

GROUNDWATER POLLUTION BY HEAVY METALS AND PESTICIDES FROM A DREDGE SPOIL DUMP

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ABSTRACT

The 3.5 square kilometre area of a polder near Rotterdam has been filled with 25 million cubic metres of dredged material from the Rotterdam harbours. The dump contains high concentrations of particulate and dissolved heavy metals and pesticides. A combined geohydrological and geochemical study was carried out to predict the fate of the metals and pesticides from the dredge spoil dump.

The original upward flow of groundwater in the polder will, after the consolidation of the former peaty top layer has ended in about the year 2020, change into a downward flow. Then pollutants from the dump will break through and enter the aquifer. Heavy metals may well up in adjacent polders between the years 2200 and 2400, pesticides several thousands of years later.

INTRODUCTION

The port of Rotterdam is situated along the only remaining open branch of the river Rhine which carries large amounts of polluted sediments. Furthermore estuarine processes transport even more marine sediments into the harbours. The continuous extension and deepening of the facilities caused the annual amount of dredging to increase from 0.3 million cubic metres in 1923 to 21 million cubic metres in 1979 (ref. 1). The latter figure is about five times the total annual mud discharge of the Rhine. Within the estuary, the metal concentrations are determined by the mixing of the polluted fluvial sediments with the cleaner marine sediments (ref. 1).

The most polluted deposits, dredged from the upstream harbours, are dumped on land. The predominantly marine spoil from the downstream parts of the estuary is released at selected locations in the North Sea.

One of the landfill areas is the 3.5 square kilometre Broekpolder (Fig. 1) in which 25 million cubic metres of dredged material were dumped between 1959 and 1976. The dump contains high concentrations of heavy metals and pesticides. Concern about the possibility of dispersion of these pollutants in the subsoil

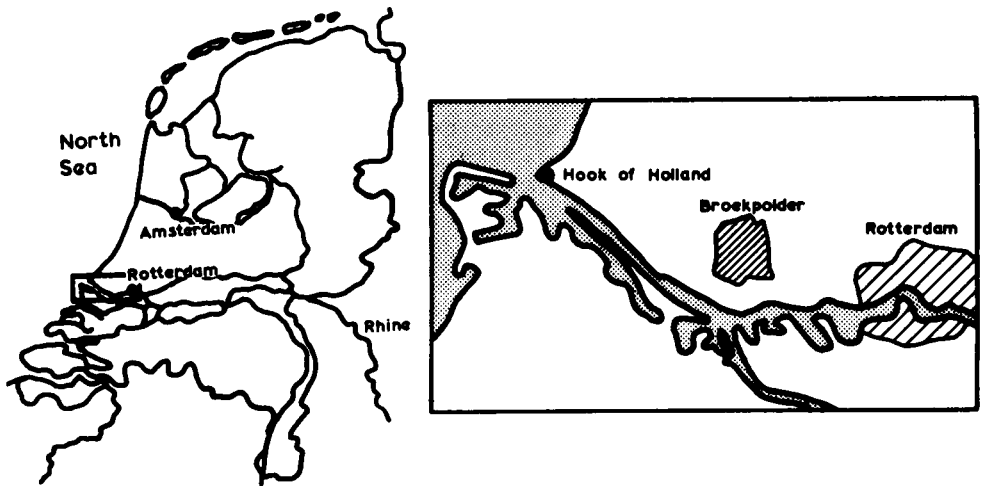


Fig. 1. Locality sketch of the Broekpolder.

and in the surrounding waters, led to this combination of geochemical and geo-hydrological studies.

DESCRIPTION OF THE SYSTEM

Originally, the land surface in the Broekpolder and its surroundings was about 2.5 metres below mean sea level; the water level was even 0.5 metre lower. The subsoil consists of 15 metres of semi-permeable peat resting on 20 metres thick permeable layer of sand and gravel. The aquifer in the latter layer is fed by the estuary along the southern boundary. The flow of the ground water is generally to the North and Northeast and it wells up through the peaty layer into the low polders.

The deposition of the dredged material locally raised the land surface and the phreatic level by about 7 metres; well above mean sea level. Moreover, the weight of the sediments causes a gradual compression of the peaty layer on which it rests. The latter process caused the water pressures in the peaty layer to rise; even higher than the phreatic level in the dump. In this way the super-stressed pore water forms a barrier between the polluted groundwater in the dump and the aquifer. With the progress of the process of consolidation, however, this barrier will fade away and, eventually, the pollutants will break through and contaminate the aquifer.

A series of geochemical and microbial reactions occurs in the dredged material after its deposition: dissolved oxygen, dissolved nitrate, particulate iron(III)hydroxide and manganese (IV)oxide, dissolved sulphate and dissolved carbon dioxide successively act as oxygen donors for the decomposition of the organic matter. Consequently, the composition of the groundwater changes:

- Depletion of oxygen, nitrate and sulphate;
- release of highly soluble iron(II) and manganese(II);
- release of organic N and organic P in the forms of ammonium and phosphate, and
- release of heavy metals and pesticides associated with the organic matter and particulate iron(III)hydroxide and manganese(IV)oxide.

The dissolved compounds, move with the flow of groundwater. En route, through the peat and the sand, phosphate, metals and pesticides will be adsorbed.

If the polluted ground water surfaces in aerobic conditions, the following reactions may occur:

- Nitrification of ammonium;
- precipitation of iron(II) and manganese (II);
- coprecipitation of heavy metals and phosphate with the iron and manganese;
- adsorption of heavy metals, phosphate and pesticides onto sediment particles, and
- (photo)oxidation of pesticides.

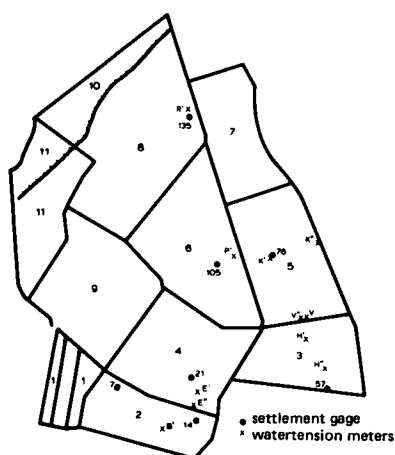


Fig. 2. Compartmentation of the Broekpolder with the localities of the water-tensionmeters and settlement gages.

ANALYSES

Four cores were taken from compartment 5 (filling completed in 1969) of the Broekpolder (Fig. 2) in 1977; another in an undisturbed polder 1.5 kilometre to the West. Samples were taken from the cores at depths of 1, 2, 3, 5 and 7 metres, stored air tight and the water was squeezed out under 60 atm. in an anoxic atmosphere. Samples were also taken from the surface water in the drainage system of the Broekpolder. The analyses carried out on the samples

TABLE 1
Analyses. in the water samples

nutrients	:	PO ₄ , NO ₃
anions	:	Cl, SO ₄
cations	:	Fe, Mn, Mg
heavy metals	:	Zn, Cu, Cr, Pb, Ni, Hg, As, Cd
pesticides	:	α-, β- and γ-HCH, heptachlor, heptochlorepoxyde, aldrin, dieldrin, endrin, isodrin, telodrin, p.p'-DDT, o.p'-DDT, p.p'-DDT, TDE
others	:	pH, NH ₄

TABLE 2
Mean composition of the groundwater in compartment 5 of the Broekpolder

Depth m	pH	NH ₄ mg N/l	NO ₃ mg N/l	SO ₄ mg/l	Cl ‰	Mg mg/l	O-PO ₄ mg P/l	Fe mg/l	Mn mg/l	Zn µg/l
1	7.1	61	0.3	<3	1.71	177	0.65	11	1.8	40
2	7.2	52	0.3	<3	1.87	271	0.84	12	1.6	17
3	7.0	45	0.5	<3	2.80	208	0.51	11	1.6	21
5	6.9	71	0.3	<3	2.50	224	0.32	21	2.0	41
7	6.8	32	0.7	<3	1.5	89	0.05	29	1.8	16

Depth m	Cu µg/l	Cr µg/l	Pb µg/l	Ni µg/l	Cd µg/l	Hg µg/l	As µg/l	aldrin µg/l	isodr. µg/l	telodrin µg/l
1	8.4	3.8	2.4	23	3.2	0.4	65	<0.05	0.06	<0.05
2	8.2	2.6	9.1	23	2.7	<0.1	38	2.5	2.9	0.21
3	11	3.2	8.5	26	2.2	0.3	42	<0.05	<0.05	<0.05
5	6.5	4.7	10	22	4.8	<0.1	68	<0.05	<0.05	<0.05
7	6.4	3.1	3.7	35	2.3	<0.1	29	0.10	0.30	0.07

are mentioned in Table 1 and the results in Tables 2 and 3.

SO₄ and Mn appear to be constant with depth, Cl, PO₄, Cu and Pb show a maximum at intermediate depths; NH₄, Zn, Cd, Hg, As and Cr are relatively high at 1 and 5 metres depth, and Fe and Ni predominate at the bottom of the cores in the Broekpolder. The pesticides show a remarkable variation. Concentrations are much lower under the reference polder.

Except for Cu, the concentrations of heavy metals in the surface waters are lower than in the groundwater of the Broekpolder. Dieldrin, missing in the groundwater, appears in the surface water due to the transformation of aldrin under oxic conditions. All other pesticides, found in the groundwater, are also present in the surface water. Phosphate is somewhat lower in the surface water. These results of the analyses confirm the picture of the processes.

By far the greater part of the metals and pesticides present in the dump are bounded to the solids as is shown in Table 4. Not all of the particulate pollutants will be leached in the future. If it is assumed that only 0.5 per cent of the metals and pesticides, now bound to the solids, will be released,

the presently observed concentrations in the groundwater can be maintained for hundreds, and in some cases even thousands, of years to come.

TABLE 3

Comparison between the concentrations in the groundwater of the Broekpolder, the groundwater of the reference polder and the surface water of the Broekpolder

Parameter	Groundwater Broekpolder	Groundwater reference polder	Surface water Broekpolder
pH	7.0	7.2	-
NH ₄ mg N/l	52	39	-
NO ₃ mg N/l	0.4	0.4	-
SO ₄ mg/l	<3	109	655
Cl ‰	2.10	1.58	1.22
Mg mg/l	194	104	-
O-PO ₄ mg P/l	0.47	3.6	0.21
Fe mg/l	17	0.03	0.06
Mn mg/l	1.8	0.63	0.76
Zn µg/l	27	<12	19
Cu µg/l	8.1	< 5.3	11
Cr µg/l	3.5	< 0.8	1.2
Pb µg/l	6.7	< 3.3	1.5
Cd µg/l	3.0	< 0.6	0.46
Ni µg/l	25	<11	14
Hg µg/l	0.15	< 0.1	< 0.02
As µg/l	48	12	7.6
aldrin µg/l	<0.55	< 0.05	0.02
isodrin µg/l	<0.67	< 0.06	0.03
telodrin µg/l	<0.08	< 0.05	0.03
dieldrin µg/l	<0.05	< 0.05	0.27

TABLE 4

Ratio of particulate to dissolved metals and pesticides per unit of soil volume

Parameter	Ratio	Parameter	Ratio
Fe	2,500	Cd	4,200
Mn	560	Ni	2,500
Zn	43,000	aldrin	>16,000
Cu	28,000	isodrin	>11,000
Cr	98,000	telodrin	>18,000
Pb	50,000		

COMPUTATIONS

The dispersion of contaminants in the ground is mainly caused by the flow of groundwater. A mathematical model of the geohydrological processes in the area has been made with the use of a finite element computer programme (GROMULA). It represents, two dimensionally, the horizontal flows in the permeable aquifer as well as the vertical flows through the semi-permeable upper layers in the system (Fig. 3). Its boundaries are situated along the Rhine estuary in the South and further at a distance where the influence of the dumping in the Broekpolder becomes insignificant. Withdrawal of water by industries is included as well as the effect of the consolidation process. The soil parameters were

- + leakage into the aquifer
- seepage from the aquifer
- direction of horizontal flow
- waterbalance

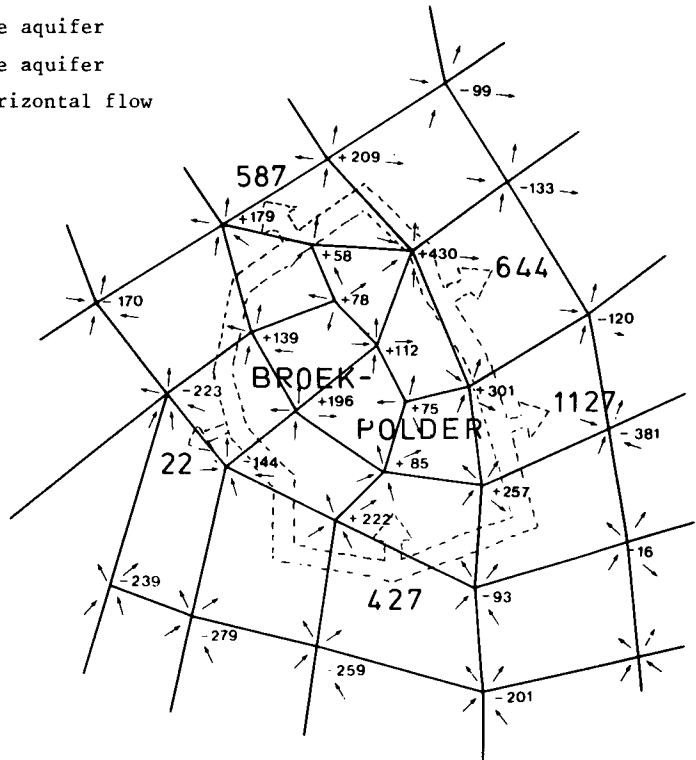


Fig. 3. Flow of the groundwater in the summerperiod of the final situation in a part of the polder area considered.

estimated from available data from many borings. The transmissivity (kD) of the aquifer was $1,250 \text{ m}^2/\text{day}$ and the resistivity (c) of the semi-permeable layer increased from 5,000 days before to 12,000 days after the dumping. The model was calibrated and verified with data about the undisturbed hydrological situation and about the consolidation observed in various compartments of the polder (Fig. 2).

Before the dumping started, the upward seepage in the Broekpolder was $480 \text{ m}^3/\text{day}$ during Winter and $570 \text{ m}^3/\text{day}$ during Summer. The consolidation process will block all vertical throughflows until a time between 1990 and 2090, depending on the location within the polder. Finally, there will be a downward flow of some $2150 \text{ m}^3/\text{day}$ in Winter and $1950 \text{ m}^3/\text{day}$ in Summer. The latter situation is given in Fig. 3.

The computed flow patterns were used as a basis for a model of the transport of the contaminants from the dump into its surroundings. A significant flow line was chosen, running from the dump downward, then horizontally in the

aquifer and finally upward into an undisturbed polder. Along this U-shaped path the transports were calculated using a one-dimensional programme (DIVAN) which simulates the advection (v), the dispersion (D) and the adsorption (R) according to

$$(1+R) \frac{\delta C}{\delta t} = v \frac{\delta C}{\delta x} + D \frac{\delta^2 C}{\delta x^2} \quad (1)$$

Values of D and R were taken from literature as given in Table 5. No other

TABLE 5

Values for the distributioncoëfficiënt R (ref. 2,3,4) and the dispersion-coëfficiënt (ref. 5,6) used in equation (1)

Parameter	Distributioncoëfficiënt R			Dispersioncoëfficiënt $10^5 \cdot D$ (m ² /day)		
	branch 1	branch 2	branch 3	branch 1	branch 2	branch 3
Cl	0	0	0	4.3	73	4.9
Fe	1.6	0	1.6	2.3	71	2.9
Zn	2.8	0	2.8	2.3	71	2.9
Cu	4.2	0	4.2	2.3	71	2.9
Pb	4.2	0	4.2	2.3	71	2.9
Cd	1.8	0	1.8	2.3	71	2.9
Ni	2.5	0	2.5	2.2	70	2.8
aldrin	600	0	600	2.3	71	2.9

chemical processes were taken into account, which means that, eventually, the same concentrations as observed in the Broekpolder will show up in the adjacent polders, the worst case.

The results for these computations for the various compounds are given in Fig. 4. It appears that chloride from the Broekpolder, being conservative, will show up as first in the adjacent polders around the year 2100. For heavy metals the process will take one to three centuries due to adsorption along the way and the pesticides will arrive thousands of years later.

CONCLUSIONS

The dump contains enormous amounts of pollutants, e.g. 5,000 tons of lead. It will be able to release them for a long time to go at a considerable rate, e.g. about 5 kilograms of lead per year. The geohydrological processes develop very slowly and therefore the penetration of the pollutants will take a long time; even retarded by the consolidation of the peaty soil.

REFERENCES

- 1 W. Salomons and W.D. Eysink, in S.D. Nio, R.T.E. Schüttenhelm and I.C.E. van Weering (Eds), Holocene Marine Sedimentation in the North Sea Basin, I.A.S. Special Publication 5, Blackwell Scientific Publishers, 1981 (In press).

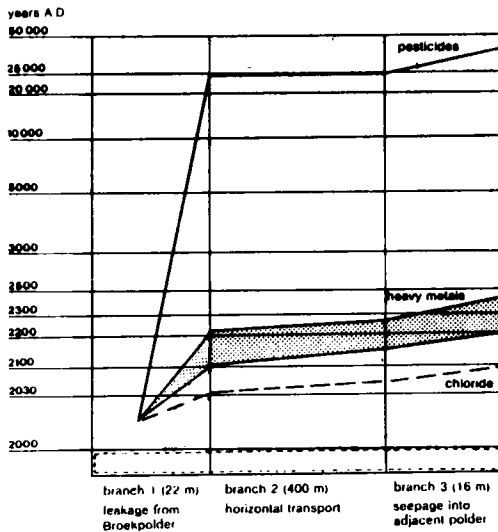


Fig. 4. Dispersion of chloride, heavy metals and pesticides after the year 2020.

2. R.C. Sidle, L.T. Kardos and M.Th. van Genuchten, *J. Envir. Quality*, 6 (1977) 438-443.
3. D. Beker, Report 959, Instituut Cultuurtechniek en Waterhuishouding, 1977, (In Dutch).
4. D. Eye, *J. Water Poll. Contr. Fed.*, 40 (1968) R316-R322.
5. F.T. Manheim, in J.P. Riley and R. Chester (Eds.), *Chemical Oceanography*, Vol. 6, London Academic Press, 1978.
6. M.J. Frissel, P. Poelstra and P. Reiniger, *Plant and Soil*, 33 (1970) 161-176.