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Use of XAD-2 Macroreticular Resin for the Recovery of Ambient Trace Levels of Pesticides and Industrial Organic Pollutants from Water

G. A. V. Rees and L. Au

Ontario Ministry of the Environment, Pesticide Section, P. O. Box 213, Rexdale, Ontario, M9W 5L1 Canada

Recently there has been considerable increase in concern about the biological significance of ultra-trace levels of many biological control agents, and industrial pollutants such as PCBs in water. Due to high potential for bio-accumulation of many of these compounds, concentrations in water previously of little concern, and below existing analytical detection limits now require study. Given the current analytical limitations, it becomes necessary to extract large volumes of water to isolate sufficient compound for quantitative analysis.

Although liquid-liquid extraction procedures are available these are cumbersome and require transportation of large volumes of water to the laboratory. We, therefore, decided to investigate the various integrative sampling systems available, where a solid adsorbent is used in a flow-through system to extract large volumes of water. Such a system has the advantage of field, as well as laboratory applications.

ROSEN and MIDDLETON (1959) evaluated adsorption of pesticides on a filter containing activated charcoal. This method, although providing high adsorption efficiency involved several difficulties in the desorption step. Rigorous extraction with hot solvents caused losses, alteration of the chemical form of some residues, and co-extraction of interfering compounds.

UTHE et al. (1972) investigated the use of polyurethane foams for the adsorption of organochlorine pesticides and PCBs from waters and sediment suspensions. Whilst foam alone gave good recoveries for PCBs, a coating of stationary phase such as DC-200 was required to permit recovery of organochlorine pesticides.

The use of Tenax GC, a 2,6-diphenyl-p-phenylene oxide polymer for pesticide recovery from water has been documented by LEONI et al. (1976) but due to the high cost of the polymer, was not considered for our work.

Recently, JUNK et al. (1974) and MUSTY & NICKLESS (1974) have documented methods for the use of XAD resins for extracting trace levels of organic pollutants from water, using flow-through resin cartridges, solvent desorption and gas chromatographic analysis.

The work presented in this paper was undertaken with the objective of evaluating the applicability of XAD-2 resin to as

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wide a range of biological control chemicals as possible, at levels similar to those encountered in natural water bodies. Recovery data are reported for organochlorine and organophosphorus pesticides, triazine and chlorophenoxy acid herbicides, phthalate ester plasticizers and PCBs at concentrations ranging from 0.001 ppb to 50 ppb.

METHODOLOGY

All solvents were commercially distilled in glass, glass wool and Na_2SO_4 were solvent washed prior to use.

Diethyl ether was redistilled daily over metallic sodium to remove alcohol preservative.

XAD-2 Resin, 20-60 mesh, was purified by sequential extraction with methanol, acetonitrile and diethyl ether in a Soxhlet extractor for 8 h per solvent. Purified resin was stored under methanol.

Florisil, PR grade, 60-80 mesh was stored at 130°C.

Standard solutions were made up in hexane or benzene. Appropriate dilutions for fortifications were made in acetone.

Resin column was Pyrex, 1.0 x 20 cm with Teflon stopcock and 1-L integral reservoir.

Concentration flask was 250-mL r.b. flask with 10-mL graduated conical extension.

Florisil column was Pyrex, 0.6 x 20 cm with Teflon stopcock and 100-mL reservoir.

For Organochlorine pesticides the GC conditions were: Pyrex column, 190 cm x 2 mm, packed with 11% OV17/QF1 on Gas Chrom Q was operated at 215°C while the Ni 63 detector was operated at 300°C.

For Chlorophenoxy Acids: The same conditions were used except for the column temperature (170°C) while for PCBs the column packing was 3% Dexsil 300 on Chromosorb W.

For Phthalates: The flame ionization detector at 300°C was used and the column temperature programmed from 90° to 250°C at 10°/min. The packing was Carbowax 20M on Chromosorb W as described by AUE et al. (1973).

For Organophosphates: A flame photometric detector in the reversed flow mode (air:40 mL/min, oxygen:20 mL/min, hydrogen:200 mL/min) was operated at 200°C. The column (3% Dexsil 410) was programmed from 100 to 220°C at 7°/min.

For Triazines: The column packing was 6% Carbowax 20M on Chromosorb W, conditioned at 260°C. The oven temperature was programmed from 190 to 250°C at 4°/min. The AFID detector was operated at 260°C.

PROCEDURE

The resin column was set-up and the lower end plugged with glass wool. XAD-2 resin was added as a methanol slurry, until a 6 cm bed was formed. A second glass wool plug was inserted to cap off the bed. The methanol was drained until the level reached the top of the bed; then the bed was rinsed with 3 x 30 mL portions

of pre-purified distilled water in order to wash off the methanol and aid in reduction of air bubble formation.

For higher concentrations of pesticides, one L of pre-purified distilled water was added to the reservoir, fortified with the appropriate acetone solution (1 mL) swirled to mix for one min, then drained through the column at approximately 35-40 mL/min. The reservoir was then further rinsed with 30 mL pre-purified distilled water, which was also drained through the column. For lower concentrations, where 20 L of water were used, fortifying was carried out in one gallon pre-rinsed bottles as alternating supplies. Fortified water was transferred to the reservoir by syphoning through 1/8" Teflon tubing.

After all the water was passed through the resin, the bed was allowed to drain for 5 min, then absolute diethyl ether was run through the resin and collected in a 250-mL separatory funnel, until no more water was co-eluted. The column tap was then closed, and dry ether (approx. 20 mL) allowed to stand in the resin bed for approximately 10 min. This was run off and added to the contents of the separatory funnel. Equilibration was repeated with two further 20 mL portions of ether, adding each eluate to the separatory funnel.

After separation, the water in the funnel was run off and discarded. The remaining ether was dried by passing through sodium sulphate, and collected in a 250-mL concentrating flask. The extract was vacuum rotary evaporated (30°C) to 0.5 mL, blown gently to dryness, made up in hexane, and submitted for gas chromatographic analysis under the conditions mentioned previously. In the case of organochlorine pesticides and PCBs, extracts were cleaned up using a 16 cm hexane slurry packed Florisil column pre-washed with 40 mL hexane. The sample was transferred to the column then eluted with 15 mL 25% dichloromethane/hexane, containing PCBs, lindane, heptachlor, aldrin, DDT group (HCB, methoxychlor, mirex not studied), and 15 mL dichloromethane containing heptachlor epoxide, dieldrin, endrin (endosulphan not studied).

For chlorophenoxy acid recoveries, fortified solutions were acidified to pH 2, before resin extraction and concentrated eluates were methylated with diazomethane/diethyl ether prior to Florisil clean up, and gas chromatography.

RESULTS AND DISCUSSION

Results for the recovery of various groups of pesticides, herbicides, and industrial chemicals from fortified tap water are shown in Table 1 - 6.

Organochlorine Pesticides: Recoveries of 9 pesticides at levels ranging from 0.001 to 0.20 ppb are shown. Recoveries are excellent for 8 pesticides, ranging from 83-120%. The exception is aldrin, with consistently low (75-78%) recoveries, MUSTY & NICKLESS (1974) using XAD-4 resin to test the recovery of organochlorine pesticides suggested that the low recoveries of aldrin obtained were due to poor desorption from the resin.

TABLE 1

RECOVERY (%) OF ORGANOCHLORINE PESTICIDES FROM TAP WATER

Pesticide	0.20 ppb	0.10 ppb	0.02 ppb	0.01 ppb	0.002 ppb	0.001 ppb
Lindane		100±4		110±10		93±5
Heptachlor		97±2		99±5		99±10
Aldrin		78±5		78±10		77±10
Heptachlor-Epoxide	91±5	85±4	83±8	97±9	87±9	
Dieldrin	94±5	88±5	88±6	105±5	110±8	
Endrin	99±4	89±1	92±5	120±10	96±10	
ppDDE	87±4	85±5	83±6	97±1	79±10	
ppDDD	96±4		90±8	100±7	89±10	
ppDDT	92±8		95±9	95±9	105±2	

Organophosphorus Pesticides: Five organophosphorus compounds were tested with excellent recoveries (90-103%).

TABLE 2

RECOVERY (%) OF ORGANOPHOSPHORUS PESTICIDES FROM WATER

Pesticides	8 ppb	40 ppb
Dichlorvos	97 ± 5%	100 ± 0%
Chlorpyrifos	103 ± 4%	97 ± 5%
Parathion	97 ± 2%	96 ± 3%
Malathion	92 ± 4%	90 ± 1%
Ethion	101 ± 4%	96 ± 4%

S-Triazine Herbicides: At the fortification levels of 10, 50 ppb the five triazines evaluated gave good recoveries (80-95%).

TABLE 3

RECOVERY OF TRIAZINES FROM WATER

Triazines	10 ppb	50 ppb
Sencor	86 ± 2%	79 ± 2%
Prometon	95 ± 1%	94 ± 5%
Propazine	96 ± 3%	90 ± 9%
Atrazine	92 ± 4%	88 ± 8%
Simazine	90 ± 5%	86 ± 5%

Polychlorinated Biphenyls: Good recoveries at all fortification levels (down to 0.01 ppb) were obtained for Aroclor 1248 and 1260. As can be anticipated, the less water soluble 1260 is recovered with a higher efficiency (average 94%) than 1248 (average 85%). This trend was also noted on examining the distribution of PCB components in a given mixture before and after recovery.

TABLE 4

RECOVERY OF PCBs FROM TAP WATER

PCB Type	Concentration		
	1.0 ppb	0.10 ppb	0.01 ppb
Aroclor 1248	88 ± 3%	85 ± 5%	82 ± 5%
Aroclor 1260	98 ± 3%	94 ± 4%	92 ± 4%

Chlorophenoxy Acid Herbicides: Recoveries of free chlorophenoxy acid herbicides were fair, (70-85%) at 1 and 20 ppb.

TABLE 5

RECOVERY (%) OF CHLOROPHENOXY ACID HERBICIDES FROM WATER

Herbicide	20 ppb	1 ppb
2, 4-D	84 ± 5%	82 ± 6%
2, 4, 5-T	89 ± 2%	85 ± 4%
Silvex	83 ± 6%	79 ± 5%

Dialkyl Phthalate Plasticizers: Dimethyl, diethyl, dipropyl and dibutyl phthalate esters gave excellent recoveries (90-98%) in the range 10-100 ppb. However, dioctyl phthalate and dinonyl phthalate gave much lower recoveries. Further experiments indicated that whilst up to 12% of the phthalates were lost in the work-up and concentration steps, the major loss of the higher chain length compounds occurred because they were not adsorbed as dected quantitatively in the aqueous effluent from the resin column.

TABLE 6

RECOVERY OF PHTHALATES FROM WATER

Phthalates	100 ppb	200 ppb	10 ppb
Dimethyl Phthalate	93 ± 8%	94 ± 5%	90 ± 7%
Dipropyl Phthalate	94 ± 5%	98 ± 5%	90 ± 5%
Dibutyl Phthalate	85 ± 7%	98 ± 3%	91 ± 3%
Dioctyl Phthalate	44 ± 14%	31 ± 7%	23 ± 9%
Dinonyl Phthalate	41 ± 15%	24 ± 4%	14 ± 3%

Techniques used for desorption appeared to be one of the more critical operations affecting recovery. Initial recoveries were performed using diethyl ether containing 2% ethanol as preservative. This proved quite difficult to remove, and interfered with both clean up (if necessary) and GC quantitation. Daily preparation of approximately 500 mL absolute ether enabled us to reduce handling steps and improve recoveries.

The equilibration of the ether with the resin was originally performed immediately after draining the water from the column. This gave low recoveries, especially for PCBs. Elution of residual water with ether prior to equilibration increased PCB recoveries by 15-20%.

CONCLUSIONS

These recovery studies have shown that ambient levels of pesticides, and related industrial materials can be recovered from water with good efficiency using small XAD-2 columns. Work with PCBs has also demonstrated that samples as large as 10 gallons may be extracted without re-elution of the compounds under study, thus permitting very low concentrations to be detected and measured.

The adsorption efficiency of the Resin was tested by running large samples (47 L) of natural river water through two successive cartridges. Individual desorption of each cartridge showed that there was no trace of carry through and the organochlorines and PCBs were completely adsorbed on the first cartridge, at levels of 3 ppt for PCBs and 0.009 ppt of pp-DDD. Thus concentrations of 0.1 ppt of PCB and 0.1 ppt of organochlorinated pesticides can be detected in natural waters. The capability of detecting such low levels of pesticides and PCBs prompted collection of large (47 L) water samples from two Ontario rivers as well as samples of suspended sediments, invertebrates, plankton and fish, to study the bio-accumulation of these compounds. While the highest residue in water was PCB at 0.05 ppb, the corresponding levels in plankton, invertebrates, suspended solids and fish were 20, 40, 400, and 1400 ppb, respectively. Similarly, bio-accumulation was found to progress up the food chain for organochlorines: ppb levels were detected in fish where the water contained only 0.001 ppt.

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