

Report on the analysis of industrial wastewaters from the Frutarom VCM/PVC plant, near Haifa, Israel, and adjacent shoreline sediments for organic contaminants.

David Santillo, Irina Labounskaia, Ruth Stringer and Paul Johnston

Greenpeace Research Laboratories Technical Note 03/97

27th June 1997

Introduction

Between November 1994 and October 1996 a total of 12 samples were collected in order to characterise wastes discharged from the Frutarom complex. The study focused on two principal discharge pipes, one in front of the VCM tanks and a second shorter pipe discharging in front of the main plant. Discharges from this second pipeline had been discontinued by 1996. In 1994 a third discharge, arising beneath a concrete bunker on the shoreline, was also sampled. In each case, effluents were being discharged directly onto the foreshore, above or at the water line.

Samples taken included wastewaters collected directly from the pipelines and from open channels on the shoreline below the plant and sediments from the shoreline adjacent to these discharges. Samples were characterised in terms of the nature of organic contaminants present. What follows is a brief description of the samples collected, the analytical methods employed, the results obtained and their significance in relation to the hazards associated with the contaminants identified.

Materials and Methods

Sample collection

November 1994

Four samples were collected on 20th November 1994;

MI4047 - wastewater from sea-level outfall in front of main plant

MI4048 - wastewater from pipe in front of VCM tanks

MI4049 - wastewater from discharge beneath concrete bunker adjacent to reservoir

MI4050 - sediment from foreshore adjacent to discharge MI4049

August 1996

Six samples were collected on 21st August 1996. The longer of the two pipes, running from a position in front of the VCM storage tanks, was in use at the time of sampling. There was no discharge from the second, shorter pipeline at this time.

Two samples were taken of waste water discharging from the pipe in front of the VCM tanks; MI6107 from immediately below the pipe and; MI6111 from the same channel but further down shore from the point of discharge.

Four sediment samples were taken from the shoreline directly in front of the plant; MI6110 and 6112 from the side of the channel receiving wastewater from the operational discharge pipe and; MI6108-6109 from two points along the dry channel in front of the inoperative discharge pipe.

October 1996

On 21st October 1996, two (duplicate) samples (MI6170-6171) were collected of effluent discharging from the pipe in front of the VCM tanks.

In each case, 1 litre of liquid effluents and 100g of sediments were collected for analysis. All samples were cooled immediately after collection and transported to the UK for analysis at the Greenpeace Research Laboratories, University of Exeter, UK.

Sample preparation

Samples were prepared for analysis using extraction methods based on those described in Swindlehurst *et al.* (1995). Organic contaminants were extracted using standard liquid:liquid or liquid: solid solvent extraction techniques and analysed using gas chromatography/mass spectrometry (GC/MS). In addition, in 1994 only, analysis of volatile organic compounds was conducted for all liquid samples using a purge and trap system linked to a GC/MS. Samples for heavy metal analysis were prepared using microwave digestion techniques and analysed using Inductively Coupled Plasma Atomic Emission Spectrophotometry (ICP-AES). A range of heavy metals were quantified, including mercury, cadmium and lead, using certified reference materials as part of a QC procedure. Full details of analytical techniques employed are included in Appendix 1.

Results and Discussion

Organic results are included in Appendix 2 and discussed in turn below.

Organic analytical results

November 1994

A total of 64 compounds were isolated from the wastewater discharging at sea-level (MI4047). Of these, 11 were reliably identified, all of which were organohalogens. In addition, of 18 compounds more tentatively identified, 15 were also organohalogens. Many of the compounds

identified were volatile (including the chlorinated methanes and ethanes); the wastewater discharge would therefore result in localised inputs of halogenated organic compounds to the atmosphere in addition to inputs to receiving waters. Of the compounds identified, only one (1,2-dichloroethane or ethylene dichloride) is required to be monitored under Environment Ministry legislation in Israel.

Many, if not all, of the compounds reliably identified in this sample are acutely toxic to animals in high doses. For example 1,2-dichloroethene, 1,1,2-trichloroethane and tetrachloroethene (perchloroethylene or PERC) are all strong skin, eye or respiratory irritants, while trichloroethene and tribromomethane act directly on the nervous system. In addition, many also exhibit chronic toxic effects in animals over longer exposure periods; for example, 1,1,2,2-tetrachloroethane is a potent liver poison (Merck 1989). Moreover, 1,2-dichloroethane and trichloroethene are confirmed animal carcinogens, while trichloromethane (chloroform), 1,1,2-trichloroethane and PERC are suspected carcinogens. 1,4-Dichloro-2-butene, identified more tentatively in this wastewater sample, is also listed as a confirmed carcinogen in animal tissues (Sittig 1994).

In recognition of the hazardous nature of volatile organohalogenes, many of the compounds identified in this sample have been prioritised for input reductions under Annex 1A of the 3rd North Sea Ministerial Declaration, including trichloromethane, 1,2-dichloroethane, trichloroethene and PERC (MINDEC 1990). 1,1,2-Trichloroethane and 1,1,2,2-tetrachloroethane are also being considered for prioritisation.

Fewer compounds were isolated or identified in the two other wastewater samples analysed (MI4048 and 4049). Nevertheless, the carcinogen 1,2-dichloroethane was reliably identified in both cases.

August 1996

No organohalogen compounds were identified in either of the two wastewater samples taken from the foreshore in front of the VCM tanks in 1996 (MI6107 and 6111). It is possible that the discharge arises from petrochemical processes or solvent use on site other than those involved in the manufacture of EDC, VCM or PVC. Note, however, that analysis of the volatile organic contaminants was unfortunately not possible in 1996 (as equipment was out of commission at that time). Any volatile organochlorines which may have been present in the samples, such as 1,2-dichloroethane, would not, therefore, have been detected using the analytical techniques employed with these samples.

Of an estimated 97 analytes isolated in total from MI6107, only 5 could be identified reliably. As many as 70 of the compounds isolated could not be identified. However, of those which were identified, the majority were simply long-chain aliphatic hydrocarbons. Fewer compounds (although, as expected, of a similar nature) were isolated from the second effluent sample, MI6111, possibly as a result of dispersion through the sediments and evaporation of the more volatile components. A similar range of compounds were isolated and identified in the two sediment samples from the same channel (MI6110 and 6112). There is little information available relating specifically to the chronic toxicity of these compounds to humans and marine

organisms. The discharge to the environment of such complex mixtures of compounds is, nevertheless, of concern.

Results for the two sediment samples from the dry channel are of greater concern. The first of these, MI6108, contained a greater range of organic contaminants, including hydrocarbons, alcohols and organic acids. Of particular significance are 2,6-bis(1,1-dimethylethyl)-4-methylphenol (butylated hydroxytoluene or BHT) and the organobromine compound 1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane.

BHT is used as an antioxidant in a wide variety of products, including food, fuels, paints, plastics and a wide variety of other petroleum-derived products (Merck 1989). It appears to have a relatively low acute toxicity to laboratory animals (hence its use in foods), but is known to engage in complex interactions with other chemicals in the body through its stimulation of liver enzyme activity (Pitot and Dragan 1996). Its presence in the sediments of the dry channel could be indicative of its historic or periodic discharge resulting from use in plastics formulation.

No toxicological information exists in the open literature for the complex organobromine identified. It is likely, however, that this compound would be toxic to marine and other organisms and may tend to accumulate in body tissues and bioaccumulate through the food chain. The likely source of this compound is unclear.

The second sample from this same channel (MI6109), described as pink sand, contained significant concentrations of organochlorines, most importantly hexachlorobenzene (HCB). This compound is generated as a by-product in a number of industrial processes, particularly the initial oxychlorination of petroleum fractions in order to generate organochlorine chemicals. It is widely dispersed throughout the environment as a result of global transport, primarily via the atmosphere. The levels in the current sample do, however, indicate a very significant point source of HCB at the Frutarom plant.

HCB is highly toxic, persistent and bioaccumulative. Howard *et al.* (1991) estimates half lives for HCB in soils and aerobic aquatic systems of between 2.7 and 5.7 years; in anaerobic sediments this could be as long as 10-23 years. HCB is acutely toxic in high doses (Merck 1989, USPHS 1990), but also exerts a wide range of toxic effects in a range of organisms exposed chronically to lower doses. It can be lethal to humans exposed to high doses, particularly in the womb, but may also lead to wide-ranging sub-lethal effects following lower exposures, including toxicity to the liver, kidneys, skin and thyroid, interference with bone development, complex changes to blood biochemistry, and damage to the immune and nervous systems (Thomas 1990, USPHS 1990).

HCB is a known initiator and promoter of cancer in a number of laboratory organisms, targeting the liver and thyroid in particular (Newhook and Meek 1994). Direct effects on the reproductive system in mammals have also been described, particularly in female monkeys, where low chronic doses of HCB have led to degeneration of ovarian epithelial and germ cells (Jarrell *et al.* 1993) and alteration of levels of steroid sex hormones circulating in the blood. These effects may occur at levels of exposure which do not cause any other visible

symptoms of toxicity. On the basis of such observed effects on hormone levels, Colborn *et al.* (1993) list HCB as a hormone disrupting chemical.

Although many studies report levels of HCB in marine organisms, relatively few address the potential or actual toxicity of this compound in marine systems. Part of the problem relates to the fact that HCB is generally one of many organochlorine and other chemical contaminants isolated from the tissues of marine organisms, whose concentrations may co-vary (ie. follow similar patterns of contamination levels). Identifying one agent as a causal factor for an observed effect is, therefore, largely impossible (Myers *et al* 1994). Nevertheless, direct toxicity of HCB to marine organisms has been demonstrated. For example, Anderson *et al.* (1981), in a study of bacterial infection in the clam *Mercenaria mercenaria*, reported complete suppression of antibacterial activity in the haemolymph resulting from exposure to relatively low doses of HCB. This has obvious implications for disease resistance in marine organisms and suggests that HCB may act on the immune systems of a very wide range of organisms.

On the basis of its toxicity, persistence in the environment and tendency to bioaccumulate in tissues, HCB is included on the UK "Red List" of priority substances for control (Agg and Zabel 1990), and is listed as a moderate to high priority for reduction under the Canadian Environmental Protection Act (Newhook and Meek 1994). It also appears on the priority list of the 3rd North Sea Ministerial Declaration (MINDEC 1990).

Two other compounds identified more tentatively in this sample, 1,3-dichloro-1-propene and 1,4-dichloro-2-butene, are listed as confirmed animal carcinogens (Sittig 1994). Both may be present as a result of their use as solvents or of their formation as waste by-products of chlorination reactions.

Note that in both sediment samples from the dry channel (MI6108 and 6109), derivatives of 1,2-benzenedicarboxylic acid, or phthalic acid, were identified. Esters and other derivatives of phthalic acids are used as plasticisers in the formulation of flexible PVC. Phthalates are among the most widespread and abundant global contaminants resulting from human activity. Nevertheless, the identification of similar compounds in the wastewater discharge to this channel in October 1996 (see below) suggests that their presence in these sediments may well relate to their manufacture or use on site.

October 1996

Both samples were found to be contaminated with a range of organic compounds, many of them organohalogens (both chlorinated and brominated), some of which were present at what appeared to be substantial concentrations. The analytical technique employed is essentially qualitative and so it is not possible even to approximate the levels present; such determinations should form part of a more detailed quantitative investigation to be carried out by the relevant authorities.

Of 26 compounds isolated as discrete peaks from sample MI6170, only one could be identified with high reliability, the bis(2-methoxyethyl) ester of 1,2-benzenedicarboxylic acid (phthalic acid). Given the nature of the operations at the Frutarom plant, it seems likely that the presence of this and related compounds in the wastewater discharge reflects usage of phthalates on site in the compounding of PVC resin for soft applications.

This is also the case for one of the compounds more tentatively identified, bis(2-ethylhexyl) ester of 1,2-benzenedicarboxylic acid, the phthalate DEHP (identification match quality 87%). Despite its toxicity, this is still widely used as a softener in a wide range of PVC applications. It is known to bioaccumulate in a range of aquatic organisms, particularly crustaceans and other invertebrates and, although its acute toxicity appears to be relatively low, it is known to exert a variety of chronic effects, including effects on the reproductive system (Lundberg 1994).

The primary target organ for DEHP toxicity in laboratory animals is the liver, where it may stimulate rapid cell division and enhanced enzyme activity. High doses over longer periods can be lethal. At lower doses, chronic exposure in rats can lead to testicular atrophy and effects on the kidney; in the case of testicular effects, juvenile rats are generally more sensitive. Several studies have suggested that DEHP is a selective carcinogen (particularly liver cancer), a mutagen in mammalian cell lines and a possible teratogen (causing birth defects) in mice. In mice exposed to DEHP during mating, decreased incidences of pregnancy have been reported (Nilsson 1994). In addition, more recent research has suggested that DEHP, along with other phthalates, may be capable of binding to the oestrogen receptor in a range of organisms (Jobling *et al.* 1995). This aspect of its activity, and the activity of other phthalates, is currently the focus of intensive scientific research.

Of the 8 compounds tentatively identified in this sample, 5 were organohalogens, including 1,4- and 2,4-dibromopentane and, again, 1,4-dichloro-2-butene. It is likely that such compounds may be used on site as solvents, or generated as intermediates and by-products from other reactions. Note that organobromines may be formed through substitution reactions involving organochlorines and bromides, particularly if seawater is used at any stage in the process (perhaps as cooling water which is subsequently mixed with effluents for dilution prior to discharge).

Very little toxicological information is available for any of these compounds, although 1,4-dichloro-2-butene, as mentioned above, is a confirmed animal carcinogen (Sittig 1994). Its identification in effluents from the plant in both 1994 and 1996 further supports the tentative identification of this compound in associated sediments (MI6109). It is likely that the other compounds would be toxic in high doses and may have significant chronic toxic effects under conditions of long-term exposure to lower concentrations. As with other organohalogens, the liver and kidney are likely target organs for toxic effects. Predicting the toxicity related to such complex mixtures of contaminants is, as always, extremely difficult, particularly as, of the 26 compounds isolated, only 9 could be identified with any degree of reliability.

The second sample (MI6171) contained compounds of a similar nature (including pentachloropropane and 1,4-dichloro-2-butene), although a range of long-chain hydrocarbons were also identified in this case.

Again, as a result of the solvent extraction technique employed, volatile organic compounds (such as those identified in 1994) would have been lost during sample preparation. The range of more volatile organohalogen described in this sample may, therefore, be a considerable underestimate of the range existing in the effluent at the time of sampling.

Conclusions

On the basis of the analytical data presented in this study, it appears that the synthesis of organochlorine chemicals at the Frutarom plant has resulted in significant contamination of the adjacent shoreline sediments with organochlorine compounds. This is indicative of long-term discharge of organohalogen, along with a range of other organic compounds, to the marine environment from the plant. Some of these chemicals are highly persistent, exert a wide range of toxic effects both in and via the marine environment, and have the ability to bioaccumulate in animal tissues. Organohalogen are listed in Annex I of the Barcelona Convention Protocol for the Protection of the Mediterranean Sea Against Pollution from Land-Based Sources (UNEP 1992) and, as such, should be targeted for elimination from discharges to the aquatic environment from land-based sources.

Under Israeli Environment legislation, vinyl chloride monomer (VCM) and ethylene dichloride (EDC) are the only two organochlorine compounds which must be included in analysis of effluents from the Frutarom plant. The results of this study clearly demonstrate that such a monitoring strategy overlooks a wide range of organochlorine and other organic compounds which are discharged to the marine environment from the plant, many of which are also of toxicological significance. This is a common shortfall of regulatory regimes and leads to potentially severe underestimation of the toxicity of complex effluent discharges (Johnston *et al.* 1996).

Although the qualitative analyses described above provide firm evidence for the presence of organohalogen and their release to the open environment, it is essential that further investigations are carried out by the relevant regulatory authorities to determine the range and concentrations of organohalogen and other organic compounds which are being discharged to the Mediterranean by the Frutarom plant. The sources of organohalogen to the shoreline sediments, particularly HCB, must be identified. Since the contaminated sediments were sampled from a channel which was dry at the time of sampling, it should be established whether such contamination relates to historical release or to continued periodic release from the adjacent pipeline. In any event, measures must be taken to determine the extent of contamination and options explored for remediative clean-up of the site to prevent wider contamination resulting from dispersal of sediments and/or incorporation into the food chain.

It is also important to bear in mind that this study has focused only on the discharges of contaminants to the marine environment as part of the waste effluents. Such a study takes no account of the nature of solid, semi-solid, non-aqueous liquid, and gaseous wastes which may also be generated as by-products of manufacturing processes at the Frutarom plant. Comparison with other integrated PVC plants suggests that such waste streams will be substantial at

Frutarom. Little information is available on the precise nature of the wastes generated within the Frutarom complex and on the waste management strategies employed. Nevertheless, it is widely recognised, even within industry, that it is not possible to manufacture VCM and PVC without generating extremely hazardous organohalogenes, including dioxins, as unwanted by-products (ICI 1994). A survey of PVC production wastes carried out in the US confirmed that many processes, particularly the use of EDC tar residues for the synthesis of organic solvents, do indeed generate substantial concentrations of dioxins (Stringer *et al.* 1995). Onward handling of such wastes, including incineration, may result in the release of dioxins and other harmful organic compounds to the atmosphere or other environmental compartments and may, therefore, ultimately contribute further to land-based sources of organochlorines to the marine environment.

Although such analyses did not form part of the current investigation, there is clearly an urgent need to evaluate and address all of the waste streams generated at the Frutarom plant. It is only through such studies that the full extent of the impact of the plant on the environment can be assessed.

References.

Agg, A.R., and T.F. Zabel (1990). Red-list substances: selection and monitoring. *J. IWEM* 4: 44-50.

Anderson, R.S., C.S. Giam, L. Ray and M.R. Tripp (1981). Effects of environmental pollutants on immunological competency of the clam *Mercenaria mercenaria*: Impaired bacterial clearance. *Aquatic Toxicology* 1: 187-195.

Colborn, T., F.S. vom Saal and A.M. Soto (1993). Developmental effects of endocrine-disrupting chemicals in wildlife and humans. *Environmental Health Perspectives* 101(5): 378-384.

Fernandez, P., M. Grifoll, A.M. Solanas, J.M. Bayona and J. Albaiges (1992). Bioassay-directed chemical analysis of genotoxic components in coastal sediments. *Environmental Science and Technology* 26(4): 817-829.

Howard, P.H., R.S. Boethling, W.F. Jarvis, W.M. Meylan and E.M. Michalenko (1991). *Handbook of Environmental Degradation Rates*. Lewis Publishers, Inc., Michigan, USA:

ICI (1994). Report to the Chief Inspector HMIP, Authorisation AK6039, Improvement Condition part 8, Table 8.1, Item 2: Formation of dioxins in oxychlorination, significance for human health and monitoring proposals. ICI Chemicals and Polymers Ltd. Report NWJP/BMTD, 27th April 1994: 16 pp.

Jarrell, J.F., A. McMahon, D. Villeneuve, C. Franklin, A. Singh, V.E. Valli and S. Bartlett (1993). Hexachlorobenzene toxicity in the monkey primordial germ cell without induced porphyria. *Reproductive Toxicology* 7: 41-47.

- Jobling, S., T. Reynolds, R. White, Malcolm Parker and J.P. Sumpter (1995). A variety of environmentally persistent chemicals, including some phthalate plasticisers, are weakly estrogenic. *Environmental Health Perspectives* 103(6): 582-587.
- Johnston, P.A., R.L. Stringer and D. Santillo (1996). Effluent complexity and ecotoxicology: regulating the variable within varied systems. *Toxicology and Ecotoxicology News* 3(4): 115-120.
- Lundberg, G., (1994). Ecotoxicological Risk Assessment. In *Phthalic Acid Esters Used as Plastic Additives, Volume 1*. The Swedish National Chemicals Inspectorate (KEMI), Report No. 12/94: 13-210
- MINDEC (1990). Final Declaration of the Third International Conference on the Protection of the North Sea. Ministry of Transport and Public Works, The Hague: 36pp.
- Myers, M.S., C.M. Stehr, O.P. Olsen, L.L. Johnson, B.B. McCain, S.-L. Chan and U. Varanasi (1994). Relationships between toxicopathic hepatic lesions and exposure to chemical contaminants in English Sole (*Pleuronectes vetulus*), starry flounder (*Platichthys stellatus*) and white croaker (*Genyonemus lineatus*) from selected marine sites on the Pacific Coast, USA. *Environmental Health Perspectives* 102(2): 201-215.
- Newhook, R., and M.E. Meek (1994). Hexachlorobenzene: evaluation of risks to health from environmental exposure in Canada. *Environ. Carcino. & Ecotox. Revs.*, C12(2): 345-360.
- Nilsson, C., (1994). Comparison of Toxicological Effects. In *Phthalic Acid Esters Used as Plastic Additives, Volume 2*. The Swedish National Chemicals Inspectorate (KEMI), Report No. 12/94: 211-285
- Merck (1989). *The Merck Index: An Encyclopaedia of Chemicals, Drugs and Biochemicals*. S. Budavari, M.J. O'Neil, A. Smith and P.E. Heckelman [Eds], 11th Edn. Merck and Co., Inc., Rahway, N.J., USA.
- Pitot, H.C., and Y.P. Dragan (1996). Chemical Carcinogenesis. In *Casarett and Doull's Toxicology: The Basic Science of Poisons*. C.D. Klaasen, M.O. Amdur and J. Doull [Eds], 5th Edn: 201-267.
- Sittig, M., (1994). *World-Wide Limits for Toxic and Hazardous Chemicals in Air, Water and Soil*. Noyes Publications, New Jersey, USA.
- Stringer, R.L., P.A. Johnston, R. Clayton and R.J. Swindlehurst (1994). Back to basics: the case for intensification in the monitoring of point source discharges. Submitted by Greenpeace International to the 19th Meeting of the Joint Monitoring Group of the Oslo and Paris Commissions, Dublin, 24-28th January 1994.
- Stringer, R.L., P. Costner and P.A. Johnston (1995). PVC manufacture as a source of PCDD/Fs. *Organohalogen Compounds* 24: 119-123

Swindlehurst, R.J., P.A. Johnston, S. Troendle, R.L. Stringer, A.D. Stephenson and I.M. Stone (1995). Regulation of toxic chemicals in the Mediterranean: the need for an adequate strategy. *The Science of the Total Environment* 171: 243-264.

Thomas, P.T., (1990). Approaches used to assess chemically induced impairment of host resistance and immune function. *Toxic Substances Journal* 10: 241-278.

UNEP (1992). *Mediterranean Action Plan and Convention for the Protection of the Mediterranean Sea Against Pollution and its Related Protocols*. United Nations Environment Programme, Athens.

USPHS (1994). *Toxicological Profile for Hexachlorobenzene, Draft Update for Public Consultation*. U.S. Public Health Service, Agency for Toxic Substances and Disease Registry. August 1994.

Appendix 1: Details of analytical techniques.

Organic compounds

Liquid samples

Following removal of a sub-sample of 100ml for analysis of heavy metals (see below) the remaining 900ml of sample was spiked with a small volume of a standard solution of deuterated-naphthalene (to a final concentration of 100 ppm) to act as an internal standard. 25ml of analytical grade pentane were added to the spiked sample and the bottle rolled for 2 hours in order to improve contact between solvent and sample matrix. The solvent fraction was removed using a separating funnel, the remaining sample acidified (to enable extraction of organic acids), 25 ml of fresh solvent added and the sample rolled for a further two hours before separation.

For each sample the two solvent fractions (before and after acidification) were combined and the whole volume cleared of very high molecular weight compounds by one or more passages through an activated Florasil column. Following clean-up, the extract was evaporated down to approximately 2 ml under a stream of analytical grade nitrogen. A small volume of a standard solution of brominated naphthalene was added to allow accurate determination of the final volume of extract.

Solid samples

A sub-sample of approximately 30g was taken for analysis from each sediment sample. This was spiked with deuterated naphthalene as for the liquid samples, and 20 ml of a 3:1 (by volume) mixture of analytical grade pentane:acetone added. Subsamples were sonicated for two hours to improve efficiency of extraction. This first extract was decanted off, the sediment acidified, and the extraction process repeated.

Following the two extraction phases, the two extracts were again combined and prepared for analysis as described for the liquid:liquid extracts above.

Sample analysis

Extracts were analysed using a Hewlett Packard GC/MS system, injecting 1 μ l on to a 25m BPX-5 fused silica capillary column held in an HP 5890 GC connected in line to an HP 5972 Mass Selective Detector (MSD). Analytes were identified through a combination of computer matching of mass spectra, against a library of 136 000 compounds, and expert interpretation.

Note that in 1994, liquid effluent samples were also analysed for volatile organic compounds using a Tekmar purge and trap system. 5 ml of sample, stored in a sealed vial from the time of sampling, was introduced into a clean glass vessel and sparged for several minutes with analytical grade helium. VOCs were carried on the helium stream and concentrated on a Tenex

trap, before being desorbed and injected directly on column to a HP GC/MS system as described above. Further details can be made available on request. Data collection and interpretation protocols were identical to those used for the non-volatile compounds in the solvent extracts.

Data are reported for each sample as the number of individual compounds isolated as discrete peaks and a list of those identified. Compounds identified to a match quality of 90% or greater are assumed to be reliable identifications. Those with match qualities between 50 and 89% are assumed to be tentatively identified only. All compounds yielding lower match qualities than 50% are assumed to be unidentified.

Appendix 2: Analytical results

Organic Analytical Results

Frutarom PVC plant, Israel, 1996

Sample type: Wastewater

Sampling date: 20/11/94

Lab. code: MI4047

Other information: Colourless wastewater from sea-level outfall, Frutarom PVC plant, Israel.

Analysis method: GC/MS screen

Number of compounds isolated: 64

Compounds identified to better than 90%:

(Z)-1,2-dichloroethene

Trichloromethane

1,2-dichloroethane

Trichloroethene

1-bromo-2-chloroethane

1,1,2-trichloroethane

Tetrachloroethene

3,4-dichlorocyclobutene

Tribromomethane

1,1,2,2-tetrachloroethane

1,1,3,4-tetrachloro-1,3-butadiene

Compounds tentatively identified:

1,1-dichloroethane

(e)-1,4-dichloro-2-butene

1,2-dichlorobutane

1,4-dichloro-2-butyne

2-chloro-1,3-butadiene

1,3-dichlorobutane

Chlorobenzene

1,3-dichlorocyclobutane

2,2-dichloropropanoyl chloride

Trichlorobutane

1,1,3-trichloro-2-methyl-1-propene

N,n-dimethylmethanethioamide

1,1,1,3-tetrachloropropane

1,1,2-trichloro-1-propene

1,2,3,4-tetrachlorobutane

(e)-1,4-dichloro-2-butene

Dodecane

3,3'-oxybis[2-chloro]-1-propene

Organic Analytical Results

Frutarom PVC plant, Israel, 1996

Sample type: Wastewater

Sampling date: 20/11/94

Lab. code: MI4048

Other information: Foamy turbid wastewater from small pipe in front of VCM tanks, Frutarom PVC plant, Israel.

Analysis method: GC/MS screen

Number of compounds isolated: 10

Compounds identified to better than 90%:

1,2-dichloroethane

Compounds tentatively identified

Pentane

4,4-dimethyl-2-oxetanone

Octanal

Tetrachlorocyclopentene

Organic Analytical Results

Frutarom PVC plant, Israel, 1996

Sample type: Wastewater

Sampling date: 20/11/94

Lab. code: MI4049

Other information: Turbid wastewater from discharge under concrete bunker adjacent to reservoir, Frutarom PVC plant, Israel.

Analysis method: GC/MS screen

Number of compounds isolated: 14

Compounds identified to better than 90%:

2-methyl-1-pentene

1,2-dichloroethane

Dodecanoic acid

Compounds tentatively identified:

2,3-dichloro-1-propanol

2-methylpentane

Hexane

Cyclohexane

Bromodichloromethane

(2-tetradecyloxy)-ethanol

Organic Analytical Results

Frutarom PVC plant, Israel, 1996

Sample type: Sand

Sampling date: 20/11/94

Lab. code: MI4050

Other information: Sand near discharge under concrete bunker adjacent to reservoir, Frutarom PVC plant, Israel.

Analysis method: GC/MS screen

Number of compounds isolated:

Compounds identified to better than 90%:

Decanoic acid

Decanoic acid, trimethylsilyl ester

Dodecanoic acid

Dodecanoic acid, trimethylsilyl ester

5-bromo-4,6-dichloro-2-pyridinamine

Tetradecanoic acid

Tetradecanoic acid, trimethylsilyl ester

1-pentadecanol

Hexadecanoic acid, trimethylsilyl ester

Trans-9-octadecenoic acid (1tms)

Pentacosane

Heptacosane

Compounds tentatively identified:

Tetradecane

1-octanol

2,4,6-trimethyloctane

Octanoic acid

Octanoic acid, trimethylsilyl ester

Cyclooctane

Docosane

Hexadecane

(2-tetradecyloxy)-ethanol

2,6,10,15-tetramethylhexadecane

11-decyldocosane

1,4-bis(trichloromethyl)benzene

(z)-octadecanoic acid

(hexadecyloxy)dimethyl-2-propenyl silane

Palmitolaidic acid (1tms)

3,6,9,12,15-pentaoxanonadecan-1-ol

Octacosane

11-decyldocosane

Organic Analytical Results

Frutarom PVC plant, Israel, 1996

Sample type: Industrial wastewater

Sampling date: 21.08.96

Lab code: MI6107

Other information: Wastewater in open channel immediately below operational discharge pipe, in front of VCM tanks.

Analytical method: GC/MS screen

Number of compounds isolated: 97

Compounds identified to better than 90%:

Eicosane

Octadecane

Docosane

Hexadecane

Nonadecane

Compounds tentatively identified:

1-Nonadecene

Tricosane

Cyclopentasiloxane, decamethyl-

Hexatriacontane

Hexatriacontane

Tetradecane

Heptacosane

Nonacosane

Tetratriacontane

(+)-(S)-5-Ethyl-octane-4-one

1,2-Benzenedicarboxylic acid, dicyclohexyl ester

Decane, 2,3,5,8-tetramethyl-

Heptadecane, 2,6,10,15-tetramethyl-

Hexacosane

Triacontane

1-Dodecene

Hexadecane, 2,6,10,14-tetramethyl-

Decane

Hahnfett

Pentacosane

Tetradecane, 2-methyl-

1,1-dimethyl-2-propylcyclohexane

Organic Analytical Results

Frutarom PVC plant, Israel, 1996

Sample type: Sediment

Sampling date: 21.08.96

Lab code: MI6108

Other information: Sediment from dry channel on foreshore in front of plant, SE from operational discharge pipe

Analytical method: GC/MS screen

Number of compounds isolated: 82

Compounds identified to better than 90%:

1-Octadecene

Docosane

Hexacosane

Eicosane

Phenol, 2,6-bis(1,1-dimethylethyl)-4-methyl-

Cyclododecane

Cyclohexane, 1,2-dibromo-4-(1,2-dibromoethyl)-

Cyclotetradecane

Compounds tentatively identified:

Hexadecane

Nonacosane

Decane, 2-methyl-

Tetratriacontane

Octacosane

1,2-Benzenedicarboxylic acid, 3-nitro-

1-Hexadecene

Dodecane

Tricosane

1-Dodecene

Octadecane

1-Tetradecanol

Tetradecane

Boninic Acid

Pyridine, 3,4-dimethyl

Cyclopentane, 1-methylene-3-(1-methylethylidene)-

Naphthalene, 1,2,3,4-tetrahydro-2-phenyl-

Nonahexacontanoic acid

.Beta.-d3-1-phenylethanol-1

Nonadecane

Tridecanol

Organic Analytical Results

Frutarom PVC plant, Israel, 1996

Sample type: Sediment

Sampling date: 21.08.96

Lab code: MI6109

Other information: Pink sand from dry channel on foreshore in front of plant, SE from operational discharge pipe

Analytical method: GC/MS screen

Number of compounds isolated: 78

Compounds identified to better than 90%:

Benzene, hexachloro-
Octadecane
Tricosane
Pentacosane
5-Undecene
Cyclododecane
Eicosane
Nonacosane
Tetracosane
1-Tetradecene
Heneicosane
Heptacosane
1-Eicosane
Nonadecane
Tetradecane
1-Tridecene
Hexadecane
Cyclotetracosane
1-Tetradecanol
5-Octadecene, (E)-
Triacontane
Undecane

Compounds tentatively identified:

1-Hexadecene
1-Propene, 1,3-dichloro-, (E)-
Tridecane
3-Dodecene, (Z)-
Pyridinium, 1-hexadecyl-, chloride, monohydrate
1-Butene, 1,4-dichloro-
Acetic acid, [(2-methylpropyl)thio]-
Nonadecane, 9-methyl-
2-Propenamide, 2-methyl-N-phenyl-
1,2-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester
Dodecane
Decane, 1-chloro-
Butachlor

2-Butene, 1,4-dichloro-
Phenol, 2,6-bis(1,1-dimethylethyl)-4-methyl-
Phosphonic acid, dioctadecyl ester

Organic Analytical Results

Frutarom PVC plant, Israel, 1996

Sample type: Sediment

Sampling date: 21.08.96

Lab code: MI6110

Other information: Sediment from kink in channel receiving discharge from pipe in front of VCM tanks.

Analytical method: GC/MS screen

Number of compounds isolated: 28

Compounds identified to better than 90%:

1-Octadecene

Cyclododecane

Octadecane

Docosane

Hexadecane

Eicosane

1-Tetradecene

Compounds tentatively identified:

Cyclopentasiloxane, decamethyl-

Tetracosane, 2,6,10,15,19,23-hexamethyl-

Tetratriacontane

Pentacosane

Tetradecane

Nonadecane

Dodecane, 2,7,10-trimethyl-

1-Hexadecanol, 3,7,11,15-tetramethyl-

Organic Analytical Results

Frutarom PVC plant, Israel, 1996

Sample type: Industrial wastewater

Sampling date: 21.08.96

Lab code: MI6111

Other information: Wastewater from mid channel, below operational discharge pipe in front of VCM tanks.

Analytical method: GC/MS screen

Number of compounds isolated: 28

Compounds identified to better than 90%:

1-Octadecene

Compounds tentatively identified:

Docosane

1-Dodecene

Tetradecane

Hexadecane, 2,6,10,14-tetramethyl-

Cyclohexane, 1,2,4-trimethyl-

Organic Analytical Results

Frutarom PVC plant, Israel, 1996

Sample type: Sediment

Sampling date: 21.08.96

Lab code: MI6112

Other information: Sediment from side of channel receiving wastewater from discharge in front of VCM tanks.

Analytical method: GC/MS screen

Number of compounds isolated: 23

Compounds identified to better than 90%:

1-Dodecene
Octadecane
Nonadecane
Eicosane
Heneicosane
Docosane

Compounds tentatively identified:

Cyclododecane
Undecane
Undecane, 3,9-dimethyl
3-Eicosane, (E)-
1-Tetradecanol
Docosane
Hentriacontane
1-Octadecene

Organic Analytical Results

Frutarom PVC plant, Israel, 1996

Sample type: Industrial waste water

Sample name: Frutarom, IS01

Sampling date: 21.10.1996

Lab. code: MI6170

Other information: Waste effluent from pipeline discharging in front of VCM tanks.

Analysis method: GC/MS screen

Number of compounds isolated: 26

Compounds identified to better than 90%:

1,2-Benzenedicarboxylic acid, bis(2-methoxyethyl) ester

Compounds tentatively identified:

1,2-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester

Acetamide, N-(3-methylphenyl)-

Pentane, 2,4-dibromo-

2-Butene, 1,4-dichloro-

1,1,2,4-Tetrachlorobut-1-ene

Pentane, 1,4-dibromo-

1,1,3,3,3-Pentachloropropane

Benzoic acid, 3-methyl-

Organic Analytical Results

Frutarom PVC plant, Israel, 1996

Sample type: Industrial waste water

Sample name: Frutarom, IS02

Sampling date: 21.10.1996

Lab. code: MI6171

Other information: Waste effluent from pipeline discharging in front of VCM tanks.

Analysis method: GC/MS screen

Number of compounds isolated: 17

Compounds identified to better than 90%:

Octadecane

Heneicosane

Hexadecane

Tetradecane

Hexadecane, 2-methyl-

Tridecane

Nonadecane

Heptacosane

Compounds tentatively identified:

Docosane

Triacotane

1,1,3,3,3-Pentachloropropane

2-Butene, 1,4-dichloro-

Dodecane

Butane, 1,2,3,4-tetrachloro-

Heptane, 2,6-dimethyl-