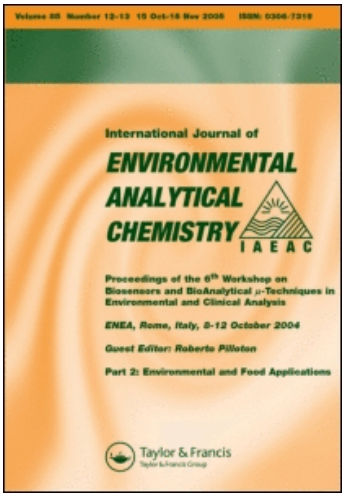

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QUANTITATIVE ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN LANDFILL LEACHATES*

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Selective determination of chlorinated hydrocarbons and alkylated benzenes in leachate of sanitary landfills and hazardous waste landfills was performed by headspace analysis.

Identification was achieved by headspace GC/MS analyses, quantitation by headspace GC, after spiking of the samples with all compounds in two concentrations (0.2 μg/250 μg). Within the hazardous waste landfills, the concentrations of chlorinated hydrocarbons ranged from 10 to 20000 ppb, with methylene chloride, trichloroethylene and tetrachloroethylene as main constituents.

They were detected only singularly up to 14 ppb in the sanitary landfill samples. Benzene and alkylated benzenes were found in concentrations of 10 to 13000 ppb in the leachates of the hazardous waste landfills and determined up to 500 ppb within the sanitary landfill leachates.

The total contents of the chlorinated headspace compounds are discussed in terms of total organic chlorine with respect to the landfill type and to the corresponding AOX-values.

KEY WORDS: Headspace gas chromatography, chlorinated hydrocarbons, alkylated benzenes, landfill leachates, AOX.

INTRODUCTION

In recent years, analysis of organic pollutants in landfill leachates has become the subject of increasing concern with respect to possible groundwater pollution and convenient methods of leachate treatment. Yet there is little information available from literature. There are few papers dealing with selective analysis of nonvolatile organic pollutants in leachates.[1–4] With regard to the determination of volatile leachate compounds, there are neither reports investigating leachates of different landfill types nor performing both sum parameter and single component analysis. This paper deals with a systematic investigation of volatile organic pollutants detected by headspace analysis in the leachates of hazardous waste landfills and of sanitary landfills. The quantitative results obtained for the chlorinated headspace

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compounds are evaluated with respect to the corresponding AOX- and POX-values.

EXPERIMENTAL

Materials

All reference compounds (puriss., >99.5%) were obtained from Fluka (Neu-Ulm, F.R.G.). Activated charcoal for AOX-determination was supplied by LHG (Karlsruhe, F.R.G.).

Samples

Samples were taken in 4 liter amber glass bottles. The bottles were completely filled and stored at 4 °C.

Standard Solutions

For quantitative analysis, stock methanol solutions were prepared, containing all of the chlorinated hydrocarbons (2%, tetrachloroethylene 4%) and alkylated benzenes (1%). The stock solutions were diluted with methanol in the ratios 1:10 (standard solution A), 1:100 (standard solution B) and 1:1000 (standard solution C).

Analytical Procedure

The leachate samples were homogenized by shaking for 10 min. For the identification of the volatile compounds, 50 ml were transferred into a 100 ml-headspace vial, thermostatically kept at 40 °C and analyzed by headspace GC/MS.

For quantitation, three 50 ml aliquots were taken for each analysis. One sample was treated as described above and analyzed by headspace GC. The other two samples were spiked either with 100 μL of standard solutions A and B, or with 100 μL of standard solutions B and C, corresponding to the leachate.

Headspace GC/MS Analyses and Headspace GC Analyses

The headspace GC/MS analyses were carried out with a Finnigan Mod. 4500 quadrupol mass spectrometer and an Incos data system. The headspace GC measurements were performed with a Carlo Erba Mod. 4160 Fractovap gas chromatograph equipped with FID/ECD (simultaneous detection). The GC conditions were as follows: 60 m DB 5 fused silica capillary column (0.32 mm I.D.),

carrier gas helium (2 ml/min), column temperature 8° for ten min, then programmed at 5 °C/min to 250 °C. Sample size 100–300 μL, splitless injection with cryogenic focusing on the column by liquid nitrogen.

Analyses of Adsorbable Organic Halogens (AOX) and Purgeable Organic Halogens (POX)

The AOX- and POX-measurements were carried out according to (5). The POX was determined by purging the organic halogenated compounds from a 100 ml aliquot of the sample directly into a pyrolysis furnace, combustion at 950 °C and subsequent microcoulometric measurement.

The AOX-analyses were performed with the samples after preliminary separation of POX, followed by adsorption of the halogenated compounds to activated charcoal, removal of anorganic chloride, pyrolysis of the charcoal at 950 °C and microcoulometric measurement.

For the AOX-analyses, a TOX-apparatus (Ebi/Kiwa-LHG/Euroglas) and a POX unit (LHG) was used.

RESULTS AND DISCUSSION

Figure 1 shows the headspace gas chromatograms of leachates from the hazardous waste landfills A1, A5 and from the sanitary landfill B1.

Almost all headspace compounds are chlorinated hydrocarbons and alkylated benzenes. The distribution pattern of A1 and A5 is very similar, with methylene chloride, trichloroethylene and tetrachloroethylene as main components of the chlorinated hydrocarbons and benzene, toluene and xylenes as main components of the aromatic compounds. In the sanitary landfill leachates, the chlorinated hydrocarbons are detected only singularly. Benzene, toluene and xylenes are main peaks of the aromatic compounds, although detected at concentrations in orders of magnitudes lower. Tables 1 and 2 list the quantitative results for the hazardous waste landfill leachates A1–A5 and the sanitary landfill samples B1–B4. Within the leachates of the hazardous waste landfills, methylene chloride, trichloroethylene and tetrachloroethylene are found in concentrations ranging from 10–20 000 ppb. Within the sanitary landfill leachates, they are detected only singularly up to 14 ppb. Benzene, toluene and xylenes are found in concentrations up to 13 000 ppb within the hazardous waste landfill samples, and reach maximal levels of 200 and 600 ppb in the sanitary landfill leachates.

Figure 2 shows the headspace gas chromatograms of hazardous waste landfill sample A5, performed by ECD-detection. Additional control and quantitation of chlorinated hydrocarbons, hardly detected by FID (i.e. chloroform, 1,1,1-trichloroethane) is achieved. The same holds true for chlorinated benzenes and chlorinated phenols, otherwise unresolved or not detected by FID.

To evaluate the quantitative results obtained by headspace measurement with respect to the total organic chlorine, AOX- and POX-analyses were performed.

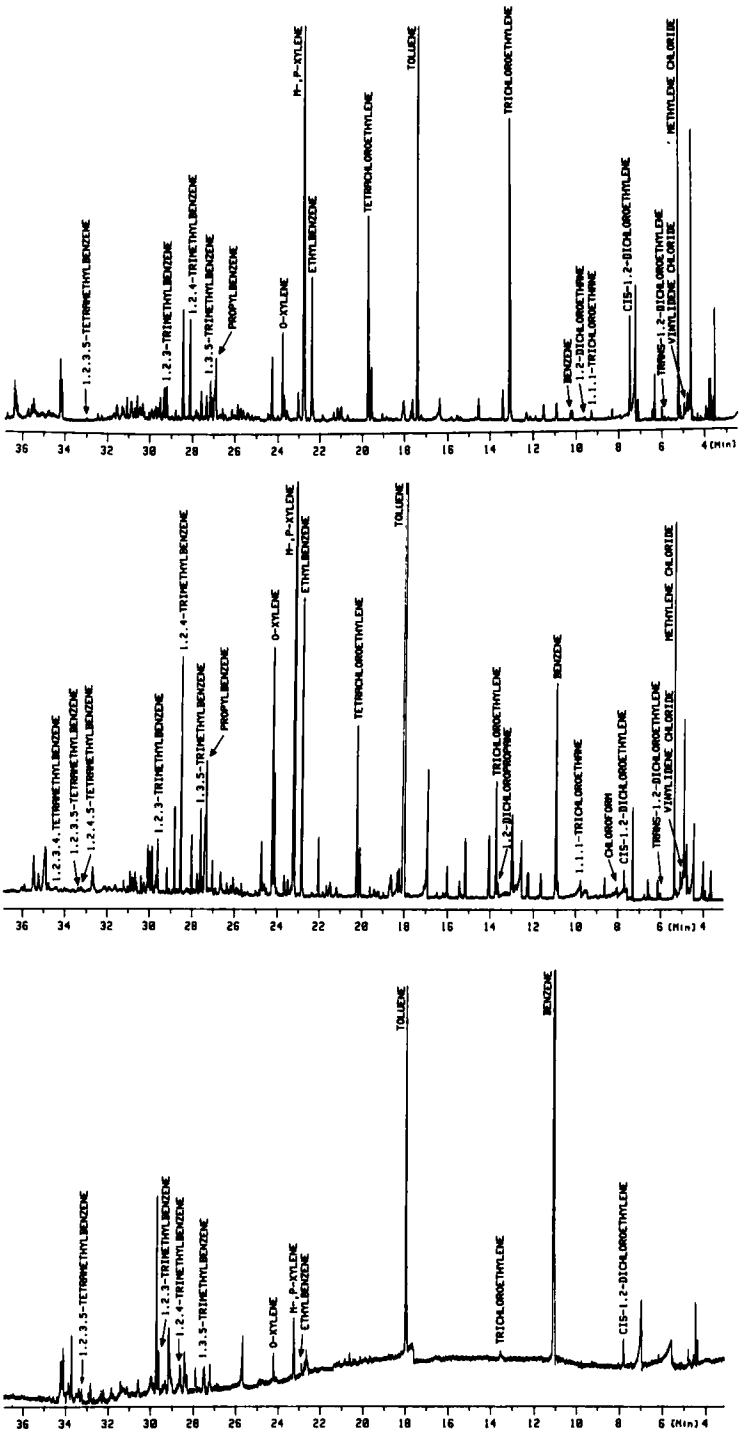

Figure 1 Headspace gas chromatograms of leachate from the hazardous waste landfills A1, A5 (top) and from the sanitary landfill B1 (bottom). Detection with FID.

Table 1 Concentrations (μg/l) of chlorinated hydrocarbons in leachate samples of hazardous waste landfills A1–A5 and sanitary landfills B1–B4

Compound	*A1*	*A2*	*A3*	*A4*	*A5*	*B1*	*B2*	*B3*	*B4*
Vinylidene chloride	140	90	950	460	360	n.d.	n.d.	1.9	n.d.
Methylene chloride	4770	5330	80	740	21290	n.d.	n.d.	6.0	n.d.
trans-1,2-Dichloroethylene	80	70	1430	70	60	n.d.	1.6	n.n.	n.d.
cis-1,2-Dichloroethylene	1500	4750	900	80	1150	14.2	2.7	1.9	1.9
Chloroform	n.d.	n.d.	n.d.	n.d.	1270	n.d.	n.d.	6.6	8.5
1,1,1-Trichloroethane	350	60	n.d.	10	1020	n.d.	1.9	n.d.	4.5
1,2-Dichloroethane	500	530	40	50	830	n.d.	n.d.	n.d.	n.d.
1,2-Dichloropropane	n.d.	n.d.	n.d.	n.d.	650	n.d.	n.d.	n.d.	n.d.
Trichloroethylene	9500	640	200	30	9440	7.2	2.3	3.5	7.9
Tetrachloroethylene	15110	70	70	20	23600	n.d.	2.8	n.d.	n.d.

n.d. = not detected at a detection limit of 1.1 ppb for trans-1,2-Dichlorethylene (with a signal to noise ratio of 3:1)

Table 2 Concentrations (μg/l) of alkylated benzenes in leachate samples of hazardous waste landfills A1–A5 and sanitary landfills B1–B4

Compound	*A1*	*A2*	*A3*	*A4*	*A5*	*B1*	*B2*	*B3*	*B4*
Benzene	150	50	380	20	1180	178	572	1.1	1.2
Toluene	3060	330	1790	120	13180	48	18	3.6	4.3
Ethylbenzene	2310	120	100	10	2120	1.7	20	7.3	20
m-/p-Xylene	3260	210	370	10	4400	8.3	3.7	n.d.	n.d.
o-Xylene	1570	90	90	10	1920	4.2	38	n.d.	n.d.
1,3,5-Trimethylbenzene	1380	20	10	10	720	2.9	4.8	2.6	4.7
Propylbenzene	580	30	10	n.d.	700	n.d.	n.d.	n.d.	n.d.
1,2,4-Trimethylbenzene	2020	30	40	10	3160	8.1	7.9	0.94	1.6
1,2,3-Trimethylbenzene	2450	40	20	10	1200	9.1	n.d.	1.0	3.0
1,2,4,5-Tetramethylbenzene	n.d.	n.d.	10	n.d.	180	n.d.	n.d.	1.2	n.d.
1,2,3,5-Tetramethylbenzene	710	20	10	10	240	5.1	n.d.	n.d.	3.7
1,2,3,4-Tetramethylbenzene	n.d.	n.d.	20	n.d.	200	n.d.	n.d.	n.d.	n.d.

n.d. = not detected at a detection limit of 0.85 ppb for toluene (with a signal to noise ratio of 3:1)

Figure 3 demonstrates the relations of AOX, POX and Volatile Organic Chlorine (VOC). The VOC-values were calculated from the concentrations of the chlorinated aliphatic headspace compounds. The VOC- and POX-levels are in good agreement with deviations in the 10% range, although originating from two completely different methods. With respect to AOX, the VOC reach levels up to 80%.

Figure 4 shows the corresponding VOC- and AOX-relations, as determined within the sanitary landfill samples. In contrast to the hazardous waste landfills, the VOC reaches only 1–2% of AOX. The VOC-concentrations between 0.01 and 0.02 ppm were below the detection limit of the POX-procedure.

Summarizing, the following conclusions are possible:

The leachates of hazardous waste landfills and sanitary landfills can be characterized by headspace analysis.

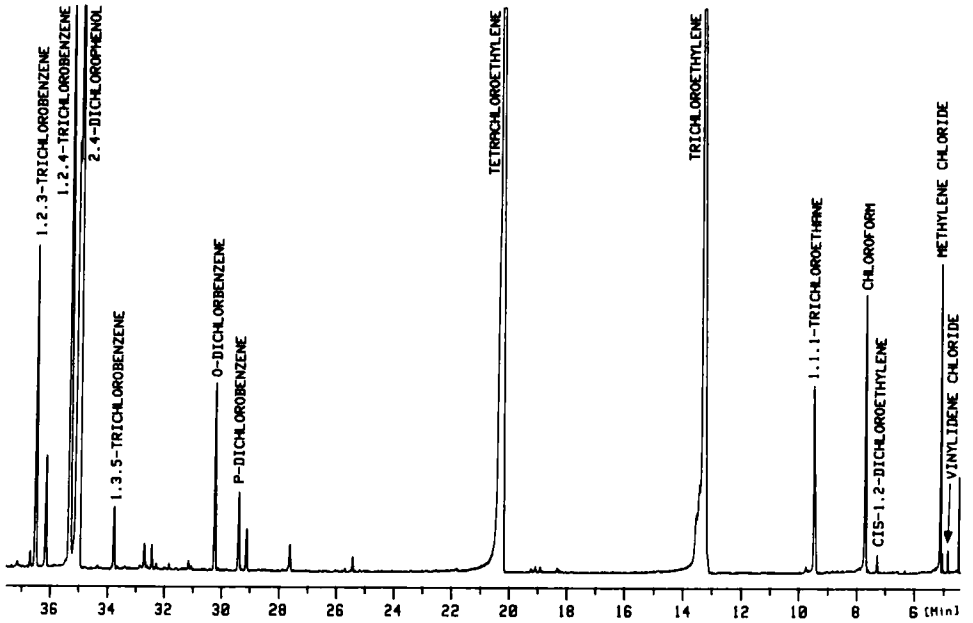

Figure 2 Headspace gas chromatogram of leachate from the hazardous waste landfill A5. Detection with ECD.

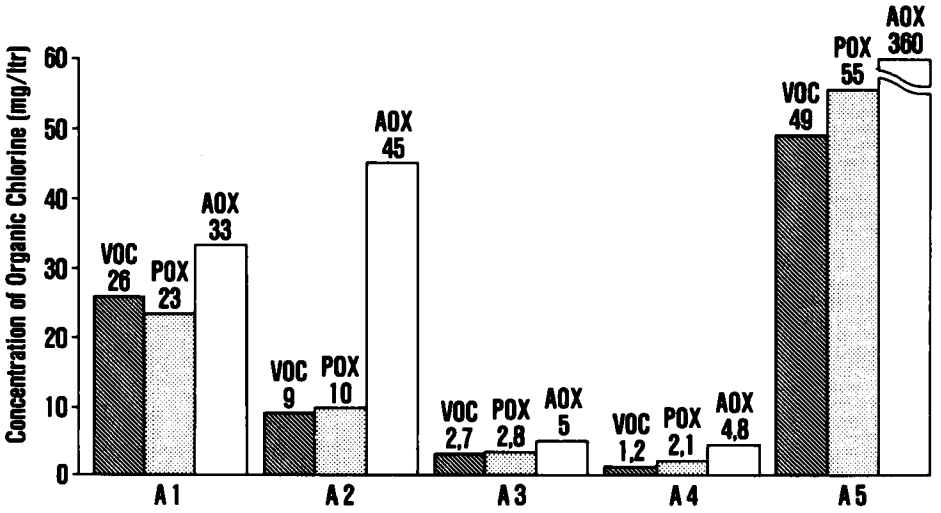

Figure 3 Organic chlorine in leachate of hazardous waste landfills A1–A5.
AOX = Adsorbable Organic Halogens
POX = Purgeable Organic Halogens
VOC = Volatile Organic Chlorine

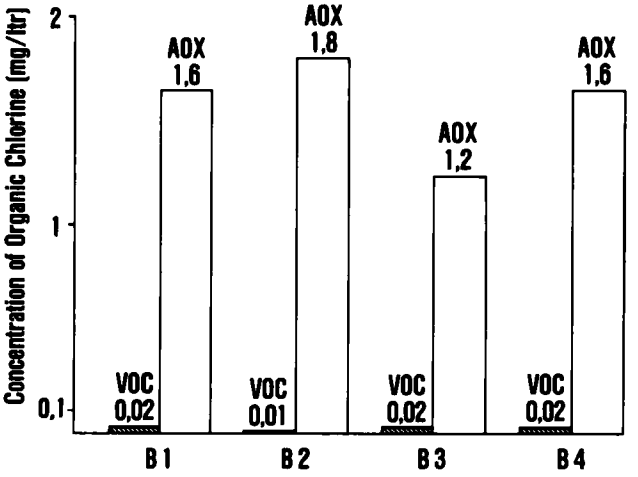

Figure 4 Organic chlorine in leachate of sanitary landfills B1–B4.
AOX = Adsorbable Organic Halogens
VOC = Volatile Organic Chlorine

Concerning the concentrations of the headspace compounds, significant differences are obtained for each landfill type, with main components of chlorinated hydrocarbons and alkylated benzenes at maximal concentrations of 20 000 ppb in the hazardous waste landfills, and of 500 ppb in the sanitary landfill samples.

Concerning the total chlorine contents, up to 80% of AOX are determined by headspace GC within the hazardous waste landfills, whereas 1–2% of AOX are determined within the sanitary landfill samples.

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