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Extraction of Pesticides from Soil Leachate Using Sorbent Disks

Kathryn L. Crepeau, Glen Walker, and Wray Winterlin

Department of Environmental Toxicology, University of California,
Davis, California 95616, USA

Solid phase extraction (SPE) which uses silica particles chemically bonded with an organic substrate has been well developed and used by many laboratories for several years. An extension of SPE has been introduced recently by enmeshing these silica particles in a inert polytetrafluroethylene matrix to provide a near physically stable sorbent disk. The sorbent disks were designed primarily for extracting organic chemicals such as priority pollutants, pesticides, phthalates and PCB's from an aqueous medium. Both C8 and C18 sorbents are available and are reported to be 8 μm diameter silica particles with an 600 nm pore size. One of the main advantages as reported by the manufacturer was the high flow rates through the disks (1-2 L/min/cm^2) which should reduce the extraction time for large volume samples. In addition, just as in other SPE methods, reduced volume of solvent is needed to recover the analyte from the sorbent disk.

Therefore, with the advantages listed above, the purpose of this study was to test the sorbent disks effectiveness as an extraction and cleanup method with soil leachate containing representative classes of pesticides. All of the six pesticides and two oxidation products studied had relatively high water solubilities.

MATERIALS AND METHODS

The pesticides used in this study were all analytical grade as supplied by the manufacturer and included a carbamate insecticide (carbofuran), a phenoxy acid herbicide (2,4-D), a substituted phenolic herbicide (dinoseb), two s-triazine herbicides (prometryn and prometon), and a organophosphorus nematicide (fenamiphos), plus its two oxidation products namely fenamiphos sulfoxide (f. sulfoxide) and fenamiphos sulfone (f. sulfone). Table 1 shows the supplier along with the water solubility and vapor pressure for each of the 6 pesticides. The ethyl acetate, acetone, and methanol used were all Baker "Resi-analyzed." The 47 mm diameter sorbent disks with C8 bonded phase used in this study were manufactured by 3-M Corporation and purchased from Analytichem International.

The leachate used in this study was prepared by eluting deionized water through a 90 mm ID coarse fritted disk funnel layered with glass wool, 1 cm of sand pre-rinsed with ethyl acetate and dried, and 4 cm of sandy loam soil covered with glass wool. The pesticides were added to the leachate to give a concentration of 1.0 ppm for each pesticide.

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*Send reprint requests to Wray Winterlin.

Table 1. Supplier, water solubility and vapor pressure for the six pesticides used.

Pesticide	Supplier	Water Solubility in ppm (°C)*	Vapor Pressure in mm Hg (°C)*
Carbofuran	Chemical Service	700 (25)	2×10^{-5} (33)
2,4-D	Dow Chemical	600 (20)	0.4 (160)
Dinoseb	Dow Chemical	52 (25)	1 (151.1)
Prometryn	Ciba-Geigy	48 (20)	1.0×10^{-6} (20)
Prometon	Ciba-Geigy	750 (20)	2.3×10^{-6} (20)
Fenamiphos	Mobay Corp.	560 (20)	4.7×10^{-5} (20)

* Water solubility and vapor pressure data was obtained from Khan (1980) except for Fenamiphos which was obtained from Mobay Corporation (1988).

Sorbent disk were used to extract the pesticides from the soil leachate. The sorbent disk was placed in the filtering apparatus and pre-washed with 10 mL of ethyl acetate, then allowed to air dry under vacuum for 5 minutes. Ten mL of methanol was added under vacuum followed by 10 mL of deionized water. To maintain conditioning of the C8 sorbent, 1.5 mL of methanol was added to the sample and mixed well. The sample leachate was then transferred to the apparatus under vacuum and the entire sample volume was extracted through the disk. Air was then pulled through for 10 minutes. The filter holder assembly was transferred to a 125 mL vacuum flask for sample elution. Ten mL of ethyl acetate was added to the filter reservoir and the vacuum slowly applied until half of the ethyl acetate had passed through the disk. The remaining ethyl acetate was allowed to stand for 1 minute before turning the vacuum back on. This process was repeated twice with a second and third 10 mL aliquot of ethyl acetate. Each 10 mL aliquot of ethyl acetate was kept separate for analysis. However, for the experiments using the centrifuge and Durapore filters only two 10 mL aliquots of ethyl acetate were used and these were combined for analysis. The extracted sample was dried over anhydrous Na_2SO_4, and transferred to a round bottom flask. A 50 μl portion of 1% OV-101 in ethyl acetate was added as a keeper to prevent loss of fenamiphos, f. sulfoxide, and derivitized 2,4-D (Peterson 1986). The samples were evaporated on a rotary evaporator just to dryness and brought up to final volumes in ethyl acetate. The samples were kept in amber vials and stored under refrigeration until analyzed.

Four methods of treating the pesticide laden leachate prior to extraction were tested, which include no treatment (unfiltered), two filtering methods, and centrifuging. The sorbent disks were also tested for their effectiveness when used two or three times.

For the first experiment, 300 mL of unfiltered leachate was extracted using the sorbent disk. The process was repeated with a second 300 mL of unfiltered leachate so the same disk was used twice. Because the clay suspensions in the leachate plugged up the disk resulting in several hours for extraction the leachate was filtered through a glass mirco fibre filter (Whatman GF/F, 5.5 cm) prior to extraction. The 300 mL portions of filtered leachate were extracted separately so the same sorbent disks was used a total of three times.

However, even the glass fibre filter did not remove all of the fine clay particles, but only those >.07 μm. Therefore, to further reduce the time for the extraction process a Dupont Sorvall RC-48 refrigerated centrifuge was used. A 100 mL sample of the soil leachate was transferred to four 30 mL Corex centrifuge tubes and centrifuged with an angular velocity of 9000 rpm at a temperature of 20°C for 3 min. Following centrifugation the solids were separated from the liquid by decanting the liquid into a 250 mL Erlenmeyer flask prior to extraction through the sorbent disk. The tubes were rinsed with 2 mL of deionized water and added to the sample. In this case the sorbent disk was used only once.

Although centrifugation was effective for reducing the time required through the sorbent disks, not everyone has the necessary equipment for handling large volumes of solutions. Therefore, one additional experiment was conducted for separating the clay particles by filtering a 300 mL portion of the leachate through a Durapore hydrophilic 0.45 μum filter. Although the clay particles also plugged up the Durapore filters slowing down the filtering process this was circumvented by using one Durapore filter per 150 mL of leachate. The total time for filtering 300 mL of leachate ranged from 20 to 40 min depending on the amount to clay in the leachate.

All pesticides except 2,4-D were analyzed on a Varian 3500 gas chromatograph equipped with a thermionic specific detector. A 5.5 m J&W DB-1701 fused silica capillary column with a 0.25 mm id and a film thickness of 0.25 μm was used with a split ratio of 1:18. The injector temperature was 250°C and the helium carrier gas had a flow rate of 3.3 mL/min. The detector was operated at 300°C with gas flows of 4 mL/min for hydrogen, 26 mL/min for helium and 176 mL/min for air. The initial oven temperature of 150°C was held for 2.9 minutes, followed by an increase of 25°C/min to 185°C which was held for 1.3 minutes, followed by an increase of 25°C/min to 210°C which was held for 2 minutes. The limit of detection for all of the pesticides was less than 1 ng.

The pesticide 2,4-D (after derivitization with diazomethane) was analyzed on a Hewlett-Packard HP-5880A gas chromatograph equipped with a Ni 63 electron capture detector. A 17.5 m J&W DB-5 fused silica capillary column with a 0.25 mm id and a film thickness of 0.25 μm was used with a split ratio of 1:18. The injector temperature was 250°C and the helium carrier gas had a flow rate of 1.6 mL/min. The detector was operated at 300°C with a nitrogen gas flow of 84 mL/min. The initial oven temperature of 165°C was held for 3.10 minutes, followed by an increase of 25°C min to a final value of 250°C which was held for 7 minutes. The limit of detection for 2,4-D was 0.05 ng.

RESULTS AND DISCUSSION

During the first experiment the leachate (unfiltered and filtered) was acidified to a pH of 2.2 prior to extraction. Prometon was not included in this experiment. The percent recoveries of the pesticides extracted from the sorbent disk are shown in Table 2. Carbofuran, dinoseb and f. sulfone gave recoveries ranging from 89 to 112% when using the disk twice with either the unfiltered or filtered leachate. However, the recovery for the other pesticides was dependent on whether the leachate was filtered. When the leachate was filtered through the glass fiber filter the recovery for prometryn improved from 50.3% to 71.8% and for fenamiphos from 51.9% to 85.9%. Clay particles in the leachate reduced the flow through the disk even under vacuum. The first extraction of 300 mL of unfiltered leachate through the sorbent disk took 2 hr, whereas, the second extraction

Table 2. Percent recovery of original concentration from 300 ml of leachate spiked at 1 ppm then filtered or left unfiltered prior to elution thru sorbent disk. Three 10 ml aliquots of ethyl acetate were used for extraction from disk.

Sample	Ten mL aliquot of ethyl acetate	Carbofuran	Dinoseb	Prometryn	2,4-D	Fenamiphos	F. Sulfoxide	F. Sulfone
Unfiltered	1	43.1	47.9	27.4	20.2	27.7	72.7	45.3
1st time	2	36.2	35.9	18.5	32.6	19.5	53.9	35.7
disk used	3	20.8	19.3	4.4	17.5	4.7	25.4	17.4
	total	100.1	103.1	50.3	70.3	51.9	152.0	98.4
	1	53.5	61.5	25.6	29.5	29.6	64.1	46.3
2nd time	2	41.2	39.2	16.3	26.6	23.5	43.5	36.7
disk used	3	8.8	6.4	1.0	2.7	ND*	13.8	9.2
	total	103.5	107.1	42.9	58.8	53.1	121.4	92.2
Filtered	1	98.6	110.9	70.1	77.9	85.9	116.5	94.6
1st time	2	0.7	0.7	1.3	0.5	ND*	1.7	1.2
disk used	3	0.3	0.4	0.4	ND*	ND*	0.3	0.3
	total	99.6	112.0	71.8	78.4	85.9	118.5	96.1
	1	44.8	51.3	36.3	20.2	28.2	68.0	43.0
2nd time	2	19.6	21.8	18.4	14.8	4.0	35.5	18.0
disk used	3	30.2	30.1	23.3	20.5	13.8	46.2	28.0
	total	94.6	103.2	78.0	55.5	46.0	149.7	89.0
	1	0.5	0.5	0.2	ND*	ND*	0.4	0.5
3rd time	2	8.2	9.6	7.3	5.8	ND*	13.1	8.8
disk used	3	27.8	35.9	29.1	20.8	17.3	49.4	30.3
	total	36.5	46.0	36.6	26.6	17.3	62.9	39.6
rinsed	1	35.4	42.7	37.1	19.2	29.2	47.3	35.2

* ND = none detected and the limit of detection for 2,4-D was < 0.05 ng and for all others < 1 ng.

of 300 mL took 16 hr. During this length of time fenamiphos was converted to its sulfoxide oxidation product as can be seen by the increased recovery of 152% for the sulfoxide in the unfiltered sample. Filtering the leachate through the glass fibre filter decreased the time to 1 hr 15 min and, although some oxidation occurred, this reduced time resulted in only limited oxidation as shown by the 118.5% recovery of f. sulfoxide. Using the disk a second time for the filtered leachate increased the time for total extraction to 3 hr and fenamiphos recovery was similar to that of the unfiltered leachate resulting in a 46.0% recovery of fenamiphos and 149.7% for f. sulfoxide. The third time the disk was used for the filtered leachate the extraction time increased to 14 hr even under vacuum and resulted in poor recoveries for all pesticides.

Desorption of the pesticides from the sorbent disks compared well with the number of times the disks were used. The first time the disk was used with filtered leachate, the pesticides recovered ranged between 71.8% for prometryn to 118.5% for f. sulfoxide in the first 10 mL of ethyl acetate (Table 2). The second and third 10 mL aliquots of ethyl acetate added only 2% or less to the total recovery. In contrast, the third time the disk was used with filtered leachate the first 10 mL eluted less than 1% of the pesticide while the largest percentage was in the third 10 mL of ethyl acetate and the total recovery of the pesticides following three elutions with ethyl acetate was low ranging between 17.3 and 62.9%. When the disk clogged with clay particles, other problems were also apparent as the ethyl acetate evaporated before it could be collected in the flask leaving a pesticide residue on the lower part of the extraction apparatus. This residue was carefully rinsed with solvent and analyzed as a separate sample. The residues listed as "rinsed" are shown at the bottom of Table 2.

Table 3. Percent recovery of original concentration from 100 mL of leachate spiked at 1 ppm and centrifuged prior to elution through sorbent disks.

Pesticide	Mean	S.D.	RSD%
Prometon	89.2	4.8	5.4
Carbofuran	96.4	1.6	1.7
Dinoseb	100.2	1.9	1.9
Prometryn	84.5	5.5	6.6
Fenamiphos	60.2	2.4	4.1
F. Sulfoxide	107.2	3.7	3.5
F. Sulfone	86.5	2.6	3.0
2,4-D	76.6	3.6	4.7

In Table 3, the mean percent recovery, standard deviations and relative standard deviations are shown for all pesticides used when the leachate was centrifuged prior to extraction. By centrifuging the leachate, the extraction time was shortened to 10 minutes for 100 mL and the pesticides recovered ranged from 60.2% for fenamiphos to 107.2% f. sulfoxide following elution with ethyl acetate. Since 2,4-D is a phenoxy acid herbicide, the leachate had to be protonated by adjusting the solution to a pH of 2.2 in order for it to be adsorbed and to complete the extraction. If the leachate was left unadjusted at pH of 5.5, 86.5% ± .5 of the 2,4-D passed through the disk without being adsorbed. However, under acidic conditions prometon becomes protonated and does not adsorb well to the sorbent disk, and fenamiphos has been observed to undergo oxidation to the sulfoxide. Therefore, prometon, fenamiphos, and the sulfoxide were run separately under neutral conditions to give the values in Table 3. It was also found that using 4:1 mixture of ethyl acetate:acetone rather than 100% ethyl acetate improved the recovery of prometon from 80.6% to 89.2% and the recovery of fenamiphos from 38.4% to 60.2%.

The recoveries indicate that all the pesticides eluted with the water rather than adsorbing to the clay particles when the leachate was centrifuged, which is not surprising since these pesticides are all water soluble at the concentrations used in this study (Table 1). Processing a 100 mL sample required 30 min. Although this may be acceptable for those having the proper equipment, not all laboratories are so equipped. Therefore, another filtering method was studied.

Table 4. Percent recovery of original concentration from 300 ml of leachate fortified at 1 ppm and filtered with Durapore hydrophilic 0.45 μm filter prior to elution through the sorbent disks.

Pesticide	Mean	S.D.	RSD%
Neutral Conditions and First Time Empore Disk Used			
Prometon	82.5	3.6	4.4
Carbofuran	83.0	3.4	4.1
Dinoseb	27.0	0.6	2.2
Dinoseb*	61.5	2.5	4.0
Prometryn	82.0	3.7	4.5
Fenamiphos	74.0	3.5	4.7
F. Sulfoxide	94.2	1.6	1.7
F. Sulfone	84.6	1.8	2.1
2,4-D*	67.3	4.2	6.3
Acidic Conditions and Second Time Empore Disk Used			
Prometon	48.6	2.6	5.4
Carbofuran	83.1	2.6	3.1
Dinoseb	80.5	2.5	3.1
Prometryn	77.3	2.1	2.7
Fenamiphos	67.2	3.5	5.3
F. Sulfoxide	101.4	6.9	6.8
F. Sulfone	83.8	3.5	4.2
2,4-D	74.3	8.8	11.8

* Leachate acidic

The Durapore filters were found to be very effective in separating the clay particles from the leachate. Extraction of 300 mL of filtered leachate through the sorbent disk required only 12 minutes. The pesticide recovery was good (Table 4) and was dependent on the pesticide and pH of the leachate. Using the best conditions for each pesticides, the amount recovered ranged from 74 to 94%.

As mentioned previously, the pH of a solution obviously effects the hydrolysis and sorption of many pesticides. As noted in Table 4, leachate fortified with 2,4-D and dinoseb had to be extracted separately under acidic conditions in order for adsorption to take place. However, since the pH can frequently effect pesticide stability, prometon, prometryn, and fenamiphos were significantly reduced in concentration under the acidic conditions resulting in recoveries of 48.6%, 77.3%, and 67.2% respectively as compared to 82.5%, 82.0% and 74.0% respectively for the non-acidified leachate. Prometon was protonated increasing its affinity for water as is evidenced by the reduced recovery. As expected, the decrease in fenamiphos resulted in a corresponding increase in f. sulfoxide due to oxidation. Carbofuran and f. sulfone do not appear to be effected by the pH of the leachate since their recoveries under both the neutral and acidic conditions were virtually identical. The values for carbofuran were 83% and 83.1% and for f. sulfone 84.6% and 83.8%.

In summary, the sorbent disks can provide a good clean-up method for leachate samples with acceptable recoveries for pesticides which have relatively high water solubilities. Small volumes of leachate may be extracted through the sorbent disks without removing the clay particles. However, for large volumes of leachate it is necessary to filter or centrifuge the sample prior to extraction. Durapore filters were found to provide the most effective way to remove the clay particles, which shortened the time for extraction and elution of the leachate while allowing for acceptable recoveries of the pesticides studied. Acidic herbicides must be treated differently be adjusting the pH of the leachate prior to extraction through the sorbent disks.

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