

Tetrachloroethylene in Contaminated Ground and Drinking Waters

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Chlorinated compounds derived from C_1 and C_2 hydrocarbons are manufactured industrially in quantities exceeding a total annual world production of $36 \cdot 10^6$ tons. More than $4 \cdot 10^6$ tons are used either as aerosol propellants or as solvents in dry cleaning and metal degreasing (PEARSON and McCONNELL 1975). Because of their dispersive use and biological resistance these compounds have been identified in various parts of the atmospheric and aquatic environment. Of particular interest is their occurrence in finished drinking waters, where some (e.g. chloroform and other trihalomethanes) are attributed to the impact of water chlorination, and others (e.g. carbon tetrachloride) must be derived from contamination of the raw waters (SYMONS et al. 1975).

Traces of tetrachloroethylene (also perchloroethylene or 1,1,2,2-tetrachloroethene) have been detected in various drinking waters (GROB and GROB 1974, DOWTY et al. 1975, REPORT TO CONGRESS 1975). The predominance of tetrachloroethylene (up to $80 \mu\text{g/l}$) among the volatile organic trace constituents in the River Glatt, Switzerland, has also been reported (GIGER et al. 1976, ZURCHER and GIGER 1976). Analyses of the trace organic constituents in the tap water at our laboratory in Dübendorf, Switzerland, likewise revealed a predominance of tetrachloroethylene.

In this paper we report on a study aimed at the evaluation of the source of the tetrachloroethylene contamination in the water supply of the town of Dübendorf. For this purpose a quantitative method was applied which is based on conventional solvent extraction and glass capillary gas chromatography.

MATERIALS AND METHODS

Water samples were collected after the particular taps had been left open for five minutes. One liter volumetric flasks were rinsed once with the sample water and then filled completely. The glass flasks were closed with glass stoppers without leaving a head space volume. The samples were then transferred as soon as possible to a cold room (4°C) and worked up between 2 and 24 hours after collection. Water volumes of one liter were extracted three times with 5 ml of pentane (Nanograde, Mallinckrodt) by vigorous manual shaking in the volumetric flasks. After adding 1-chlorohexane (5-100 µl of a pentane solution containing 1.21 g/l) as internal standard, the combined extracts were concentrated to approximately 0.2 ml in a Kuderna-Danish evaporator.

Gas chromatography was performed on a Carlo Erba instrument (Fractovap Model GI) equipped with a Grob-type injector (GROB 1972), a glass capillary column, and a flame ionization detector. The glass capillary (28 m x 0.27 mm I.D.) coated with UCON LB 550 was prepared and supplied by K. and G. Grob according to GROB and GROB (1976 and 1977). The injector was held at a temperature of 200°C. Hydrogen served as carrier gas (approx. 1 ml/min). Aliquot samples of 0.6 - 2.0 µl were injected without stream splitting onto the column which was cooled in an ice bath. After 10 sec the split valve was opened allowing the septum and injection port to be purged at a flow approximately sixty times higher than the flow through the column. Subsequent to the elution of the solvent, the ice bath was removed, and the column temperature was raised at 3°C per minute. Our GC procedure is based on the description given by GROB and GROB (1972). Electronic integration of gas chromatographic peak areas was performed by a digital integrator (Minigrator, Spectra Physics).

The average relative standard deviation in the range from 1 to 400 µg/l was $\pm 3.5\%$. The detection limit was 0.15 µg/l. Recoveries have been measured for concentrations from 1.8 to 465 µg tetrachloroethylene per liter. A mean recovery of $84 \pm 8\%$ was found.

For mass spectrometric identification a Finnigan GC/MS system (Model 1015D) combined with an on-line computer (Model 6000) was used. The glass capillary was directly coupled to the mass spectrometer by means of a platinum capillary. Helium was used for carrier gas.

RESULTS AND DISCUSSION

Fig. 1 shows the gas chromatographic analysis of the pentane extract of the tap water from our laboratory at the EAWAG, Dubendorf, Switzerland. This sample taken in February 1976 contained 45.7 μg or 0.28 μmoles of tetrachloroethylene per liter. Identification was based on co-injection experiments and on GC/MS. The possibility of an interference by one of a series of organic compounds which had been found as trace constituents in drinking waters (GROB and GROB 1972, REPORT TO CONGRESS 1976) was checked; it was evident that sufficient separation was achieved by capillary gas chromatography.

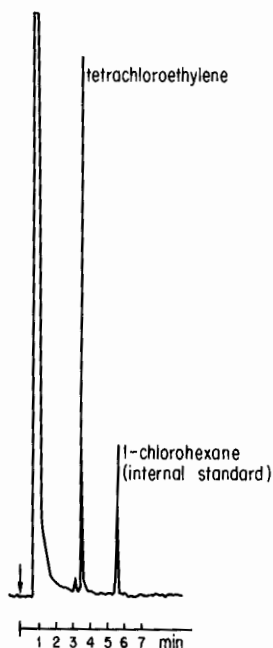


FIGURE 1

Gas chromatogram
of a drinking
water extract

During a period of 12 days, the levels of tetrachloroethylene were determined on a daily basis. In addition, the analyses of deionized, doubly-distilled, and UV irradiated (24 h, 254 nm) water showed that these three water purifications did not completely remove tetrachloroethylene. Tap water from another location at Dubendorf (location A, Table 1), however,

contained much smaller amounts of tetrachloroethylene than the tap water at EAWAG. Table 1 summarizes the data.

TABLE 1

Concentrations of tetrachloroethylene in various water samples

Sample	Number of de-terminations	Tetrachloroethylene µg/l	
		average	min.- max.
Tap water, EAWAG	15	28.3	7.4 - 82.5
Doubly-distilled water	3	1.7	0.4 - 2.5
Deionized water	2	4.2	3.5 - 4.9
UV irradiated water	1	2.9	-
Tap water, location A	5	1.3	n.d.- 2.5
Tap water, location B	7	69.1	0.5 -451
Groundwater, well I	6	763	473 -954

With the aim of locating the source of this contamination, we inquired about the origin of the water which is distributed by the water supply of Dubendorf. The following situation was discovered: Half of the water supplied by the Water Works of Zurich is treated water from Lake Zurich. Most of the remainder is drawn from three groundwater wells in and near Dubendorf. A minor part is delivered by a few springs. Subsequently, water samples from all these sources were analyzed for tetrachloroethylene. The result was that only the groundwater well I was contaminated, with levels ranging between 500 and 1000 µg/l (Table 1). Well I is located in the center of the town of Dubendorf.

The wells are not continuously operated and the water is pumped directly into the distribution system. Thus, the water from a particular tap is composed irregularly of water of different origins, depending on time and location. Close to the contaminated well and at a time when the pump was working, we detected a maximum concentration of 451 µg/l in a tap water sample (location B, Table 1).

The bulk of EAWAG tap water is composed of varying amounts of lake water and of water from the contaminated groundwater well. Therefore, the tetrachloroethylene concentration correlated positively with some parameters which are typically elevated in these groundwater samples, such as nitrate, chloride, and alkalinity.

It is worthwhile mentioning that this tetrachloroethylene contamination was not detected by presently used methods for routine control of drinking water (i. e.: total dissolved organic carbon or chemical oxygen demand).

Based on these results, the official chemist of the Canton of Zurich prohibited further use of the contaminated well. An assessment of the toxicity of tetrachloroethylene in drinking water is presented by UTZINGER and SCHLATTER (1977).

The aquifer upstream of the contaminated well was surveyed as a consequence of the results reported here. This led to the discovery of a location, about 300 meters distant from the polluted well, where tetrachloroethylene exceeds the solubility limit (150 mg/l at 25°C) and a solvent/water emulsion exists. How the organic solvent reached the aquifer is presently under investigation. Of particular interest is that the center of the contamination was found in the backyard of a dry-cleaning facility.

This case study shows that the widely used tetrachloroethylene is of particular concern as a potential pollutant of sub-surface waters. This organic solvent is reasonably soluble in water, has a low tendency to adsorb compared to pesticides and petroleum hydrocarbons, and is only very slowly degraded. Thus, it is likely to be transported with the water flow and to be quite mobile as well as longlived in the groundwater environment. Volatilization, the most effective mechanism for removal from surface waters, proceeds at much lower rate in groundwater. It is hoped that this study will contribute to a better awareness of this potential threat to groundwaters and to drinking water derived from such sources.

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