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IDENTIFICATION OF NON-BIODEGRADABLE ORGANIC POLLUTANTS IN RIVERWATER

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Over 100 non-biodegradable organic compounds, accumulated on a carbon filter of a Rhine waterworks, were isolated and identified by means of combined gas chromatography — mass spectrometry. The identified pollutants belong to five different classes: aliphatic as well as aromatic chlorinated hydrocarbons, nitro aromatic compounds, aromatic ethers, tert-butyl substituted phenols and phthalic acid esters. The potential toxicological hazard of the non-biodegradable organic compounds is briefly discussed.

The Rhine is an international river and, hence, an internationally polluted river. All countries lying along i.e. Switzerland, Germany, France and the Netherlands, use the Rhine as a canal for waste water. Every day about 10.000 t of organic pollutants are discharged into the Rhine and its tribunales (1). About 75% of this load is destroyed by the biological process of self-purification. The capacity of self-purification of the Rhine is reflected by a value of 10—20 t of organic compounds per day and kilometer of river (2). The non-biodegradable organic compounds, however, adversely affect the quality of water for human consumption (3, 4) because they are a toxicological hazard. Furthermore, they produce secondary effects by influencing the ecology of the river.

We report here the isolation and identification of non-biodegradable organic pollutants from Rhine river water.

EXPERIMENTAL

Non-biodegradable or scarcely degradable organic compounds accumulate on the charcoal filters of waterworks, which have been used for more than six months.

An air dried charcoal filter sample of 22 kg from a waterworks at the end of the German part of the Rhine, was extracted in a Soxhlet appara-

tus with benzene, followed by acetone and methanol. Over 180 m^3 of shore filtered surface water was passed through every kg of carbon. A total weight of 290 g of a brown tar was collected.

Separations of the fractions are achieved by column and thin layer chromatography.

After having achieved the best separation possible by vapor phase chromatography (Aerograph 1860 and 1400, VARIAN) the gas-chromatographic peaks were analyzed by means of a mass spectrometer (CH5, VARIAN MAT) in combination with a gas chromatograph (Aerograph 1740. VARIAN).

Further analytical work was performed for identification by a second independent analytical method; either by measuring the relative retention time and/or, after trapping a peak, by IR-spectroscopy.

RESULTS

Over 100 non-biodegradable organic compounds have been identified in the three solvent extractions. The organic pollutants belong to five different classes of organic compounds, which are summarized in Table 1.

A sizeable number of the identified compounds in Table 1 were found in the Dutch Rhine by *Meyers* (5) and were also identified in the direct analysis of various Rhine water samples taken in the German Rhine and in the fatty tissue of Rhine fish (7).

Table 1

Identified non-biodegradable organic pollutants in shore filtered surface Rhine water

Compound	Concentration*	Literature
1. *Chlorinated hydrocarbons*		
a) aliphatic		
tetrachloroethylene	M	
tetrachlorobutadiene	M	
pentachlorobutadiene	M	
hexachlorobutadiene	M	5
pentachlorobutene	M	
pentachlorocyclohexene	M	
γ-hexachlorocyclohexane	M	
α-hexachlorocyclohexane	T	
δ-hexachlorocyclohexane	T	
b) aromatic		
o-dichlorobenzene	M	5
m-dichlorobenzene	T	5
p-dichlorobenzene	M	5
1,2,3-trichlorobenzene	T	
1,3,5-trichlorobenzene	T	5
1,2,4-trichlorobenzene	M	

M = main component, identified in one of the solvent extractions
T = trace component, identified after column and/or thin layer chromatography separation

1,2,3,4-tetrachlorobenzene	T	
1,2,3,5-tetrachlorobenzene	T	
1,2,4,5-tetrachlorobenzene	T	
pentachlorobenzene	M	
hexachlorobenzene	M	
dichloro methylbenzene	M	
trichloro methylbenzene	M	
tetrachloro methylbenzene	T	
pentachloro methylbenzene	T	
trichloro dimethylbenzene	T	
chlorobiphenyl	T	
4,4'-dichlorobiphenyl	M	
trichlorobiphenyl	T	
dichlorodibenzyl	T	5
tetrachlorodibenzyl	T	
c) miscellaneous		
2,6-dichloro benzonitrile	T	
chlorobenzophenone	T	
chloro methylquinoline	T	
chlorophenyl-methyl sulfone	T	
chlorophenyl-ethyl sulfone	T	
4,4'-dichlorophenyl sulfone	T	
2,4,5-trichlorophenyl 4-chlorophenyl sulfone	T	
bis-(3,5-dichloro-2-hydroxyphenyl)sulfide	T	
dichloro azobenzene	T	
2. *Nitroaromatic hydrocarbons*		
nitrobenzene	M	
o-dinitrobenzene	T	
m-dinitrobenzene	T	
p-dinitrobenzene	T	
2-nitro methylbenzene	M	5
2,4-dinitro methylbenzene	T	5
2,6-dinitro methylbenzene	T	5
2-nitro-m-dimethylbenzene	M	
1-nitronaphthalene	T	
2-nitrobiphenyl	T	
2-chloro nitrobenzene	T	5, 6
chlorodinitrobenzene	T	
dichloro nitrobenzene	M	
trichloro nitrobenzene	T	
2-chloro-4-nitro methylbenzene	M	5
2,5- or 3,4-dichloro nitrobenzene	T	
p-nitrobenzoic acid	T	
methyl nitrobenzoic acid	T	
dimethyl nitrobenzoic acid	T	
3-nitro-benzotrifluoride	T	
3. *Ethers*		
bis-(chloroisopropyl) ether	M	6
bis-(dichloro butyl) ether	T	
dichloro methoxybenzene	M	
trichloro methoxybenzene	M	5
tetrachloro methoxybenzene	T	
pentachloro methoxybenzene	M	
chloromethoxy pentachlorobenzene	T	

o-nitro methoxybenzene	T	
o-nitro ethoxybenzene	T	
chloro-dimethoxybenzene	T	
dichloro-dimethoxybenzene	T	
propyl phenyl ether	M	
diphenyl ether	T	5, 6
ditolyl ether	T	
nitrophenyl phenyl ether	T	
diphenyl phenyl ether	T	
benzofuran	T	
diphenylene oxide	T	
diphenylene sulfide	T	
2-methylthiobenzothiazole	M	20
benzothiazolyl-2-methyl sulfon	T	
β-picolyl propyl ether	T	
4. *Phenols*		
2-tert-butyl-4-methyl phenol	M	
2-tert-butyl-4-methoxy phenol	M	
2,6-ditert-butyl-4-methyl phenol	M	
2,6-ditert-butyl 4-ethyl phenol	T	
2,6-ditert-butyl-4-methoxy phenol	M	
2,6-ditert-butyl-4-ethoxy phenol	T	
4-carboxyl-2,6-ditert-butyl phenol	T	
4,6-ditert-butyl-2-hydroxymethyl phenol	T	
bis-(3,5-ditert-butyl-2-hydroxyphenyl) methan	T	
nitro methylphenol	T	
nitro dimethylphenol	T	
p-isopropylphenol	T	
1-chloro-2-naphthol	T	
5. *Esters*		
tetradecanoic acid, methyl ester	M	
pentadecanoic acid, methyl ester	M	
hexadecanoic acid, methyl ester	M	
heptadecanoic acid, methyl ester	M	
phthalic acid, dipropyl ester	M	
phthalic acid, dibutyl ester	M	
phthalic acid, bis-2-ethylhexyl ester	M	
tributylphosphate	M	
adipic acid, bis-2-ethylhexyl ester	T	

DISCUSSION

All non-biodegradable organic compounds listed as main compounds in Table 1 are chemicals each of which is produced on a technical scale in quantities of more than 10.000 t per annum. Some of the persistent chelicals, such as diphenyl ether, o-chloronitrolbenzene and bis-(chloro-isopropyl) ether were identified by *Middleton* in 1960 in four industrially polluted rivers in the east of the United States (6).

Only a few of the non-biodegradable compounds are well known pesticides or herbicides, such as hexachlorcyclohexane, 2,6-dichlorobenzonitril and 2,4,4',5-tetrachlordiphenyl sulfon. This is not surprising since only

2% of the world-wide annual production of organic chemicals (approximately 100 million t) are pesticides. The largest class of non-biodegradable pollutants of industrial origin (8) are chlorinated hydrocarbons. Half of the compounds identified in this class contain more than two chlorine atoms. Chlorinated hydrocarbons, especially the polychlorinated ones, are toxic. Since they are lipophilic, they accumulate in the food chain and some of them, such as hexachlorocyclohexane, hexachlorobenzene and polychlorinated biphenyls, have been found in human fat tissue and even in mothers milk (9). In this respect it is questionable that chlorinated aromatics, such as o- and p-dichlorobenzene together with trichlorobenzene are used in large quantities to cover the bad odour of waste water. The world-wide occurrence and significance of polychlorinated biphenyls has been the subject of many investigations during the last five years (10).

The nitro aromatic compounds, important chemicals for the synthesis of dyes, drugs etc, are highly toxic to fish in very low concentrations (8). Nitrochloro substituted aromatics are known as strong blood poisons (11). o-Chloro nitrobenzene is known to accumulate in the human body. So far however, there have been no reports in the literature on the persistence of the nitro aromatic compounds.

In the third class of non-biodegradable organic compounds, the ethers, it is surprising to find polychlorinated anisols, while in the fourth class, the phenols, no chlorinated phenols are listed. Since only chlorophenols are produced on a large scale it may be argued that chloroanisols are the results of a bacteriological methylation process in the polluted river or on the carbon filters. There are some indications (12) that bacteria produce chlorinated anisols, such as 4-methoxy-2,3,5,6-tetrachlorophenol (13). The 2-methyl thio benziothiazole, which is used to improve the vulcanization process, retards the production of thyroxine (14). Furthermore, it is questionable that the persistant diphenyl ether, which has been identified in varous polluted rivers (5,6,7) dissolved in ethylene glycol, is used in the winter time to clear the roads from ice and snow.

Phenols, especially those bearing teritary butyl groups, are obviously resistant to biodegradation. This class of compounds are ubiquitously used as antioxidants in oil, grease, varnish etc. Although they are known to be non-toxic (15) the accumulation in the environment could cause secondary effects by retarding or preventing oxidation processes in nature. Thus, it is reported that in polluted water tert-butyl substituted phenols are inhibitors of the photosynthesis of chlorella pyrenoidosa (16).

The fifth class of non-biodegradable organic pollutants, the phthalic acid esters, which are ubiquitous in their use as plasticisers, are identified as water pollutants. Although their biological impact is uncertain (17) a sizeable number of reports during the last few years indicate their wide distribution in the environment (18).

The most difficult question to be answered is that of the effect of these non biodegradable toxic compounds when they are taken up by human

bodies over prolonged periods of time, especially in very low doses of a few micrograms per day. There have been indications that people take up some of these non-biodegradable organic compounds via their daily drinking water (6).

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Sažetak

IDENTIFIKACIJA BIOLOŠKI NERAZGRADIVIH ZAGAĐIVAČA U RIJEČNOJ VODI

Biološki nerazgradivi organski spojevi djeluju nepovoljno na kvalitetu riječne vode koja služi za ljudsku upotrebu i prouzrokuju sekundarne efekte utječući na ekologiju rijeke. Ti se biološki nerazgradivi organski spojevi nakupljaju na ugljenim filtrima vodovoda. Za identifikaciju biološki nerazgradivih organskih spojeva, uzorak ugljenog filtra njemačkog vodovoda s donjeg toka rijeke Rajne, ekstrahiran je s organskim otapalima. Ekstrakti su separirani kromatografskim tehnikama te identificirani pomoću spektrometra masa vezanog uz plinski kromatograf. Neovisno o tome spojevi su identificirani mjerenjem vremena zadržavanja te pomoću infracrvene spektroskopije nakon hvatanja uzorka s maksimuma. Identificirano je više od 100 organskih spojeva. Većina pripada klasama kloriranih alifatskih i aromatskih ugljikovodika, aromatskih nitrospojeva i terc.-butil supstituiranih aromatskih ugljikovodika.

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