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# Sodium Monofluoroacetate (1080) Leaching through Soils

R. L. Parfitt,[1] C. T. Eason,[2] H. Hoff,[3] L. K. Heng[4]

[1]Manaaki Whenua—Landcare Research, Private Bag 11-052, Palmerston North, New Zealand
[2]Manaaki Whenua—Landcare Research, P.O. Box 31-011, Christchurch, New Zealand
[3]Hydrology Department, Bayreuth University, Germany
[4]Soil Science Department, University of Melbourne, Australia

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Sodium monofluoroacetate (Compound 1080) is used in New Zealand for the control of animals such as the rabbit and the brush-tail possum. Since more than one tonne of this pesticide is applied annually in New Zealand a clear understanding of possible risks to the environment is essential. Research has been conducted on the toxicity of 1080 to a number of target and non-target species (Atzert 1971; Rammel and Flemming 1978; Eason et al. 1993). Work on biodegradation of 1080 has shown that it is defluorinated both by organisms which have been isolated from soil (Walker and Bong 1981; Wong et al. 1991) and within soils themselves (David and Gardiner 1966; Parfitt et al. 1994). In Australia where fluoroacetate occurs naturally in 41 plant species from two genera of Leguminosae at concentrations of from <100 mg/kg to in excess of 6000 mg/kg (Twigg 1994), biodegradation of fluoroacetate takes place in soils and none has been detected in waters (D. R. King, Agricultural Protection Board of Western Australia; pers. comm).

To our knowledge no studies have been conducted on the leaching of 1080 through soil. Peters (1975) speculated that 1080 is adsorbed by soil and is not leached but this appears to have been based on the mistaken assumption that 1080 could be adsorbed on cation-exchange sites in soils; fluoroacetate, however, is an anion and it cannot be held on cation-exchange sites. Therefore it may possibly be held on anion-exchange sites which occur on hydrous iron oxides, hydrous aluminium oxides and the clay mineral allophane. Since fluoroacetate, like chloride and nitrate, is a large monovalent ion, we suggest that fluoroacetate has a low preference for adsorption on soil minerals and that traces which are not removed by biodegradation may be leached through soils.

Here we report on the adsorption of 1080 by soil samples with large amounts of hydrous oxides, including samples of Andisols formed from volcanic ash and which contain allophane. We also investigate the possibility that traces of 1080 may be leached through soils.

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*Correspondence to:* R. L. Parfitt

## MATERIALS AND METHODS

Soil samples were collected in a field moist condition. The samples were sieved moist through a 6 mm screen and stored in sealed plastic bags. The soil samples were Stratford silt loam (0-100 mm, 200-300 mm) (Andisol), Westmere silt loam (0-100 mm) (Inceptisol 1), and Holmes Bay (0-140 mm) (Inceptisol 2). The pH values of the samples ranged from 5 to 6.

Adsorption experiments were conducted with 3.0 g moist soil which was equilibrated with the anion being studied in 5 mL solution for four hours in the presence of a drop of toluene, which was added to prevent microbial activity. After analysis of the supernatant solution, using anion chromatography, adsorption was calculated by difference between the initial and final concentrations.

Leaching experiments were conducted with moist 30 g soil samples which were loosely packed in glass tubes 20 mm diameter and 150 mm long to give columns of soil 100 mm in length. The tubes were fitted with a plug of cellulose at the base to hold the soil in position. Chloride and nitrate were first removed by leaching with distilled water to give a similar low ionic strength in all samples. A solution containing 0.04 mmol (4 mg) 1080 in 5 mL water was added to the top of the column and leaching was continued by adding 10 (5 mL) pulses of water over an eight hour period; this was equivalent to 160 mm rain. The same experiment was carried out using nitrate, chloride and sulfate. Sulfate was used last because of the possibility that it may have been strongly sorbed by the soil column. The eluate was collected in 5 mL samples and analysed using anion chromatography.

Undisturbed cores of Holmes Bay soil were collected in sleeves 100 mm in diameter and 140 mm long. After the addition of 0.03 mmol (3 mg) 1080 in 1 mL of water to the top of the column, the column was leached with 0.001 M chloride at a rate of 12 mm $h^{-1}$ for 15 h. A suction equivalent to 100 mm of water was applied to the base of the column and the leachate was collected in 50 mL aliquots. The 1080 in the leachate was acidified with hydrochloric acid and converted to the dichloroanilide derivative by using dicyclohexylcarbimide (DCC) and 2,4-dichloroaniline (DCA). The derivative was extracted with ethyl acetate and cleaned up on a silica column. The derivative in toluene was quantified by gas chromatography with electron-capture detector (Ozawa and Tsukioka 1987).

## RESULTS AND DISCUSSION

Small amounts of 1080 were adsorbed by the sample of Andisol (Figure 1). The amounts adsorbed were very similar to those of nitrate but were significantly less than for sulfate. Andisols contain large amounts of allophane and hydrous oxides, and the data in Figure 1 are probably representative of soils with the greatest adsorption of 1080 at pH values near 5.5. Because of their relatively high affinity for adsorption sites, sulfate and other polyvalent anions when present may reduce 1080 adsorption by blocking some adsorption sites (Parfitt 1978). Anion adsorption generally increases with decrease in pH, with the charge on the anion and with the amount of hydrous iron/aluminium oxide in soil (Parfitt 1978).

The 1080 moved through the sample of Andisol in the leaching tube at a similar rate to that of nitrate and chloride (Figure 2). The 1080 was first detected in the eluate after one pore volume of solution had been displaced from the column; maximum concentration in the eluate was reached after 1.7 pore volumes. The 1080, nitrate and chloride were completely recovered from the 100 mm column after displacing 3.5 pore volumes, equivalent to 160 mm of rainfall in eight hours. No microbial decomposition was detected during this time.

In the leaching experiment using Inceptisol 1, which had less hydrous oxides than the Andisol, 1080 movement was similar to that of nitrate and chloride. Sulfate leaching was a little slower than for 1080, nitrate or chloride (Figure 3). The 1080, nitrate and chloride were again completely recovered but in this experiment after 2.8 pore volumes, equivalent to 130 mm of rainfall. Less water was required for complete leaching from the column partly because the monovalent anions were not adsorbed by this soil (data not presented). Here the sulfate was adsorbed with a low preference and was completely recovered after 3.8 pore volumes had been displaced. When the data in Figures 2 and 3 were modelled with the convective-dispersive equation (Biggar and Nielsen 1967) a good fit was obtained.

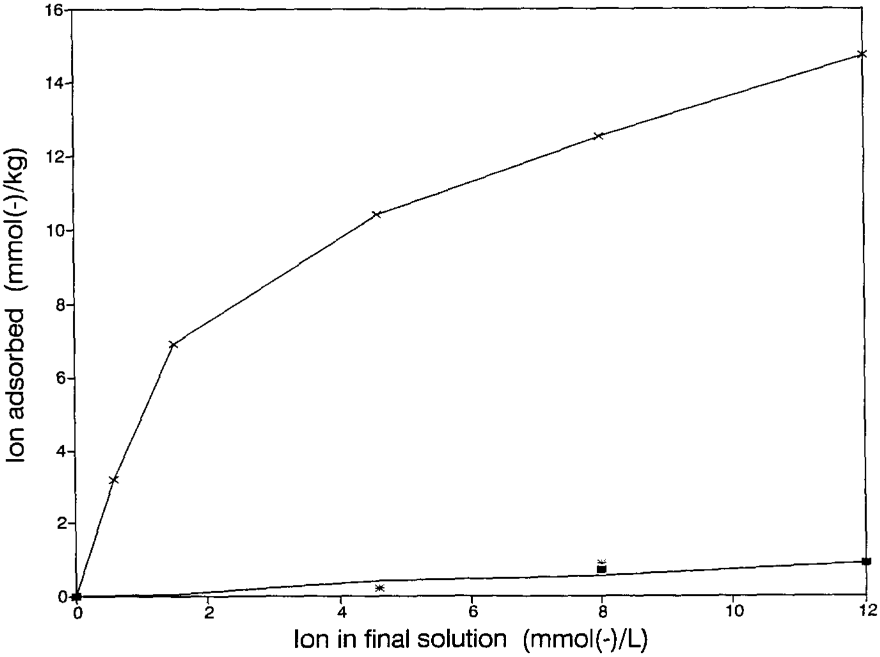

Figure 1. Adsorption of 1080 (■), nitrate $NO_3$ (*), and sulfate $SO_4$ (x) onto an Andisol (200-300 mm) at pH 5.5 after 16 hours.

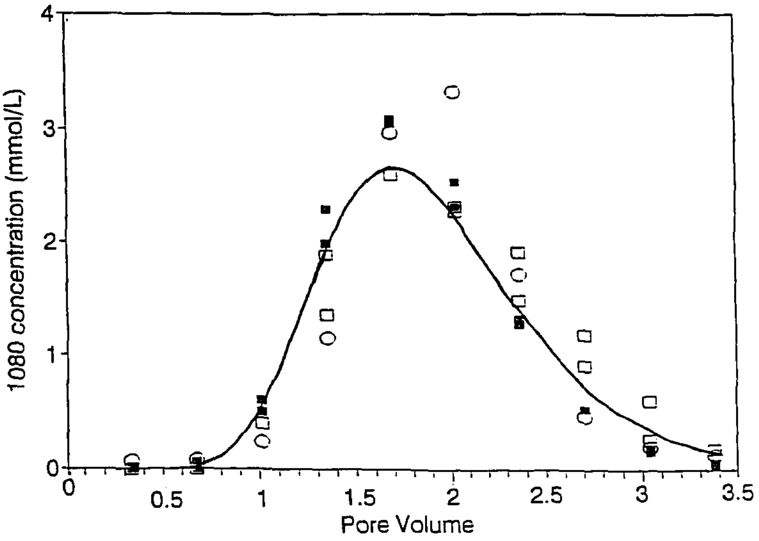

Figure 2. Leaching of 1080 (□), nitrate (■), and chloride (○) through an Andisol (200-300 mm). The curve is fitted from the convective-dispersive equation.

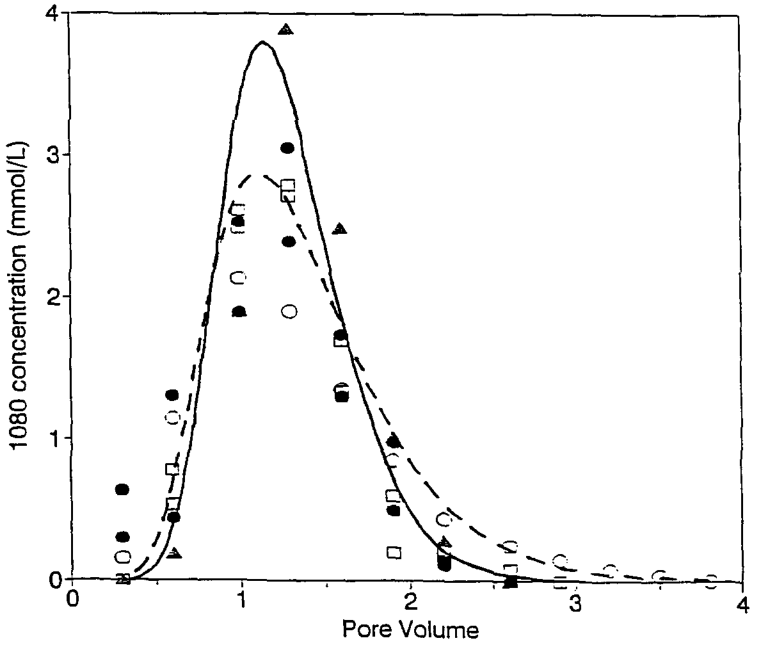

Figure 3. Leaching of 1080 (•), chloride (□), nitrate (▵), and sulfate (○) through Inceptisol 1 (0-100 mm). Curves for the monovalent and sulfate ions are fitted from the convective-dispersive equation.

Sulfate was adsorbed onto the Andisol with a stronger preference than for nitrate, and hence was more slowly leached (Figure 4) (Bolan et al. 1986). Whereas the nitrate was recovered after 2.8 pore volumes of solution had been displaced, some sulfate was still being eluted after seven pore volumes had been displaced. When the 200-300 mm sample of the Andisol was used, the sulfate was not completely recovered within 13 pore volumes (data not shown). This demonstrates the effect of adsorption on leaching.

In the leaching experiment with intact cores of Inceptisol some 1080 appeared in the eluate after 0.4 pore volumes had been displaced; possibly some 1080 was translocated through the macropores and was eluted rapidly. The 1080 peak occurred after about 1.6 pore volumes (Figure 5a). This is similar to the results with the repacked soil (Figure 3). The 0.03 mmol of 1080 was completely leached from the intact core after four pore volumes which was the equivalent of 180 mm of rainfall.

When the previous experiment was repeated with a second core of soil, the results differed in that 1080 was leached in two obvious pulses (Figure 5b). Only 0.0135 mmol of 1080 was recovered in the eluate and 0.0032 mmol was extracted from the soil; possibly some 1080 was degraded in the soil after the leaching experiment was completed and before the soils were analysed. The two pulses may arise from the different rates of movement of 1080 through both the larger pores and the smaller pores in this core of soil.

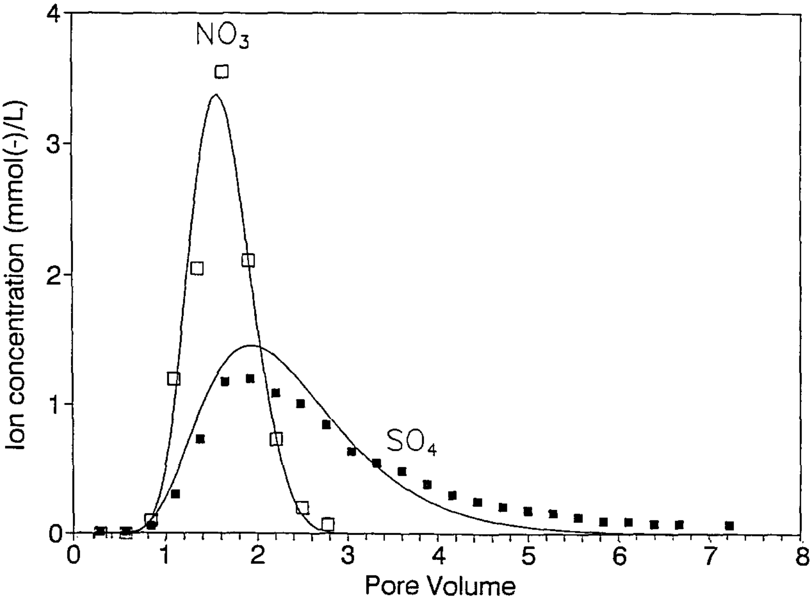

Figure 4. Leaching of nitrate (□), sulfate (■) through an Andisol (0-100 mm). The curves are fitted from the convective-dispersive equation.

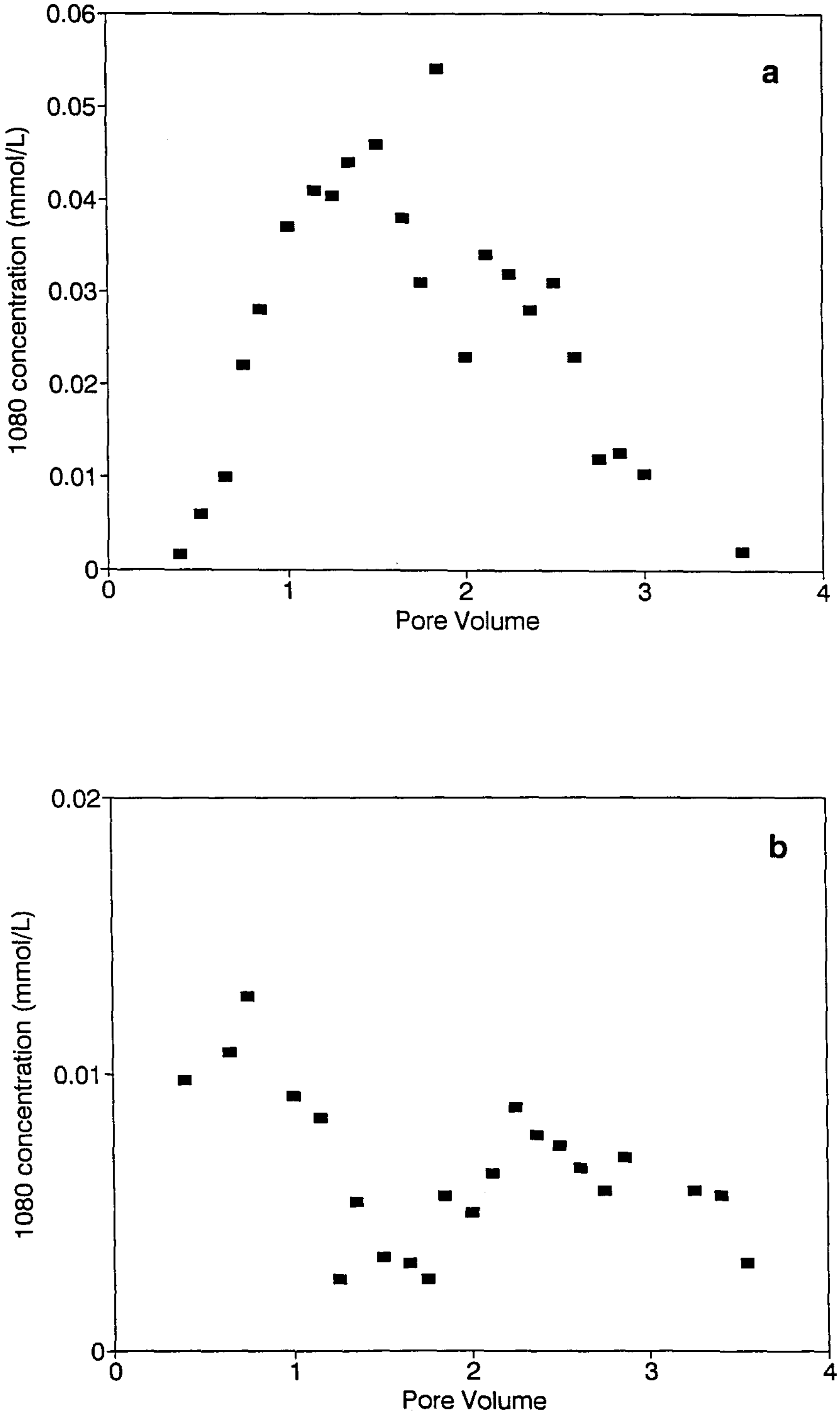

Figure 5. Leaching of 1080 through two intact cores from Inceptisol 2.

These results indicate that there is the potential for some 1080 to be leached through soil particularly if intense rainfall events occur shortly after 1080 is placed on the surface of soil. Some 1080, however, will probably be retained in soil pores where biodegradation can occur.

Amounts of 1080 applied per ha in New Zealand, for the control of possums and rabbits, are very small (4-15 g $ha^{-1}$). If 100 mm rain fell and washed all the 1080 into the soil, the concentration in soil solution is calculated to be equivalent to 0.004-0.015 mg $L^{-1}$. No 1080, however, has been detected, at a level of detection of 0.0003 mg $L^{-1}$, in groundwater after animal control operations and the 1080 is probably degraded either within the bait itself or in the animal carcass or in the soil (Parfitt et al. 1994).

Small amounts of 1080 were adsorbed by soils containing large amounts of hydrous oxides of iron and aluminium. The amounts adsorbed were similar to the amounts of nitrate adsorbed. In contrast sulfate was adsorbed in larger amounts since it has a higher charge.

Leaching experiments showed that 1080 could be leached through soils at a similar rate to nitrate and chloride. The 1080 was completely recovered in the leachate. Sulfate was leached more slowly as a result of the greater sorption preference. In the field situation, however, biodegradation and dilution would probably be important factors in detoxifying and removing fluoroacetate in and from the environment.

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