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ENVIRONMENTAL POLLUTION BY A CHEMICAL WASTE DUMP

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ABSTRACT

Drums containing chemical waste products have been found on a domestic waste dump in a polder north of Amsterdam. The wastes were analyzed and found to contain polychlorinated benzenes, chlorophenols, 2,4,5-T, hexachlorocyclohexanes and tetradifon. The concentrations found were at the weight % level. 2,4,5-T was contaminated with 2.5 mg kg^{-1} 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD).

Since 1960 about 10000 drums were dumped in the polder. The origin of most of the drums was a chemical plant producing pesticides. The waste was a by-product of a purification process.

In 1963-1969 the dump was covered with soil and sediment of watercourses, and after that partly used for grazing cows and sheeps. Setting of the dump was the cause that in later years the drums came to the surface of the pasture soil and to the surface of the sides of the surrounding watercourses. Several drums which were rusted through came in direct contact with the surface water. Samples were analyzed from water, sediment, farm animals and wildlife.

INTRODUCTION

In the period 1925-1930 a domestical waste dump came into use 10 km north of Amsterdam in a polder area with many ditches and canals. Until now yearly about 7.10^7 kg of refuse were dumped in an area of 6.10^5 m^2. The dump was situated from 3-5 m below the original soil surface until 5 m above this level. Since 1960 also chemical waste products were dumped. After dumping, the domestical waste and drums were covered with soil and sediment of watercourses and after that used for grazing of cows, ponies and sheep.

In spring 1980 a worker of the Municipal Environmental Laboratory of Amsterdam observed a great number of rust-eaten and mechanically damaged drums dispersed over the surface of the soil and in the water of ditches and canals. About 250 drums were visible of which 28 were selected and the contents analyzed. After the analysis contact was made with the chemical industry which dumped these drums.

Since 1960 about 10000 drums were dumped, of which 8000 containing by-products of the tetrachlorobenzene production and 2000 containing by-products of the lindane (γ-hexachlorocyclohexane) production. The tetrachlorobenzenes were used for the production of 2,4,5-T.

Besides samples of the contents of the drums, also samples were taken of the environment of the dump e.g. surface water and sediment, fat of farm animals which grazed for years on the dump and wildlife. In Fig.1 a map of the dump is given with sampling sites of surface water and sediment indicated.

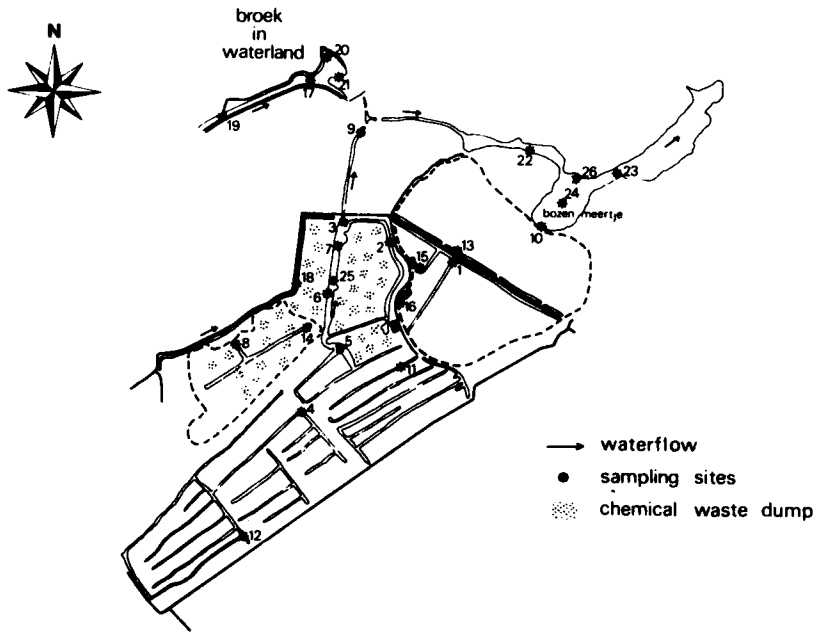

Fig.1 Map of the dump with sampling sites. 5 (centre, C), 3 (lock, S), 9 (bridge, J) and 10 (Bozenmeertje, B) are of special interest. Distance 3 to 5: 1000 m.

ANALYTICAL METHODS

The analytical methods used are summarized in Table 1.

RESULTS

Drums

From the 250 visible drums on the dump 28 drums were selected for analysis. It was tried to select drums with different contents. In Table 2 the concentrations (in weight %) of chlorobenzenes and HCH's in some characteristic drums are given. In view of the low concentrations found, the concentrations of β-HCH, aldrin, dieldrin, heptachloor, heptachloorepoxide, endrin, TDE, o.p'-DDT, p.p'-DDE and p.p'-DDT are not given in the table. In Table 3 the concentrations (in weight %) of the chlorophenols in the same drums are given. I.R.-spectra were made of all the chemical waste samples.

TABLE 1

Summary of analytical methods

Compound	Matrix	Extraction	Clean-up	Detection	Reference
chloroben-zenes	waste	PE	none	GLC-ECD	
	water	PE	none	GLC-ECD	
	sediment	acetone	L/L partition	GLC-ECD	
	fat	PE	alumina column	GLC-ECD	
	milk	PE	none	GLC-ECD	
chloro-phenols	waste	toluene	L/L partition	der. GLC-ECD	1
	water	toluene	L/L partition	der. GLC-ECD	1
	sediment	toluene	L/L partition	der. GLC-ECD	2
	fat	PE	L/L partition	der. GLC-ECD	
	milk	toluene	L/L partition	der. GLC-ECD	
organochlo-rines e.g. HCH's, DDT's, "drins"	waste	PE	none	GLC-ECD	3
	water	PE	alumina column	GLC-ECD	3
	sediment	acetone	L/L partition, alumina column	GLC-ECD	4
	fat/milk	PE/acetone	alumina column	GLC-ECD	5
tetradifon	waste	acetone	none	GLC-ECD	
2,4,5-T	waste	chloroform	preextraction of alkaline solution	der. GLC-ECD	6
	water	chloroform		der. GLC-ECD	6
volatile organohalogens e.g. $CHCl_3$	water	purging and trapping	none	GLC-ECD	7
toluene, benzene, ethylbenzene	water	purging and trapping	none	GLC-ECD	7
polycyclic aromatics	water	cyclohexane	alumina column	HPLC	
	sediment	acetone/cyclohexane (1:1), cyclohexane	silicagel column	HPLC	
heavy metals	water	none	none	AA	8, 9
	sediment	Parr bomb	none	AA	8, 9
TCDD	waste	PE	none	GLC-MS	10
extractable organic chlorine	waste	PE	pyrolysis	microcoulometer	11

PE = petroleum ether (b.r. 40-60°C)
der. = derivatization
waste = chemical waste products

TABLE 2

Chlorobenzenes and hexachlorocyclohexanes (in weight %) in drums containing chemical waste products

Drum	Chlorobenzenes							HCH	
	1,2- + 1,3- + 1,4-	1,2,3- + 1,3,5-	1,2,4-	1,2,3,4-	1,2,4,5-	Penta	Hexa	α-	γ-
A	-	-	1.7	44	22	30	2.3	0.09	0.29
B	-	-	1.9	0.93	95	1.2	-	-	-
C	-	-	-	-	-	-	1.9	96	2.6
D	-	-	-	-	-	-	0.08	0.81	-
E	1.2	0.02	0.17	0.61	0.32	0.21	-	0.06	-

"-" non detectable (<0.05%)

TABLE 3

Chlorophenols (in weight %) in drums containing chemical waste products

Drum	Mono	Di	Tri excl. 2,4,5-	2,4,5-Tri	Tetra	Penta
A	-	0.14	-	0.044	-	0.44
B	-	0.04	-	0.006	-	0.006
C	-	0.23	-	0.061	-	0.93
D	-	0.018	0.32	2.9	0.26	0.027
E	-	-	-	-	-	-

"-" non detectable (<0.005%)

It showed that drum D, which contained 2.9% trichlorophenol, contain 2,4,5-T and drum E tetradifon. 2,4,5-T appeared to be contaminated with 2.5 mg kg^{-1} 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). TCDD was determined by high resolution mass spectrometry (Ref.10).

13 of the 28 drums contained a mixture of chlorobenzenes with low concentrations of chlorophenols (up to 1%), 5 drums contained a mixture of HCH's, 2 drums contained 2,4,5-T, 1 drum contained tetrachlorodifon and 7 drums contained soil. Besides the individual organochlorine compounds, also the sum of extractable organic chlorine was determined. The results of this parameter confirmed the gas chromatographic results.

Surface water and sediment

Samples of surface water and sediment were analyzed for chlorobenzenes, organochlorines, chlorophenols, heavy metals and polycyclic aromatics. The water samples were also analyzed for aromatics, 2,4,5-T and volatile organic halogen compounds. Samples were taken at 24 sites in and around the dump. The results of 4 sampling sites are given in Fig.2-4 and in Table 4 and 5.

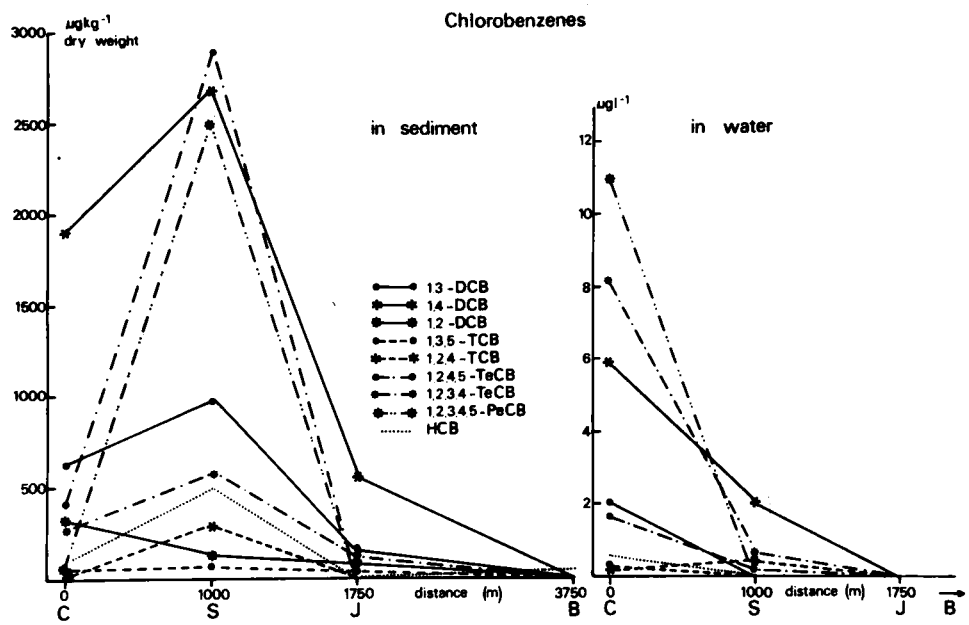

Fig.2 Chlorobenzenes in sediment (in µg kg^{-1}, dry weight) and in water (in µg l^{-1}) at C, S, J and B (see Fig.1).

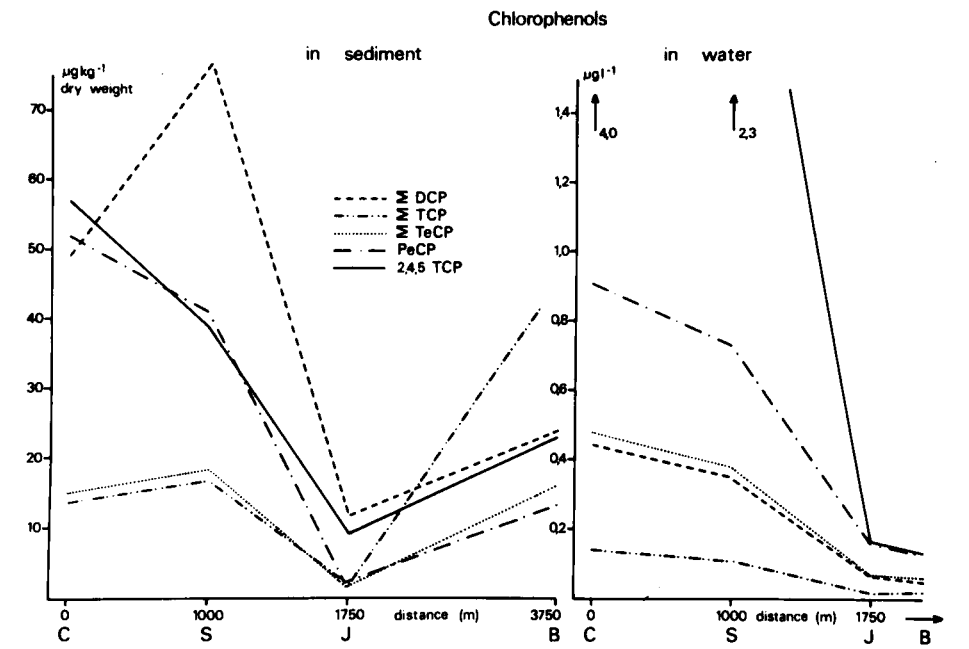

Fig.3 Chlorophenols in sediment (in µg kg^{-1}, dry weight) and in water (in µg l^{-1}) at C, S, J and B (see Fig.1). DCP = dichlorophenols, TCP = trichlorophenols, TeCP = tetrachlorophenols, PeCP = pentachlorophenol.

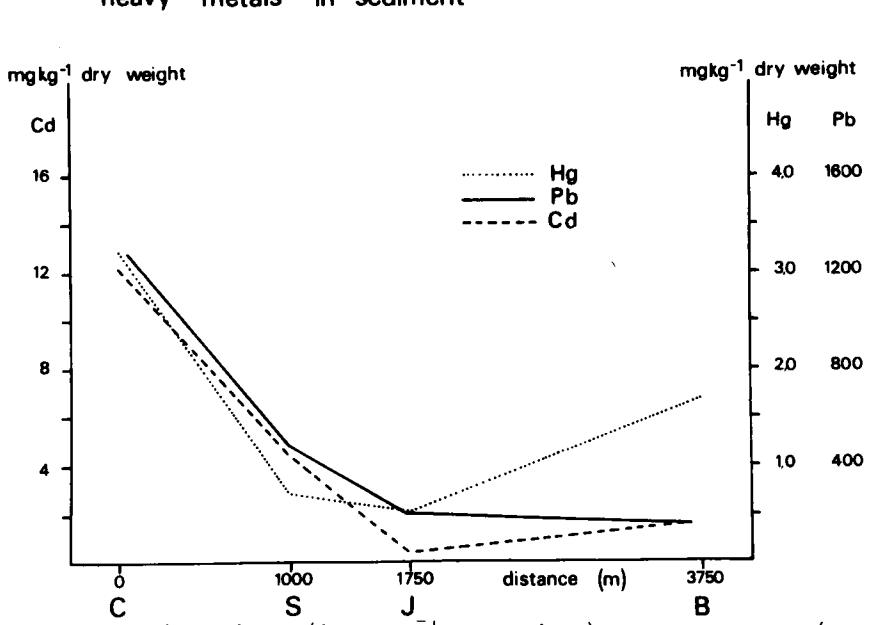

Fig.4 Heavy metals in sediment (in mg kg^{-1}, dry weight) at C, S, J and B (see Fig.1).

TABLE 4

Volatile organic halogens in water (in µg l^{-1}) of 4 sampling sites (see also Fig. 1) and in river Rhine (Ref.12)

Compound	Centre (5)	Lock (3)	Bridge (9)	Bozenmeer-tje (10)	Rhine 1979
dichloromethane	<0.01- 0.30	0.02-1.60	<0.01-0.01	<0.01	2.0 -20
1,1-dichloroethene	<0.01- 2.8	0.01-0.10	<0.01-0.01	≤0.01	0.3 -80
trichloromethane	0.01- 1.2	<0.01-0.05	0.01-0.90	0.01-0.03	1.5 - 6.0
1,1,1-trichloroethane	<0.01- 10	<0.01-0.02	0.01-0.10	≤0.01	<0.01- 0.5
tetrachloromethane	0.50-250	0.03-4.2	0.20-2.5	0.20-0.40	0.5 -10
trichloroethene	0.01- 1.0	0.02-0.06	3.6	<0.01	0.2 - 1.5
1,1,2,2-tetrachloroethane	0.06- 4.0	0.01-1.4	0.01-5.7	0.01-0.04	ni

ni = not investigated

TABLE 5

Maximum concentration of HCH's in water (in µg l^{-1}) and sediment (in mg kg^{-1}, dry weight) at sampling site 3

Compound	Water	Sediment
α-HCH	0.27	0.13
γ-HCH	0.05	0.04

The 2,4,5-T concentrations in water were at sampling site 5: 6.5 µg l^{-1}, 3: 5.0 µg l^{-1}, 9: 2.5 µg l^{-1} and 10: 0.06 µg l^{-1}.

Water and sediment samples taken at sampling site 5 were analyzed for polycyclic aromatics. The sum of fluoranthene, benz (k) fluoranthene, benz (b) fluoranthene, 1-12 benzperylene, benz (a) pyrene and indenopyrene was in water 0.49 µg l^{-1} and in sediment 8.5 mg kg^{-1} (dry weight).

Farm animals

Samples of lamb, pony and cow which grazed on the dump were analyzed. The results and the maximum residue limits are given in Table 6. The milk was also analyzed for chlorophenols. 2,3,6-, 2,3,5- and 2,4,5-trichlorophenol and pentachlorophenol were found. After removing the cows from the dump, the chlorophenol concentrations decreased below the limit of detection.

TABLE 6

Chlorobenzenes and organochlorines (in mg kg^{-1} fat base) in farm animals

Compound	Lamb n=7	Pony	Cow n=2	Cowmilk	MRL (Ref.13)	
					Pork meat	Milk
1,2,4,5-tetrachlorobenzene	ni	0.24	ni	-		
1,2,3,4-tetrachlorobenzene	ni	-	ni	-		
pentachlorobenzene	ni	0.08	ni	-		
HCB	1.57	0.09	0.02	0.11	0.5	0.3
α-HCH	0.02	17	0.02	0.03		
β-HCH	0.15	15	0.01	0.04		
γ-HCH	0.02	0.65	0.01	0.01	2	0.3
p.p'-DDE	0.04	0.02	0.03	-	1.25*	1.25*
TDE	-	-	0.02	-		
dieldrin	-	0.03	-	-	0.2**	0.15**
heptachlorepoxide	0.02	0.01	0.01	-	0.5***	0.15***

ni = not investigated * = sum of DDT's *** = including heptachlor
"-" = non detectable ** = including aldrin

Wildlife

Fat samples of buzzard, pheasant, pigeon, duck, rabbit, daphnia magna, white bait, eal and a goose-egg were analyzed for chlorobenzenes and organochlorines. The results are summarized in Table 7. The concentrations in rabbit, duck, pheasant and pigeon were very low and are not given. In goose-egg on fat base were found 1,2,4,5- and 1,2,3,4-tetrachlorobenzene (2.6 resp. 1.3 mg kg^{-1}), pentachlorobenzene (6.6 mg kg^{-1}), HCB (0.9 mg kg^{-1}) and β-HCH (0.7 mg kg^{-1}).

TABLE 7

Chlorobenzenes and organochlorines (in mg kg^{-1}, fat base) in wildlife

Compound	Environment chemical waste dump				Hollandsch Diep	Lauwersmeer
	Buzzard	Daphnia magna	White bait	Eel	Eel 1977 (Ref.14)	Eel 1977 (Ref.14)
1,2,4,5-tetrachlorobenzene	19	13	2.0	6.7	ni	ni
1,2,3,4-tetrachlorobenzene	25	14	8.0	12	ni	ni
pentachlorobenzene	185	17	1.2	13	ni	ni
HCB	73	4.3	2.0	1.9	10	0.11
α-HCH	2.9	1.4	-	1.8	0.28	0.17
β-HCH	460	2.9	-	1.4	0.15	0.04
γ-HCH	-	-	-	0.2	0.98	0.35
p.p'-DDE	40	-	-	0.5		
p.p'-DDT	0.6	4.3	-	0.3	2.7*	0.39*
TDE	1.0	14	6.0	3.6		
dieldrin	4.2	-	-	-	0.51	0.12
heptachlorepoxide	2.9	-	-	-	ni	ni

ni = not investigated
"-" = non detectable
* = sum of DDT's

DISCUSSION

From the results presented in Fig.2-3 it follows that the concentrations of chlorobenzenes and chlorophenols in water decrease with the distance of the sampling sites to the centre of the dump. From the results in Table 4 it follows that the contamination of volatile organic halogens near the dump are lower than measured in the river Rhine in 1979.

In sediment relatively high concentrations of chlorobenzenes, HCH's and chlorophenols are found near the lock. Chlorophenols are also found at a greater distance to the dump. The concentrations of heavy metals in sediments near the lock were lower than at the centre of the dump.

The concentrations of chlorobenzenes and HCH's in water and sediment are at the Rhine water level (Ref.3 and 15). Chlorophenols, especially 3,5-, 2,3,6-, 2,4,5-, 2,3,5,6- and pentachlorphenol in sediment are higher than in an area with Rhine sediment, the Ketelmeer (Ref.2). So the aquatic environment of the dump can be compared with a surface water polluted by chemical industry.

HCB was found in lamb in concentrations above the Dutch maximum residue limit. High concentrations of α-, β- and γ-HCH were found in fat of pony. Chlorophenols were found in cowmilk. After removing the cows from the dump the concentrations decreased below the limit of detection.

High concentrations of chlorobenzenes and organochlorines were found in fat of daphnia magna, white bait and eel. Especially eel was contaminated with HCH's in comparison with eel from other polluted area's in the Netherlands e.g. Hollandsch Diep, tributary of the river Rhine.

The concentrations of chlorobenzenes and organochlorines were low in fat of rabbit, pheasant, duck and pigeon.

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