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Recovery of Trace Organic Chemicals from a Large Mass of Water Using a Newly Developed Liquid-Liquid Continuous Extractor

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Recovery of trace chemicals from a large mass of water is one of the most important analytical procedures done by environmental chemists. Trapping on an adsorbent, such as Amberlite XAD resins, and extraction with an organic solvent are the most commonly used methods. For example, Burnham et al. (1972) enriched some organic compounds from potable water using macroreticular resins, Amberlite XAD resins. The Amberlite XAD resins efficiently adsorb certain chemicals, but reextraction from the filter material often gives poor recovery due to contamination with unknown materials such as fatty substances, inorganic chemicals, and certain polymers (Ahling and Jensen 1970). More recently, a convenient and disposable C-18 solid-phase extraction cartridge has been made commercially available. For example, using these cartridges, certain herbicides such as atrazine, alachlor, and methoxychlor were satisfactorily recovered from a large mass of water from the Great Lakes (Schottler and Eisenreich 1994). However, use of these cartridges has some drawbacks. Water containing particulates can plug a cartridge in a short time, and require a high-pressure water pump to draw the water sample through. If a cartridge is used for a prolonged length of time, solid-phase materials (styrene polymers) begin to breakdown. These breakdown products significantly interfere with gas chromatographic analysis when a flame ionization detector is used

Batch or continuous solvent extraction methods have also been developed to recover trace chemicals from a large mass of water. The batch methods are limited because using a large quantity of solvent introduces more contaminants upon concentration. Ahnoff and Josefsson (1974) used liquid-liquid continuous extraction to recover pesticides and PCBs from river water. They recovered ppb levels of PCBs by this method, in which water is fed into the container continuously and the extraction solvent stays in the container. The system used was complicated, and the apparatus was expensive. Once extraction begins, fresh solvent cannot be added because the system is closed. We have attempted to develop a simple liquid-liquid continuous extractor for a large mass of water. An apparatus was prepared for a solvent heavier than water because its construction is much simpler than that of an apparatus for a solvent lighter than water.

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MATERIALS AND METHODS

All standard pesticides were purchased from Chem Service Inc., West Chester, PA. Dichloromethane was bought from J. T. Baker Chemical Co., Phillipsburg, NJ. Phthalates and alkyl halogens were from Aldrich Chemical Co., Milwaukee, WI.

The first step of this study was to prepare a liquid-liquid continuous extractor capable of handling a large mass of water. The apparatus was prepared as shown in Figure 1. The procedure is as follows: Dichloromethane (300 mL) is poured into a boiling flask and sample water (2 L) is placed in the extractor. The solvent refluxes up the side arm, is condensed, and drops through the sample where extraction occurs. The condenser temperature is kept at 10 °C by a Brinkman RM6 constant-temperature water circulator. The solvent stream carries the extracted sample to the boiling flask. The sample is thus continuously extracted with fresh solvent and the extract accumulates in the boiling flask over time. After a certain time, stop cocks A and D are closed and B is opened; the used water sample is drained by opening stop cock C. After draining, C is closed and a fresh water sample is placed in the apparatus through B; B is closed and A and D are opened. The extraction starts again at this point. If a lower reflux temperature is desired, this system is easily placed under reduced pressure by attaching a vacuum outlet at the top of the condenser. If A and D are closed, the vacuum can be released by opening B without disturbing the boiling system of the solvent. Then the water sample can be changed using C and B.

Aqueous parathion solution (100 ppt) was prepared by spiking 2 µg of standard parathion into 20 L of tap water. Part of this sample (2 L) was placed in the extractor and extraction with 300 mL of dichloromethane was conducted over various periods of time (2, 6, 12, 24, and 48 hr). The extract was dried over anhydrous sodium sulfate for 12 hr. After removal of the sodium sulfate, the solvent was evaporated using a Kuderna-Danish evaporator under reduced pressure (50 mm/Hg). Further concentration of the sample was performed under a nitrogen stream until the volume of the sample became exactly 1 mL. Quantitative analysis was done by a gas chromatographic method (Ettre 1967) with nonadecane as an internal standard. The experiment was repeated three times.

Using this apparatus, the chemicals shown in Table 2 were tested for their recovery efficiencies from water. A 20 L aqueous solution containing 10 ppt of each chemical was prepared. Each batch of sample (2 L) was extracted for a 24 hr period so that the entire sample (20 L) was extracted in ten days. The analysis was done in the same manner as the parathion experiments. The experiment was repeated three times.

Water samples were collected from the Sacramento River, Sacramento County, California on December 10, 1993, from Putah Creek, Yolo County, California on November 26, 1993, and from Clear Lake, California on April 5, 1994. The water samples (10 L) were extracted with 300 mL of dichloromethane using this extractor for 12 hr per 2 L portions for 5 times (10 L total). The extracts were dried over anhydrous sodium sulfate for 12 hr. The solvent was removed using a Kuderna Danish evaporator under reduced pressure and further concentration was performed with a nitrogen stream.

Identification of chemicals recovered from water samples was made by comparison of their Kovat's gas chromatographic retention indices and mass spectra to those of authentic compounds. For some compounds, authentic samples were not available

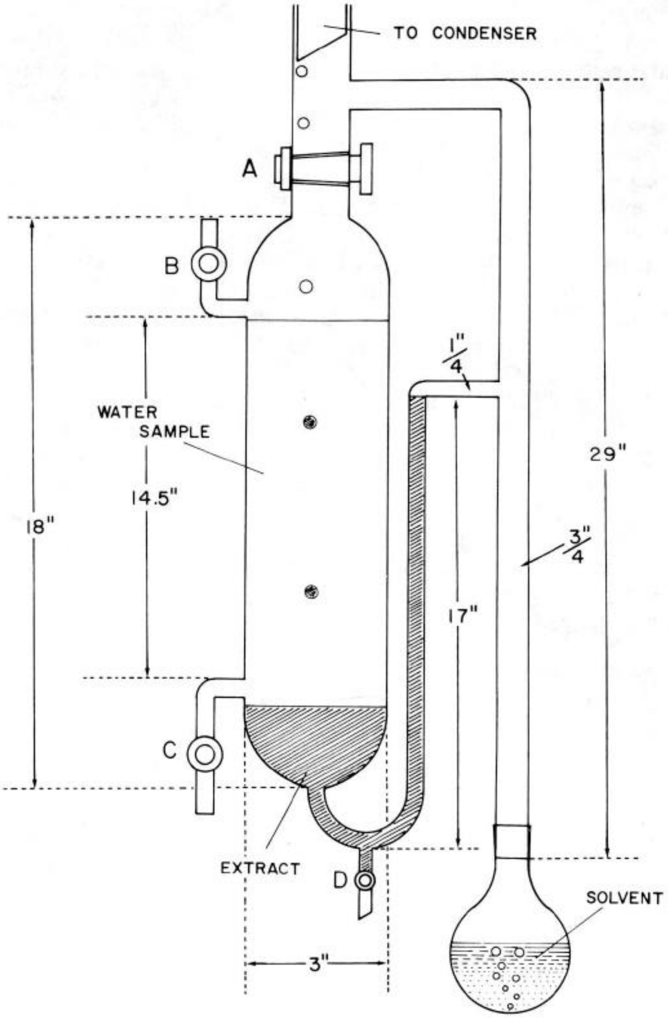

Figure 1. A liquid-liquid continuous extractor prepared for a large mass of water

to confirm positive identification. If the mass spectrum matched precisely that of published data and the retention time could be estimated from the published data, the compound was listed as tentatively identified

A Hewlett-Packard Model 5890A gas chromatograph (GC) equipped with flame ionization detector (FID) and a 30 X 0.25 mm i.d. DB-1 bonded-phase fused-silica capillary column (J & W Scientific, Folsom, CA) was used. The column temperature was programmed from 70 to 230 °C at 4 °C/min. The linear velocity of the helium carrier gas was 30 cm/sec with a split ratio of 1:30. The injector temperature was 250 °C and the detector temperature was 300 °C.

Hewlett-Packard Model 5971A Mass Selective Detector interfaced to a HP 5890 Series II GC equipped with a 30 m X 0.25 mm i.d. (df = 0.25 µm) bonded-phase DB-1 fused-silica capillary column was used to identify organic chemicals recovered from the water samples. The GC oven conditions were the same as that described above. Splitless injection was used.

RESULTS AND DISCUSSION

Dichloromethane (300 mL) was refluxed alone for 120 hr and condensed to 1 mL in volume. The gas chromatogram of condensed dichloromethane showed no peaks which might interfere with the peaks of the chemicals used. This gas chromatogram was used as a blank for all experiments.

Table 1 shows the recovery efficiencies of parathion from water at the level of 10 ppt over different periods of extraction time. The values are mean & standard deviation (n = 3).

Table 1. The recovery efficiencies of parathion from 2 L of water (100 ppt).

Extraction time (hr)	Recovery (%)
2	10.1 ± 1.2
6	16.3 ± 2.5
12	76.8 ± 4.3
24	93.5 ± 4.7
48	94.7 ± 12.4

Parathion can be recovered at over 75% efficiency with a 12 hr extraction and over 90% with a 24 hr extraction. If the recovery was 90%, a 300 mL dichloromethane extract would contain 0.18 µg of parathion. This sample can be condensed to exactly 1 mL and 1 µL of this solution injected into a GC at a split ratio of 1:30. Therefore, the calculated amount of parathion reaching the detector would be 6 ng, an amount detectable by an FID. The amount of parathion introduced to a detector can be increased by increasing the sample concentration or reducing the split ratio. Accordingly, splitless injection was used for GC/MS analysis of water samples from rivers and a lake. A nitrogen-phosphorus detector (NPD) or a flame ionization detector (FPD) can detect parathion at pg levels. Assuming 10 L of water at an extraction rate of 2 L per 24 hr (for > 90% effeciency) is necessary to recover a sufficient amount for GC and GC/MS analyses, a total of 120 hr extraction time (5 days) is required using this apparatus. This may be too long for routine analysis. However, once continuous extraction is set up, it is not necessary to observe it constantly. Moreover, because the extractor is simple, samples can be run in many extractors at the same time.

Table 2 shows the recovery efficiencies of pesticides and industrial chemicals. The values are mean ± standard deviation (n = 3).

Table 2. The recovery efficiencies of pesticides and industrial chemicals from 20 L of water (10 ppt).

Chemical	Recovery (%)
Trichlorophenol	62.5 ± 4.3
Tetrachlorophenol	69.4 ± 5.7
Pentachlorophenol	74.0 ± 3.6
2,4-Dichlorophenoxyacetate	42.3 ± 7.7
Aldrin	80.0 ± 6.9
Atrazine	80.9 ± 3.7
Carbaryl	87.7 ± 3.5
Diazinon	50.0 ± 5.3
Diuron	50.0 ± 5.7
Ethion	42.7 ± 10.1
Azinphos-methyl	19.8 ± 8.2
Heptachlor	76.1 ± 7.7
Molinate	63.4 ± 7.2
Parathion	92.2 ± 7.3
Dimethyl phthalate	75.5 ± 3.4
Diethyl phthalate	80.3 ± 5.5
Di-n-butyl phthalate	98.2 ± 12.4
Dibenzyl phthalate	77.9 ± 6.3
1,2-Dichloropropane	0
Trichloroethylene	0
Ethylene dibromide	0

The pesticides atrazine, carbaryl, aldrin, and parathion were recovered at over 80% efficiency, whereas ethion, azinphos-methyl, diuron, and diazinon were recovered at less than 50%. Moderate recovery efficiencies (63-74%) were obtained in the case of chlorophenols. Widely used plasticizer phthalates were recovered satisfactorily ranging from 76% (dimethyphthalate) to 98% (Di-n-butylphthalate). Some low boiling point compounds such as chlorinated hydrocarbons could not be recovered by this apparatus. Trace amounts of these highly volatile compounds may escape from the system during the extraction or removal of the solvent.

Tables 3, 4, and 5 show compounds recovered from the Sacramento River, Putah Creek, and Clear Lake, respectively, along with their Kovats Index on DB-1. Figure 2 shows a typical gas chromatogram of an extract from Sacramento River water.

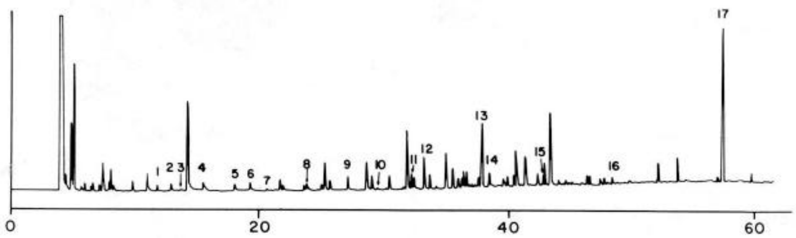

Figure 2. A typical gas chromatogram of the extract from Sacramento River water.

Table 3. Chemicals isolated from Sacramento River water.

Peak# Figure 2	Compound	Kovats Index
1	Phenol	990
2	Olefin derivate	1017
3	2-Nitropyridine	1040
4	Methyl benzyl ether	1098
5	Olefin derivate	1170
6	Benzene derivate	1188
7	Benzene derivate	1206
8	Benzene derivate	1321
9	4-Chloro-2-hydroxybenzyl mercaptan (tentative)	1369
10	2,6-Bis(1,1-dimethyl ethyl)-methylphenol	1470
11	Diethyl phthalate	1586
12	2,3-Dinitro-tetrahydro-thiapyran	1586
13	Benzyl benzoate	1744
14	2,6-Bis(1,1-dimethyl ethyl)-4-methylanisole (tentative)	1766
15	di-n-Butyl phthalate	1923
16	Dibenzyl phthalate	2160
17	Bis(2-ethyl-n-hexyl)phthalate	2513

Table 4. Chemicals isolated from Putah Creek water.

Compound	Kovats Index
Benzaldehyde	965
Phenol	989
Benzyl alcohol	1050
Olefin derivate	1097
Benzene derivate	1188
2-(Methylthio)thiophene (tentative)	1192
Benzene derivate	1321
Methyl-2-oxobenzofuran	1333
Benzene derivate	1570
Diethyl phthalate	1584
Benzene derivate	1615
Benzene derivate	1630
2-Chloro-4,6-bis(ethylamino)-s-triazine (tentative)	1690
Benzylbenzolate	1742
Chlorinated benzene derivate	1765
Methyl-4-methylbenzyl sulfide (tentative)	1776
Benzene derivate	1787
di-n-Butyl phthalate	1919
1,1,-Dichloro-2,2-bis(p-chlorophenyl)ethylene	2078
Dibenzyl phthalate	2154
di-n-Octyl phthalate	2504

Table 5. Chemicals isolated from Clear Lake water.

Compound	Kovats Index
Ethylbenzene	858
p-Xylene	863
Alkyl chloride	958
Acetophenone	1048
Alkylchloride	1317
2,4-Dimethylhenzenamide (tentative)	1435
Dodecanoic acid	1586
Diethyl phthalate	1587
Tetradecanoic acid	1786
Hexadecanoic acid	1986
Octadecanoic acid	2180
Bis(2-ethyl-n-hexyl)phthalate	2513

Pesticides were not found in any water samples. However, some benzene derivates found in Putah Creek and Sacramento River waters suggest the presence of pesticide breakdown products. The water from Clear Lake contained different chemicals from those found in the Putah Creek and Sacramento River waters. The major organic compounds isolated from the Clear Lake water were long chain fatty acids. The major contaminants in the water samples analyzed were phthalates, which have been used as plasticizers for many products such as automobile tires. For example, synthetic rubbers, such as Buna-N. G.R.S., and Neoprene, are plasticized with di-(2-ethyl hexyl) phthalate to increase their resistance to stretching. As a result of the increased use of synthetic rubber products, phthalates might be deposited into the environment in large quantities from industrial disposals. Moreover, it should be noted that great amounts of these chemicals have been released into the environment from automobile tires as they are being worn out. Phthalates have not received much attention from environmental chemists. Also, there is virtually no data on phthalate contamination in the environment. This may be due to a lack of sensitive detection methods for phthalates because they do not contain atoms such as nitrogen and phosphorus which respond to sensitive GC detectors.

Levels of chemicals present in the water samples analyzed were estimated using mass spectral ion current values. The calculated level of diethyl phthalate was 220 ppt. Accordingly, the levels of chemicals present in the water samples were roughly estimated as ranging from 10 to 1000 ppt based on the peak area of gas chromatograms. This newly developed extractor has proven to be useful in isolating ppt levels of certain organic chemicals, such as pesticides and plasticizers, from a large mass of water. Investigation and discussion of the role of the chemicals found in the present study in the environment are not within the scope of this report.

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