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# A REVIEW OF THE EXTRACTION OF HERBICIDE RESIDUES FROM AGED SASKATCHEWAN FIELD SOILS

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Polar solvents based on aqueous methanol and aqueous acetonitrile are good extractants of herbicides from Saskatchewan field soils that had received treatments of the individual chemicals 6 to 17 months previously. The addition of small amounts of acetic acid or ammonium hydroxide to aqueous acetonitrile resulted in greater recovery of most herbicides. In general, 50 ml of the extraction solvent were added to 20 g of soil and the soils were then initially extracted for 1-hr on a wrist-action shaker and then allowed to stand overnight before being shaken for a further 1-hr period.

**KEY WORDS:** Herbicides, solvent extraction, aged residues, soils.

## INTRODUCTION

Herbicides, whether directed at the soil or growing crops, come into contact with the soil. Once present in the soil, some herbicides are rapidly degraded while others are persistent and may remain in the soil for several months, or years, after the application. When persistent residues remain in contact with field soils for prolonged periods, a phenomenon referred to as ageing, or weathering, occurs which renders them more resistant to solvent extraction<sup>1-5</sup>. This resistance to extraction can present difficulties to analysts responsible for the monitoring of herbicide residues in field soils. Although reactions that take place during ageing are poorly understood, such mechanisms as increased adsorption of the herbicide to soil colloids and a diffusion into, or reaction with, humic colloids are assumed to occur<sup>1,2,6-8</sup>.

In most laboratories, the recovery of herbicides from soils is studied by fortification of the soils with known amounts of the chemicals under test for a few hours or a few days prior to extraction. Although under such conditions, a particular extraction may recover over 90% of the applied residues, there are no means of knowing whether the recovery efficiency of the same herbicide from field soils treated several months previously will be the same. A practical approach to overcome such difficulties has been to take soil samples from a field, treated several months previously with a particular herbicide, and compare various extraction procedures selecting for routine laboratory analysis the method which extracts the greatest amount of a particular herbicide<sup>4,9-13</sup>.

In this presentation, studies are reviewed in which field plots at different locations in Saskatchewan were treated with different herbicides. Following natural weathering for 6 to 17 months, homogeneous soil samples from the plots were sampled and extracted using a variety of solvent systems and extraction procedures to determine which solvent systems and extraction procedures resulted in the greatest amounts of herbicide being recovered.

## EXPERIMENTAL

### *Chemicals*

The herbicides used in these studies included atrazine (2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine), benzoilprop acid (2-[*N*-(3,4-dichlorophenyl)benzamido]propionic acid), diclofop acid (2-[4-(2,4-dichlorophenoxy)phenoxy]propanoic acid), flumprop acid (2-[*N*-(3-chloro-4-fluorophenyl)benzamido]propionic acid), nitrofen (2,4-dichlorophenyl 4-nitrophenyl ether, picloram (4-amino-3,5,6-trichloropicolinic acid), profluralin (*N*-cyclopropylmethyl-2,6-dinitro-*N*-propyl-4-trifluoromethylaniline), simazine (2-chloro-4,6-diethylamino-1,3,5-triazine), triallate (*S*-2,3,3-trichloroallyl di-isopropylthiocarbamate) and trifluralin ( $\alpha,\alpha,\alpha$ -trifluoro-2,6-dinitro-*N,N*-dipropyl-*p*-toluidine).

The herbicides used in these studies have all been reported to be persistent in Saskatchewan soils with residues being carried over from spring applications to the following crop year<sup>14,15</sup>. In general, the observed carry-over was approximately 10 to 30% of the initially applied herbicide, depending on field moisture conditions. However, with herbicides such as nitrofen, picloram and simazine the carry-over can be higher<sup>14</sup>. Adsorption data is available for some of these herbicides in Saskatchewan soils, and mean  $K_{oc}$  values ( $\mu\text{g}$  herbicide adsorbed  $\text{g}^{-1}$  organic matter) for atrazine (64), picloram (5), triallate (1250) and trifluralin (4270) have been reported<sup>16,17</sup>.

### *Field soil treatments*

Individual commercial formulations of the herbicides were applied at a rate of about  $1.5 \text{ kg ha}^{-1}$  to bare plots at several locations in Saskatchewan during early May. Representative soil samples were removed from the top 5 cm of all treated plots 6 to 17 months later. The soils were air dried at laboratory temperature, ground and thoroughly mixed in a laboratory mixer for 20 min to ensure an even distribution of the herbicides throughout the soils. Full details of these procedures have been reported<sup>11-13</sup>. The physical characteristics of the soils are summarized in Table 1.

### *Extraction procedures*

Typical solvent systems and the extraction procedures are indicated in Tables 2, 3 and 4. Generally, replicate (2 or 3) soil samples (20 g) were weighed into 150-ml glass-stoppered flasks and shaken with their respective solvent system (50 ml) on a wrist-action shaker as required. In certain cases, the aqueous component of the

**Table 1** Composition and physical characteristics of field soils

Soil	Clay (%)	Silt (%)	Sand (%)	Organic content (%)	pH
Heavy clay	70	25	5	4.2	7.7
Sandy loam	10	25	65	4.0	7.6
Clay loam	30	40	30	11.7	6.0

**Table 2** Comparison of extraction procedures for the recovery of atrazine residues from a heavy clay field soil following weathering for 12 months (Adapted from Reference 12)<sup>a</sup>

Solvent	Extraction procedure	Recovered $\mu\text{g/g}^{-1}$
CH <sub>3</sub> CN/H <sub>2</sub> O/NH <sub>4</sub> OH (70:18:12)	Shake 0.5 hr; stand 18 hr; shake 0.5 hr	0.30
CH <sub>3</sub> OH/H <sub>2</sub> O (90:10)	Wet soil with water 18 hr; methanol reflux 2 hr	0.24
CH <sub>3</sub> OH/H <sub>2</sub> O (90:10)	Soxhlet 24 hr	0.23
CH <sub>3</sub> CN/H <sub>2</sub> O/CH <sub>3</sub> COOH (70:30:2.5)	Shake 1 hr	0.20
CH <sub>3</sub> OH/H <sub>2</sub> O (90:10)	Shake 18 hr	0.18
CH <sub>3</sub> CN/H <sub>2</sub> O (90:10)	Shake 1 hr	0.16

<sup>a</sup> Average from duplicate extractions.**Table 3** Comparison of extraction procedures for the recovery of picloram residues from a clay loam field soil following weathering for 12 months (Adapted from Reference 13)<sup>a</sup>

Solvent	Extraction procedure	Recovered $\mu\text{g/g}^{-1}$
CH <sub>3</sub> CN/H <sub>2</sub> O/NH <sub>4</sub> OH (70:18:12)	Shake 0.5 hr; stand 18 hr; shake 0.5 hr	0.93 <sup>a</sup>
CH <sub>3</sub> CN/H <sub>2</sub> O/NH <sub>4</sub> OH (70:18:12)	Shake 1 hr	0.71 <sup>b</sup>
CH <sub>3</sub> OH/H <sub>2</sub> O/NH <sub>4</sub> OH (70:18:12)	Shake 0.5 hr; stand 18 hr; shake 0.5 hr	0.47 <sup>c</sup>
CH <sub>3</sub> CN/H <sub>2</sub> O/CH <sub>3</sub> COOH (70:30:2.5)	Shake 0.5 hr; stand 18 hr; shake 0.5 hr	0.29 <sup>d</sup>
CH <sub>3</sub> OH/H <sub>2</sub> O (40:10)	Shake 1 hr	0.18 <sup>e</sup>
H <sub>2</sub> O/Ca(OH) <sub>2</sub> (50 mL:1 g)	Shake 1 hr	0.18 <sup>e</sup>
0.1N KOH/KCl (50 mL:5 g)	Shake 1 hr	0.07 <sup>f</sup>

<sup>a</sup> Average from triplicate extractions; means within a column followed by a common letter are not significantly different at the 0.05 level according to Duncan's multiple range test.

**Table 4** Comparison of extraction procedures for the recovery of triallate residues from a sand loam field soil following weathering for 12 months (Adapted from Reference 13)<sup>a</sup>

<i>Solvent</i>	<i>Extraction procedure</i>	<i>Recovered <math>\mu\text{g g}^{-1}</math></i>
CH <sub>3</sub> CN/H <sub>2</sub> O/CH <sub>3</sub> COOH (70:30:2.5)	Shake 0.5 hr; stand 18 hr; shake 0.5 hr	0.55 <sup>a</sup>
CH <sub>3</sub> OH/H <sub>2</sub> O (40:10)	Wet soil with water 18 hr; shake with CH <sub>3</sub> OH 1 hr	0.56 <sup>a</sup>
CH <sub>3</sub> CN/H <sub>2</sub> O/CH <sub>3</sub> COOH (70:30:2.5)	Wet soil with water 18 hr; shake with acidic CH <sub>3</sub> CN 1 hr	0.52 <sup>b</sup>
CH <sub>3</sub> CN/H <sub>2</sub> O/CH <sub>3</sub> COOH (70:30:2.5)	Shake 1 hr	0.52 <sup>b</sup>
CH <sub>3</sub> CN/H <sub>2</sub> O/NH <sub>4</sub> OH (70:18:12)	Shake 0.5 hr; stand 18 hr; shake 0.5 hr	0.49 <sup>c</sup>
CH <sub>3</sub> OH/H <sub>2</sub> O (40:10)	Shake 1 hr	0.45 <sup>d</sup>

<sup>a</sup> Average from triplicate extractions; means within a column followed by a common letter are not significantly different at the 0.05 level according to Duncan's multiple range test.

extractant was added to the soil 18 hr before addition of the acetonitrile or methanol and the commencement of the extraction. After extraction the slurry was centrifuged at 3500 rpm for 5 min and the supernatant (25 ml, equivalent to 10 g soil) was taken for partitioning and gas chromatographic analysis as previously described<sup>11-13</sup>. Soxhlet extractions, in duplicate, were carried out by continuously extracting soil samples (20 g) with the designated solvent system (200 ml) under reflux conditions. After the specified time, the volume of solvent remaining in the flask was measured and half the volume (equivalent to 10 g soil) taken for analysis. Full experimental details can be found elsewhere<sup>11-13</sup>.

## RESULTS AND DISCUSSION

A comparison of solvent extraction systems for herbicide residues from weathered Saskatchewan soils has been reported<sup>11-13</sup>. Some of the recovery data for atrazine, picloram and triallate from field soils one year after application are summarized in Tables 2, 3 and 4. From these and data reported from other herbicide recovery studies<sup>2,9-13</sup> certain conclusions can be drawn regarding the extraction of residues from weathered soils:

1) The solubility of a herbicide in a solvent is not a measure of its recovery. Thus although nitrofen, profluralin, triallate and trifluralin are very soluble in such solvents as acetone or a mixture of benzene and isopropanol, significantly greater amounts can be recovered using more polar solvents based on methanol or acetonitrile<sup>11-13</sup>. The polar solvents may be necessary to overcome the high soil adsorption coefficients of these herbicides.

2) It has also been noted that the addition of water to the extraction solvents results in a significant increase in herbicide recovery<sup>2,9-13</sup>. The water most probably affects desorption of the herbicides adsorbed to soil colloids<sup>18</sup>. The pre-wetting of

the soils prior to extraction did not appear to significantly increase the recovery of any of the herbicides when water was a component of the extraction solvent<sup>11-13</sup>.

3) The addition of small quantities of acetic acid to aqueous methanol or acetonitrile resulted in improved extraction of most acidic herbicides from weathered field soils, though in the case of the triazines and picloram the addition of ammonium hydroxide to the acetonitrile proved to be superior to the addition of acetic acid<sup>11-13</sup>.

4) In general, an extended shake where the soil and solvent were shaken on a wrist-action shaker for 0.5 or 1 hr before being allowed to stand overnight and receiving a further shake, resulted in significantly greater (and more reproducible) amounts of herbicides being recovered than did shorter shaking periods<sup>11-13</sup>. The extended shake also resulted in gas chromatogram traces that showed the presence of less co-extracted impurities than those obtained from soxhlet extractions. The former extraction is much simpler to carry out than the latter.

For the analysis of herbicides in soils, the extraction should be practical and reasonably simple. The above data (Tables 2, 3 and 4) and similarly reported data<sup>11-13</sup> obtained with residues from aged Saskatchewan field soils indicate that polar solvents based on methanol and/or acetonitrile consistently recover greater amounts of 10 different herbicide residues than less polar solvents. Although a universal solvent for the extraction of all herbicides from soils is still a dream, acetonitrile is a versatile extractant and with most of the 10 herbicides tested (*cf* Refs. 10, 11, 12 and Tables 2, 3 and 4) is superior to methanol based extractants. Table 5 summarizes the solvent systems used, in conjunction with the extended shaking, at the Regina Research Station for the recovery of classes of herbicides commonly used in Canada. Although the extraction of some of these herbicides has not been attempted from aged field soils, studies indicate that the recovery of such residues from air dry soils fortified several days prior to solvent extraction is satisfactory.

**Table 5** Extraction solvent systems used in conjunction with the extended shaking procedure for the recoveries of classes of herbicides from Saskatchewan soils

<i>Solvent system</i>	<i>Herbicides</i>	<i>Refs.</i>
CH <sub>3</sub> CN/H <sub>2</sub> O/NH <sub>4</sub> OH (70:18:12)	Clopyralid	19
	Picloram	13
	Phenoxypropanoic acids	20, 21, 22
CH <sub>3</sub> CN/H <sub>2</sub> O/CH <sub>3</sub> COOH (80:20:2.5)	Aliphatic acids	23
	Benzoic acids	24
	Benzonitriles	25
	Diclofop acid	13
	Diphenylethers	11
	Dinitroanilines	11, 12
	Herbicide esters	26
	Phenoxyalkanoic acids,	27, 28
	Sulfonylureas	29, 30
	Thiocarbamates	13

More studies on the comparative extraction of herbicide residues from aged field soils are necessary to determine whether similar recovery differences are experienced with weathered soils from different parts of the world. The experience with Saskatchewan soils may, to some extent, be a phenomenon of hot dry summer conditions and the long freezing winter temperatures which might result in greater extraction problems.

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