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A BIOASSAY-DIRECTED METHOD FOR THE SEPARATION OF VOLATILE COMPOUNDS FROM LANDFILL LEACHATES

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Abstract:

A bioassay-directed method for the separation of volatile compounds from landfill leachates based on a destillation in a closed system is presented. The method supplies a volatile fraction containing compounds with Henry's law constants down to 0.01 (20°C) concentrated in destilled water, which can be investigated directly using bioassays and chemical analysis. © 1997 Elsevier Science Ltd. All rights reserved

Introduction:

Landfill leachates are known to contain volatile compounds such as halogenated alkanes, alkenes and benzenes, alkylated benzenes and sulfur compounds in concentrations up to several mg/L (FÖRST ET AL., 1989; FÖRST ET AL., 1993). For estimation of the ecotoxicological risk using bioassays the volatile fraction must be separated from the leachate.

In principle, there are two different possibilities to fractionate complex environmental samples for their toxicity assessment: indirect and direct fractionation (MOUNT & ANDERSON-CARNAHAN, 1988)

For indirect estimation the respective fraction is removed, the toxicity of the remaining mixture is determined and compared to the efficacy of the original sample. This kind of method is often used for estimation of the toxicity of volatile fractions (for example JOP ET AL., 1991) because the latter is easily stripped from the sample. However, the validity of results is questionable if the toxicities of different fractions are not strictly additive (KOPPE ET AL., 1990). The same fraction may contribute to very different extents to the toxicity of different leachates.

It is therefore preferable to prepare fractions which can be directly investigated without any interference from other compounds of a complex environmental sample. Organic solvents which interfere with the bioassays should not be used. A method for direct separation of volatile compounds of landfill leachates which fulfills this assumption is presented.

Volatile compounds are defined here as substances the transfer of which from the water phase to gas phase is limited by molecular diffusion through the liquid phase interfacial layer according to the two-layer model presented by LISS & SLATER (1974). Diffusion is independent of the Henry's law constant (H). With decreasing H the resistence in the gas phase interfacial layer is increasing and becomes dominant when H falls below about 0.01 (20 °C), depending upon the experimental conditions. For compounds with lower H, the transfer from water to gas phase decreases with decreasing H. The presented method based on distillation takes advantage of this principle.

Methods

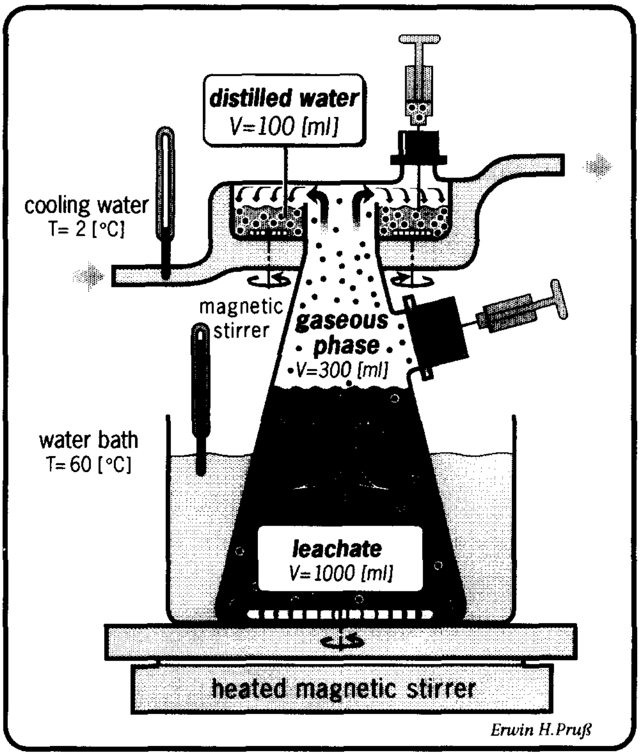

Fig. 1: Destillation apparatus

Volatile compounds from landfill leachates are separated by distillation in a closed system as shown in Figure 1. The vessel is composed of two reservoirs for liquids interconnected by the gas phase. The upper reservoir is filled with 100 mL destilled water, cooled to 2 °C with a cooling jacket and permanently agitated by means of two magnetic stirrers. The lower reservoir containing 1 L of the leachate is heated to 60 °C and is also stirred. The volume of the gas phase is 300 mL. Volatile compounds evaporate from the leachate and accumulate in the distilled water. The resulting solution can be subjected to bioassays without any further treatment and can be analyzed after micro extraction with organic solvents or by headspace gas chromatography.

The fugacity of organic compounds from an aquous sample depends upon the physico-chemical properties of the sample such as ionic strength and dissolved organic carbon. Therefore, the reliability of the approach was tested using two leachates with different properties (Table 1). Sample I represents leachate with high conductivity and high content of dissolved organic carbon (DOC). The conductivity of sample II is seven times lower, the DOC sixty times.

Table 1: Properties of the leachates

Leachate	I	II
Conductivity	64 mS/cm	9.2 mS/cm
DOC	1300 mg/L	22 mg/L

Both leachates have been spiked with a mixture of organic compounds with Henry's law constants between 0.0018 and 1.26 (Table 2) and destilled for 6 hours. Every 30 min a sample of aqueous destillate was taken from the upper reservoir through a septum, using a gas tight 100-µL-syringe. It was injected through a septum into a 2-mL-vial containing 1 mL hexane with bromotrichloromethane as internal standard. After 1 min micro extraction using a Vortex-mixer, the supernatant hexane was analyzed by GC/ECD under the following conditions:

GC:	Gas chromatograph (HP 5890)
Detector:	ECD, constant current mode (280°C)
Column:	30 m * 0.53 mm coated with trifluoro propyl silicone (VOCOL), 3 µm film thickness
Carrier gas:	nitrogen, linear gas velocity (5.9 mL/min)
Temperature programme:	50°C (7 min) - 15°C/min - 90°C (2 min) - 15°C/min - 160°C
Injection:	splitless (250°C)

The distillation rate over time t was calculated according to the equation

$$y = a * (1 - \exp(-b * t))$$

using the statistic program SAS (SAS Institute Inc., Cary, North Carolina). The constant b was used for determination at which time 95 % of the equilibrium concentrations in the distillate is reached.

Table 2: Compounds used for the evaluation of the destillation method

	Compound	**Henry's law constant (20-25°C)** [1]	**Molecular weight**
a	**1,1-Dichloroethylene**	1.26	96.94
b	**1,1,1-Trichloroethane**	0.91	133.42
c	**Tetrachloroethylene**	0.83	165.82
d	**Trichloroethylene**	0.34	131.40
e	**Trichloromethane**	0.12	119.39
f	**1,1,2-Trichloroethane**	0.029	133.42
g	**1,1,2,2-Tetrachloroethane**	0.01	167.86
h	**ortho-Chloronitrobenzene**	0.0018	157.56

1) Henry's law constants from R*IPPEN (1995)*

Results

As shown in Figure 2 for leachate I and 8 compounds (Table 2) with Henry's law constants from 0.0018 to 1.26 (20 °C), the equilibrium concentration of more than 95 % is reached within 2 hours for substances with H larger than 0.01. The equilibration times do not differ significantly for these compounds. For ortho-chloronitrobenzene (H = 0.0018) equilibration is a much slower process.

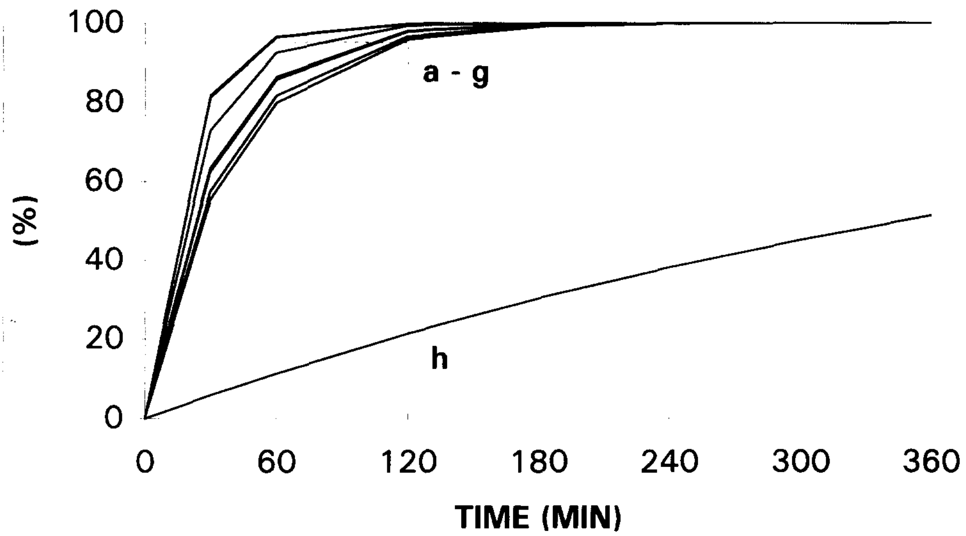

Figure 2: Time courses for the concentrations of 8 chemicals in the distillate of leachate I. For abbreviations see Table 2.

The transfer from the lower to the upper reservoir for less volatile compounds decreases strongly with H so that those do not reach the test solution in significant amounts within 2 hours. Compounds with 0.001 < H < 0.01 are not very common in landfill leachates, so that codistillation of these compounds does not create a great disadvantage.

Considering the t(95%) values and their 95 %-confidence intervals (Table 3), no significant differences in t(95%) between the leachates I and II can be seen despite their different composition. Therefore, applicability of this method for a wide range of leachates may be assumed.

As shown in Figure 3, the concentration factors depend on the volatility of the compound. With H increasing from 0.01 to 1.26, the concentration factors decrease from almost tenfold to approximatively five-fold. This is due to the increasing fraction remaining in gas phase. The compounds a to g do not exhibit any significant differences between the concentration factors after 120 and 360 minutes.

Table 3: Equilibration parameters for eight compounds and the leachates I and II

		I		II	
	Compound	**b(min^{-1})**	**t(95%) (min)** [1]	**b(min^{-1})**	**t(95%) (min)** [1]
a	**1,1-Dichloroethylene**	**0.057**	**53**	**0.042**	**72** *(48 - 140)*
b	**1,1,1-Trichloroethane**	**0.043**	**69** *(47 - 130)*	**0.039**	**77** *(50 - 170)*
c	**Tetrachloroethylene**	**0.033**	**92** *(63 - 170)*	**0.039**	**77** *(48 - 190)*
d	**Trichloroethylene**	**0.027**	**110** *(98 - 130)*	**0.046**	**65** *(47 - 100)*
e	**Trichloromethane**	**0.056**	**54** *(30 - 300)*	**0.040**	**75** *(56 - 110)*
f	**1,1,2-Trichloroethane**	**0.028**	**110** *(80 - 150)*	**0.028**	**110** *(79 - 160)*
g	**1,1,2,2-Tetrachloroethane**	**0.033**	**90** *(58 - 200)*	**n.d.**	**n.d.**
h	**ortho-Chloronitrobenzene**	**0.0020**	**1500** *(1100 - 2500)*	**0.0024**	**1250** *(970 - 1800)*

1) 95 %-Confidence intervals in brackets

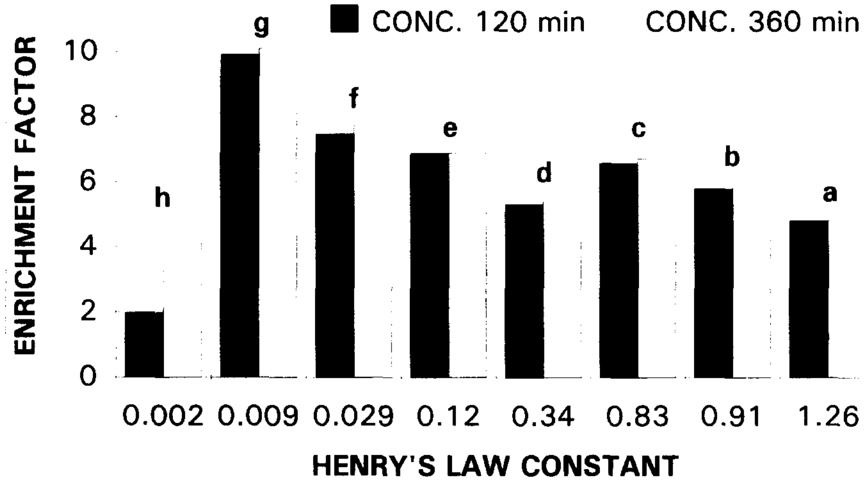

Figure 3: Enrichment factors in leachate I after 120 and 360 min as a function of Henry's law constant. The letters represent the compounds from table 2.

In Table 4, the optimized parameters for the separation of the volatile fraction from landfill leachates by destillation are summarized.

Table 4: Distillation parameters

Principle	Destillation		
Duration	120 min		
Distilled compounds	Compounds with H $\geq$ 0.01 and small amounts of compounds with lower volatility		
Enrichment factors	5 to > 9		
Lower reservoir	Leachate	**Upper reservoir**	dest. water
Temperature	60 °C	**Temperature**	2 °C
Volume	1000 mL	**Volume**	100 mL
Stirring velocity	500 rpm	**Stirring velocity**	100 rpm

Conclusions

The method presented in this paper allows the bioassay-directed separation of volatile fractions from complex aquous environmental samples. These fractions contain compounds with Henry's law constants of higher than about 0.01 (20°C). Compounds with H lower than 0.01 are codistilled to a small extent. Enrichment of volatile compounds up to 1000 % may be achieved, depending on the volumes of the liquid phases. A somewhat lower enrichment of compounds with increasing H is the only disadvantage. Organic solvents which are not compatible with bioassays are completely avoided. The resulting distillate can be directly investigated using bioassays and chemical analysis.

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