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Syringe Filtration as a Source of Error in Pesticide Residue Analysis in Environmental Samples

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Filtration is an essential step to remove solid particles from the soil solution or particulate matter from aqueous solution prior to the pesticide analysis. The membranes and housing of commonly used syringe microfilters are made of synthetic polymers which can potentially react, and hence may be incompatible, with some pesticides. For example polyethylene has been reported to sorb atrazine (Xing et al. 1996) and poly(isobutyl methacrylate) to sorb phenanthrene (Leboeuf and Weber 1997). While sorption of pesticides from aqueous solution onto the materials used for flasks and tubes has been fairly well documented (Topp and Smith 1992), little attention has been given to filters. General guidelines regarding membranes and filter housing are provided by the manufacturers. However, there are generally no specifications available for their suitability for use with pesticides. The objective of this study was to investigate sorption of 7 pesticides namely bifenthrin, phosalone, carbaryl, ametryn, imazethapyr, monocrotophos and dichlorvos by various syringe microfilters and to evaluate the compatibility of the filters with these pesticides.

MATERIALS AND METHODS

The specifications of the filters are given in Table 1. The seven pesticides tested in this study were ametryn (N^2-ethyl-N^4-isopropyl-6-methylthio-1,3,5-triazine-2,4-diamine), 99.3% purity; imazethapyr ((RS)-5-ethyl-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinic acid), 99% purity; carbaryl (1-naphthyl methylcarbamate), 99.8% purity; phosalone (S-6-chloro-2,3-dihydro-2-oxobenzoxazol-3-ylmethyl O,O-diethyl phosphorodithioate), 99.7% purity; bifenthrin (2-methylbiphenyl-3-ylmethyl(Z)-(1RS,3RS)-3-(2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate), 97.8% purity; monocrotophos (dimethyl(E)-1-methyl-2-(methylcarbamoyl)vinyl phosphate, 98% purity and dichlorvos (2,2-dichlorovinyl dimethyl phosphate), 99.8% purity. These pesticides represent a wide spectrum of chemical properties. Imazethapyr was purchased from Chem Service, West Chester, PA, USA; carbaryl was donated by Rhône-Poulenc Rural Australia; bifenthrin was a gift from FMC International A. G., Australia; ametryn, phosalone, dichlorvos and monocrotophos were obtained from the Pesticide Division of the Plant Protection Institute, Faisalabad, Pakistan, where these compounds were originally supplied by various international pesticide

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Table 1. Specifications of the filters tested for their suitability

No	Filter code	Membrane type	Housing material	Source/manufacturer	Diameter (mm)	Pore size (μm)
1	PTFE	Polytetrafluoroethylene	Polypropylene	Adelab Scientific, Australia	25	0.45
2	Nylon	Nylon	Polypropylene	Adelab Scientific, Australia	25	0.45
3	SS	Cellulose acetate	Polycarbonate	Schleicher and Schuell GmbH	25	0.45
4	SLHV	Durapore*	EASTAR**	Millipore, Australia Pty, Ltd.	25	0.45
5	RC	Regenerated cellulose	Polypropylene	Sartorius Australia Pty, Ltd	25	0.45
6	B101	316 stainless steel	Polypropylene	US Upchurch Scientfic, USA	3	0.50
7	SLS Frit	316 stainless steel	Stainless steel holder	Adelab Scientific, Australia	25.4	0.50
8	Polypure	Polypropylene	Polypropylene	Alltech, Australia	13	0.45
9	AGS	Nylon	Polypropylene	Adelab Scientific, Australia	25	0.45

*Durapore is a trademark of Millipore Corporation or affiliated company.
**EASTAR is a trademark of Eastman Chemical Company.

marketing companies.

Because of the low aqueous solubilities of most of the pesticides studied, pesticide stock solutions had to be prepared in a suitable organic solvent. Stock solutions of each of all compounds except bifenthrin containing 1000 μg mL^{-1} were prepared separately in methanol. Bifenthrin stock solution containing 1000 μg mL^{-1} was prepared in acetone due to its very low solubility in water and methanol. Aliquots of 200 μL of stock solution of each pesticide were taken into 100 mL volumetric flasks, evaporated the solvent to just dryness under very gentle stream of nitrogen and volume was made with Milli-Q water with the help of ultrasonic agitation to obtain a target concentrations of 2 μg mL^{-1}. Aqueous bifenthrin solution was prepared containing 0.5% v/v acetone owing to its low aqueous solubility.

Aliquots (~1 mL) of each pesticide in aqueous solution were filtered through the various syringe filters directly into HPLC autosampler vials using Hamilton gastight glass syringes. Unfiltered samples were used as references. The determinations were done in triplicate. The samples were analyzed for the pesticides immediately after filtration using a high performance liquid chromatograph (Waters Chromatography Division) equipped with a variable wavelength UV detector (Lambda-Max Model 481), a degasser (Model ERC-3310, ERMA Optical Works, Tokyo), an HPLC pump (Model 510) and an autosampler (Model 710B WISP). The mobile phase compositions were acetonitrile:water (85:15) for bifenthrin; acetonitrile:water (70:30) for phosalone; acetonitrile:water (35:65) for carbaryl, ametryn and dichlorvos; methanol:water:acetic acid (40:60:0.5%) for imazethapyr and methanol:water (25:75) for monocrotophos. The wavelengths used were 220 nm for carbaryl, ametryn and monocrotophos, 205 nm for bifenthrin, phosalone and dichlorvos and 254 nm for imazethapyr. The pesticides were separated on a Waters Radial-pack C18 cartridge (100 mm × 5.0 mm ID, 4 μm particle size) using isocratic elution at a flow rate of 1 mL min^{-1} with injection volume of 15 μL. A Nova-pack guard column (Waters) was used as a precolumn. Data were processed using the Millennium^{TM} Chromatography Manager (Version 2.1). The sorption by filters was calculated from the concentration difference between the reference and filtered solutions. Selective filters after use were extracted for the sorbed bifenthrin, phosalone and carbryl onto the membrane and/or housing of the syringe filters by passing 5×2 mL methanol (acetone for bifenthrin), concentrated and determined for the respective pesticide.

RESULTS AND DISCUSSION

It is evident from the Table 2 that there were significant losses of pesticides from the solutions during filtration. The decrease in solution concentration was due to sorption on the filter membrane and/or housing material, as almost complete recoveries of bifenthrin, phosalone and carbaryl from the selective filters were obtained (data not shown). As the membrane and housing of each syringe filter was used as one sealed unit, it was not possible to distinguish between proportions of the pesticides retained on the membrane and housing separately. The loss through sorption by filters was in the order of SLVH (95%) > SS (87%) > AGS (82%) >

Table 2. Average loss (%) of pesticide solutions filtered through various syringe filters. Standard errors (±) are shown in parentheses, n =3.

Pesticide	PTFE*	Nylon	SS	SLVH	RC	B101	SLS-Frit	Polypure	AGS
Bifenthrin	63.8 (±4.4)	78.8 (±3.9)	87.3 (±4.3)	94.8(±2.5)	54.7 (±3.2)	0.9 (±0.4)	55.1 (±3.0)	27.6 (±2.8)	82.4 (±2.1)
Phosalone	51.2 (±1.4)	66.3 (±2.7)	75.4 (±3.7)	79.4 (±0.6)	0.2 (±0.2)	0.3 (±0.3)	10.8 (±1.7)	N.T.	N.T.
Carbaryl	10.4 (±2.1)	9.3 (±1.0)	25.1 (±1.5)	N.T.	0.3 (±0.3)	0.5 (±0.3)	0.8 (±0.3)	N.T.	N.T.
Ametryn	2.4 (±1.1)	1.1 (±0.6)	40.6 (±3.2)	N.T.	0.4 (±0.3)	0.4 (±0.2)	0.2 (±0.4)	N.T.	N.T.
Imazethapyr	0.2 (±0.2)	0.2 (±0.2)	0.3 (±0.2)	N.T.	0.2 (±0.2)	0.7 (±0.4)	0.6 (±0.9)	N.T.	N.T.
Monocrotophos	0.3 (±0.3)	0.3 (±0.2)	0.5 (±0.3)	0.3 (±0.2)	0.1 (±0.1)	2.8 (±0.3)	5.3 (±0.5)	N.T.	N.T.
Dichlorvos	N.T.	0.6 (±0.2)	12.4 (±3.3)	2.0 (±0.4)	0.7 (±0.4)	0.2 (±0.7)	1.0 (±0.6)	N.T.	N.T.

N.T. = not tested

* For types of filters see Table 1.

Nylon (79%) > PTFE (64%) > SLS-Frit (55%) = RC (55%) > Polypure (28%) > B101 (1%) for bifenthrin, SLVH (79%) > SS (75%) > Nylon (66%) > PTFE (51%) > SLS-Frit (11%) > B101 (0.3%) = RC (0.2%) for phosalone, and SS (25%) > PTFE (10%) > Nylon (9%) >SLS-Frit (1%) > B101 (0.5%) = RC (0.3%) for carbaryl. The Nylon and PTFE filters, which are very frequently used in pesticide studies, showed significant amounts of sorption of the more hydrophobic pesticides.

Irrespective of the filters used, sorption of the pesticides decreased in the order bifenthrin (95%) > phosalone (79%) > ametryn (41%) > carbaryl (25%) > dichlorvos (12%). Bifenthrin was the pesticide for which the authors observed a loss with all filters except B101. In contrast, higher efficiencies (<1% loss) were observed for imazethapyr and monocrotophos for all filters, except for some loss of monocrotophos on the stainless steel filters B101 (2.8%) and SLS-Frit (5.35%). It appeared that some decomposition of monocrotophos occurred on the steel; this was also evident from a slight corrosion of the frit. Monocrotophos has been reported to corrode stainless steel (Charles and Hance 1991) and such filters are clearly not suitable for monocrotophos. The other pesticides studied do not corrode stainless steel. The SS filter showed high sorption during filtration of aqueous solutions of dichlorvos and ametryn (the loss from solution being 12% and 41% for dichlorvos and ametryn, respectively), whereas other filters were found compatible with these chemicals. The differences in sorption by the various filters can be attributed to the different types of organic polymers used in their construction. The sorption mechanisms are unknown and beyond the scope of this study. However, the difference between the binding affinities of the pesticides may be attributed to their hydrophobicities.

The extent of sorption of pesticides by filters was greater for more hydrophobic compounds like bifenthrin (aqueous solubility, 0.1 $\mu g\ mL^{-1}$) and phosalone (aqueous solubility, 10 $\mu g\ mL^{-1}$). Bifenthrin was highly retained by the all filters tested except B101. The stainless steel frit used with a stainless steel holder gave a loss of 55% for bifenthrin, whereas the B101 syringe filter containing polypropylene housing and a stainless steel frit of the same material as that in the SLS frit (316 stainless steel) gave highest efficiency (>99%) even for highly hydrophobic compounds. Further investigation on this anomaly revealed that the stainless steel frit was heat passivated, whereas the B101 filter frit was heat passivated in the presence of hydrogen (hydrogen passivated). It is likely that the hydrogen passivation changed the characteristics of the material such that high recoveries of the pesticides were possible.

As shown in Table 1, the SS filter, which showed maximum sorptive capacity for the more hydrophobic compounds, has a cellulose acetate membrane and a polycarbonate housing. The high interaction of pesticides with the SS filter is supported by a study on sorption of pesticides to centrifuge tubes conducted by Baskaran (1994) who observed 63 and 68% sorption of phorate and terbufos from their aqueous solutions onto the polycarbonate tubes after shaking time of 4 h.

The results of this study highlight that filtration of aqueous solutions of pesticides through microfilters may be a major source of error during residue analysis of the pesticides. Choice of filters is critical and their suitability must be tested before they are used, particularly for pesticides with low aqueous solubilities.

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REFERENCES

Baskaran S (1994) Sorption and movement of ionic and non-ionic pesticides in selected soils of New Zealand. Ph. D. Dissertation, The Massey University, New Zealand

Charles RW, Hance RJ (1991) The pesticide manual. A world compendium. 9th edition. The British Crop Protection Council

Leboeuf EL, Weber Jr WJ (1997) A distributed reactivity model for sorption by soils and sediments. 8. Sorbent organic domains: Discovery of a humic acid glass transition and an argument for a polymer-based model. Environ Sci Technol 31:1697-1702

Topp E, Smith W (1992) Sorption of herbicides atrazine and metolachlor to selected plastics and silicone rubber. J Environ Qual 21:316-317

Xing B, Pignatello J J, Gigliotti B (1996) Bisolute competetive sorption between atrazine and other organic compounds in soils and model sorbent. Environ Sci Technol 30:2432-2442