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Emission of Volatile Organic Compounds to the Atmosphere in the Solvent Sublation Process. II. Volatile Chlorinated Organic Compounds

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ABSTRACT

The mass of trichloroethylene, chlorobenzene, and 1,3-dichlorobenzene removed from an aqueous solution and emitted to the atmosphere during solvent sublation was determined experimentally. It was shown that the emission of these compounds in solvent sublation was reduced by 30 to 85% over air stripping under the same experimental conditions. The efficiency of removal of these compounds from water was also studied. The reduction of emissions over air stripping was more effective for the more hydrophobic and less volatile compounds. Emissions are reduced as the thickness of organic layer on the top of the column is increased. The use of decyl alcohol as the layer compound decreases emissions to a greater extent than does paraffin oil. Removal of these chlorinated volatile organic compounds from water by solvent sublation at an elevated temperature of 45°C is significantly faster than at room temperature. However, the emissions to the atmosphere are also increased.

INTRODUCTION

Solvent sublation, also called flotoextraction, is a process designed to remove dissolved or dispersed hydrophobic organic compounds from water more efficiently than conventional air stripping (1, 2). In this process, contaminants are transported both on the surface of air bubbles and in their interior. The removed material is deposited in a thin overlying layer of an immiscible organic liquid, such as paraffin oil. The only difference between solvent sublation and air stripping is the presence of this layer at the top of the stripping column.

Solvent sublation has been investigated for the removal of various toxic chlorinated organic compounds from water solutions. These include methyl chloroform (3), chlorobenzene (4), 1,4- and 1,2-dichlorobenzene (4, 6), heptachlor and hydroxychlordene (7), hexachlorobutadiene (8), 2,4,6-trichlorophenol (6, 8, 9), 2,3,6-trichloroanisole (6), Arochlor 1254, a commercial PCB mixture (5), pentachlorophenol (6, 9–11), and chlorinated organic pesticides *p,p'*-DDT (4), endrin, and lindane (5).

The effectiveness of solvent sublation and air stripping have been compared (4, 6–8). Both processes remove very volatile and hydrophobic compounds, those with a higher Henry's law constant more rapidly than more soluble and less volatile ones. However, solvent sublation is more effective than air stripping for the removal of less volatile compounds such as trichlorobenzene, pentachlorophenol, and some chlorinated pesticides (4–7). With more volatile compounds the primary mechanism for transport of the contaminants is in the interior of the bubbles. Therefore, there is less improvement in the removal efficiency when solvent sublation is compared to air stripping for these compounds.

The other important advantage of solvent sublation over air stripping is the reduction in emissions of volatile organic compounds (VOCs) to the air during the process. Experimental data including determination of both the mass of pollutant removed from the water and that emitted to the air have been absent from the literature for a long time. We recently submitted experimental results including the determination of toluene concentrations in both aqueous and gaseous phases during solvent sublation (12). On the basis of these experiments, it was shown that the amount of toluene emitted to the atmosphere during solvent sublation is 34–82% less than that released by air stripping under the same experimental conditions. Emission is reduced as the thickness of the organic layer is increased and as the air flow decreases. When decyl alcohol is used as the overlying layer, the efficiency is improved when compared to paraffin oil.

The objective of this study was to determine the atmospheric emissions of some chlorinated VOCs during solvent sublation and to compare these with the emissions from air stripping. The efficiency of removal of these compounds from water was also determined. Compound concentrations in both the air and water phases during both air stripping and solvent sublation were measured and compared at intervals during the process under the same experimental conditions. Three chlorinated VOCs were selected as test compounds: trichloroethylene, chlorobenzene, and 1,3-dichlorobenzene. The physical and chemical properties important for sol-

TABLE 1
Physical and Chemical Properties of the Test Compounds

Compound	Molecular mass	bp (°C)	Density (g/mL)	Solubility in water (mg/L)	Henry's law constant	Log K_{ow}
Trichloroethylene	13.4	87.0	1.46	1000	0.42	2.42
Chlorobenzene	112.6	131.7	1.11	448	0.165	2.92
1,3-Dichlorobenzene	147.0	172.8	1.29	123	0.125	3.13

vent sublation of these compounds are presented in Table 1 (13, 14). Density, solubility and Henry's law constants are given at 20°C, and the octanol–water distribution coefficient, K_{ow}, at 25°C. In Table 1, volatility, solubility, and Henry's law constants decrease and hydrophobicity increases as one moves down the list.

It is known that the efficiency of removal of organics by air stripping is improved by elevating the temperature of the solution being stripped. A significant improvement was noted for chlorobenzene and 1,3-dichlorobenzene as the temperature was raised over the range 15 to 55°C (14). No experimental data were found in the literature on the effect of temperature changes on the solvent sublation process. In the present study, air stripping and solvent sublation experiments were carried out at 45°C and were compared with data obtained at room temperature (22°C). The emission of the stripped compounds to the air at elevated temperature was also estimated.

EXPERIMENTAL

A nearly saturated aqueous solution of 1,3-dichlorobenzene (Fluka), was prepared by overnight stirring of an excess of the compound with water. To 600 mL of this solution 60 μL of chlorobenzene and of trichloroethylene (both Fluka) were added and the solution was stirred for 2 hours. The solution was then filtered through a 0.45-μm membrane filter, and the concentrations of the target VOCs were determined by direct injection into a gas chromatograph. The chromatograph was calibrated by injection of a standard composed of the three compounds dissolved in ethyl ether. The concentrations of the solutions prepared by this method were reproducible, with VOC concentrations within a range of 5%. The solutions contained 60 mg/L of 1,3-dichlorobenzene, 80 mg/L of chlorobenzene, and 45 mg/L of trichloroethylene. These solutions were used for solvent sublation or air-stripping experiments immediately after preparation.

All experiments were carried out at an air flow of 94 mL/min. Solvent-refined paraffin oil (Ivax Ind., Inc.), and decyl alcohol (Fisher Scientific) were used as overlying layers.

A bench-scale laboratory apparatus was constructed, and a Varian 3700 gas chromatograph with FID detector was used for VOC determination in the liquid and gaseous phases. A similar apparatus was used for toluene emission experiments (12), and a diagram of the equipment is presented there. The stripping column, 60 cm tall and with an internal diameter of 3.8 cm, was constructed of glass reactor tubing. Pure compressed air was introduced through a fine glass frit into the bottom of the column. The flow was controlled by a needle valve and monitored with a calibrated rotameter. The gas emerging from the top of the column was vented until a sample was needed.

The column was fitted with a contact thermometer, and an electrical heating tape was installed around the column to maintain the water at a constant temperature during the experiment. For experiments at an elevated temperature, the column was preheated before the test solution was poured in. The solution was allowed to heat for 8–10 minutes to bring it to 45°C, at which point the stripping air was turned on and the experiment began. All the tubing delivering the gas samples from the stripping apparatus to the gas chromatograph was fabricated of stainless steel, and it was also heated to prevent adsorption of the VOC during the experiment.

For analysis of the effluent air, the gas from the top of the column was drawn through a trap chilled with isopropanol slush (−89°C). After passing through the trap, the gas flowed into a previously evacuated container and its pressure was monitored using an accurate vacuum gauge. In each run the final pressure was brought to the same value, so the sample volume was kept constant. Then the valve was turned to allow the carrier gas to sweep the sample into the GC column, and the trap was heated using a hot bath at 90°C. The column used was a 15 m, 0.54 mm ID capillary coated with a bonded methyl silicone stationary phase (Alltech). The separation was carried out at 130°C using helium carrier at 2 mL/min.

Aqueous phase samples were drawn from the lower part of the column using a syringe with a needle inserted through a rubber seal in a side port on the stripping column. The water samples were analyzed by direct injection into the GC. A 1/8-in. ID, 31 m Carbopack B 1% SP 1000 column (Supelco) was used at 170°C for the water analysis. The GC was calibrated against liquid standards made up in ether for the water analyses.

Both air and aqueous phases were analyzed in the air stripping and the solvent sublation experiments. In the case of air stripping, the total amount of each compound lost from the aqueous phase was equal to that found in the air, as there was no other mechanism for loss of VOC. By direct comparison of the peak area vs time curves obtained for each target compound in air stripping and in solvent sublation under comparable conditions, the emissions with and without the overlying layers were determined. It was, therefore, not necessary to do an absolute calibration for the gas-phase samples.

The sizes of the air bubbles at 25°C and 94 mL/min flow with paraffin oil and with decyl alcohol were estimated by comparing their diameters with the diameter of a calibrated glass capillary inserted in the column. A series of photos was made approximately in the middle of the column after the experiment had progressed for about 15 minutes. The slides were projected, the diameters of about 100 bubbles were measured, and the average was calculated.

RESULTS AND DISCUSSION

Paraffin oil is very insoluble in water. Therefore, the average bubble size for air stripping and for solvent sublation with an oil layer is identical at the same air flow rate and solute concentration. The range of air bubble diameters in our experiments was 0.1–0.8 mm and the average was 0.45 mm. When decyl alcohol was used in the overlying layer the average diameter was lower, approximately 0.35 mm. This is due to the solubility of decyl alcohol, 37 mg/L at 20°C. While the concentration of decyl alcohol in the water did not reach saturation, the amount which did dissolve lowered the surface tension and reduced the bubble size.

In our experiments the rate of VOC removal from water by either air stripping or solvent sublation was found to follow first-order kinetics.

$$\ln C/C_0 = -Kt$$

where C_0 = initial concentration in water, ppm
C = current concentration, ppm

The values of the rate constant K (min^{-1}) in both air stripping and solvent sublation at different air flows, using different thicknesses of the organic layer at the top of the column at two temperatures, are presented in Table 2.

The rate of VOC removal from water for both air stripping and solvent sublation increased with their volatility: trichloroethylene > chlorobenzene > 1,3-dichlorobenzene. There is a larger difference in removal rate constants between the two methods for the less volatile compounds. For trichloroethylene, solvent sublation does not provide any improvement

TABLE 2
Rate of Removal of Test Compounds from Water at 22°C

Overlying layer	Layer thickness (mm)	Temperature (°C)	Rate constant (10^{-4} min^{-1})		
			Trichloroethylene	Chlorobenzene	1,3-Dichlorobenzene
Air stripping	—	22	4.71	1.90	1.73
Paraffin oil	5	22	4.81	2.08	2.10
"	10	22	4.66	2.60	2.43
"	20	22	4.89	3.01	2.75
Decyl alcohol	5	22	4.88	2.29	2.01
"	10	22	4.90	2.81	2.58
"	20	22	5.09	3.32	3.03
Air stripping	—	45	—	3.33	3.34
Paraffin oil	10	45	—	4.85	4.31

in comparison with air stripping. However, for 1,3-dichlorobenzene and chlorobenzene, the enhancement of removal is significant, especially when a thicker overlying organic layer is used. When decyl alcohol is used as the layer material, the rate of removal of VOC is increased because of the smaller bubble diameter and concomitant increase in bubble surface area. In addition, the lower surface tension between the decyl alcohol and water allows the bubbles to penetrate the layer more easily.

To calculate the total emission of each test compound to the atmosphere during solvent sublation, plots of concentration in the emitted air vs time were prepared for both air stripping and solvent sublation experiments done under the same experimental conditions. The VOC peak areas from the chromatograms, which are proportional to concentration, were measured in arbitrary units and plotted against the elapsed time from the start of the air flow. Figure 1 shows, for example, plots for the concentrations of trichloroethylene in the emitted air with and without a 10-mm paraffin oil layer. The total amount of trichloroethylene emitted is calculated by integrating the area under the curve.

The area under the peak area vs time curve was divided into 15 minute time periods, and the amount emitted was calculated for each integrated time period. In Fig. 1 the shaded area (A + B) is proportional to the amount of test compound emitted to the air during 15 minutes of air stripping. From the water concentration data obtained in the same experiment, the actual mass of test compound removed from water, corresponding to

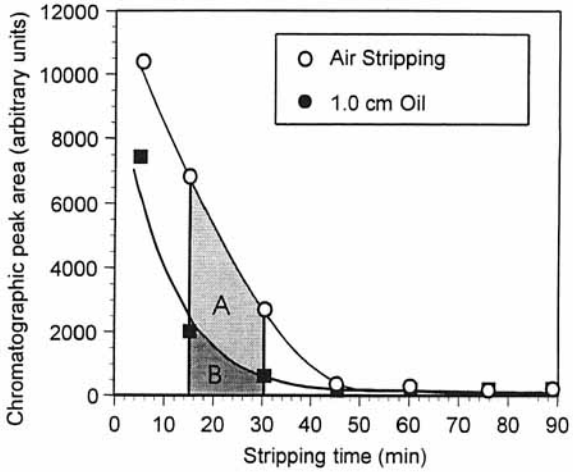

FIG. 1 Chromatographic peak areas for trichloroethylene from emitted air samples in air stripping and solvent sublation using a 10-mm paraffin oil layer.

area A + B, was determined. This is necessarily equal to the amount found in the air. The shaded area marked B is proportional to the trichloroethylene emitted under the same experimental conditions with a 10-mm paraffin oil layer present. From the ratio B/(A + B), the absolute amounts emitted in the solvent sublation experiments were calculated.

From the measured emissions for each compound during each 15 minute period, the cumulative mass was calculated and plotted vs time. From these plots the reduction of emissions when solvent sublation is used is evident. One can also calculate the amount of each VOC in the oil layer at any point from the difference between the air and water amounts. The results of these measurements and calculations for different thickness of paraffin oil and decyl alcohol layers are shown in Fig. 2 for trichloroethylene, in Fig. 3 for chlorobenzene, and in Fig. 4 for 1,3-dichlorobenzene.

The oil layer on the top of the column reduces the emission to the atmosphere of all the test compounds. Less is emitted when a thicker layer is used. The oil layer is more effective in reducing the emission of the VOCs which have lower Henry's law constants.

When the overlying layer is composed of decyl alcohol, the emissions of all tested compounds is less than those found with a similar layer of paraffin oil (Figs. 2–4). The same trend was observed in previous work

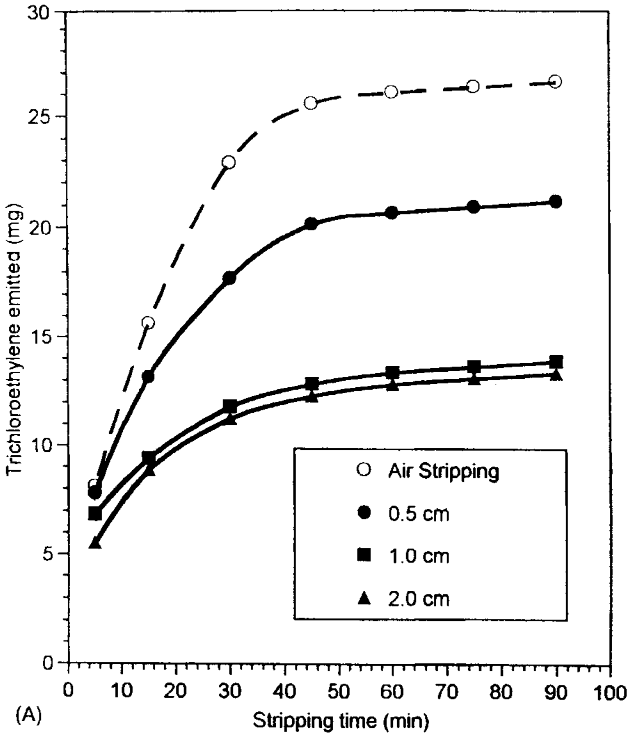

FIG. 2 Effect of layer thickness on the cumulative mass of trichloroethylene emitted during air stripping and solvent sublation using paraffin oil (A) and decyl alcohol (B).

with toluene (12). The lowered surface tension caused by the dissolution of some of the alcohol in the aqueous phase produces smaller, slower-rising bubbles, which transfer the adsorbed and included volatiles to the organic layer more efficiently. Also, the interface between the water and the layer is lower, so the bubbles penetrate more readily. When paraffin oil is used, the bubbles tend to coalesce and slide across the interface, exiting along the column wall. Despite the improvement in efficiency with decyl alcohol, the use of the less expensive and much less soluble paraffin oil may be preferable in practice.

For both the paraffin oil and decyl alcohol layers, the greatest emission reduction is found for the most hydrophobic and least volatile compounds.

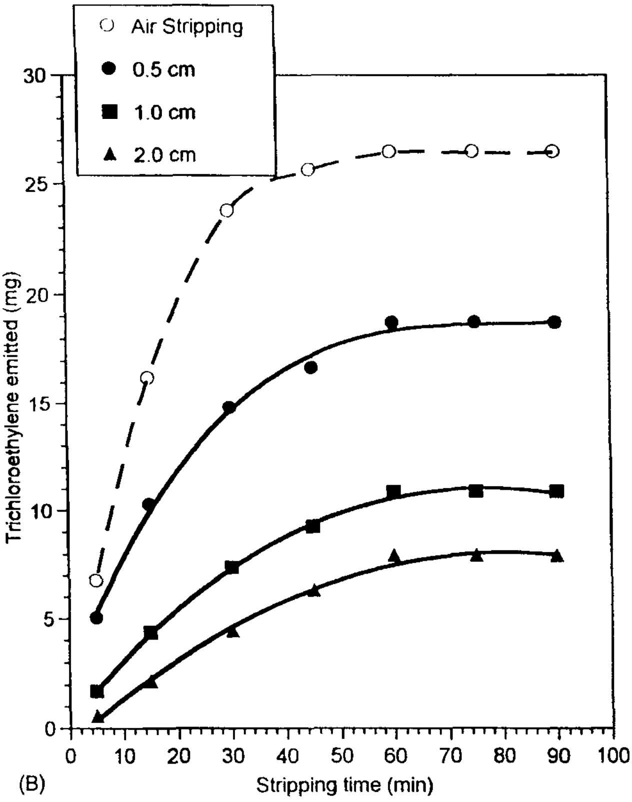

FIG. 2 Continued

Although the initial concentrations were not identical for each compound, it can be concluded that the reduction in emissions compared to air stripping is in the order 1,3-dichlorobenzene > chlorobenzene > trichloroethylene. Therefore, for low volatility hydrophobic organic compounds, solvent sublation produces two major benefits. First, these compounds are removed from water more quickly and more efficiently than in air stripping, and second, emission to the air is greatly reduced.

Solvent sublation with a 10-cm paraffin oil layer and air stripping were also carried out at 45°C. Rate constants for the removal of chlorobenzene and 1,3-dichlorobenzene are shown in Table 2. Reliable results were not obtained for trichloroethylene because a significant fraction of this com-

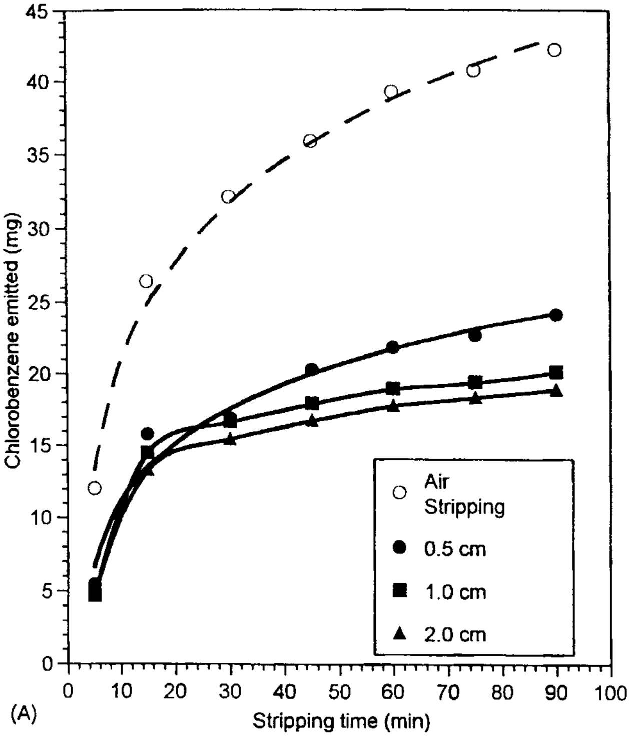

FIG. 3 Effect of layer thickness on the cumulative mass of chlorobenzene emitted during air stripping and solvent sublation using paraffin oil (A) and decyl alcohol (B).

pound was lost during the preheating of the solution, before stripping began.

In Fig. 5 the kinetics of removal of 1,3-dichlorobenzene from water are shown at the two temperatures. It is evident that the elevated temperature dramatically increases the removal of these chlorinated VOCs from water. Removal of these same compounds was studied by air stripping from packed columns, and similar improvements were observed as temperatures were raised (14). It is also remarkable that solvent sublation at the higher temperature still improves the removal rate compared to air stripping to approximately the same extent as it did at 22°C.

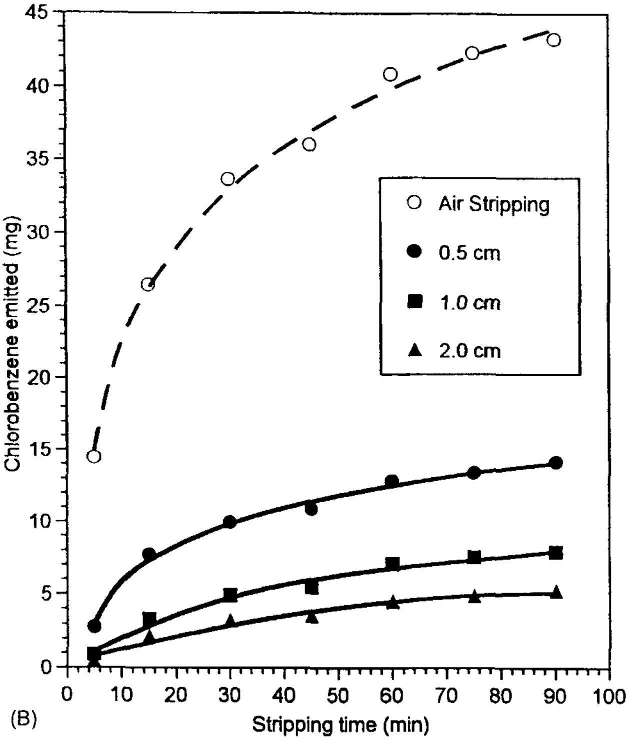

FIG. 3 Continued

The percent reduction in the emitted quantity of the compounds during 90 minutes of solvent sublation compared to that under identical conditions with air stripping for all the experiments carried out in this study are shown in Table 3.

The reduction of emissions to the atmosphere in solvent sublation with a 10-mm layer of paraffin oil for the two compounds was not as efficient at the higher temperature as it was at room temperature. It appears that the compounds are less easily absorbed in the oil layer at the higher temperature, or that they are more readily revolatilized from the layer as the air passes through.

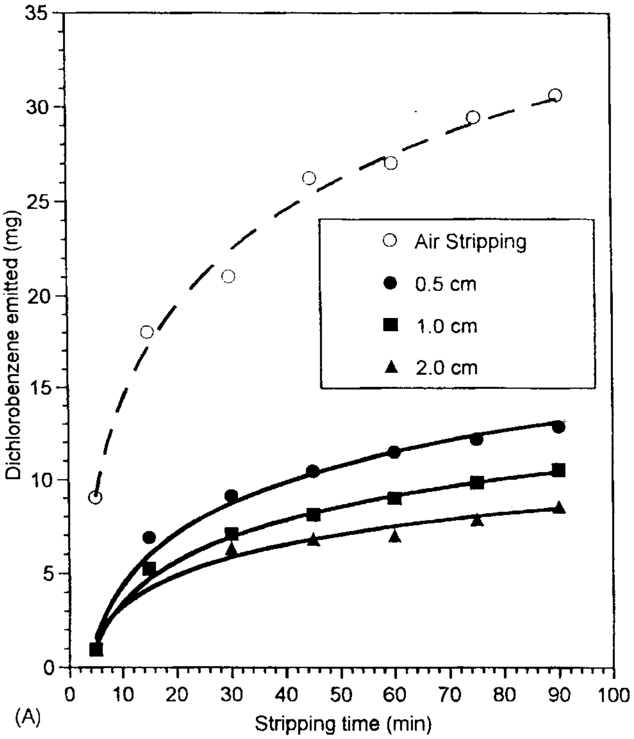

FIG. 4 Effect of layer thickness on the cumulative mass of 1,3-dichlorobenzene emitted during air stripping and solvent sublation using paraffin oil (A) and decyl alcohol (B).

TABLE 3
The Reduction of Emission of Chlorinated VOC to the Atmosphere in Comparison with Air Stripping under the Same Conditions

Layer composition	Temperature (°C)	% Reduction in emission Trichloroethylene	Chlorobenzene	1,3-Dichlorobenzene
5 mm paraffin oil	22	22	45	57
10 mm paraffin oil	22	45	53	66
20 mm paraffin oil	22	49	56	73
5 mm decyl alcohol	22	30	66	80
10 mm decyl alcohol	22	57	87	86
20 mm decyl alcohol	22	69	87	89
10 mm paraffin oil	45	—	43	41

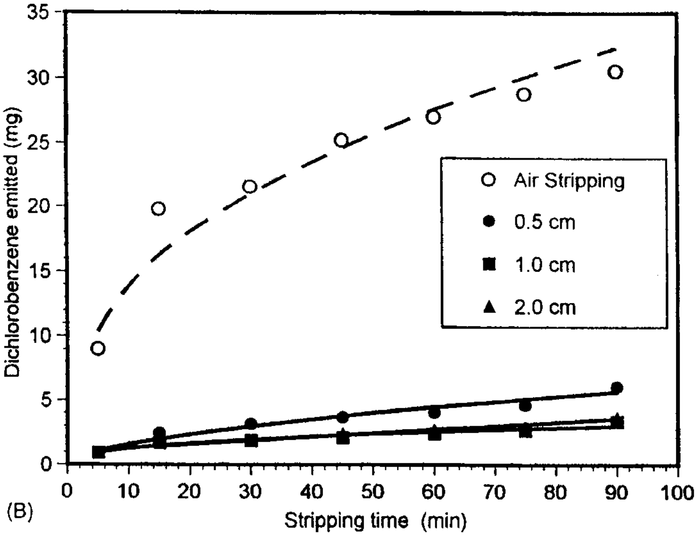

FIG. 4 Continued.

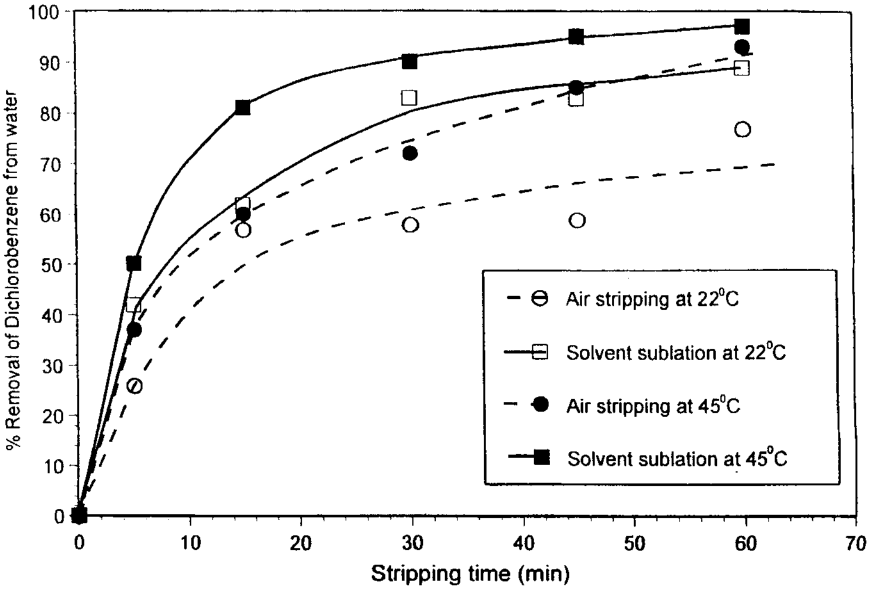

FIG. 5 Effect of layer thickness on the cumulative mass of trichloroethylene (A), chlorobenzene (B), and 1,3-dichlorobenzene (C) emitted during air stripping and solvent sublation using paraffin oil at 22 and 45°C.

The data presented here are a first attempt to evaluate the effect of temperature on the removal of VOC from water and their emission to the atmosphere in solvent sublation. Additional experiments at a series of different temperatures and different thicknesses of overlying organic layer are needed before more general conclusions can be drawn.

CONCLUSION

Solvent sublation can significantly reduce the emission of chlorinated volatile organic compounds in comparison with air stripping under identical conditions. Depending on the nature and the thickness of the overlying layer, emissions of the test compounds to the air, at ambient temperature, were reduced by 22–69% for trichloroethylene, 45–87% for chlorobenzene, and 57–89% for 1,3-dichlorobenzene.

The advantages of solvent sublation over air stripping increase for compounds with lower Henry's law constants both from the water treatment and emission reduction points of view. Emission reduction also increases with the thickness of the overlying layer. Decyl alcohol gives improved results over paraffin oil. The removal of the tested compounds by both solvent sublation and air stripping was significantly improved at a higher temperature.

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