Determination of Bromacil in Groundwater and in High Organic Matter Soils

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Solid phase extraction (SPE) technology for the determination of bromacil in environmental water samples was compared with traditional liquid/liquid partitioning methods. SPE was found to be more cost effective and safer due to the use of smaller volumes of solvent. Detection of less than 0.05 μg/L of bromacil was possible with the analysis of large (1 L) samples. A practical and beneficial enhancement of the existing methods for soil extraction with aqueous sodium hydroxide, is described. Holding the extraction mixture at a temperature of 30 or 50 °C for 18 h increased the recovery of bromacil in nine of 12 soils studied, and minimized the use of solvents. The method was effective on high organic matter soils. HPLC was used for analysis of both water and soil extracts.

Keywords: *Bromacil; groundwater; soil extraction*

INTRODUCTION

Since its discovery in the early 1960s, the herbicide bromacil (5-bromo-6-methyl-3-(1-methylpropyl)-2,4-(1*H*,3*H*)-pyrimidinedione, CA; 5-bromo-3-*sec*-butyl-6-methyluracil, IUPAC) has been used in a variety of agricultural and nonagricultural situations for control of annual and perennial weeds. It has been shown to be both persistent (Gardiner *et al.*, 1969) and mobile (Smith *et al.*, 1975) in the environment, depending on soil properties and climate. Bromacil is more strongly adsorbed by organic matter than by clay particles and thus was more persistent and less mobile in soils with a high organic matter content (Rhodes *et al.*, 1970; Gerstl and Yaron, 1983a,b). Also, Webber and Best (1972) reported that bromacil was more persistent in an acid soil compared to a neutral soil.

In New Zealand bromacil is widely used for controlling weeds in asparagus (*Asparagus officinalis*) and is often applied to large areas on an annual basis. Sandy soils are usually chosen for asparagus crops and these have been reported as highly prone to leaching of bromacil with consequent groundwater contamination (Hebb and Wheeler, 1978; Zandvoort *et al.*, 1980; Gómez de Barreda *et al.*, 1991; Tucker, 1978). However most New Zealand soils are acid and have a high organic matter content (Burney *et al.*, 1975; Wells and Luke, 1968). Because of this it is unlikely that bromacil would leach.

Determination of bromacil is relatively straightforward. The chemical is usually extracted, concentrated, and then analyzed without derivatization. Solid phase extraction (SPE) methods have been successfully used for extraction and concentration of a wide range of pesticides from water (e.g. Wolkoff and Creed, 1981; Wells and Michael, 1987; Junk and Richard, 1988; Sherma, 1991) but are not without complications. For example, Johnson *et al.* (1991) demonstrated reduced recovery of bromacil from water with a high humic acid content. Gas chromatography (GC) was traditionally used for analysis of bromacil; however, more recently, high-performance liquid chromatography (HPLC) has also been used for analysis (Lawrence and Turton, 1978; Barceló, 1988; Lauren *et al.*, 1988).

Most of the extraction methods for bromacil residues in soil (Pease, 1966; Jolliffe *et al.*, 1967; Caverly and Denney, 1977; Byast *et al.*, 1977), although efficient, appear to have been developed on low organic matter soils with little reference to weathered residues. Also, some of the methods use solvents, such as chloroform (Pease, 1966; Caverly and Denney, 1977), which if possible should be avoided due to safety concerns.

Bromacil is highly soluble in polar organic solvents and alkaline aqueous solutions (Jolliffe *et al.*, 1967; Kidd and James, 1991). Therefore a wide range of solvents are available for extraction of bromacil from soil. Many factors might influence the choice of solvent such as the soil type, coextractive interferences, recovery, and quantification or the method of detection used. For example, Leistra *et al.* (1974) extracted bromacil into ethyl acetate from the soil (sandy loam and silty clay loam) and injected directly into GC.

The purpose of the work reported here was to investigate the use of SPE, compared to existing methods, for recovery of bromacil from groundwater and to establish a reliable extraction technique for New Zealand soils.

EXPERIMENTAL PROCEDURES

Apparatus and Reagents. HPLC was performed using a Shimadzu LC-6A gradient system which included an autoinjector, column oven, and a Shimadzu SPD-6A variable-wavelength UV detector. Data was collected on a CR-4AX data system. All analyses were performed on a Zorbax ODS 4.6 mm i.d. × 15 cm reversed-phase column. For some analyses a Linear 206 Programmable Hi-Speed Detector was used for multiwavelength scanning.

SPE extractions were performed using Extract-Clean C18 (500 mg × 2.8 mL) columns from Alltech Associates Inc., Deerfield, IL, unless otherwise noted when Empore C18 Extraction Disks (47 mm × 500 μm) from 3M, St. Paul, MN, were used.

Anatop syringe filters and Anatop membranes were also from Alltech Associates Inc.

Modified soxhlet extraction was performed on a Soxtec System HT6 from Tecator AB, Höganäs, Sweden.

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Table 1. Comparison of Bromacil Recovered from Spiked Water Samples[a] by Liquid/Liquid Extraction and SPE Methods

Liquid/Liquid Extraction

extraction medium	bromacil recovered[b] (%)			
	10 mL sample		100 mL sample	
	0.01 mg/L	0.1 mg/L	0.01 mg/L	0.1 mg/L
chloroform	90	93	90	98
dichloromethane	85	96	96	93
ethyl acetate	90	100	96	97
n-hexane	0	0	0	0
toluene	70	91	90	83
C18 (columns)	89	98	82	91
C18 (disks)	–[c]	–	94	97

Solid Phase Extraction

	bromacil recovered[b](%)			
	100 mL sample		1 L sample	
	0.1 μg/L	1 μg/L	0.1 μg/L	1 μg/L
C18 (columns)	89	86	–	–
C18 (disks)	–	–	95	99

[a] All extractions performed in duplicate according to the method except for dichloromethane and C18 tubes which, as the selected methods, were replicated four times. [b] Overall cv for table = 3.1%. [c] Samples not evaluated.

Bromacil, technical grade (>99%), was obtained from DuPont, Wilmington, DE.

Standard solutions of bromacil were made in methanol/water (10:90 v/v) from a stock solution of 50 mg/L in methanol/water (25:75 v/v).

All solvents were HPLC grade from Mallinckrodt or BDH. Water was glass distilled and further purified through a Millipore Milli-Q water purifier.

Soil samples containing weathered residues were obtained from field sites where bromacil had been applied at 1.6–2.0 kg/ha, 3–6 months previously. All soil samples were passed through a 2 mm sieve.

HPLC Analysis Conditions. All HPLC analyses were run isocratically using a mobile phase flow rate of 1 mL/min and a column temperature of 35 °C. The mobile phase used was methanol/water, either 52:48 (v/v) (bromacil retention time 5.7 min) for water samples (see Figure 1) or 44:56 (v/v) (retention time 9.3 min) for soil extracts (see Figures 3 and 4) where coextractive interferences occurred in some samples. Sample injection volumes from 20 to 100 μL were used. External standards of bromacil were run after every 4–8 samples. The detection wavelength was generally set at 280 nm. Where necessary, confirmation of bromacil was obtained using relative absorbance at four different wavelengths (220, 245, 265, and 280 nm) which had absorbance ratios of 1.3:0.35:0.6:1.

Water Extraction. *a. SPE.* The C18 column (or disk) was conditioned with 2 mL (10 mL) of methanol and washed with 5 mL (20 mL) of water as described by the supplier. The sample (usually 100 mL and 1 L, respectively, for columns and disks) was aspirated through the C18 medium (flow rate approximately 10 mL/min) and the eluate discarded. The C18 medium was then dried by pulling air through for 5 min before the adsorbed material was eluted with methanol (2 and 10 mL respectively for columns and disks). The methanol eluate was collected, evaporated to dryness (N_2, 35 °C), and then redissolved in 1 mL methanol/water (10:90) for HPLC analysis. Generally, 1 L samples of unpurified groundwater required prefiltering with Anodisc 47 Filter Membranes (0.2 μm) before they were passed through the disk.

b. Liquid/Liquid Partitioning. Liquid/liquid partitioning was performed with 50 and 250 mL (for 10 and 100 mL samples) separatory funnels. The water sample was extracted three times with solvent (see Table 1) (5 and 25 mL, respectively, for 10 and 100 mL water samples). The solvent fractions were combined and rotary evaporated (45 °C) to dryness, and the residue was redissolved in 1 mL of methanol/water (10:90) for HPLC analysis.

Table 2. Efficiency of Various Solvent Compositions (Methanol:Water) in Dissolving Bromacil from Dried Residue[a] Obtained after Dichloromethane Partition of Acidified Sodium Hydroxide Extract Solutions from Three "Weathered" Soil Samples

soil sample	bromacil concentration[b] (mg/L)					
	10:90	25:75	50:50	100:0	25 + 75[c]	50 + 50[d]
1A	2.25	2.43	2.61	2.67	2.70	2.64
2A	0.93	1.11	1.26	1.23	1.26	1.29
3A	3.36	3.27	4.32	4.35	4.56	4.38

[a] Several batches of soil extract were collected and thoroughly mixed before duplicate subsamples (10 mL) were taken, partitioned into dichloromethane (5 mL), and evaporated (N_2, 30 °C) before being redissolved for analysis. [b] Data was subjected to analysis of variance using soils as replicates. This analysis showed that significantly less ($P < 0.05$) bromacil was dissolved in the 10:90 and 25:75 solutions compared with the other four treatments. The cv for the duplicates = 2.7%. [c] 0.25 mL of CH_3OH used to dissolve residue followed by addition of 0.75 mL of H_2O and filtering. [d] 0.5 mL of CH_3OH used to dissolve residue followed by addition of 0.5 mL of H_2O and filtering.

c. Experiments. Detection limits for SPE extraction were determined for unpurified groundwater using C18 columns with 100 mL samples and C18 disks with 1 L samples. Comparisons of SPE extraction with conventional liquid/liquid extraction were also made using spiked samples (Table 1). Storage of environmental water samples was tested using both acidified (2 mL of 5 N hydrochloric acid/L) and nonacidified (natural pH 4.2–6.5) samples stored at 4 °C in amber glass bottles. Subsamples (100 mL) were taken for extraction after 1, 5, 9, 13, and 53 weeks.

Soil Extraction. *a. Sodium Hydroxide.* Soil samples collected from field sites where bromacil had been applied approximately 6 months earlier were used as received, or partially air dried if they contained more than 30 mL of water/50 g dry soil. In all cases soil moisture was taken into account when adding solvents. Duplicate subsamples (50 g dry weight) of soil were mixed with 100 mL of 1.5% w/v aqueous sodium hydroxide/water (70:30 v/v) in 250 mL stoppered Erlenmeyer flasks and shaken on an orbital shaker for 1 h. The samples were allowed to settle overnight at 30 °C before drawing off 10 mL of supernatant liquid for workup. The samples of extract were acidified (to pH 2–3) with 1 mL of 5 N hydrochloric acid then reextracted into dichloromethane (5 mL). The samples were vortex mixed in test tubes (1 min) and then centrifuged at 2000*g* (10 min) to separate the layers. Then 3 mL of dichloromethane was drawn off with a pipet and evaporated to dryness (N_2, 30 °C). The residues were first redissolved in 0.25 mL of methanol to which 0.75 mL of water was added and the samples centrifuged at 2000*g* (20 min) and filtered (Anatop 10, 0.2 μm syringe filters) in preparation for HPLC analysis.

b. Experiments. (i) Extractions. Several solvents were evaluated for extraction of soil samples (both freshly spiked as well as those containing weathered residues). They were methanol/water (70:30 and 20:80 v/v), 1.5% w/v aqueous sodium hydroxide/water (70:30 v/v) and methanol/1.5% w/v aqueous sodium hydroxide/water (70:20:10 v/v). Ammonium sulfate was evaluated as an additive (Jolliffe *et al.*, 1967) to facilitate the settling of the soil after shaking with aqueous sodium hydroxide. A modified soxhlet extraction (15 min boiling, 40 min rinsing, and 5 min recovery) was tested on 10 g of dry weight soil using 50 mL of methanol/water (70:30 v/v). An aliquot (10 mL) of extract solution was taken for further treatment. The sodium hydroxide soil extract samples were worked up as above. Reextraction of the methanol-based soil solution was similar except that water (10 mL) plus saturated sodium chloride solution (1 mL) was added to the methanol extract to aid the partition into dichloromethane.

(ii) Solvent for HPLC Analysis Solution. The efficiency of different methanol–water combinations for redissolving bromacil prior to analysis were evaluated (Table 2). Dried residues of bromacil were obtained for this work by evaporating aliquots of dichloromethane solution collected from the partition step.

Table 3. Comparison of Number of Dichloromethane Partition Extractions (1–4) for Recovery of Bromacil from Acidified Aqueous Sodium Hydroxide Solutions

soil sample	bromacil concentration in soil[a] (mg/kg)			
	1[b]	2[c]	3[c]	4[c]
1B	0.92	0.74	0.83	0.88
2B	0.30	0.27	0.28	0.27
3B	1.52	1.34	1.42	1.48
4	0.42	0.37	0.42	0.38
5	1.19	1.09	1.18	1.19
6	0.07	0.06	0.06	0.06

[a] Cv for duplicates = 4.0% (back transformed). [b] Workup as described in methods and corrected for proportion of dichloromethane recovered from partition for evaporation. [c] For multiple extractions the total of each dichloromethane layer was collected and combined for subsequent evaporation and analysis.

(iii) Partition. The use of single and repeated dichloromethane partition extractions for recovery of bromacil from acidified aqueous sodium hydroxide solutions were compared (Table 3). For the single extraction the workup is as described and final concentrations were corrected for the proportion of dichloromethane recovered (3 mL) compared to that added (5 mL). For the multiple extractions, as much dichloromethane as possible was collected after each partitioning, and the combined extracts were then evaporated and redissolved for analyses. No correction factor was applied to these results.

(iv) Time of Extraction. The effect of time and temperature on the extraction of bromacil from soil with sodium hydroxide solution was evaluated using 12 different soils containing naturally weathered bromacil residues (Table 4). Eight replicate extractions for each soil were carried out as above except that after shaking for 1 h duplicate samples were held at either ambient (15–20 °C), 30, 50, or 80 °C, and 5 mL aliquots were removed for analysis after 18, 42, and 90 h. The 5 mL aliquots were acidified with 0.5 mL of 5 N hydrochloric acid and extracted once with 5 mL of dichloromethane, using a 3 mL aliquot as above. Also two soils (1 and 2, 50 g dry weight) were refluxed with aqueous sodium hydroxide (18 h) and 5 mL aliquots collected and treated as above.

All data were analyzed using standard analysis of variance techniques. For Tables 3 and 4 data were $\log_{10}$ transformed before analysis.

RESULTS AND DISCUSSION

Groundwater. Bromacil was readily extracted from water samples by SPE. Results of the comparison of liquid/liquid extraction and SPE are presented in Table 1. These show that SPE was equivalent in performance to solvent extraction and had the added benefit that large samples (up to 1 L using C18 disks) could be processed with relative ease. When using C18 disks and samples larger than 100 mL, prefiltering was required, since the environmental samples often contained fine particles and water from this region often contains iron hydroxide complexes. No prefiltering was required for the C18 columns with samples of 100 mL or less, although some environmental samples did cause the flow rate to be reduced as the frits became clogged. In general, however, C18 columns could be reused up to six times by washing after use with an extra 2 mL of methanol in addition to the 2 mL of methanol used for preconditioning. Tests with samples of pure water and spiked water showed that there was no cross-contamination and recovery efficiency was not affected by reuse.

Several benefits result from the use of SPE technology including, reduced costs, higher sample throughput, and greater safety. For example, when used only once, C18 columns are about 2.5 times more expensive than an ethyl acetate extraction. However if used five or six times they are about half the cost. There is also a reduced solvent disposal cost with SPE. Also, it was found that several SPE extractions could be carried out simultaneously which resulted in an increase in the number of samples able to be handled in a given time. Greater user safety comes from the use of less solvent in the SPE process.

Figure 1e shows that environmental concentrations as low as 0.1 μg/L could readily be analyzed using SPE of 100 mL samples on a C18 column. Detection limits (signal/noise ratio of 3:1) in environmental samples for the SPE methods described were close to 0.05 and 0.01 μg/L for 100 mL and 1 L samples respectively using detector settings of 0.002 AUSF at 280 nm. These limits could potentially be reduced either by making a larger HPLC injection or by reducing the quantity of solvent used to redissolve the extract residue. We have found the above detection limits to be satisfactory in routine analysis where having enough solution to run the analysis more than once is often advantageous. The detection limits established here are comparable to those for other pesticides using SPE methods (Marvin *et al.*, 1990; Moltó *et al.*, 1991; Brooks *et al.*, 1989) and slightly better for bromacil than those reported by Gómez de Barreda *et al.* (1991) and Hebb and Wheeler (1978) using traditional methods. For example Marvin *et al.* (1990) and Moltó *et al.* (1991) could detect a range of pesticides at 0.03 μg/L while Gómez de Barreda *et al.* (1991) and Hebb and Wheeler (1978) could detect bromacil to 0.1 and 0.4 μg/L respectively using methods described by Pease (1966) and Jolliffe *et al.* (1967).

Results of the storage study show that there was no reduction in bromacil recovered from the environmental water samples stored for up to 53 weeks at 4 °C. The standard deviations of the analyses carried out on five occasions (1, 5, 9, 17, and 53 weeks after collection) ranged from 5 to 16% for the nine samples evaluated, and were similar to normal samples variability. There were no differences between the acidified and unmodified samples. These results demonstrate that prolonged storage in appropriate containers under refrigeration did not adversely affect sample integrity and that acidification was not required.

Soil. A preliminary comparison of extraction conditions for weathered residues of bromacil from soil samples showed that although methanol/water was as efficient as sodium hydroxide for extraction of bromacil from freshly spiked soil samples it was less efficient for the weathered residue from field applications even when shaken for 24 h (data not presented). Further tests showed that recovery using the modified Soxhlet extraction method was about half that of the sodium hydroxide method in two out of four cases and, also, that a mixture of methanol and aqueous sodium hydroxide was less efficient than sodium hydroxide alone. We also tested the addition of ammonium sulfate to the sodium hydroxide extraction mixtures. This is a common method of speeding up the settling of soil particles (Jolliffe *et al.*, 1967). In our hands the addition of 5 g of ammonium sulfate to the two soils followed by extraction with sodium hydroxide gave reduced recovery of bromacil by 30–80%. Therefore for all future tests the soil extract solutions were simply allowed to settle naturally overnight.

During these initial experiments with sodium hydroxide extractions, it was noticed that when the dichloromethane partition layer was evaporated, a large residue was deposited. It was possible that these

Table 4. Determination[a] of Bromacil in 12 Soils Held at Different Temperatures for a Range of Times during Extraction

	bromacil concentration[b] (mg/kg)											
	18 h				42 h				90 h			
soil	amb[c]	30 °C	50 °C	80 °C	amb[c]	30 °C	50 °C	80 °C	amb[c]	30 °C	50 °C	80 °C
1	0.51	0.57	0.63	0.53	0.65	0.67	0.57	0.43	0.59	0.64	0.75	0.53
2	0.16	0.22	0.27	0.21	0.25	0.29	0.30	0.11	0.34	0.32	0.19	0.13
3	2.41	2.85	3.35	2.78	2.44	2.75	3.32	2.71	2.19	3.01	2.97	0.71
7	0.17	0.25	0.23	0.15	0.09	0.25	0.23	0.13	0.09	0.25	–	–
8	0.47	0.53	0.51	0.36	0.50	0.51	0.49	–[d]	0.42	0.49	–	–
9	1.96	1.73	2.02	1.46	2.16	1.77	2.19	1.09	2.05	1.84	1.77	0.35
10	0.63	0.63	0.67	0.67	0.71	0.63	0.71	0.55	0.71	0.64	0.58	0.24
11	1.01	1.05	0.76	0.91	1.09	1.08	0.89	0.85	0.99	1.19	0.76	0.69
12	0.22	0.30	0.25	0.27	0.25	0.31	0.37	0.33	0.23	0.32	0.27	0.24
13	0.44	0.47	0.59	0.51	0.51	0.49	0.67	0.39	0.47	0.53	0.57	0.09
14	0.03	0.04	0.05	0.06	0.03	0.03	0.08	0.04	0.03	0.03	0.05	–
15	0.82	0.82	0.95	0.85	0.91	0.81	0.83	0.74	0.86	0.82	0.73	0.19

[a] Fifty grams of soil (duplicates for each soil at each temperature) was shaken with 100 mL of aqueous sodium hydroxide for 1 h at room temperature and then held at different temperatures. Five milliliter aliquots were removed for dichloromethane (5 mL) partitioning after 18, 42, and 90 h. [b] Results expressed as bromacil residues measured in the soil sample. Average cv for duplicates = 16.3% (back transformed). Note that this includes soil sampling error as well as analytical method error. [c] Ambient temperature, from 15–20 °C. [d] Insufficient soil extraction solution for sampling.

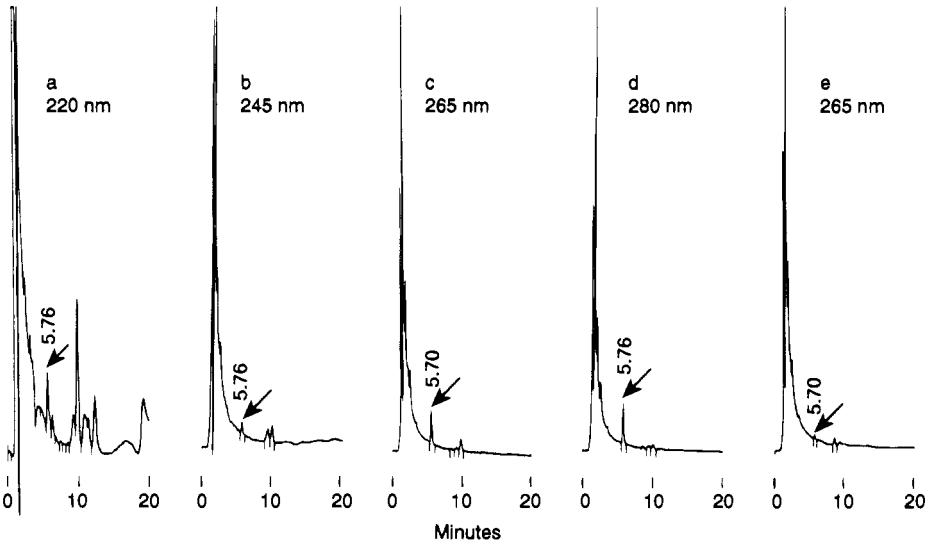

Figure 1. Analysis of bromacil at four wavelengths (220, 245, 265, and 280 nm). 100 mL samples of well water were spiked to 1 μg/L (a–d) or 0.1 μg/L (e) and extracted with C18 tubes and resolubilized in 1 mL of methanol/water (10:90). Injection size 50 μL, mobile phase 52:48 methanol/water. Detector sensitivity 0.01 AUSF.

deposits would interfere with resolubilizing of bromacil if methanol/water (10:90) solution (as used in the water extraction method) was used for the soil extracts. Therefore several mixtures of methanol and water were tested for redissolving the bromacil containing residues from three different soils. The results, expressed as solution concentrations of bromacil (Table 2), show that as the percentage of methanol to water increased up to 50% the resolubilizing efficiency for bromacil significantly ($P < 0.05$) increased. It was also found that significantly better recovery was obtained by first dissolving the residues in 0.25 mL of methanol and then adding 0.75 mL of water. While this did result in the precipitation of some material which required the samples to be filtered before analysis, filtration did not appear to affect the recovery of bromacil, and the more dilute solutions of methanol allowed the injection of up to 100 μL into the LC with consequent improvement in sensitivity.

The suitability of a single partition extraction of the acidified sodium hydroxide extract with dichloromethane was tested by comparing it to a more exhaustive extraction involving up to four successive dichloromethane partitions (Table 3). This comparison was evaluated on six different soils containing different amounts of bromacil and in all cases the corrected recovery from the single extraction was not significantly ($P < 0.05$) different compared to those of the multiple extractions. This allowed the development of a simplified method which is much quicker and uses considerably less dichloromethane.

The final aspect studied was the time and temperature used for extraction with sodium hydroxide solution. It had been noticed that some soil extracts showed increasing estimates for bromacil concentration depending on the time the mixtures were allowed to stand after shaking. To fully evaluate this effect 12 soils containing weathered residues of bromacil were shaken for 1 h with sodium hydroxide solution at room temperature according to the method and then held at different temperatures up to 80 °C, and 5 mL aliquots of the supernatant solution were removed at various times (up to 90 h) for workup by the method. The results are presented in Table 4. Results from the first sampling made after 18 h show that the recovery of bromacil from most of the soils was enhanced when the mixtures were held at elevated temperatures during extraction. Two examples of the increased recovery are demonstrated in Figures

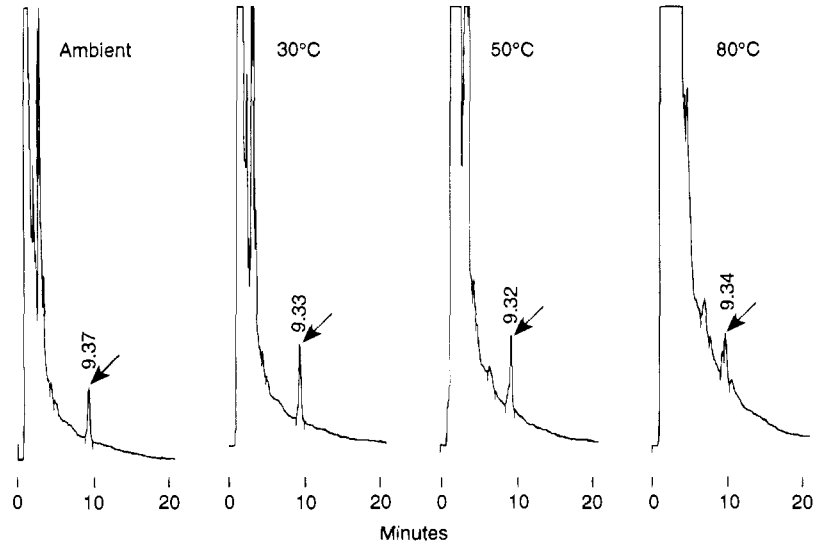

Figure 2. Analysis of bromacil in weathered soil (soil 7) held at four different temperatures (ambient, 30, 50, and 80 °C) for 18 h during extraction with aqueous sodium hydroxide according to the experimental method. HPLC injection 35 μL, mobile phase 44:56 methanol/water, wavelength 280 nm. Detector sensitivity 0.01 AUSF.

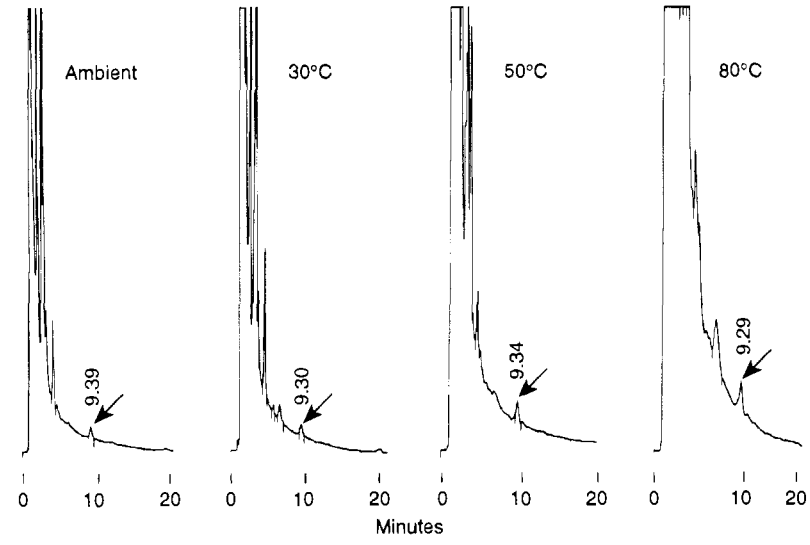

Figure 3. Analysis of bromacil in weathered soil (soil 14) held at four different temperatures (ambient, 30, 50, and 80 °C) for 18 h during extraction with aqueous sodium hydroxide according to the experimental method. HPLC injection 35 μL, mobile phase 44:56 methanol/water wavelength 280 nm. Detector sensitivity 0.01 AUSF.

2 and 3. Compared to ambient, the 30 and 50 °C temperatures gave increased recovery in 9 of 12 soils. It was also noted that at 80 °C, the recovery was beginning to decline in some soils. After 42 h recoveries from the ambient samples were higher than after 18 h in about half the soils while results from the 30 and 50 °C samples were in most cases very similar to those collected after 18 h. It was noticeable at 42 h that recoveries from the 80 °C samples were reduced in most soils. This was probably due to the instability of bromacil in harsh alkaline conditions (Jolliffe *et al.*, 1967). After 90 h recovery from the ambient and 30 °C samples were similar to those measured after 42 h while those from 50 and 80 °C were reduced in many soils.

These results demonstrate that the extraction of bromacil from many soils can be considerably enhanced by allowing the samples to stand at elevated temperatures after they have been shaken. On the basis of the present studies, it appears that standing at 50 °C for 18 h is both an effective and practical way to optimize recovery with 30 °C being nearly as good in many cases. It should be noted, however, that at the higher temperatures of 50 and particularly 80 °C many more coextractants were found in the final worked up sample (see Figures 2 and 3) and in some soils these interfered with the analysis of bromacil. While a change of mobile phase generally gave adequate separation, this was at the expense of lower sensitivity and increased overall analysis run time. This means that in most instances the use of the 30 °C temperature (as recommended under Experimental Procedures) is the most practical as it increases the recovery of bromacil without producing a high concentration of interfering coextractants.

The detection limit of this method for soil extraction (0.01 mg/kg for a 50 g soil sample) is lower than that of Caverly and Denney (1977) and Cotterill (1980) both with limits of 0.1 mg/kg and equal to Jolliffe *et al.* (1967) who had a detection limit of 0.01 mg/kg from 100 g soil sample. The reproducibility of this method was also good. Replicated extractions (5) on six different soils (1, 2, 3, 4, 5, and 6) gave standard deviations of 5.2, 2.9, 2.8, 5.7, 10.3, and 11.2% respectively. This statistic includes both analytical method and soil sampling errors.

Table 5. Soil Properties for the Soil Types Used in the Experiments

site	% clay[a]	% silt[a]	% sand[a]	% organic C[b]	pH[c]	CEC[d]
1	2	10	88	2.3	6.1	103
2	11	23	65	6.6	6.7	98
3	4	18	78	4.2	5.4	56
4	14	16	70	2.4	5.2	–
5	14	11	75	3.5	7.3	–
6	1	4	94	1.6	6.9	–
7	2	24	74	4.5	6.3	117
8	5	21	74	5.4	5.8	134
9	4	24	72	4.3	6.2	157
10	2	14	84	4.1	6.0	98
11	26	28	46	2.1	6.0	131
12	1	3	96	1.3	6.4	46
13	3	22	75	5.5	6.3	153
14	3	27	70	6.6	6.1	153
15	7	17	76	4.1	6.3	172

[a] Mechanical analysis was by the pipet method, by pretreating soil samples with H_2O_2 and sodium hexametaphosphate and dispersing ultrasonically for 10 min. [b] Organic carbon was determined by Walkley–Black method as modified by Smith and Weldon (1940). [c] Soil pH was determined in a 1:2.5 soil/water slurry using a glass electrode. [d] Cation exchange capacity (mmol kg^{-1}) was determined by leaching the soil with ammonium acetate followed by ethanol, distilling off the ammonia in boric acid, and titrating with standard HCl.

The use of enhanced temperatures in the extraction of herbicides from soil is not new but has traditionally been confined to either reflux or Soxhlet extractions and often for extended periods of time. For example, Cotterill (1980) extracted lenacil by refluxing with chloroform or acetonitrile for 8 h while Huang and Pignatello (1990) used a 24 h Soxhlet extraction for atrazine. However, our studies with aqueous sodium hydroxide extraction suggest that these conditions are too harsh for bromacil. In our hands, soils 1 and 2 refluxed with aqueous sodium hydroxide for 18 h yielded no bromacil. More recently Huang and Pignatello (1990) showed that weathered residues of atrazine were more effectively extracted by shaking with solvent at 75 °C for 2–4 h compared to either Soxhlet or shaking at room temperature. Optimal conditions for extraction of bromacil from soil with aqueous sodium hydroxide with minimal degradation appear to be standing for 18 h at 30–50 °C after shaking for 1 h at room temperature.

By using several soils containing weathered residues, an effective method for extraction of bromacil from soils, including those with an high organic matter content, has been developed.

All the soils studied were from asparagus growing sites and most of them are very sandy with a very low clay fraction but with high organic carbon contents (Table 5). Organic carbon is frequently cited as being highly sorptive (Gerstl and Yaron, 1983a; Huang and Pignatello, 1990) and could be responsible for the difficulty in extraction of bromacil in some of the soils examined here. There was a weak relationship (r = 0.661) between the increase in recovery of bromacil and increasing soil organic carbon content ($\log_{10}$[50 °C at 18 h/ambient at 18 h] vs soil OC). However, there was no relationship with other soil properties (clay content and pH) that are often cited as having some influence on the sorption, and hence extraction, of other herbicides. Thus it appears that there is no easy way to predict the degree of difficulty in the extraction of weathered bromacil residues from field soil samples. The equilibrium period for weathered residues is obviously quite different from that of freshly spiked samples. This is possibly influenced by the nature of the sorptive sites, in particular those associated with the soil organic matter, rather than simply the presence of large amounts of organic matter.

CONCLUSION

Determination of bromacil in environmental water samples by SPE was more effective than liquid/liquid partitioning as it enabled the practical analysis of large samples with consequent improvement in sensitivity. Also the SPE methods are more cost effective and safer due to the handling of smaller volumes of solvents. For soil extraction, the methods by Pease (1966) and Jolliffe *et al.* (1967) have been improved by holding the extraction mixture at an elevated temperature (30 °C) for 18 h and simplified by using only one partitioning into dichloromethane, as opposed to exhaustive partitioning. The method developed was also demonstrated to be effective on high organic matter soils containing weathered residues of bromacil from field applications.

LITERATURE CITED

Barceló, D. A Review of Liquid Chromatography in Environmental Pesticide Analysis. *Chromatographia* **1988**, *25*, 928–936.

Brooks, M. W.; Jenkins, J.; Jimenez, M.; Quinn, T.; Clark, J. M. Rapid Method for the Determination of Alachlor, Atrazine and Metolachlor by Solid-Phase extraction. *Analyst* **1989**, *114*, 405–406.

Burney, B.; Rahman, A.; Oomen, G. A. C.; Whitham, J. M. The Organic Matter Status of some Mineral Soils in New Zealand. *Proc. N. Z. Weed Pest Cont. Conf.* **1975**, *28*, 101–103.

Byast, T. H.; Cotterill, E. G.; Hance, R. J. Methods of Analysis for Herbicide Residues. ARC Weed Research Organization. Tech. Report 15 (2nd ed.), 1977, pp 99.

Caverly, D. J.; Denney, R. C. Determination of Residues of the Herbicides Bromacil, Lenacil and Terbacil in Soils by Gas Chromatography. *Analyst* **1977**, *102*, 576–579.

Cotterill, E. G. The Efficiency of Methanol for the Extraction of Some Herbicide Residues from Soil. *Pestic. Sci.* **1980**, *11*, 23–28.

Gardiner, J. A.; Rhodes, R. C.; Adams, J. B.; Soboczenski, E. J. Synthesis and Studies with 2-C^{14}-Labelled Bromacil and Terbacil. *J. Agric. Food Chem.* **1969**, *17*, 980–986.

Gerstl, Z.; Yaron, B. Behaviour of Bromacil and Napropamide in Soils: I. Adsorption and Degradation. *Soil Sci. Soc. Am. J.* **1983a**, *47*, 474–478.

Gerstl, Z.; Yaron, B. Behaviour of Bromacil and Napropamide in Soils: II. Distribution After Application from a Point Source. *Soil Sci. Soc. Am. J.* **1983b**, *47*, 478–483.

Gómez de Barreda, D.; Lorenzo, E.; Gamón, M.; Monteagudo, E.; Saez, A.; De la Cuadra, J. D.; Del Busto, A.; Ramos, C.; Carbonell, E. A. Survey of Herbicide Residues in Soil and Wells in Three Citrus Orchards in Valencia, Spain. *Weed Res.* **1991**, *31*, 143–151.

Hebb, E. A.; Wheeler, W. B. Bromacil in Lakeland Soil Groundwater. *J. Environ. Qual.* **1978**, *7*, 598–601.

Huang, L. Q.; Pignatello, J. J. Improved Extraction of Atrazine and Metolachlor in Field Soil Samples. *J. Assoc. Off. Anal. Chem.* **1990**, 73, 443–446.

Johnson, W. E.; Fendinger, N. F.; Plimmer, J. R. Solid-Phase Extraction of Pesticides from Water: Possible Interferences from Dissolved Organic Material. *Anal. Chem.* **1991**, *63*, 1510–1513.

Jolliffe, V. A.; Day, B. E.; Jordan, L. S.; Mann, J. D. Method of Determining Bromacil in Soils and Plant Tissues. *J. Agric. Food Chem.* **1967**, *15*, 174–177.

Junk, G. A.; Richard, J. J. Organics in Water: Solid Phase Extraction on a Small Scale. *Anal. Chem.* **1988**, *60*, 451–454.

Kidd, H.; James, D. R., Eds. *The Agrochemicals Handbook,* 3rd ed.; Royal Society of Chemistry: Cambridge, England, 1991.

Lauren, D. R.; Taylor, H. J.; Rahman, A. Analysis of the Herbicides Dicamba, Clopyralid and Bromacil in Asparagus by High-Performance Liquid Chromatography. *J. Chromatogr.* **1988**, *439*, 470–475.

Lawrence J. F.; Turton, D. High-Performance Liquid Chromatographic Data for 166 Pesticides. *J. Chromatogr.* **1978**, *159*, 207–226.

Leistra, M.; Smelt, J. H.; Zandvoort, R. Persistence and Mobility of Bromacil in Orchard Soils. *Weed Res.* **1975**, *15*, 243–247.

Marvin, C. H.; Brindle, I. D.; Hall, C. D.; Chiba, M. Automated High-Performance Liquid Chromatography for the determination of Pesticides in Water using Solid Phase Extraction. *Anal. Chem.* **1990**, *62*, 1495–1498.

Moltó, J. C.; Picó, Y.; Font, G.; Mañes, J. Determination of Triazines and Organophosphorous Pesticides in Water Samples using Solid-Phase Extraction. *J. Chromatogr.* **1991**, *555*, 137–145.

Pease, H. L. Determination of Bromacil Residues. *J. Agric. Food Chem.* **1966**, *14*, 94–96.

Rhodes, R. C.; Belasco, I. J.; Pease, H. L. Determination of Mobility and Adsorption of Agrichemicals on Soils. *J. Agric. Food Chem.* **1970**, *18*, 524–528.

Sherma, J. Pesticides. *Anal. Chem.* **1991**, *63*, 118R-130R.

Smith, H. W.; Weldon, M. D. A comparison of some methods for the determination of soil organic matter. *Proc. Soil Sci. Soc. Am.* **1940**, *5*, 177–182.

Smith, A. E.; Grover, R.; Emmond, G. S.; Korven, H. C. Persistence and Movement of Atrazine, Bromacil, Monuron and Simazine in Intermittently-Filled Irrigation Ditches. *Can. J. Plant Sci.* **1975**, *55*, 809–816.

Tucker, D. P. H. Bromacil and Diuron Residue Levels in Florida Citrus Soils. *Pestic. Monit. J.* **1978**, *12*, 47–50.

Webber, J. B.; Best, J. A. Activity and Movement of 13 Soil-applied Herbicides as Influenced by Soil Reaction. *Proc. South. Weed Sci. Soc.* **1972**, *25* 403–413.

Wells, N., Luke, J. Eds. Soils of New Zealand Part 3. Soil Bureau Bulletin (3), N. Z. Dept. of Scientific and Industrial Research, Wellington. 1968.

Wells, M. J. M.; Michael, J .L. Reversed-Phase Solid-Phase Extraction for Aqueous Environmental Sample Preparation in Herbicide Residue Analysis. *J. Chromatogr. Sci.* **1987**, *25*, 345–350.

Wolkoff, A. W.; Creed, C. Use of SEP-PAK^{R} C_{18} Cartridges for the Collection and Concentration of Environmental Samples. *J. Liq. Chromatogr.* **1981**, *4*, 1459–1472.

Zandvoort, R.; Van den Born, G. W.; Braber, J. M.; Smelt, J. H. Leaching of the Herbicide Bromacil after Application on Railroads in the Netherlands. *Water, Air Soil Pollut.* **1980**, *13*, 363–372.

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