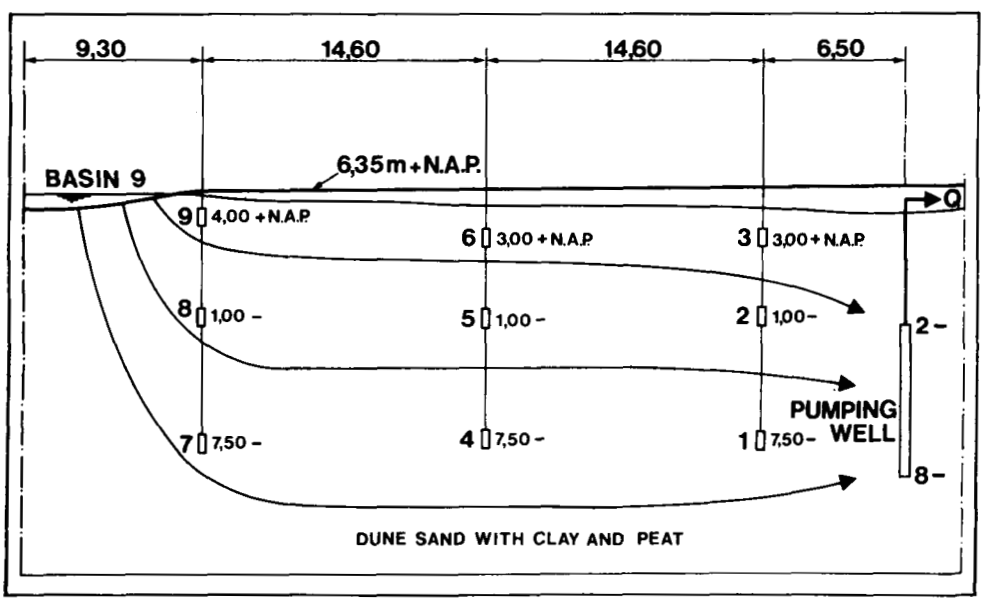
Dune-infiltration South-Holland



Dune infiltration North-Holland



Dune infiltration North-Holland



clay and lens-shaped peat-layers. It has been used continuously during the last 4 years for infiltration purposes.

Sampling for the analysis of organic compounds was carried out in the same way as described for the model and field studies at Leiduin.

The average concentration of nitrate (in mg/l nitrogen) and oxygen (in mg/litre) in the basin and at wells 8 and 5 are shown in table 1.

TABLE 1

Nitrate and oxygen levels (averages over November, December 1980 and January 1981) of sampling wells at North-Holland (10 observations)

Location	Nitrate (mg N/l)	Oxygen (mg/l)
Basin 9 (infiltrating water)	4.3	11.1
Well 8 and 5	3.8	5.4

3. Analytical Program

The organic compounds in the XAD eluates are analysed by high resolution gaschromatography using 50 m OV-1 capillary columns and on-column injection techniques combined with computerised massspectrometry (Finnigan 4000 - Incos system).

The XAD concentrates relate to identical water bodies as sampling of the water at a second well (e.g. number 5) started when the water body from the first well (e.g. number 8) had moved to that location (after 18 days).

FIRST ANALYTICAL RESULTS

A. Leiduin

At the Leiduin site it was demonstrated that nitrobenzene, nitrotoluene and chloronitrobenzene were completely eliminated in the first 50 cm of the soil after infiltration. Some phthalates which were not present in the infiltrating water, were present in a sample after passing 50 cm of the soil.

Less polar organic chlorine compounds were strongly reduced in the first 50 cm of the soil while more polar organic chlorine compounds pass. This is demonstrated by the measurement of extractable and adsorbable organic chlorine compounds (table 2).

TABLE 2

Organic chlorine sum parameters in the infiltrated water before and after passage of 50 cm of the soil (concentration in microgram/litre).

	Extractable Organic Chlorine	Adsorbable Organic Chlorine
Before infiltration	12 (± 2)	40 (± 5)
After infiltration	3 (± 2)	45 (± 5)

B. North-Holland

More than 400 organic compounds in the infiltrating water and the water from well 5 and 8 were registered in one GC-MS run. Only the major compounds at a microgram/litre level were listed. Over 60% of the list are unknown substances, part of them are present in infiltrating water, part are only found after infiltration through the soil. Not all identified substances were confirmed by calibrating substances. In table 3 compounds are listed that decrease in concentration due to infiltration.

TABLE 3

Organic compounds in the infiltrating water which were considerably reduced in concentration in the water of well 8 (% reduction).

Compound		Compound	
Nitrobenzene	(60)	a-Chloronitrobenzene	(90)
Chlorocresol	(100)	Dichlorobenzene methanol, α-methyl	(60)
Triethylphosphate	(70)	Dinitrotoluene	(95)
Ethylmethylpyridine/N-ethylaniline	(80)	10 unknown major compounds	(50-100)
a-Nitrotoluene	(70)		

In table 4 compounds are mentioned which were found at much higher concentrations in the water of well 8 than in the infiltrating water.

TABLE 4

Organic compounds in infiltrating water which increased in concentration due to infiltration (% increase)

Compound		Compound	
Benzene	(500)	Bis(2-chloroisopropyl)ether	(70)
Toluene	(600)	Alkane-C_{11}	(100)
Tetrachlorethene	(100)	Naphthalene	(500)
o-Xylene	(3000)	Tri(2-chloroethyl)phosphate	(400)
Phosphorothio acid, o,o,o-trimethyl	(200)	2 Phthalates	(500-5000)
		22 unknown major compounds	

In table 5 those compounds are listed that were not found in the infiltrating water but were detected at well 8.

TABLE 5

Compounds not present in the infiltrating water but detected after infiltration (concentration in µg/litre)

Compound		Compound	
Dibromochloromethane	(2)	Trichloro aniline isomer	(trace)
Bromodichloromethane	(2)	Tributylphosphate	(0.1)
Dichlorotoluene	(0.1)	a-Phthalate isomer	(3)
Dichloromethoxybenzene	(0.1)	3 unknown major compounds	

In table 6 compounds are listed that are found at the same levels at well 8 and well 5.

TABLE 6

Compounds that are almost unchanged to concentration at well 8 and well 5

Dibromochloromethane	a-Chloronitrobenzene
Bromodichloromethane	2-Methylthiobenzothiazole
m/p-Xylene	Tri-butylphosphate
Alkane-C_{10}	Tri(2-chloroethyl)phosphate
Triethylphosphate	Tetradecanoic acid
Napthalene	Several Phthalates
	17 unknown major compounds

Some isomers of compounds changed in concentration during passage through the soil, other isomers of the same compounds did not change in concentration (table 7). The % increase (+) or reduction (-) is related to the concentration in the infiltrating water.

TABLE 7

Compound	After 3 days		After 21 days	
	change	unchanged	change	unchanged
m/p-Xylene Δ		x		x
o-Xylene	+ 800		- 500	
a-Nitroluene	- 70		- 90	
a-Nitrotoluene		x	- 30	
a-Chloronitrobenzene	- 90		- 100	
a-Chlronitrobenzene Δ		x		x
13 isomers of 6 unknown compounds (5 marked with Δ)				

The compounds marked with Δ are of special interest because they show a tendency to break through and are sometimes present in drinking water (6).

DISCUSSION

A field study of the effect of the soil of the dunes on organic compounds present in water of the river Rhine showed that several nitro aromates are almost completely eliminated in the water under aerobic conditions. At the Leiduin site this took already place in the first 50 cm of the soil. This is of importance because nitro aromates are major compounds in Rhine water.

Of interest are also the chloronitro aromates, major compounds in the Rhine. Some of these compounds are eliminated in the first metres of the soil even after prolonged infiltration, but a chloronitrobenzene-isomer was not reduced in concentration during passage of the soil under aerobic conditions. As chloroanilines seem to be formed in the soil it is of importance to study the behaviour of chloronitro aromates as possible precursors particularly under anaerobic conditions.

Compounds which are found at increased concentrations compared to the infiltration water are some haloforms, tetrachloroethene, dichlorotoluene, bis(2-chloroisopropyl)ether. This could be due to the fact that the soil acts as a kind of chromatographic column in which a zone-formation takes place. It should be studied whether this is mainly caused by sorption- and displacement effects because these compounds will break through in the course of the time if no bio-degradation affects them. Some polar compounds which break through are somewhat soluable in water and are of interest too. To these belong organic phosphates, chloro-phosphates and probably phthalates. In this respect the adsorbable organic chlorine compounds have to be studied more in detail. As several major organic compounds with an unknown character are present after passage through the soil additional identification techniques have to be applied to verify their character and impact.

The movement and behaviour of organic micropollutants in the soil are governed by numerous processes. For this reason well-defined column studies will be carried out for selected compounds in conjunction with the Leiduin semi-technical studies and the field studies in the dunes.

The possible mathematic modelling and description of seperate processes (7) may enable identification of critical processes regulating the behaviour and possible fate of organic compounds during passage through the soil.

To this end not only soil surface boundary conditions, initial solution concentration, dispersion coefficients and other characteristics of the soil are relevant but also rate constants for decay partly depending on biodegradability and the presence of micro-organisms in the soil.

ACKNOWLEDGEMENTS

The assistance of Mr. A. den Boer and Mrs. N. Ruygrok who did the analytical work and Mr. A. van Eck who assisted in the field made it possible to write this report.

REFERENCES

1 Baardolf, B., M.F.M. Jansen, J. van Puffelen. The occurrence and removal of some pesticides as to the dune water supply of the Hague (in Dutch). Report Municipal Water Supply, The Hague. 1973.
2 Sontheimer H., W. Nissing. 'Anderung der Wasserbeschaffenheit bei der Bodenpassage unter besonder Berücksichtigung der Uferfiltration, Gas, Wasser-Abwasser, 77, 639 (1977).
3 Smeenk J.G.H.M., Survey of data concerning quality aspects of dune-infiltration.

3 Report Municipal Water Supply of Amsterdam, 1979.
4 G.J. Piet, B.C.J. Zoeteman. Organic Water Quality Changes during Sand Bank and Dune Filtration of Surface Waters in The Netherlands, JAWWA, 72, 400-404, 1980.
5 J.C. Sybrandi (Municipal Water Works Overijssel) Personal communications.
6 B.C.J. Zoeteman. Sensory Assessment of Water Quality. Pergamon Series on Environmental Science Volume 2, 1980.
7 M.Th. van Genuchten, Analytical solutions for chemical transport with simultaneous adsorption, zero-order production and first-order decay. Journal of Hydrology, 49 213-237, 1981.