

## Soil Retention of Trifluoroacetate

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The phase out of chlorofluorocarbons (CFCs) has resulted in the use of hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) as environmentally acceptable alternative chemicals. Trifluoroacetic acid (TFA) has been identified as a degradation byproduct of these compounds, which largely returns to Earth's surface via precipitation. Little is known about the environmental and ecological fate of TFA. Soil retention studies were conducted to evaluate the potential accumulation of TFA in soil of terrestrial ecosystems. Batch equilibrium studies showed that detectable TFA was retained by 34 of 54 soils collected from diverse locations. Retention ranged from a high of 280 to 25  $\mu\text{mol kg}^{-1}$  (0-80% of added TFA). Most soils (43 of 54) did not retain TFA strongly ( $>25\%$ ), but soils high in organic matter and some mineral soils with high iron and aluminum content exhibited strong retention. Trifluoroacetate retention was correlated ( $r = 0.80$ ) with % organic matter content. Organic soils from wetlands, peatlands, and a boreal forest showed the greatest retention. The retention of TFA increased with decreasing pH. The magnitude of TFA retention was similar to  $\text{Cl}^-$  and  $\text{Br}^-$ . Trifluoroacetate retention decreased with increasing concentrations of  $\text{F}^-$ ,  $\text{Cl}^-$ , and  $\text{SO}_4^{2-}$ . The ultimate fate of TFA retained in soils is uncertain.

### Introduction

The Montreal Protocol and subsequent Amendments have called for the phase out of chlorofluorocarbons (CFCs) because of their role in stratospheric ozone depletion (1, 2). The search for environmentally acceptable replacements for CFCs has led to partially halogenated compounds, hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) (1, 3). Trifluoroacetic acid (TFA) has been identified as an atmospheric degradation byproduct of HCFC-123, HCFC-124, and HFC-134a and is the only byproduct not considered to be a naturally occurring compound (4). Trifluoroacetic acid will be produced in the atmosphere and transported via precipitation to the Earth's surface (4, 5). The global average TFA concentration in rainwater for the year 2010 is estimated to be in the range of  $8 \times 10^{-9}$ - $1 \times 10^{-7}$  M (6). The environmental fate of TFA deposition is uncertain, and the ecological consequences need to be evaluated.

The extent of sorption to soil particles can influence the transport, bioavailability, and toxicity of solutes. Inputs of TFA to natural ecosystems may be biodegraded by microbial processes, assimilated by vegetation, adsorbed by organic and/or mineral soil, or transported with drainage water.

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Microbial degradation of trace levels of TFA has been reported by Visscher et al. (7) in lake and saltmarsh sediments by reductive defluorination under anoxic conditions and by decarboxylation under oxic conditions. However, microbial degradation has not been reproduced in similar soils under similar conditions (8) to those used by Visscher et al. (7), and the significance of microbial degradation as a pathway of TFA loss remains uncertain. In any event, the rate of biodegradation of most organic compounds is influenced by the degree of adsorption to soil particles (9). The soil retention of TFA may decrease the availability of TFA for biodegradation.

Current research suggests that expected environmental concentrations of TFA are of little concern with respect to human health, but there is a need to evaluate the effects on ecosystems (6). Trifluoroacetate is transported from roots via the transpiration stream and can bioconcentrate in leaf tissues of plants (10, 11). There are reports of growth inhibition (11, 12) in tomato and wheat seedlings ( $>5 \times 10^{-4}$  M), sunflowers, mung beans, and wheat ( $>9 \times 10^{-4}$  M), and two species of algae out of seven tested ( $>1 \times 10^{-4}$  M). These concentrations are 1-3 orders of magnitude above TFA concentrations anticipated in precipitation. However, a recent modeling analysis suggests that, under conditions of high evapotranspiration, TFA concentrations could be much greater ( $>10^{-4}$  M) in surface waters of seasonal wetlands within a few decades (13). Recent measurements of TFA in rain indicate that current concentrations are above estimates projected for 2010 and cannot be explained by known sources or precursors of TFA (14). Soil/sediment retention is a potentially important mechanism of TFA accumulation in the environment. Soil retention is a critical issue, because inputs of TFA over an extended period to soils that exhibit retention may eventually accumulate to ecologically significant concentrations. It is likely that retention by soils will influence bioavailability and therefore toxicity of TFA to plants.

Retention of organic compounds by soil depends upon the specific chemical properties of the compound and soil properties. The trifluoroacetic acid molecule consists of both hydrophilic ( $\text{COO}^-$ ) and hydrophobic ( $\text{CF}_3$ ) functional groups (15). Trifluoroacetic acid is an acidic organic compound that predominantly occurs as an anion ( $\text{p}K_a = 0.81$ ) (16) under environmental conditions. This class of organics is considered highly mobile and susceptible to leaching from soils. In the only study of TFA adsorption in the literature, three agricultural, non-acidic soils were found to retain only 0.1-2.6% of added TFA (17). This study did not include any soils that are known to retain organic anions, particularly soils enriched with iron and aluminum or organic matter. Moreover, the concentration of TFA used in this experiment was 4 orders of magnitude larger than values anticipated in the environment over the next 20 years.

The objectives of this study were to evaluate the sorption of TFA on a variety of soils and minerals at concentrations comparable to anticipated values and to evaluate the soil characteristics and conditions that influence TFA sorption. In addition, the retention of TFA was compared with the retention of major inorganic anions. Finally, the influence of pH and the presence of competing anions on TFA retention by soil were evaluated.

### Materials and Methods

**Field Soil Samples and Their Characterization.** Thirty-five soil samples were obtained from 15 terrestrial sites of the National Science Foundation (NSF) Long-Term Ecological Research (LTER) Program. The LTER is a network of intensively studied ecosystems that represent important ecological zones, ranging from arctic (Toolik Lake) and boreal

(Bonanza Creek) sites in Alaska to a tropical rain forest in Puerto Rico (Luquillo). These sites encompass a wide range of soil and ecological conditions (18). Soil samples were also obtained from Lake Agassiz Peatlands, Minnesota; near Found Lake, Wisconsin; Lytina and Pihuvu Bor, Czech Republic; and Manaus, Belém, and a Brazilian cation in Brazil. At most sites, a surface and subsurface soil sample were collected, but for some sites only a single surface soil was obtained. At Hubbard Brook Experimental Forest, New Hampshire) soil samples were obtained from each of the major soil horizons. A total of 54 soil samples were used in the batch equilibrium study. Adsorption isotherms were also conducted for several well-characterized soil minerals (Na-montmorillonite, kaolinite, illite, aluminum hydroxide, and silicon dioxide) to evaluate the ability of these materials to retain TFA.

Soil samples were air-dried and passed through a 2-mm sieve prior to analysis. The soils were characterized for important chemical and physical parameters, including soil pH (19), total soil C and N (20), % organic matter (LOI) (20), soil texture (% clay, % silt, % sand) (19), exchangeable cations [calcium (Ca<sup>2+</sup>), magnesium (Mg<sup>2+</sup>), potassium (K<sup>+</sup>), sodium (Na<sup>+</sup>), iron (Fe<sup>3+</sup>), and aluminum (Al<sup>3+</sup>)] (21), cation exchange capacity (CEC) (21), and water-extractable anions [chloride (Cl<sup>-</sup>), nitrate (NO<sub>3</sub><sup>-</sup>), and sulfate (SO<sub>4</sub><sup>2-</sup>)] (19). Acid-extractable pyrophosphate, and citrate-dithionite extractable Fe<sup>2+</sup> and Al<sup>3+</sup> fractions were also determined (19).

Sorption Experiments. Batch equilibrium soil sorption studies were conducted on each of the soils. A 1:5 and 1:20 soil to solution ratio was used for organic and mineral soils, respectively. A range of sorbate concentrations (0, 2, 4, 7, 10, 20, 30, 40 μmol Na-TFA L<sup>-1</sup>) were used for each soil to develop sorption isotherms at ambient pH. These concentrations of TFA were chosen to be comparable with anticipated environmental conditions. Each soil was weighed into a 50-ml polypropylene centrifuge tube, the adsorbate was added, and the suspension was equilibrated on a reciprocating shaker filtered through 0.45-μm polypropylene fiber membrane filters (Gelman Sciences, Ann Arbor, MI). The TFA concentration of the filtrate was analyzed using ion chromatography (Dionex, Model DX 500). The difference between the amount of TFA initially in the adsorbate solution and the amount remaining after equilibration was determined to be the amount of TFA retained by the soil. Instrument reproducibility studies

determined that a difference of >0.5 μmol L<sup>-1</sup> was significant within 3 μmol L<sup>-1</sup> for soils with low organic matter content (>17%) and 5 μmol L<sup>-1</sup> for soils with high organic matter content (>17%) in replicate samples. Since no specific mechanism of sorption is determined by this method, we have used the more general term "retention" to indicate the amount of TFA remaining in the soil. No detectable retention of TFA by the polypropylene tubes was found.

Langmuir and Freundlich adsorption isotherms were plotted and fitted to evaluate the extent of retention of TFA on all of the soils. The Langmuir adsorption maximum (X<sub>L</sub>) was determined using OPTIMO, an optimization program that allows for the inclusion of uncertainty when fitting data to a Langmuir model (22). The sorption distribution coefficient (K<sub>d</sub>) was determined for the special case of the Freundlich model where the Freundlich coefficient (n) = 1. When the sorption data showed better fit with the Langmuir model, the linear portion of the isotherm was used to determine K<sub>d</sub>. This procedure may introduce some error into the use of K<sub>d</sub> when evaluating the sorption of TFA, but the distribution constant is widely used as an index of chemical retention by soil, and this approach facilitates a comparison of TFA retention to other compounds. Distribution constant (K<sub>d</sub>) was reproducible within 0.09 L kg<sup>-1</sup> for soils with low organic matter content (<17%) and 0.16 L kg<sup>-1</sup> for soils with high organic matter content (<17%) in replicate samples. A description of the Langmuir and Freundlich adsorption isotherms is provided in Travis and Emler (23).

Bonanza Creek (BNZ OH) organic horizon and Coweeta Hydrologic Laboratory (CWT AF) A horizon (frigid) were selected to further examine factors that influence TFA retention because of their contrasting physical and chemical characteristics and relatively high TFA retention (Table 1). The pH dependence of TFA retention was determined using 20 samples of both of the soils. A 1:5 and 1:20 soil to solution ratio was used for BNZ OH and CWT AF, respectively. Thirty-milliliter volumes of 30 μmol L<sup>-1</sup> Na-TFA were added to 50-ml polypropylene centrifuge tubes and shaken for 1 h at 25 °C. After the initial equilibration period, acid (HNO<sub>3</sub>) or base (NaOH) was added to adjust the final pH in a range from 2 to 10. After an additional 24 h of equilibration, the pH value of each sample was measured, and this pH was used as the final reaction value. Samples were analyzed as described for the batch equilibrium samples.

TABLE 1. Characteristics and TFA Adsorption Parameters for Selected Soils

location/soil class	soil	pH	organic matter (%)	clay (%)	CEC (cmol <sub>c</sub> kg <sup>-1</sup> )	X <sub>L</sub> (μmol kg <sup>-1</sup> )	K <sub>d</sub> (L kg <sup>-1</sup> )
Bonanza Creek, AK	organic horizon	5.30	82.5	3	63.6	245	11
	mineral horizon	4.61	30.3	5	12.1	10	0.88
Coweeta, NC	A horizon (mesic)	4.16	9.4	3	2.1	26	1.5
	AB horizon (mesic)	4.20	6.2	9	1.4	47	0.68
	A horizon (frigid)	4.12	24.8	7	5.4	76	1.2
Lytina, Czech Republic	Ca horizon	2.76	38.5	5	20.6	32	0.71
	E horizon	3.11	2.9	2	4.0	27	0.30
	Be1 horizon	3.34	7.9	6	11.6	30	0.54
	Be2 horizon	3.81	7.1	7	7.3	45	0.53
	C horizon	4.05	4.0	1	3.7	60	0.60
	Ca horizon	3.04	79.5	8	17.2	54	3.9
	E horizon	3.18	1.4	2	1.0	19	0.34
	Bh horizon	3.68	17	4	12.5	21	0.68
	Be1 horizon	4.01	8.1	6	2.3	18	0.42
	Be2 horizon	4.70	0.5	3	0.05	13	0.17
	wetland	5.04	75.2	2	17.7	180	5.8
	peat core	3.22	93.3	1	17	290	20
Lake Agassiz, MN	Histosol						
	Konza Prairie, KS	5.85	10.1	27	23.1	28	1.5
	Mollisol						
	Nivot Ridge, CO	4.33	18.6	2	5.5	17	0.19
	inceptisol	4.71	6.1	11	10.4	4	0.32
	mineral horizon						
	organic horizon						
	surface soil						

Retention of TFA was compared to the retention of other major inorganic anions by conducting batch adsorption studies on BNZ OH and CWT AF using fluoride ( $F^-$ ),  $Cl^-$ ,  $TFA^-$ , bromide ( $Br^-$ ),  $NO_3^-$ , and  $SO_4^{2-}$ . A range of sorbent concentrations (0, 5, 10, 15, 20, 30, 40, 60, 80, 120, and 180  $\mu\text{mol L}^{-1}$  of a salt of each anion) was used. A 1:5 and 1:20 soil to solution ratio was used for BNZ OH and CWT AF, respectively. Anion retention was determined using the same procedure as described for studies of TFA retention.

Competitive sorption of TFA with other anions was examined on BNZ OH and CWT AF soil samples using  $F^-$ ,  $Cl^-$ , and  $SO_4^{2-}$ . The soils were leached in a column with deionized, distilled water to remove excess anions and to reduce variability of ambient anion concentration. The soils were air-dried prior to analysis. A 1:5 and 1:20 soil to solution ratio was used for BNZ OH and CWT AF, respectively. Ten milliliters of a range of sorbent concentrations of the individual anions (0, 10, 20, 30, 40, 60, 80, 120, and 180  $\mu\text{mol L}^{-1}$ , final concentrations) was added to each soil in a 50-mL polypropylene centrifuge tube. The samples were equilibrated for 24 h. After the initial equilibration, 10 mL of 40  $\mu\text{mol L}^{-1}$   $Na-TFA$  was added. The samples then were equilibrated for an additional 24 h. Trifluoroacetate retention was determined the same as described previously.

## Results

**Sorption Isotherms.** The soils investigated exhibited a range of TFA retention, ranging from no detectable retention to high retention of added TFA (up to 60%). A subset of 12 soils from the 30 soils that showed significant TFA retention were chosen as representative of the TFA retention characteristics found in this study. These soils encompass a wide range of chemical and physical characteristics. Selected chemical and physical properties of the soils, Langmuir adsorption maximum ( $X_i$ ), and distribution coefficient ( $K_d$ ) are given in Table 1.

Isotherms generally exhibited one of two characteristic shapes, either L-type (Langmuir) or C-type (constant partitioning) (24). Isotherms for soils with moderate to high clay (35–20%) content and low organic matter content (<10%) were generally characterized by linear adsorption (C-type). Isotherms for soils with high organic matter (50–90%) content and low clay content (<10%) typically showed an asymptote or adsorption maximum (L-type). Isotherms for soils with intermediate clay content and organic matter exhibited either C-type or L-type characteristics.

At all sites where TFA retention was evaluated for organic and mineral soils, the organic horizon exhibited greater retention. Soils with high organic matter content (>75% OM), such as a peat sample from the Lake Agassiz Peatlands, were found to retain the highest concentrations of TFA. In addition to differences in TFA retention between bulk organic and mineral horizons, differences were also evident between soils from horizons within the soil profile. The greatest TFA retention was found in the organic surface horizon with decreasing TFA retention down through the profile. The B horizon showed the least TFA retention.

The sorption isotherms of selected minerals indicated that aluminum hydroxide ( $K_d = 3.7 \text{ L kg}^{-1}$ ) and 2:1 clay minerals [Na-montmorillonite ( $K_d = 2.9 \text{ L kg}^{-1}$ ) and illite ( $K_d = 1.1 \text{ L kg}^{-1}$ )] retained TFA to some extent. Minerals exhibiting TFA retention were characterized by linear adsorption, similar to the pattern observed for mineral soils. Retention of TFA was not evident for kaolinite or silicon dioxide. During the investigation of TFA retention by illite, a high concentration (4600  $\mu\text{mol L}^{-1}$ ) of  $SO_4^{2-}$  was observed in the equilibrating solution. This  $SO_4^{2-}$  is believed to be contamination introduced during processing of the clay. In the presence of elevated  $SO_4^{2-}$ , little retention of TFA by illite ( $K_d = 0.03 \text{ L kg}^{-1}$ ) was evident. The influence of elevated  $SO_4^{2-}$  on TFA retention was investigated by washing the illite with deionized,

distilled water to remove the  $SO_4^{2-}$ . Aliquots of illite were washed twice ( $K_d = 0.99 \text{ L kg}^{-1}$ ) and three times ( $K_d = 1.1 \text{ L kg}^{-1}$ ), decreasing the  $SO_4^{2-}$  concentration in the equilibrating solution to 200  $\mu\text{mol L}^{-1}$ . The retention of TFA on illite increased markedly after  $SO_4^{2-}$  was removed from the clay.

**Influence of Soil Properties on TFA Retention.** Linear regression analysis between TFA retention and selected soil properties was used to identify soil constituents that influence retention and to better characterize the retention mechanisms. The correlations reported are for linear regression analysis performed with  $X_i$  quantifying TFA retention, but use of the  $K_d$  value gave similar results. Results are significant at the 0.01 probability level. The analysis was performed on the entire data set and on the surface and subsurface soil samples separately.

The analysis of the influence of surface soil characteristics on TFA retention were similar to patterns observed for the entire data set. The soil properties exhibiting the strongest positive correlations were % organic matter ( $r = 0.60$ ), total carbon content ( $r = 0.53$ ), and exchangeable  $Fe^{3+}$  ( $r = 0.65$ ). Surface soils exhibited a negative correlation with clay content ( $r = -0.48$ ). While this result may appear surprising, it probably reflects more the organic vs mineral content of the soil rather than adsorption characteristics of clays. Indeed, a strong relationship was evident between  $X_i$  and the ratio of % organic matter to clay content ( $r = 0.90$ ).

The group of subsurface soils was comprised mainly of soils from the Czech Republic (Spodosols and Inceptisols). Subsurface soils results were correlated with different soil properties than the surface soils, indicating possible differences in adsorption mechanisms. Of these, probably the most noteworthy is the positive correlation with clay content ( $r = 0.38$ ) and the negative correlation with total C content ( $r = -0.85$ ) and extractable  $SO_4^{2-}$  ( $r = -0.30$ ). While strong relationships were evident with other parameters, we believe that this reflects the role of clays in controlling the chemical characteristics of soil rather than a causal relationship.

**Effect of Suspension pH on TFA Retention.** The adsorption of ionic solutes to soil and minerals typically is pH-dependent. Anion adsorption generally increases with decreasing pH due to the protonation of soil surfaces. The CWT AF soil showed a typical adsorption edge, with a marked increase of TFA retention with decreases in pH below 5.0. In contrast, the BNZ OH soil, with a higher organic content exhibited a more gradual increase in TFA retention with decreases in pH over a wider pH range (Figure 1).

**TFA Retention Relative to Other Anions.** The results of the comparison of TFA retention to that of other anions for BNZ OH and CWT AF is shown in Figure 2. The order of decreasing retention of anions by BNZ OH was  $F^- >> SO_4^{2-} > Cl^- > TFA^- > Br^- > NO_3^-$ . Trifluoroacetate retention on the Bonanza Creek soil was similar to  $Br^-$ . The order of decreasing retention of anions by CWT AF was  $F^- = SO_4^{2-} > Cl^- = TFA^- > Br^- > NO_3^-$ . Trifluoroacetate retention on the Coweeta soil was similar to  $Cl^-$  and  $Br^-$ .

**Effect of Anion Concentration on TFA Retention.** Trifluoroacetate retention was influenced by the presence of other anions, suggesting competition between TFA and other anions for available adsorption sites (Figure 3). The addition of increasing concentrations of  $F^-$ ,  $Cl^-$ , and  $SO_4^{2-}$  to the BNZ OH soil all decreased TFA retention, but additions of increasing concentrations of  $F^-$  were more effective in decreasing TFA retention in comparison to the other anions. The addition of increasing concentrations of  $Cl^-$  and  $F^-$  to the CWT AF soil decreased TFA retention slightly, but the addition of 120  $\mu\text{mol L}^{-1}$   $SO_4^{2-}$  reduced TFA retention by approximately half. A greater decrease in the TFA retention with added anions was found on the CWT AF soil than the BNZ OH soil.

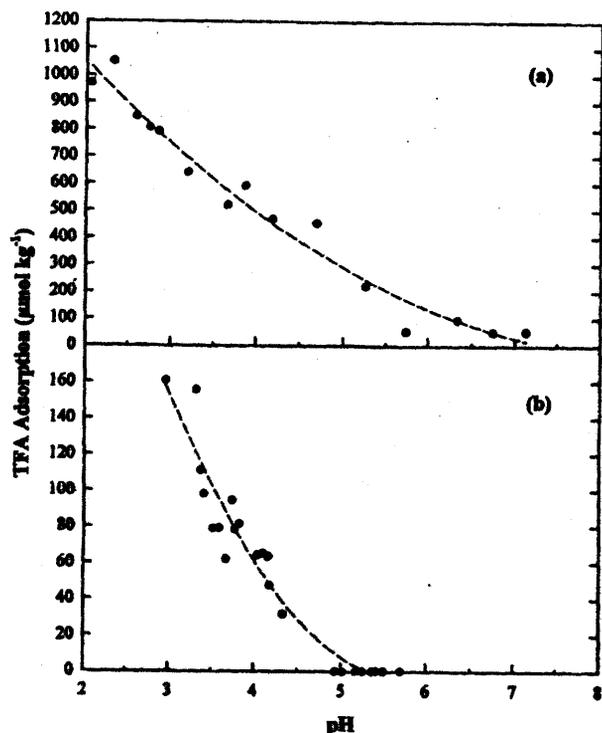


FIGURE 1. Retention of TFA as a function of pH for (a) Bonanza Creek, organic horizon, and (b) Coweeta Hydrologic Laboratory, A horizon (frigid).

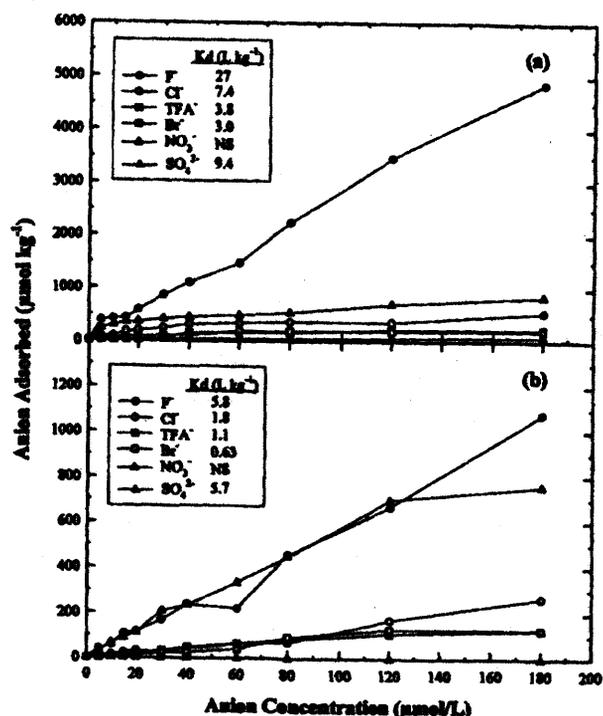


FIGURE 2. Adsorption isotherms comparing TFA retention to other anions for (a) Bonanza Creek, organic horizon, and (b) Coweeta Hydrologic Laboratory, A horizon (frigid). Distribution coefficient ( $K_d$ ) is given in the legend. No significant retention is indicated by NS.

### Discussion

In general, TFA was retained in organic soils to a greater extent than in mineral soils. Organic soils that exhibited higher retention of TFA sorbed between 20 and 60% of added TFA. In contrast, mineral soils retained 0–15% of added TFA.

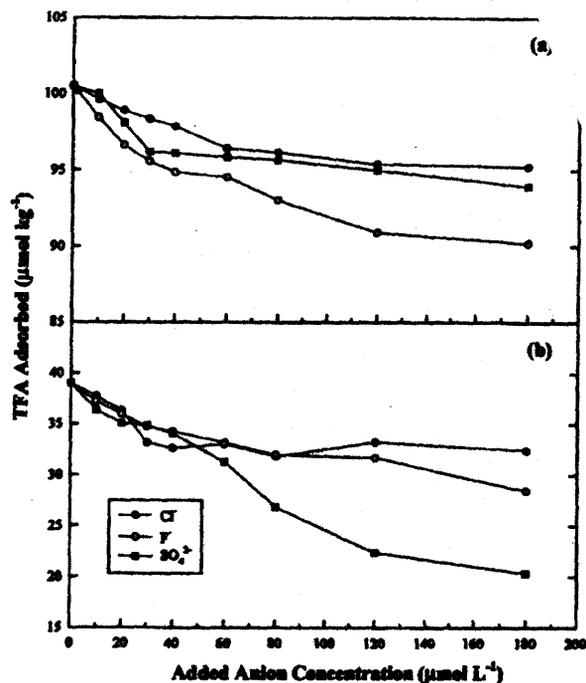


FIGURE 3. Effect of increasing concentrations of competing anions on TFA retention for (a) Bonanza Creek, organic horizon, and (b) Coweeta Hydrologic Laboratory, A horizon (frigid).

Retention ranged from a high of 260 to 25  $\mu\text{mol kg}^{-1}$ . The magnitude of TFA retention in the majority of soils studied was small and similar to that of other monovalent anions.

Classifying TFA mobility (25) on the basis of  $K_d$  values suggests that TFA would be considered immobile ( $K_d > 10$ ) in only three of 54 soils studied. These soils were all characterized by elevated organic matter content (> 70%). In addition, eight soils exhibited low TFA mobility ( $K_d = 2-10$ ), 15 soils exhibited intermediate TFA mobility ( $K_d = 0.5-2$ ), and TFA would be considered mobile in eight of the soils studied ( $K_d = 0.1-0.5$ ). No significant TFA retention was found in 20 of the soils studied. Trifluoroacetate can therefore be considered as a mobile organic compound in soils at the majority of sites investigated.

Results from this study suggest that soil organic matter and mineral surfaces influence the retention of TFA by soils. There seem to be two mechanisms of TFA retention, indicated by differing shapes of TFA isotherms, for mineral and organic soils. Conformity of water-soluble TFA to a Langmuir adsorption isotherm may indicate that the retention is site-specific. Furthermore, the retention of TFA by soil surfaces is dependent upon pH and the presence of other anions in soil solution. Retention of TFA increased with decreasing soil suspension pH and decreased with increasing concentrations of competing anions. It is expected that rates of TFA leaching from soils will depend on soil types, organic content, soil pH, inputs of competing anions (e.g., atmospheric deposition), and atmospheric deposition rates of TFA.

The ecological fate of TFA is uncertain. Trifluoroacetate was significantly retained by wetland, peatland, and boreal forest soils in this study. These ecosystems are often the habitats for rare and endangered species (26). The retention of TFA by soils in these environments is critical to assessing the impact of this substance on sensitive ecosystems.

The ultimate fate of TFA in soils is an important environmental question. In general, acidic solutes such as TFA are weakly retained in soil. However, conformity to the Langmuir adsorption isotherm can indicate a stronger mechanism of retention. Isotherms cannot be interpreted to indicate any particular mechanism of retention, but results

indicate a need for further process level studies of TFA retention by soil organic matter and mineral surfaces. If TFA is not strongly retained by soil then the transport of TFA would be governed largely by the amount and frequency of precipitation and drainage. The strong retention of TFA may indicate that soil may be a permanent sink for TFA. There is a critical need to assess the reversibility and bioavailability of TFA retained by soils.

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