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GROUNDWATER POLLUTION BY VOLATILE ORGANIC CHEMICALS

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ABSTRACT

Volatile organic groundwater pollutants were determined in Switzerland. Tetra- and trichloroethylene and alkylated and chlorinated benzenes were frequently found. An aquifer that had been contaminated by wastewater leakage from a chemical plant was investigated. Several chemicals, including brominated hydrocarbons, which had been manufactured at this plant were detected. In addition, a series of dialkylsulfides and cyclic disulfides were identified. These volatile sulfur compounds were probably formed by the reaction of alkylbromides with hydrogen sulfide under anaerobic conditions.

INTRODUCTION

Volatile organic chemicals are increasingly frequent groundwater pollutants (refs.1-3). Volatile compounds are quite mobile in groundwater. If such compounds resist biodegradation they are long-lived in the groundwater environment because volatilization, the most effective mechanism for their removal in surface waters, proceeds at a much slower rate in groundwater. This paper is a report on pollution of some Swiss groundwaters by volatile organic chemicals including several halogenated compounds. Particular emphasis is placed on the results of an investigation of an aquifer that has been contaminated by wastewater leakage from a chemical plant.

EXPERIMENTAL

Volatile organic constituents of groundwater samples were enriched by the closed-loop gaseous stripping/adsorption/solvent elution procedure described by Grob and Zürcher (ref. 4). Gas chromatographic analyses were performed on glass capillary columns supplied by K. and G. Grob. Compound identifications were based on directly coupled gas chromatography/mass spectrometry (GC/MS). Some samples were further analyzed by dual flame photometric/flame ionization detection to determine sulfur containing compounds.

RESULTS AND DISCUSSION

General

Table 1 contains a selected list of volatile organic chemicals which have been frequently detected in Swiss groundwaters. The polychlorinated compounds are of particular concern because they are little, if at all, affected by microbial degradation. The petroleum-derived benzenes and 1,4-dichlorobenzene are more easily biodegraded (refs. 5 and 6). All these volatile non-polar chemicals are reasonably soluble in water (e.g. tetrachloroethylene: 150 mg/L) and have been shown to be quite mobile in the ground (ref. 8). Therefore they are likely to be transported with the water flow and may thus contaminate large parts of an aquifer. These pollutants may be introduced into subsurface waters by acute spills (fuel oils, gasoline, solvents), by chronic input from polluted surface waters (ref. 6), or by leaching from disposed wastes (ref. 7).

TABLE 1

Volatile organic chemicals frequently found as groundwater pollutants

Compound	Use/origin	Concentrations, µg/L	Remarks
Tetrachloroethylene	solvent	0.5 - 2	bank filtrates (ref. 1 and 6)
		⩽ 240	contaminated aquifer (ref. 1)
		> 150 000 (solubility limit)	spill (ref. 2)
Trichloroethylene	solvent	2	contaminated aquifers (ref.1)
1,4-Dichlorobenzene	deodorant	< 0.1 - 0.3	bank filtrates (ref. 6)
Hexachloroethane	leachate from disposal site of chemical wastes	15 - 21	contaminated aquifer (ref. 7)
Hexachlorobutadiene		0.2 - 0.3	
Toluene, Xylenes, Trimethylbenzenes	"water soluble" constituents of gasoline and fuel oil	up to the solubility limits	oil spills

Case study: Groundwater pollution by industrial wastewater

We report here on a groundwater pollution case which occurred in Switzerland. After the operations of a chemical plant which manufactured intermediates for chemical synthesis were moved, it was discovered that the underlying aquifer was heavily polluted. The source of the pollutants was probably a leak in a wastewater treatment tank. Our investigation was undertaken seven years after the plant operations had ceased and after extensive clean-up procedures including the removal of soil and aquifer material and continuous pumping from two wells. The principal objective of our study was to determine whether the aquifer was still contaminated with compounds related to those which had been present in the chemical plant.

Figure 1 shows the total ion chromatograms for GC/MS analyses of the volatile organic chemicals which were extracted from groundwater samples taken from the two clean-up wells. The complete structures could only be determined for a few components. Molecular formula and compound type were obtained for most major components (Table 2). Several peaks were attributed to isomeric compounds.

Although the two wells were located only about 100 m apart, the patterns of volatile organic pollutants were distinctly different. The water from well 1 was more polluted; this well was closer to the presumed source of the contamination.

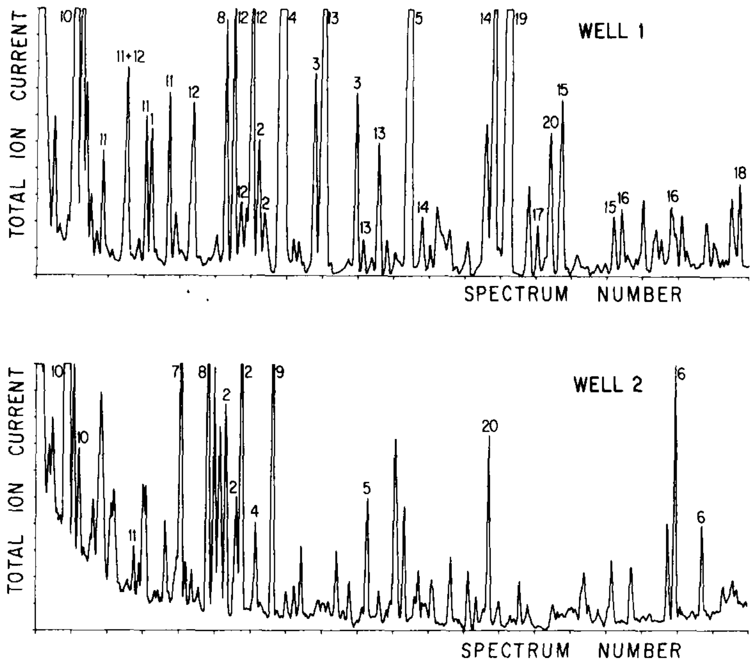

Fig. 1. Total ion chromatograms of volatile organic chemicals present in samples from a contaminated groundwater. Numbers refer to Table 2.

TABLE 2

Volatile organic chemicals identified in samples from a contaminated groundwater

	Aromatic Hydrocarbons		Halogenated C_3-hydrocarbons		Dialkylsulfides[c]	
1	Toluene	7	Bromochloropropane[b]	10	$C_4H_{10}S$	(2)
2	C_2-benzene[a]	8	Chloropropane	11	$C_5H_{12}S$	(4)
3	C_3-benzene[a]	9	Dibromopropane[b]	12	$C_6H_{14}S$	(5)
4	Chlorobenzene			13	$C_7H_{16}S$	(3)
5	Bromobenzene[b]		Cyclic disulfides	14	$C_8H_{18}S$	(2)
6	Dibromobenzene (2)[b,c]			15	$C_9H_{20}S$	(2)
		19	$C_3H_6S_2$	16	$C_{10}H_{22}S$	(2)
		20	$C_4H_8S_2$	17	$C_5H_{11}SCl$	
				18	$C_7H_{15}SCl$	

a) C_n-benzenes: isomeric benzenes with n additional alkyl carbon atoms.
b) Products of the chemical plant responsible for the contamination.
c) Number in parenthesis: number of isomers.

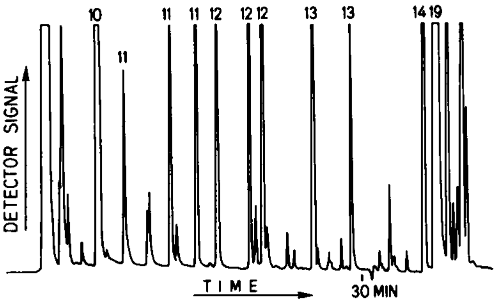

Fig. 2. Sulfur specific gas chromatogram of volatile organic chemicals present in a sample from a contaminated groundwater. Numbers refer to Table 2.

In well 1 the maximum concentrations of the major volatile constituents, bromo- and chlorobenzene, were 16 and 8 µg/L, respectively. The qualitative and quantitative differences between wells 1 and 2 were probably caused by different mobilities of the pollutants and complex hydrological processes during pumping of the two wells. This was indicated by the results of monitoring the volatile pollutants during extensive pumping of the two wells.

Bromobenzene, dibromobenzene,bromochloropropane and dibromopropane were products which had been manufactured at the chemical plant. Chlorobenzene is a solvent widely used in chemical synthesis. Thus, our investigation conclusively proved that the aquifer was still contaminated with chemicals which very likely originated from the plant.

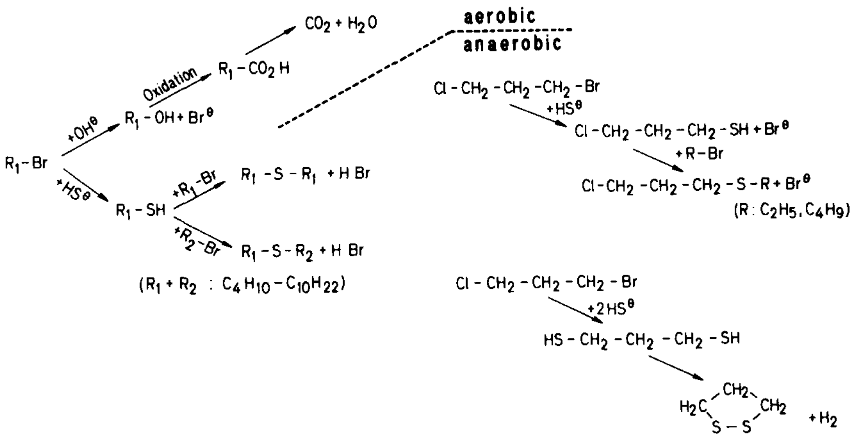

Fig. 3. Proposed formation schemes for volatile sulfur compounds.

In addition, a series of sulfur containing volatile compounds were identified. Dialkylsufides (several isomeric compounds) and cyclic disulfides were particularly abundant in samples from well 1 (Fig. 1). Additional evidence for the presence of a series of sulfur compounds was obtained by using the sulfur specific flame photometric detector (Fig. 2).

To understand the formation of sulfur compounds one should recall that alkylbromides are excellent alkylating agents. If such alkylbromides were introduced into water under aerobic conditions, they would rapidly hydrolize to the corresponding alcohols which then would be easily biodegraded (Fig. 3). Under anaerobic conditions the hydrolysis to the alcohols would also proceed, and the alcohols would be oxidized to the carboxylic acids by anaerobic microbial processes. However, in competition with hydrolysis, the alkylbromides can react with hydrogen sulfide formed by the anaerobic, microbial reduction of sulfate. In this reaction hydrogen sulfide is alkylated and thiols (R_1-SH) are produced. These thiols can be further alkylated by alkylbromides, and stable, persistent dialkylsulfides (R_1-S-R_2) are formed.

Of particular importance was the presence of two dialkylsulfides with one chlorine atom each (compounds 17 & 18). These compounds can be formed from 1-bromo-3-chloropropane, a chemical which was manufactured at the chemical plant. Therefore the chlorine atoms in the two dialkylsulfides clearly indicate the industrial origin of these pollutants. The cyclic disulfides could have been produced by similar reactions leading to dithiols and subsequent cyclisation. All of the suggested reaction pathways are shown in Fig. 3.

Laboratory experiments which will be presented elsewhere showed that the formation of dialkylsulfides from alkylbromides in an anaerobic hydrogen sulfide containing environment can be a purely chemical reaction and that biological mediation is not needed.

In conclusion, our investigation showed that some volatile organic substances, probably spilled from a chemical plant, persisted in a contaminated, anaerobic aquifer for many years. Other compounds (alkylbromides) reacted with hydrogen sulfide which was present in the anaerobic environment. These chemicals are thought to be detrimental to the water quality because of their suspected high toxicity and their impact on taste and odour of the water.

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