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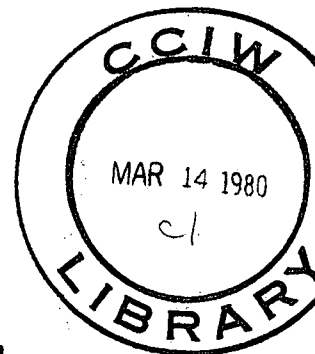


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BINDING OF FENITROTHION TO SOILS
AND SEDIMENTS

by

R. JAMES MAGUIRE

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ABSTRACT

Both the amount of fenitrothion [0,0-dimethyl-0-(p-nitro-m-tolyl)phosphorothionate] that binds to soils and sediments, and the rate of binding, increase with increasing organic carbon content of soils and sediments. Six soil and two sediment samples were used; the fenitrothion binding capacity is $5 \times 10^1 - 1.2 \times 10^3$ $\mu\text{g/g}$, and the half-life for binding ranges from 7 to 70 hr.

1 INTRODUCTION

2 Fenitrothion was used in the period 1969-1977 in New Brunswick,
3 Canada, for control of the spruce budworm (Choristoneura fumiferana
4 [Clemens]) in the province's forests. Millions of hectares were
5 sprayed annually with 150 - 300 g active ingredient per hectare. The
6 routes and rates of environmental transformation and disappearance
7 have been, and still are, subjects of a great deal of interest (1,2).

8 We have recently reported (3) on the fate of fenitrothion in
9 the surface microlayer, subsurface water, suspended solids and
10 sediment of a small pond in a spruce-fir forest in New Brunswick
11 after the spraying of a fenitrothion formulation for spruce budworm
12 control. The conclusion was that a large fraction of fenitrothion
13 which reached the surface of the pond probably volatilized rapidly,
14 while the fraction which remained in the water disappeared or degraded
15 within a few days, largely through mechanisms of photolysis and
16 microbial reduction.

17 In support of this field study, we examined some aspects of
18 the kinetics and thermodynamics of the binding of fenitrothion to
19 various soils and sediments, and the results are reported here. To
20 a lesser extent, we also examined the binding of p-nitro-m-cresol
21 and aminofenitrothion [0,0-dimethyl-0-(p-amino-m-tolyl)phosphorothionate],
22 the only transformation products detected in the field study.

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1 EXPERIMENTAL SECTION

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3 Materials

4 Technical grade fenitrothion was a gift from Chemagro Ltd.
5 Samples of six different well-characterized soils were gifts from
6 the Soil Research Institute of the Canadian Department of Agriculture.
7 All organic solvents used in this work were pesticide grade from
8 Caledon Laboratories. p-Nitro-m-cresol was obtained from Aldrich
9 Chemical Co. and purified by sublimation. All other chemicals were
10 reagent grade and were used without further purification.

11 Fenitrothion was purified by elution in benzene from a 10%
12 H₂O-deactivated column of Florisil [®] and shown to be pure by gas
13 chromatography (g.c.) with flame ionization, flame photometric (FPD-
14 P mode) and electron capture (ECD) detectors. Aminofenitrothion was
15 prepared by chromous chloride reduction of fenitrothion (4) and was
16 stable for months in oxygenated toluene or hexane.

17
18 Apparatus

19 p-Nitro-m-cresol was detected with a Cary 14 spectrophotometer
20 at 397 nm after adjustment of solution pH to 9.2 with suitable buffers.
21 Detection and quantitation of fenitrothion and aminofenitrothion were
22 done by g.c. with ⁶³Ni-ECD and FPD (P mode), respectively. A Spectra-
23 Physics 4000 integrator was used to calculate peak areas. Usually a
24 2 m x 2 mm i.d. glass column containing 4% OV 101/6% OV 210 on Chromosorb
25 WHP, 80/100 mesh, was used for fenitrothion and aminofenitrothion. Other

1 g.c. conditions were: column oven, 200°C (isothermal); inlet and
2 outlet temp., 220°C; ECD temp. 350°C; FPD temp. 240°C; ECD carrier
3 and purge gases were Ar/5% CH₄ or N₂/pentane. The minimum detectable
4 amount of fenitrothion was 500 pg by FPD (P mode), 5 pg by ECD
5 (Ar/5% CH₄) and 0.5 pg by ECD (N₂/pentane), and the detectors were
6 calibrated for linearity of response with standards of known
7 concentration. Underivatized p-nitro-m-cresol could also be
8 detected and quantitated readily by ECD using a Carbowax 20 M column.
9 Confirmations of identity were made by comparing retention times and
10 by co-chromatography with authentic samples on OV 101/210, Carbowax
11 20 M or OV 225 columns. Confirmations of identity were also made
12 with a Finnigan 1015-C gas chromatograph-mass spectrometer (electron
13 impact, 70 eV) with PDP-8 computer, Cyphernetics spectral library,
14 and reference to other published mass spectra.

15

16 Methods

17 It was difficult to obtain well-characterized sediments in
18 order to study the thermodynamics and kinetics of the binding of
19 fenitrothion to sediments of varying types; therefore, a series of
20 standard soil samples was used, as well as a sediment sample from
21 the pond examined in the field study (3), and a sediment sample
22 from a nearby stream. Table 1 contains relevant information,
23 provided by the Soil Research Institute, on these soils and the
24 dried (110°C) sediments. For the adsorption experiments, the soil
25 and sediment samples were sieved to pass an 850 µm size mesh.

1 The extent of binding of fenitrothion to the soils and sediments
2 was investigated as follows. Mixtures were prepared of 10 ml of
3 fenitrothion solution ($0.05 - 5.0 \mu\text{g } \ell^{-1}$, pH 6.0) and 10 mg of dry soil
4 or sediment (for a sediment: water weight ratio of 10^{-3}) in a 25 ml
5 volumetric flask. The flasks were shaken (Burrell wrist-action shaker,
6 speed "2") in the dark at 20°C for periods of 4 - 8 days. The mixtures
7 were then centrifuged and 5 ml portions of the supernatant were
8 (1) adjusted to pH 9.2 for spectrophotometric analysis of p-nitro-m-
9 cresol, or (2) for fenitrothion and aminofenitrothion, extracted
10 ($3 \times 10 \text{ ml}$) with n-hexane, and the n-hexane extracts were concentrated
11 to 1 ml; $3 \mu\ell$ aliquots were then analyzed by g.c. as described above.
12 Each set of binding experiments was performed three times and
13 concentrations determined by g.c. were the result of 3 - 5 injections.
14 Experiments were performed for each soil and sediment on (1) the effect
15 of pesticide concentration, (2) the effect of shaking speed, (3) the
16 effect of pH, and (4) the extraction of sediment-adsorbed fenitrothion
17 with n-hexane. Experiments were also performed on the extents of bind-
18 ing of aminofenitrothion and p-nitro-m-cresol to the pond sediment.

19 The kinetics of binding of fenitrothion to the soils and
20 sediments were investigated in a similar way, except that the fenitrothion
21 concentration used was uniformly $5 \text{ mg } \ell^{-1}$ and samples were taken for
22 analysis periodically over 8 days. Each set of kinetics experiments was
23 performed three times, and concentrations determined by g.c. were the
24 result of 3 - 5 injections. In addition, limited experiments were
25 performed on (1) the effect of shaking speed, (2) the kinetics of

1 binding of aminofenitrothion to the pond sediment, and (3) the
2 kinetics of desorption of sediment-bound fenitrothion. In the latter
3 case, the procedure was to re-suspend the sediments in pesticide-free
4 water and monitor the water for increasing fenitrothion concentration.

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6

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RESULTS

8 In the treatment of the thermodynamic data, the application of
9 the Freundlich isotherm was rejected because it has no theoretical
10 significance; for example, it predicts infinite binding at infinite
11 pesticide concentration. Since the plots of the amount of fenitrothion
12 bound to sediment vs. the concentration of fenitrothion in solution
13 resembled rectangular hyperbolas, graphical methods were used to derive
14 the maximum, or limiting, amount of fenitrothion adsorbed per g of soil
15 or sediment, in a manner analogous to the determination of the maximum
16 velocity of an enzyme-catalyzed reaction by the use of the Michaelis-
17 Menten equation (5), which is itself analogous to the Langmuir adsorp-
18 tion isotherm for gases on solids. The equation to be considered is
19 thus

20

21

$$[F]_{ad} = \frac{[F]_{ad(\infty)} \cdot [F]_{so1}}{A + [F]_{so1}} \quad (1)$$

22

23 where $(F)_{ad}$ is μg of fenitrothion bound per g of soil or sediment,

24 $[F]_{so1}$ is the concentration of fenitrothion in solution in $\mu\text{g } \ell^{-1}$,

25

1 A is a constant (the concentration of fenitrothion in solution at which
2 1/2 of the total fenitrothion is bound to the soil or sediment) with
3 units of $\mu\text{g } \ell^{-1}$, and $[F]_{\text{ad}(\infty)}$ is the maximum amount of fenitrothion
4 which can be bound to the soil or sediment under our experimental
5 conditions, in $\mu\text{g } \text{g}^{-1}$. A recommended plotting form of an equation of
6 this sort is (5):

$$[F]_{\text{ad}} = [F]_{\text{ad}(\infty)} - \frac{[F]_{\text{ad}} \cdot A}{[F]_{\text{sol}}} \quad (2)$$

11 A plot of $[F]_{\text{ad}}$ vs. $[F]_{\text{ad}}/[F]_{\text{sol}}$ yields $[F]_{\text{ad}(\infty)}$ from the ordinate
12 intercept and $-A$ from the slope. Values of $[F]_{\text{ad}(\infty)}$ were determined
13 in this way for the six soils and two sediments. Since the adsorption
14 of hydrophobic substances on soils is often correlated with the amount
15 of organic matter in the soil (e.g., 6), this approach was used here.
16 There is in general an increase in the limiting amount of bound
17 fenitrothion with increasing organic carbon content of the soils and
18 sediments; a plot of $[F]_{\text{ad}(\infty)}$ vs. % organic carbon content is
19 linear ($r^2 = 0.83$), albeit with significant experimental error as seen
20 in Fig. 1. In addition, it was determined that (1) there was no effect
21 of shaking speed within the range tested, probably because the high
22 water:sediment ratio ensured adequate exposure of the fenitrothion to
23 the sediment over a period of four days, even when the flasks were not
24 shaken; (2) all of the soil- and sediment-adsorbed fenitrothion could
25 be extracted with n-hexane; (3) there was no effect of pH, between 5.0

1 and 7.5, on the binding of fenitrothion to the soils and sediments;
2 (4) aminofenitrothion is bound about 10 times more strongly than
3 fenitrothion to the pond sediment at pH 6.0 - 7.0 (cf. [aminofenitro-
4 thion]_{ad(∞)} = $(9.72 \pm 3.88) \times 10^2 \mu\text{g g}^{-1}$ and [fenitrothion]_{ad(∞)} =
5 $(1.02 \pm 0.43) \times 10^2 \mu\text{g g}^{-1}$). All of the sediment-adsorbed amino-
6 fenitrothion could be extracted with hexane; (5) p-nitro-m-cresol
7 does not bind significantly to the pond sediment at pH 7.0, probably
8 partially because a significant fraction of it is ionized at this
9 pH value ($\text{pK}_a = 7.26$ at 25° and ionic strength 0.05 M - ref. 3). The
10 extent of binding increases as the pH is lowered, but even at pH 5,
11 p-nitro-m-cresol is bound only about 1/4 as strongly as fenitrothion
12 to the pond sediment.

13 The kinetics experiments showed that the binding of fenitrothion
14 to the soils and sediments was essentially complete within three days,
15 and that $[F]_{ad(\infty)}$ values estimated kinetically were the same, within
16 experimental error, as those determined thermodynamically. The
17 kinetics were first-order in fenitrothion concentration over three
18 half-lives, and the rate constant increased with % organic carbon
19 content of the soils and sediments, as shown in Fig. 2. Other notable
20 findings were that (1) the half-life for the binding of fenitrothion
21 to the pond sediment was 19.2 ± 2.4 hr at 20°C in unshaken buffered
22 or unbuffered solutions in the pH range 6.0 - 7.5, (2) the rate of
23 adsorption of fenitrothion to pond sediment increases with increasing
24 shaking speed, cf. $t_{\frac{1}{2}} = 19.2 \pm 2.4$ hr for unshaken pond sediment vs.
25 14.7 ± 0.7 hr for pond sediment shaken at speed "2"; (3) amino-

1 fenitrothion binds to unshaken pond sediment at about the same rate
2 as fenitrothion ($t_{\frac{1}{2}} = 17.9 \pm 3.2$ hr); and (4) the kinetics of desorption
3 of fenitrothion from pond sediment were slow and not simply first-order.
4 Only 20% of bound fenitrothion could be desorbed into distilled water
5 after shaking for two weeks.

6 No chemical reactions other than adsorption or desorption were
7 observed in these experiments with fenitrothion, aminofenitrothion and
8 p-nitro-m-cresol.

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11 DISCUSSION

12 In general, the results of this work appear to be internally
13 self-consistent but would probably only apply to a field situation in
14 a qualitative sense; thus the main conclusions are that both the amount
15 of fenitrothion that binds to soils and sediments, and the rate of
16 binding, increase with increasing organic carbon content of the soils
17 and sediments. The non-zero intercepts of Figs. 1 and 2 suggest that
18 fenitrothion does bind to some other fraction such as clay, but
19 attempted correlations along these lines were fruitless. In what
20 follows, we compare results from this work concerning only the pond
21 sediment with field observations made on the pond sediment (3).

22 Thermodynamic data from field observations and these laboratory
23 results appear to be in harmony. The limiting amount of fenitrothion
24 bound to pond sediment was determined to be about 10^2 μg per g of
25 sediment, and the highest concentration of fenitrothion observed in

1 the pond sediment after the spray was about 6×10^{-2} μg per g of
2 sediment, much less than the apparent maximum binding capacity.

3 The nature of binding of aminofenitrothion to the pond sediment
4 is different in the laboratory experiments compared with the field
5 observations. In the laboratory case, aminofenitrothion appeared to be
6 fairly loosely bound, in the sense that what was bound could be removed
7 from the pond sediment by n-hexane extraction. In the field study,
8 there was no n-hexane-extractable aminofenitrothion in the pond sediment.
9 That aminofenitrothion which could be extracted could only be extracted
10 with the use of HCl or certain hydrolytic enzymes. The inference
11 was that fenitrothion was microbially reduced in the sediment,
12 and that aminofenitrothion was somehow covalently attached to some
13 organic component of the sediment.

14 The kinetic data from the laboratory differ significantly from
15 those obtained from the field study. Basically, it appears that
16 fenitrothion binds to sediments much faster than would be predicted
17 from laboratory experiments. For example, the half-life for the
18 appearance of fenitrothion in pond sediment after the pond had been
19 sprayed was 1.8 ± 0.4 hr (3), while the half-life determined in the
20 laboratory (unshaken, and corrected for the temperature difference)
21 was 13.4 ± 2.4 hr. This discrepancy may be due to a change in the
22 ability of the pond sediment to bind fenitrothion after it had been
23 dried at 110°C prior to chemical characterization, or it may be an
24 artifact of experimental design (e.g., the sediment:water weight
25 ratio of the pond is unknown since the effective thickness of the
26 actively adsorbing layer of sediment is unknown).

1 In addition to these uncertainties with regard to "laboratory
2 kinetics" vs. "field work kinetics", it is probably also possible,
3 within the fairly large limits of experimental error, to regard the
4 kinetics of binding of fenitrothion to pond sediment determined in
5 the laboratory as resulting from the combination of a fast first-order
6 process and a slow first-order process (reflecting differing
7 accessibilities or strengths of binding sites) rather than reflecting
8 simple first-order kinetics over a period of 3 half-lives; in
9 accordance with Occam's razor, however, the latter approach was
10 adopted here.

11 The results of this work illustrate the difficulty involved
12 in trying to model anything as complex and inhomogeneous as sediment,
13 with binding sites of varying strength and accessibility, and a
14 biologically active microlayer; however, it is reasonable to conclude
15 that the organic carbon content of a sediment will play a significant
16 role in the thermodynamics and kinetics of binding of fenitrothion

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ACKNOWLEDGMENT

20 I thank Dr. R.A. McKeague of the Soil Research Institute,
21 Dept. of Agriculture, Ottawa, Canada, for the soil samples and analyses
22 of the sediment samples.

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FIGURE AND TABLE CAPTIONS

1

2

3 Table 1. Properties of Soils and Sediments.

4

5 Figure 1. Plot of $[F]_{ad(\infty)}$ vs. % organic carbon content of 6 soils
6 and 2 sediments. The slope, calculated by weighted (by
7 standard deviation) linear least squares analysis, is
8 $(9.24 \pm 1.75) \times 10^1 \mu\text{g (g sediment dry weight)}^{-1}(\% \text{ organic}$
9 $\text{carbon})^{-1}$ and the intercept is $(1.02 \pm 1.00) \times 10^1 \mu\text{g}$
10 $(\text{g sediment dry weight})^{-1}$; $r^2 = 0.83$.

11

12 Figure 2. Plot of k_{binding} vs. % organic carbon content for the
13 adsorption of fenitrothion to 6 soils and 2 sediments.
14 The slope, calculated by weighted (by standard deviation)
15 linear least squares analysis, is $(4.40 \pm 1.53) \times 10^{-3} \text{hr}^{-1}$
16 $(\% \text{ organic carbon})^{-1}$ and the intercept is $(2.11 \pm 0.54) \times$
17 10^{-2}hr^{-1} ; $r^2 = 0.81$.

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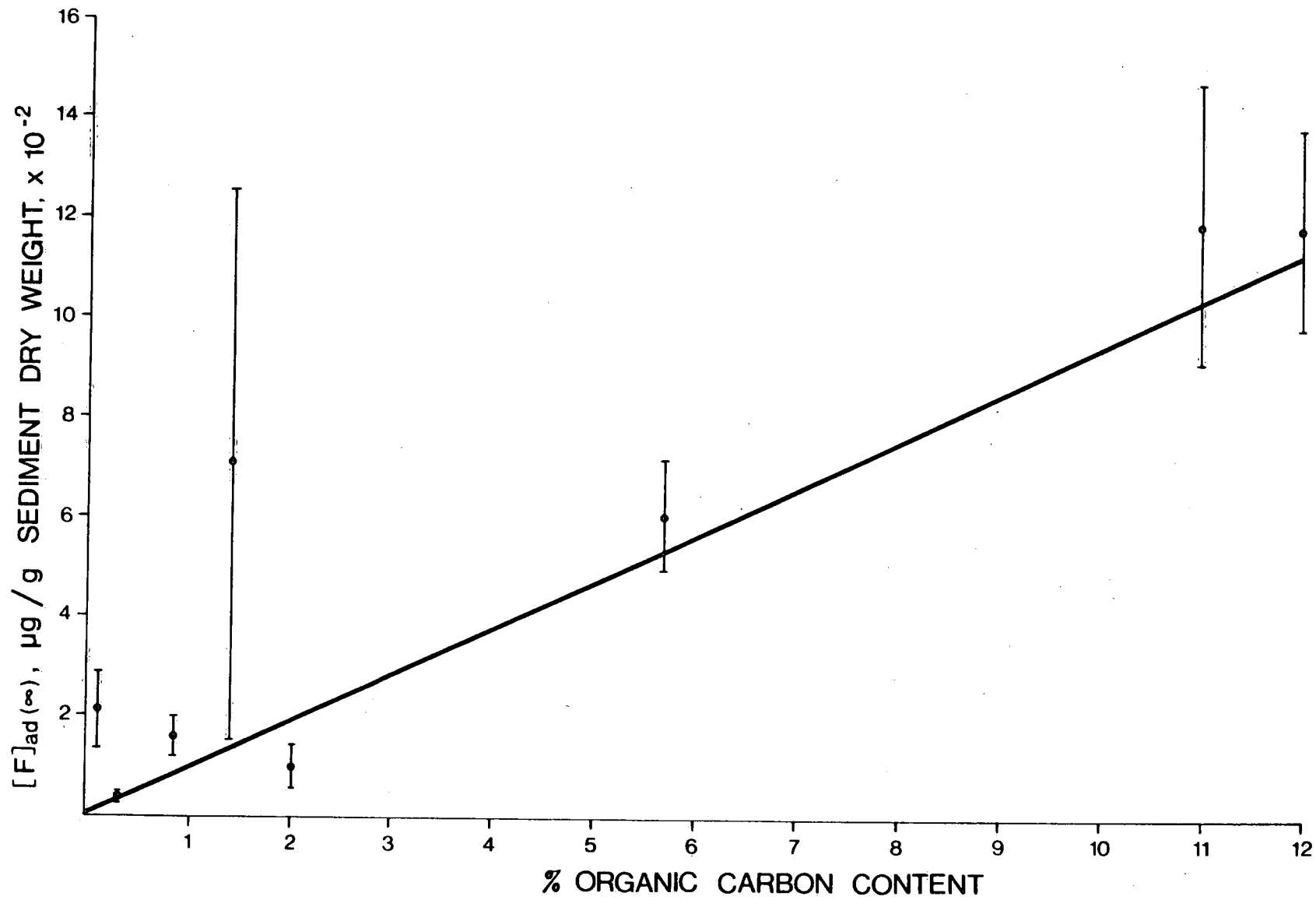
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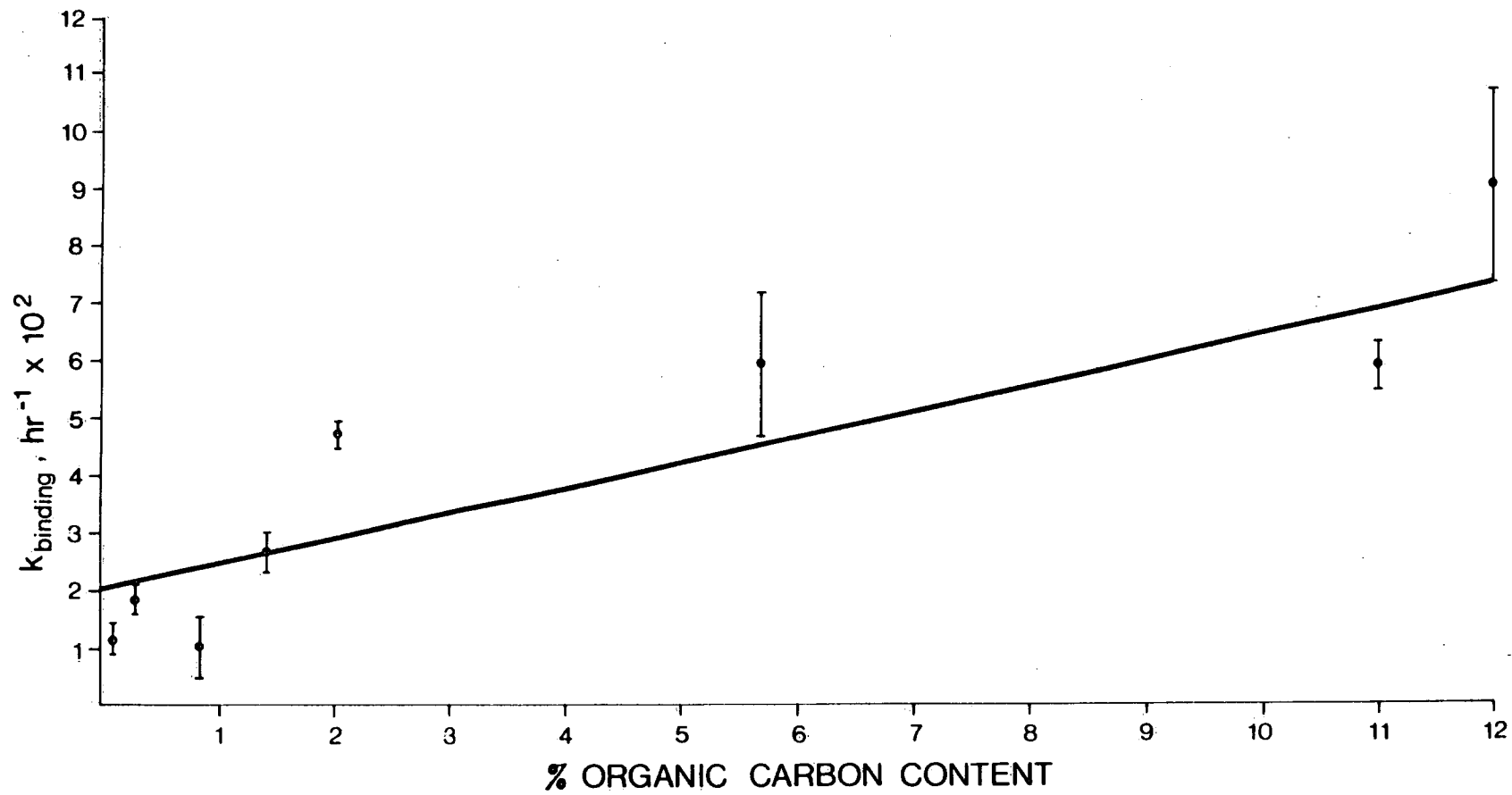
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Table 1. Properties of Soils and Sediments


Type	% Organic Carbon	% Clay	Elemental Analysis, % Total			
			Al	Fe	Ca	Mg
Victoria 1	11.0	12.0	6.0	3.0	2.0	0.9
Guelph 15	5.7	18.0	5.5	2.4	2.2	1.0
Ste. Foy 18	1.4	2.0	6.5	4.0	1.7	0.5
Ste. Foy 19	12.0	12.0	6.5	7.0	1.5	0.5
Truro 25	0.1	6.0	5.5	2.4	0.2	0.5
Ottawa 28	0.3	81.0	9.2	6.0	2.0	2.3
Pond Sediment	2.02	n.d.*	0	n.d.	4.0	0.65
Stream Sediment	0.84	n.d.	0	n.d.	2.25	0.41

* not determined





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