

Dow Sentrachem, Chloorkop: organic and metal
contaminants in wastewater and in the downstream
environment

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Summary

On two consecutive days in July 2002, a research team led by Greenpeace collected samples of wastewater being discharged by the Dow Sentrachem production facility located in the Chloorkop industrial suburb of Ekurhuleni Metro (Witwatersrand, South Africa). Samples of soil, sediment and water from the environment immediately downstream were also collected. All samples (eleven in total) were returned to the Greenpeace Research Laboratories, University of Exeter (UK) for analysis of organic and heavy metal contaminants.

Although the appearance and quality of the wastewater varied from day-to-day, the plant is clearly acting as a point source of a range of organic contaminants, including the volatile organochlorine chemicals chloroform and tetrachloromethane, and the persistent contaminants di-, tri- and tetra-chlorinated benzenes and chlorinated alkanes. Samples taken on one day also showed the presence of hexachlorocyclohexane (HCH) in the discharge, as well as very high concentrations (148 mg/l) of the toxic metal nickel and elevated levels of cobalt. Although this sample had a more or less neutral pH, samples collected the previous day were highly alkaline (pH 12-14), indicating that the effluent is periodically highly corrosive.

As this discharge channel runs across land which is openly accessible to the public, and noting that the channel was uncovered and even broken in parts, wastewaters being released from the Dow Sentrachem facility to the nearby evaporation ponds clearly represent immediate acute hazards to public health as well as the longer-term health and environmental hazards associated with the chemical contaminants themselves. Of particular concern is the potential for soil, surface and groundwater contamination to occur either from leaks of wastewater from the effluent channel or as a result of migration from the evaporation ponds.

An area of soil adjacent to one such break in the effluent channel, where there was evidence of a previous leak or spill of effluent, contained a similar range of chlorinated benzenes to that identified in the wastewater, as well as very high concentrations (almost 3 g/kg) of nickel. Residues of the persistent, toxic and bioaccumulative pesticide DDT and its degradation products (DDD and DDE) were also detected in this sample, as were traces of 2,4-dichlorophenol (possibly arising as a by-product of the manufacture of other chlorinated pesticides), although it is not possible to state conclusively that these residues have arisen as a result of discharges from the Dow Sentrachem facility.

Water collected from the Kaalspruit stream, receiving water from the evaporation pond site downstream from the effluent discharge, also contained a range of organic compounds, including organochlorines, though in this case dominated by isomers of the pesticide HCH. HCH was also detected in iron-rich flocs sampled from the stream, as well as residues of DDD and DDE. Sediments from the bed of the Kaalspruit at the same point also contained DDD, DDE and one isomer of DDT itself, as well as the chlorinated organophosphorus pesticide chlorpyrifos ("Dursban"). Direct links between the presence of these residues and past or

present pesticide formulation operations at the Dow Sentrachem plant are possible but cannot be verified on the basis of the current investigation. Further sampling and analysis, in combination with information on current and previous activities at the plant and on the possible application of such pesticides for insect control, would be necessary in order to determine the likely source. In any case, the presence of these pesticide residues represents a significant potential danger to the surrounding environment and public health, demanding urgent investigation into the extent and severity of contamination and actions to remediate the impacted areas.

Introduction

Site description

The Dow Sentrachem production facility, located in the Chloorkop industrial suburb of Ekurhuleni Metro (Witwatersrand), produces a range of chlorine-based products. A single wastewater discharge has been identified arising from the plant, carrying effluent north-east from the plant boundary across open land and under Zuurfontein Avenue to a series of evaporation ponds also operated by Dow Sentrachem. The evaporation pond site, enclosed within a concrete wall, slopes away to the north between the Phomolong and Birch Acres suburbs. At the northern-most end is a small dam impounding a lagoon from which water is pumped to join the Kaalspruit stream, which flows away to the north under Andrew Mapheto Drive.

From the point of exit from the boundary of the production facility itself, effluent is carried to the evaporation pond site through a simple channel formed from sections of concrete pipe, set into a shallow ditch. In some sections, this channel has no cover, while in other places, there are small gaps between adjacent sections of the pipe. As far as can be ascertained, this discharge channel runs through land which is openly accessible to the public.

Sample collection

In July 2002, a small research team led by Greenpeace visited the Chloorkop area and collected samples of wastewater being discharged from the Dow Sentrachem facility in order to determine the presence of any organic and/or heavy metal contaminants. Separate samples were collected on both 23rd and 24th July 2002 in order to examine day-to-day variation in effluent quality. A sample was also taken of soil adjacent to the discharge pipeline at a point at which effluent appeared to have recently leaked out over the ground. Further samples were collected of water and sediment from the Kaalspruit stream, north of the evaporation pond site, adjacent to the bridge under Andrew Mapheto Drive. Full descriptions of all eleven samples collected are given in Table 1. Sampling points are also indicated in Figure 1.

Materials and methods

Sampling

All samples were collected in pre-cleaned (acid and solvent washed) glass bottles supplied by the Greenpeace Research Laboratories. Two types of liquid sample were collected from each sampling location, one in a 250ml amber glass bottle with a ground glass stopper (for analysis of volatile organic compounds) and another in a 1 litre glass screw-cap bottle (for analysis of other organic compounds and heavy metals). Solid (soil and sediment) samples for organic and

Sample no.	Sample type	Sample description	Date	Appearance	pH
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MI02029/30	Wastewater	Collected from open effluent channel flowing from the Dow Sentrachem facility, at point of exit from plant boundary	23.07.02	Pale yellow-brown w/ brown sediment	12-14
MI02035/36	Wastewater	Collected from open effluent channel flowing from the Dow Sentrachem facility, at point of exit from plant boundary	24.07.02	Pale green w/ white sediment	7-8
MI02031/33	Wastewater	Collected from open effluent channel flowing from the Dow Sentrachem facility, at intersection of Chloorkop Rd with Andrew Mapheto Drive	23.07.02	Pale yellow-green w/ white sediment	12-14
MI02032	Soil	Collected adjacent to open effluent channel, at intersection of Chloorkop Rd with Andrew Mapheto Drive (site of previous leak or spill)	23.07.02	Grey-white sludge	N/a
MI02026/28	River water	Collected from the Kaalspruit stream, north of Dow Sentrachem evaporation ponds, by the bridge on Andrew Mapheto Drive	23.07.02	Pale brown w/ small amount of sediment	7
MI02027	Sediment	Collected from the bed of the Kaalspruit stream, by the bridge on Andrew Mapheto Drive	23.07.02	Black silt	N/a
MI02034	Sediment	Brown flocs collected from the surface of reeds and debris in the Kaalspruit stream, by the bridge on Andrew Mapheto Drive	24.07.02	Dark brown w/ high water content	N/a

Table 1: full descriptions of the samples collected from the environs of Dow Sentrachem

metal analyses were collected in 100ml glass screw-cap bottles using a pre-cleaned stainless steel spatula in each case.

Analysis

All samples were placed in the cool and dark immediately after collection and were returned to the Greenpeace Research Laboratories for analysis. Samples for volatile organic compound analysis were analysed by gas chromatography – mass spectrometry (GC-MS) using an Agilent 5890 GC linked to a 5972 MS. Other organic contaminants were also determined by GC-MS (6890 GC and 5973 MS) following liquid-liquid (or liquid-solid) extraction into analytical grade pentane (or pentane-acetone mixture), desulphurisation and clean-up on activated Florasil. For both VOC and other organics, the MS was run in both SCAN mode (to identify a broad range of contaminants) and SIM mode (to verify identities of a range of key contaminants against standard solutions). Metal concentrations were determined using inductively coupled plasma - atomic emission spectrometry (ICP-AES, Varian Liberty-100) following hot acid digestion. Further details of the analytical methods employed are available on request.

Results and discussion

The results of the analysis of the samples for organic contaminants are summarised in Table 2, and for metals in Table 3 below. Full lists of the organic compounds identified in each sample are available on request.

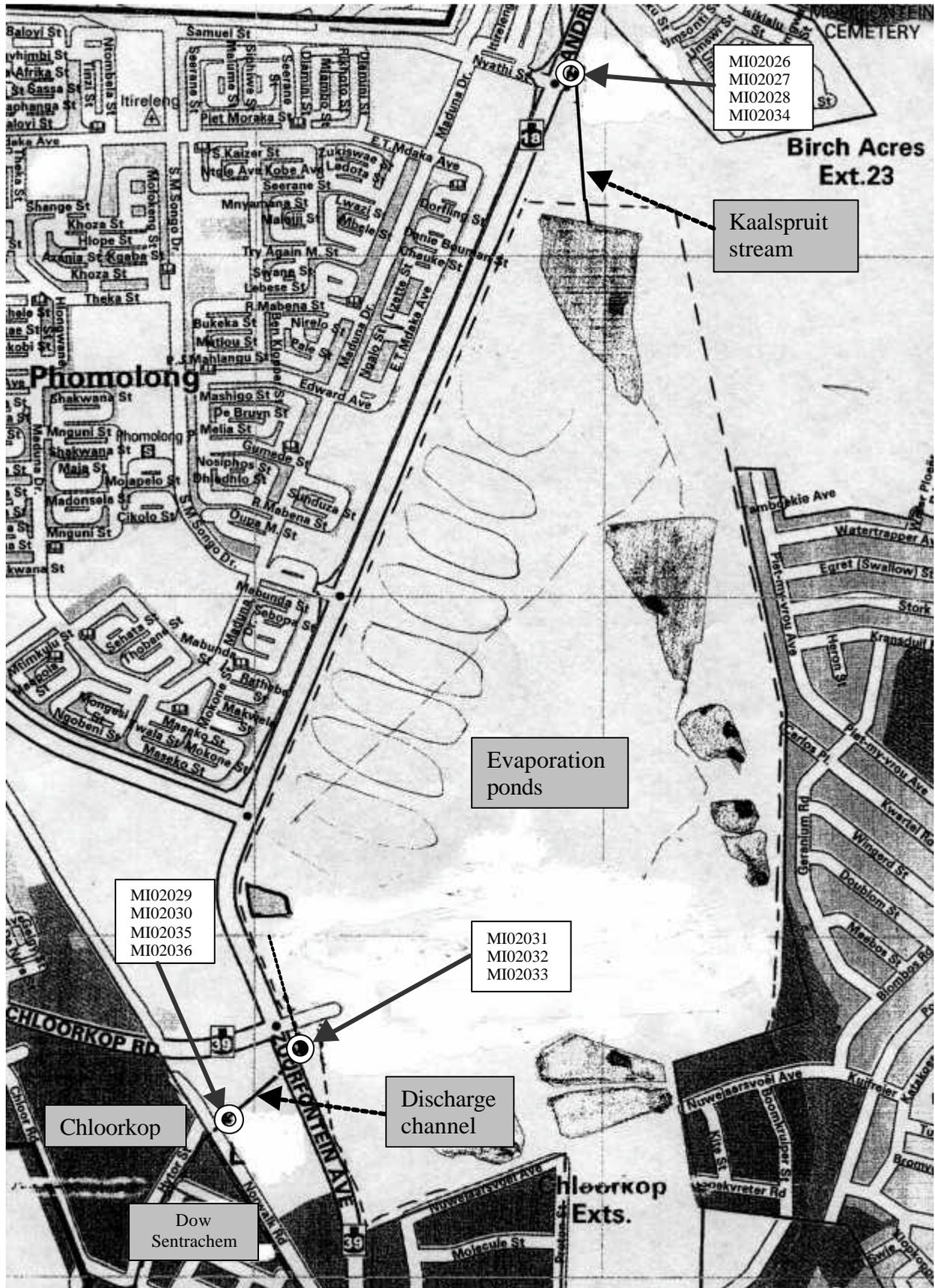


Figure 1: location of sampling sites

Sample	MI02029/30 wastewater	MI02035/36 wastewater	MI02031/33 wastewater	MI02026/28 river water	MI02032 soil	MI02027 sediment	MI02034 sediment
<i>Summary</i>							
No. compounds isolated	68	85	72	5	108	44	41
No. compounds identified	26	50	44	5	63	24	17
No. chlorinated organics	9	10	10	5	14	8	7
<i>VOCs</i>							
Chloroform	1	1	1				
Tetrachloro-methane	1	1	1				
Bromodichloro-methane		1					
<i>Chlorinated benzenes</i>							
Dichloro-benzenes	(2)	(2)	(2)	(1)	(2)	(2)	(1)
Trichloro-benzenes	1 (1)	1 (2)	1 (1)		(2)		
Tetrachloro-benzenes	(2)	(2)	(2)		(2)		
<i>Pesticides</i>							
o,p'-DDT					(1)		
p,p'-DDT					(1)	(1)	
o,p'-DDD					(1)	1	(1)
p,p'-DDD					(1)	1	(1)
o,p'-DDE					(1)	(1)	(1)
p,p'-DDE					(1)	(1)	(1)
alpha-HCH		1		(1)			(1)
beta-HCH				(1)			(1)
gamma-HCH				(1)			
delta-HCH				(1)			
Chlorpyrifos						1	
<i>Other organo-chlorines</i>							
2,4-dichloro-phenol					(1)		
Chloroalkanes	1	2	2		1		

Table 2: summary of organic analytical results for all 11 samples collected; figures indicate positive identifications for the compounds listed – for chemical groups, figure indicates the number of representatives of that group positively identified; figures in parenthesis indicate that these compounds were detected in selective ion monitoring (SIM) mode only.

Wastewater from discharge channel at point of exit from factory boundary

As noted in Table 1, samples MI02029/30 and MI02025/36 differed markedly in appearance despite being collected from the same point in the effluent channel on consecutive days. Both sample sets smelt strongly of chlorine. The variation in effluent quality was confirmed by the marked difference in pH, with samples MI02029/30 being highly alkaline (pH 12-14) while samples MI02035/36 were approximately neutral (pH 7-8). These differences may relate to variations in manufacturing or processing operations at the Dow Sentrachem facility from one

Sample number	MI02030 wastewater	MI02036 wastewater	MI02033 wastewater	MI02028 river water	MI02032 soil	MI02027 sediment	MI02034 sediment
<i>Metal concentration</i>	ug/l	ug/l	ug/l	ug/l	mg/kg	mg/kg	mg/kg
Cadmium	<10	<10	<10	<10	<1	<1	<1
Chromium	79	64	206	<20	9	84	75
Cobalt	<20	103	<20	<20	3	14	<2
Copper	<20	<20	<20	<20	<2	39	47
Iron	252	2658	<20	297	3656	31471	222700
Lead	<30	<30	<30	<30	<3	94	<3
Manganese	<10	187	<10	750	46	238	338
Mercury	<1	<1	<1	<1	0.2	0.5	1.3
Nickel	<20	148111	<20	74	2965	138	325
Zinc	<10	660	<10	14	55	229	775

Table 3: summary of quantitative results of metal analyses for all 11 samples collected

day to the next, though without detailed information on such activities, it is not possible to speculate further.

Both sample sets contained a range of organic compounds, dominated by simple linear and branched hydrocarbons, though a number of chlorinated organic compounds were also detected. Chloroform and tetrachloromethane were found in the effluent collected on both sampling days (MI02029 and MI02035). The sample collected on the second visit (24th July) also yielded bromodichloromethane. These volatile organochlorine chemicals probably arise as a result of unintended reactions between free chlorine from the hypochlorite and organic matter contained within the wastewater, although without further information on the facility itself, the possibility that these chemicals are manufactured and/or used intentionally on site cannot be ruled out.

Chloroform

Exposure to chloroform may occur when breathing contaminated air, drinking contaminated water or through skin contact (Weisel & Chen 1994, Weisel & Jo 1996). Chloroform has been specified by the International Agency for Research on Cancer in the Group 2B as possibly carcinogenic to humans (IARC 1998). Investigation on animals have shown that the main target organs for carcinogenicity from chloroform are liver, kidney, and/or intestine (Dunnick & Melnik 1993, Snyder & Andrews 1996, Chiu *et al* 1996).

Chloroform evaporates easily into the air. Most of the chloroform in air breaks down eventually, but it is a slow process. The breakdown products in air include phosgene and hydrogen chloride, which are both toxic (ATSDR 1997). It is poorly absorbed to soil and can travel through soil to groundwater where it can persist for years. Chloroform dissolves easily in water and some of it may break down to other chemicals (ATSDR 1997).

Tetrachloromethane (Carbon tetrachloride)

Carbon tetrachloride is a substance which can cause cancer in animals and humans (US EPA 1997) and has been classified as Group 2B carcinogen (possibly carcinogenic to humans) by International Agency for Research on Cancer (IARC 1999). Carbon tetrachloride induces hepatic cell proliferation and DNA synthesis. It also has a mutagenic effect and induces aneuploidy in several *in-vitro* systems (IARC 1999). High exposure to carbon tetrachloride can cause liver, kidney, and central nervous system damage.

Carbon tetrachloride is relatively stable in the environment and is included in Group II of Annex B of controlled substances of the Montreal Protocol (UNEP 1997) as an ozone depleting compound. If carbon tetrachloride released to land, it does not sorb onto soil, but migrates readily to ground water and is believed to remain in ground water for month to years (US EPA 1988). Under anaerobic conditions carbon tetrachloride can be biotransformed producing hazardous intermediates such as chloroform and methylene chloride (Hashsham *et al* 1995) and carbon disulphide under sulphate reducing conditions (Delvin & Muller 1999, Hashsham *et al* 1995).

Chlorinated benzenes

Exposure to **dichlorobenzenes** can cause adverse effects on the blood, skin, respiratory tract and nervous system in humans. Effects reported for animals are most commonly liver and kidney damage. Dichlorobenzenes are bioaccumulative in algae, aquatic invertebrates and fish (Ware 1988b).

The toxicity of all three isomers of **trichlorobenzene** appear similar, primarily damaging the liver, kidney and thyroid. There is some indication of slight fetotoxicity at high doses. There is little evidence of mutagenicity and too few data are available for the trichlorobenzenes to given a carcinogenicity classification (Giddings et al. 1994a). All three isomers are toxic to algae (Sicko-Goad et al. 1989a-d, Sicko-Goad & Andresen 1993a & b).

The toxicity of **tetrachlorobenzenes** as a group, and target organs, are again similar, with 1,2,4,5-tetrachlorobenzene appearing to be the most toxic. Again insufficient information is available to classify tetrachlorobenzenes as to carcinogenicity. In rats, 1,2,3,4- and 1,2,3,5-tetrachlorobenzene caused reduction in the number of live offspring at concentrations too low to adversely affect the mother (Giddings et al. 1994b).

Wastewater collected on both days also contained a range of di-, tri- and tetra-chlorinated benzenes (MI02030 and MI02036), relatively common contaminants from industrial processes involving the chlorination of organic compounds. Simple chlorinated linear hydrocarbons (chlorotetradecane and chlorohexadecane) were also identified in both samples. Of course, the process origin of these contaminants cannot be determined in this case. Sample MI02036 also contained residues of one isomer of the chlorinated pesticide hexachlorocyclohexane (α -HCH), suggesting that formulations including HCH were being prepared on the site during that day (or at least that HCH-contaminated wastes were being discharged). This isomer was clearly visible even in the relatively low sensitivity scan mode, and its identify was confirmed in SIM mode (through both mass spectrum and retention time matching). The absence of this compound from the effluent sampled on the previous day (MI02030) could reflect day-to-day variation in the quality of wastes discharged, though the very high pH of the effluent on this first day might also have interfered with recovery of the compound had it been present.

Day to day variations in effluent quality are also apparent from concentrations of metals in the two wastewater samples collected from the same location on consecutive days (MI02030 and MI02036). These samples contained similar (and slightly elevated) levels of chromium but markedly different concentrations of iron, cobalt, manganese and, in particular, nickel. At 148 mg/l, the nickel concentration determined on the second visit (24th July) was extremely high, though the process origins of this metal from Dow Sentrachem are not known. Elevated iron

Hexachlorocyclohexane (HCH)

The toxic, persistent and bioaccumulative organochlorine hexachlorocyclohexane (HCH) has in the past been produced and used as an insecticide on a worldwide basis. Technical grade HCH comprised five isomeric forms, referred to as alpha, beta, gamma, delta and epsilon, with alpha the most abundant. alpha, beta and gamma-HCH are the most important isomers in terms of environmental impact.

The relatively high stability, mobility and fat solubility of HCH, combined with its global use pattern, has resulted in widespread environmental contamination. Once introduced into environment, HCH may persist for many years (Martijn *et al.* 1993). The beta-isomer is more persistent than others (ATSDR 1997).

All isomers of HCH are toxic to animals, humans, and aquatic species. Chronic health effects in animals can include damage to the liver, lung, endocrine system and induction of certain types of cancer. Reproductive problems and behaviour effects have also been reported following repeated exposure (Nagata *et al* 1996). Moreover, chronic exposure to HCH can be hazardous to freshwater macroinvertebrates even at unexpectedly low concentrations (Schulz *et al* 1995).

concentrations (at over 2mg/l) probably relate to the manufacture of iron-based flocculant chemicals at the facility

Wastewater and soil from discharge channel near Zuurfontein Avenue

Samples MI02031 and MI02033 were also highly alkaline and contained a very similar mix of chlorinated and non-chlorinated organic compounds as that identified in samples MI02029 and MI02030. This is to be expected, since MI02031/33 were collected from only slightly downstream from the factory boundary and on the same day as MI02029/30. Again there was a strong smell of chlorine, presumably arising from the hypochlorite content of the wastewater. Both chloroform and tetrachloromethane were identified, as in sample MI02029, as well as a similar range of di-, tri- and tetra-chlorinated benzenes and chlorinated alkanes. Levels of chromium were higher, and of iron, lower than at the upstream site, suggesting significant changes in effluent quality over very short timescales, though for most metals, concentrations remained below limits of detection.

A sample of soil collected immediately adjacent to the discharge channel at this point (MI02032), soil which had apparently been discoloured by a previous spill of effluent from a break in the pipeline, also yielded the same chlorinated benzenes and chlorotetradecane. This sample also contained residues of the pesticide DDT and its breakdown products DDD and DDE. According to information received by Greenpeace, the Chloorkop facility did produce DDT commercially for a period after the second world war, though clearly it cannot be determined whether the presence of residues of this pesticide in the soils adjacent to the current discharge are a carry-over from previous production activities or have arisen from more recent spills or discharges of contaminated wastes. The possibility also exists that the DDT residues detected in this sample have resulted from the use of this pesticide in the region (e.g. for malaria vector control) rather than from production at the adjacent chemical complex. In any case,

DDT, DDD and DDE

The organochlorine insecticide DDT is environmentally persistent, toxic and bioaccumulative. The main ingredient, p,p'-DDT, is broken down in the environment or in the body to p,p'-DDE and smaller quantities of other chemicals. p,p'-DDE is more persistent both in the body and the environment than p,p-DDT (Smith 1991) and responsible for most of the observed toxic effects, unless there has been recent exposure to technical DDT.

DDT is moderately to slightly toxic to animals following ingestion (RSC 1991; Meister 1992; ASTDR 1997). The primary target of DDT is the nervous system and high doses can cause trembling, with convulsions at the highest doses. Chronic exposure effects include damage to the nervous system, liver, kidneys, and immune systems, and may reduce fertility (ASTDR 1997; WHO 1979).

Several of the DDT group are endocrine disruptors, exhibiting different modes of action. Several are weakly oestrogenic. Of these, o,p'-DDT is the most active. p,p'-DDE, the compound likely to be present at highest concentrations in most humans, is an anti-androgen (Longnecker et al. 1997). The IARC classified p,p'-DDT as possibly carcinogenic to humans (group 2B) and the US Department of Health and Human Services regards it as being "reasonably anticipated to be a human carcinogen" (DHHS 1998).

DDT's most severe impacts are on the environment. DDT, or rather, its metabolite, p,p'-DDE, causes the thinning of bird's eggshells through perturbation of calcium metabolism, resulting in eggs breaking prematurely or becoming dehydrated (Haegele & Tucker 1974; Newton 1995; Provini & Galassi 1999).

DDT is controlled under numerous international legal instruments, most notably the recently developed UNEP POPs Convention (Stockholm Convention 2001), which aims for its global elimination. Agricultural use of DDT is almost totally banned, but its use is retained in some countries for public health purposes, primarily malaria vector (mosquito) control.

given the hazards associated with DDT and its products of degradation, the origin of these residues and the extent of contamination demand further investigation.

Traces of 2,4-dichlorophenol were also present in this soil sample. This compound can arise as a by-product of the synthesis of certain chlorinated pesticides, including the herbicide 2,4-D (2,4-dichlorophenoxyacetic acid), although once again it is not possible to determine the origin of the residues in the current sample, nor link its presence with activities on the Dow Sentrachem site.

This soil also showed strong evidence of previous contamination with wastes rich in nickel (Ni 3g/kg in the sample collected), probably related to the visible remnants of a leakage from a break in the effluent channel at this point.

Water and sediment from the Kaalspruit stream

The samples of water collected from the Kaalspruit stream on 23rd July 2002 (MI02026 and MI02028) contained no detectable volatile organic compounds, though residues of all isomers of the pesticide hexachlorocyclohexane (alpha, beta, gamma and delta-HCH) were positively identified in SIM mode. Given that the Kaalspruit stream receives water from the evaporation pond site, downstream from the Dow Sentrachem production facility, the possibility exists that these residues have a common origin to that identified in the effluent discharge itself on 24th July 2002, though again the direct application of technical mixtures of HCH for insect control around the Kaalspruit and associated reed-beds cannot be ruled out. This aspect also demands further investigative work and analyses.

Both alpha- and beta-HCH were also detectable in a sample of brown flocculous sediment collected from the surface of plants and debris from the same location in the Kaalspruit stream on 24th July (MI02034). This sample also contained residues of DDD and DDE, degradation products of DDT, though once again these could arise from the deliberate spraying of DDT formulations in this area rather than from industrial discharge. Elemental analysis confirmed this material to be highly iron rich (22% iron by weight), presumably arising from the discharge of iron rich wastes to the evaporation ponds.

A sample of sediment from the stream bed collected from the same location on the 23rd July was also found to contain DDT, DDD and DDE residues. Among other compounds detectable in this sample were two dichlorobenzenes and residues of the chlorinated organophosphorus pesticide chlorpyrifos ("Dursban"). Again, while links with manufacture or pesticide formulation activities on the Dow Sentrachem site upstream are possible, these cannot be confirmed by the results of the current investigation.

Conclusions: hazards associated with the Dow Sentrachem discharge and contaminants in the downstream environment

It is clear from the analyses presented above that the Dow Sentrachem facility located at Chloorkop is releasing hazardous effluent and acting as a point source of a number of persistent organic and metal contaminants. Given that the effluent channel (uncovered and broken at various points) runs across open land immediately after exiting the plant boundary fence, that the wastewater is then discharged to open evaporation ponds and that residual water from the site of these ponds is thereafter pumped to the Kaalspruit stream, the potential for direct and indirect exposure of humans, wildlife and the wider environment to these chemicals is clear:-

- Effluent discharged on 23rd July 2002 was very strongly alkaline (pH 12-14), presenting a direct and immediate hazard of severe burns to skin or eye damage to anyone coming into contact with the wastewater. The strong “chlorine” smell of the wastewater on both sampling days suggesting high concentrations of hypochlorite or related chemicals in the discharge which could also present significant irritations hazards to the eyes, skin or respiratory system.
- Effluent discharged on both 23rd and 24th July contained the toxic volatile organochlorines chloroform and tetrachloromethane (carbon tetrachloride). Apart from the acute hazards associated with inhaling these chemicals close to the effluent stream (e.g. nausea, dizziness or even more severe nervous system effects), the discharge of these chemicals to the evaporation ponds will inevitably result in substantial losses to the atmosphere, adding to the overall anthropogenic burden of atmospheric VOC pollution. Moreover, any contact with the soil, either in the evaporation ponds themselves or as a result of a spill from the discharge channel, could result in rapid migration to deeper soils and/or contamination of underlying groundwater reserves. Once reaching groundwater, these VOCs can persist for many years, over which the contaminant plume can spread great distances down gradient from the initial point of contamination.
- The range of chlorinated benzenes identified in the wastewater on both days are also persistent and toxic contaminants. While 1,4-dichlorobenzene is a fairly ubiquitous environmental contaminant in urban areas, stemming from its widespread use as a disinfectant and deodoriser in public and household sanitation, the other di-, tri- and tetra-chlorinated benzenes present are more commonly generated as by-products of industrial chemical reactions involving the production of chlorinated organic chemicals. Once again, these could represent a significant and long-term hazard to soil, groundwater and receiving surface waters.
- There is some evidence for the release of the persistent pesticide hexachlorocyclohexane (HCH) from the Dow Sentrachem facility, though whether this reflects a one-off or ongoing process discharge cannot be determined from the current investigation. HCH isomers were found in two of the samples collected from the Kaalspruit stream downstream from the evaporation ponds, though the possibility that these originate from the Dow Sentrachem plant cannot be confirmed.
- Samples of wastewater collected on one of the sampling days (24th July) demonstrate that the plant is, at least periodically, acting as a very substantial point source of the toxic metal nickel to the evaporation ponds and possibly to the wider environment when pond sludges are ultimately disposed of. Nickel is especially soluble and, therefore, mobile at high pHs and can bioaccumulate in some organisms. Toxic effects in humans, most notably allergic reactions, can be far greater in some (pre-sensitised) individuals than in others.
- Whereas high concentrations of iron in the wastewater and in the Kaalspruit are probably of relatively low toxicological significance in themselves, analysis of the iron-rich flocs in the stream indicated their ability to adsorb and concentrate persistent organic compounds from the water.
- A number of the samples collected indicate that the areas immediately surrounding the effluent discharge channel and downstream from the evaporation ponds are contaminated with persistent, toxic and bioaccumulative pesticide residues (including DDT and its

degradation products DDD and DDE, various isomers of HCH and the chlorinated organophosphorus pesticide chlorpyrifos, or "Dursban"). While it is not possible from the results of this investigation to implicate previous or ongoing discharges from the Dow Sentrachem plant as being responsible for some or all of these contaminants, this possibility cannot be ruled out. Moreover, even if the presence of such residues results from deliberate application of these pesticides at some point in the past, significant risks to the environment and the health of local communities could result. This aspect demands further investigation to determine the extent of contamination and the scale of the problem such that necessary clean-up actions can be initiated.

References

- ATSDR (1997) ATSDR's toxicological Profiles on CD-ROM. Agency for Toxic Substances and Disease Registry, US Public Health Service, Publ: Lewis Publishers.
- Chiu, N., Orme-Zavaleta, J., Chiu, A., Chen, C., DeAngelo, A., Brattin, W. & Blancato, J. (1996) Characterization of cancer risk associated with exposure to chloroform. *Environmental Carcinogenesis & Ecotoxicology Reviews. Journal of Environmental Science and Health C14(2)*: 81-104
- Delvin, J.F. & Muller, D. (1999) Field and laboratory studies of carbon tetrachloride transformation in sandy aquifer under sulfate reducing conditions. *Environmental Science and Technology 33(7)*: 1021-1027
- DHHS (1998) 8th Report on Carcinogens. 1998 Summary. Publ: US Department of Health and Human Services, 252pp.
- Dunnick, J.K & Melnik, R.L. (1993) Assessment of the carcinogenic potential of chlorinated water: experimental studies of chlorine, chloramine and trihalomethanes. *Journal of the National Cancer Institute 85(10)*: 818-823
- Giddings, M., Meek, M.E. & Gomes, R. (1994a) Trichlorobenzenes: Evaluation of risks to health from environment exposure in Canada. *Environ. Carcin. Ecotox. Revs. C12(2)*: 517-525
- Giddings, M., Meek, M.E. & Gomes, R. (1994b) Tetrachlorobenzenes: Evaluation of risks to health from environment exposure in Canada. *Environ. Carcin. Ecotox. Revs. C12(2)*: 473-481
- Haegel, M.A. & Tucker, R.K.(1974) Effects of 15 Common Environmental Pollutants on Eggshell Thickness in Mallards and Coturnix. *Bulletin of Environmental Contamination & Toxicology 11(1)*:98-102
- Hashsham, S.A., Scholze, R. & Freedman, D.L (1995) Cobalamin-enhanced anaerobic biotransformation of carbon tetrachloride. *Environmental Science and Technology 29(11)*: 2856-2863
- IARC (1999) Carbon tetrachloride. IARC Monographs Vol.71, p.401
- Longnecker, M.P., Rogan, W.J. & Lucier, G. (1997) The human health effects of DDT (dichlorodiphenyltrichloroethane) and PCBs (polychlorinated biphenyls) and an overview of organochlorines in public health. *Annu. Rev. Public Health 18*: 211-244
- Martijn, A., Bakker, H. & Schreuder, R.H. (1993) Soil persistence of DDT dieldrin, and lindane over long period. *Bull. Environ. Contam. Toxicol. 51*: 178-184
- Meister, R.T. [Ed] (1992). *Farm Chemicals Handbook '92*, Meister Publishing Co., Willoughby, OH.
- Nagata K., Huang C.S., Hamilton B.J., Carter D.B., Narahashi T. (1996). Differential-effects of hexachlorocyclohexane on the gaba receptor subunits expressed in human embryonic kidney-cell line. *Brain Research, Vol.738, No.1*, pp.131-137.
- Newton, I. (1995) The contribution of some recent research on birds to ecological understanding. *Journal of Animal Ecology 64*: 675-696
- Provini, A. & Galassi S. (1999) Polychlorinated Biphenyls and Chlorinated Pesticides in Bird Eggs from Calabria (Southern Italy). *Ecotoxicology and Environmental Safety 43*:91-97
- RSC (1991) *The Agrochemicals Handbook*, 3rd Edition. Publ: Royal Society of Chemistry Information Services, Cambridge, UK.
- Schulz R., Liess M. (1995). Chronic effects of low insecticide concentrations on fresh-water *Caddisfly Larvae*. *Hydrobiologia, Vol.299, No.2*, pp.103-113.
- Sicko-Goad, L. & Andersen, N.A. (1993a) Effect of lipid composition on the toxicity of trichlorobenzene isomers to diatoms. I. Short-term effects of 1,3,5-trichlorobenzene. *Arch. Environ. Contam. Toxicol. 24*: 236-242
- Sicko-Goad, L. & Andersen, N.A. (1993b) Effect of lipid composition on the toxicity of trichlorobenzene isomers to diatoms. II. Long-term effects of 1,2,3-trichlorobenzene. *Arch. Environ. Contam. Toxicol. 24*: 243-248
- Sicko-Goad, L., Evans, M.S., Lazinsky, D., Hall, J. & Simmons, M.S. (1989d) Effect of chlorinated benzenes on diatom fatty acid composition and quantitative morphology. IV. Pentachlorobenzene and comparison with trichlorobenzene isomers. *Arch. Environ. Contam. Toxicol. 18*: 656-668

- Sicko-Goad, L., Hall, J., Lazinsky, D. & Simmons, M.S. (1989b) Effect of chlorinated benzenes on diatom fatty acid composition and quantitative morphology. II. 1,3,5-Trichlorobenzene. *Arch. Environ. Contam. Toxicol.* 18: 638-646
- Sicko-Goad, L., Hall, J., Lazinsky, D. & Simmons, M.S. (1989c) Effect of chlorinated benzenes on diatom fatty acid composition and quantitative morphology. III. 1,2,3-Trichlorobenzene. *Arch. Environ. Contam. Toxicol.* 18: 647-655
- Sicko-Goad, L., Lazinsky, D., Hall, J. & Simmons, M.S. (1989a) Effect of chlorinated benzenes on diatom fatty acid composition and quantitative morphology. I. 1,2,4-Trichlorobenzene. *Arch. Environ. Contam. Toxicol.* 18: 629-637
- Smith, A. G. (1991) Chlorinated hydrocarbon insecticides IN: *Handbook of Pesticide Toxicology, Volume 2, Classes of Pesticides*, Hayes, W.J.Jr. & Laws, E.R.Jr. (Eds.), Publ: Academic Press, Inc, pp731-915
- Snyder, R. & Andrews, L.S. (1996) Toxic effects of solvents and vapours. In: *Casarett and Doull's Toxicology: The Basic Science of Poisons. Fifth Edition*. Klaasen, C.D, Amdur, M.O. & Doull, J. [Ed]. Mc-Graw-Hill, ISBN 0-07-105476-6, pp.737-772
- UNEP (1997) The 1987 Montreal Protocol on Substances that Deplete the Ozone Layer, as adjusted and amended by the second Meeting of the Parties (London, 27-29 June, 1990), and by the fourth Meeting of the parties (Copenhagen, 23-25 November 1992), and further adjusted by the seventh Meeting of the Parties (Vienna, 5-7 December 1995), and further adjusted and amended by the ninth Meeting of the Parties (Montreal, 15-17 September 1997)
- UNEP (United Nations Environment Programme). Final Act of the Conference of Plenipotentiaries on the Stockholm Convention on Persistent Organic Pollutants, UNEP/POPS/CONF/4, 5 June 2001: 44 pp; 2001
- US EPA (1988) Reviews of environmental contamination and toxicology. Vol. 106, Environmental Protection Agency, Office of Drinking Water Health Advisories, Springer-Verlag New York Inc. ISSN 0179-5953: 21-35
- Ware, G.W. (Ed.)(1988) Ortho-, meta- and para- dichlorobenzene. *Rev. Environ. Contam.Toxicol.* 106: 51-56
- Weisel, C.P. & Chen, W.J. (1994) Exposure to chlorination by-products from hot water uses. *Risk Analysis* 14(1): 101-107
- Weisel, C.P. & Jo W-K. (1996) Ingestion, inhalation, and dermal exposures to chloroform and trichloroethene from tap water. *Environmental Health Perspectives* 104(1): 48-51
- WHO (1979) DDT and its derivatives. *Environmental Health Criteria* 9. World Health Organizations, Geneva, 1979, 194pp.