Transport and fate of trifluoroacetate in upland forest and wetland ecosystems

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ABSTRACT   Although trifluoroacetate (TFA), a breakdown product of chlorofluorocarbon replacements, is being dispersed widely within the biosphere, its ecological fate is largely unknown. TFA was added experimentally to an upland, northern hardwood forest and to a small forest wetland ecosystem within the Hubbard Brook Experimental Forest in New Hampshire. Inputs of TFA were not transported conservatively through these ecosystems; instead, significant amounts of TFA were retained within the vegetation and soil compartments. More TFA was retained by the wetland ecosystem than by the upland forest ecosystem. Using simulation modeling, TFA concentrations were predicted for soil and drainage water until the year 2040.

Chlorofluorocarbons (CFC) catalyze the breakdown of stratospheric ozone (1, 2), and future manufacture of these materials is banned by international agreements (3). In the United States, manufacture of CFCs ceased on January 1, 1996 (4). Degradation of CFC replacements HFCs and HCFCs (such as HCFC-123, HCFC-124, and HFC-134a) in the atmosphere forms trifluoroacetate (TFA) (5), which is highly soluble in water (>10 g ml^{-1}) (unpublished data) and thus is transported rapidly back to the Earth's surface in atmospheric deposition (6, 7). Manufacturers have suggested that TFA is inert and is conservatively transported in water without significant long term accumulation in ecosystem compartments. Here we report on the first experimental study of the transport and fate of TFA in natural ecosystems.

METHODS

TFA was applied to irrigated plots within an upland forest and to a small wetland ecosystem within the Hubbard Brook Experimental Forest (HBEF) (8), 43° 56′N, 71° 45′W, of the White Mountain National Forest of north central New Hampshire. We analyzed TFA in surface water, stream water, and soil water by ion chromatography. Selected water, soil, and vegetation samples were analyzed by ion-selective mass spectrometry to detect trace concentrations of TFA (6). All samples were stored at $\approx 4°C$ until analysis.

Experimental Areas

Upland Forest Plots. Twice during the summer of 1994, sodium trifluoroacetate (molecular weight, 136 g/mol) was added to plots within an upland beech (*Fagus grandifolia* Ehrh.) forest in the Norris Brook watershed of the HBEF (9). One of the six 1-m × 2-m plots received 274 mg/m² TFA, and two of the plots received 68 mg/m² TFA. No TFA was added

to three adjacent reference plots. The plots were irrigated once (40 liter/m²) or twice (80 liter/m²) per week from July to September (total 1140 liter/plot; approximately twice the mean ambient precipitation input for the experimental period) with water from nearby Mirror Lake (10) (total dissolved solids, 21 mg/liter). In each plot, soil water was collected from a pair of zero-tension lysimeters (which were installed in 1988) beneath the following horizons: Oa (at ≈ 8 cm), Bh (at ≈ 28 cm), and Bs2 (at ≈ 48 cm). We estimated the amount of TFA transported through the soil profile by multiplying the concentration of TFA in each sample of soil water by the water output from the related soil horizon (11) and summing these values during the study period. We used a modified version of the BROOK2 hydrology simulation model (12), developed and parameterized for the HBEF,¶ to estimate the water transport through the soil profile of the upland forest plots. This modification calculated flow through each soil horizon based on the assumption that water removed from the soil profile by transpiration was proportional to the distribution of roots in each soil horizon (11). We collected vegetation (September) and soil (November) samples from each plot.

Wetland Ecosystem. The small (407 m²) forest wetland (Fig. 1) was located at 701-m elevation within the Bear Brook drainage of the HBEF (13). It contained mosses (*Sphagnum* spp.) and sedges (*Carex* spp.) and was surrounded by an 80-year-old northern hardwood forest dominated by American beech (*F. grandifolia* Ehrh.), yellow birch (*Betula alleghaniensis* Britt.), and sugar maple (*Acer saccharum* Marsh.). This small wetland has organic soil extending to a maximum depth of 1 m, probably experiences both oxic and anoxic conditions, and is a net source of methane (13). Ground water wells and piezometers were installed in 1988–1989. We collected pretreatment samples of precipitation and stream water in 1993. Three times during the summer of 1994, sodium TFA dissolved in previously collected stream water from just below the weir on nearby Bear Brook, and stemflow from the surrounding forest was sprayed manually onto the wetland at ground level. The three sections of the wetland received a total of 113, 6, or 3 mg/m² of TFA (Fig. 1).

Rainfall data were collected from a standard rain gauge, located ≈ 236 m from the wetland (14). Water outflow was measured at a temporary gauging weir located on the stream draining the wetland. Samples of surface water, stream water, and soil water were collected at least weekly from June to November. We collected vegetation (September) and soil (August and November) samples after all of the treatments were applied.

Soil Adsorption Studies

Batch equilibrium studies of soil adsorption were conducted on each of the upland forest soil horizons and the wetland soil.

Abbreviations: CFC, chlorofluorocarbons; TFA, trifluoroacetate; HBEF, Hubbard Brook Experimental Forest.
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¶BROOK2 freeware and documentation: United States Department of Agriculture Forest Service, P.O. Box 640, Durham, NH 03824.
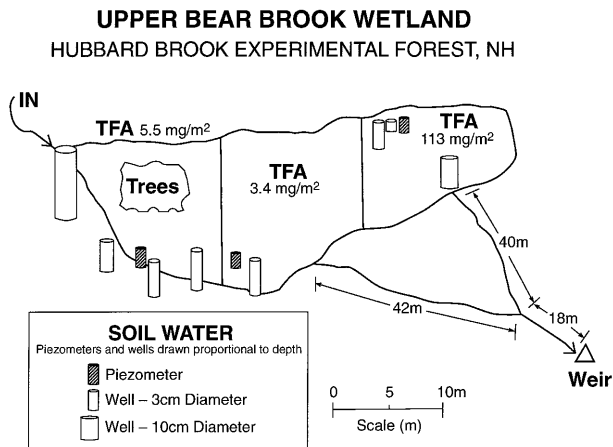
FIG. 1.   Map of wetland ecosystem study site.

Adsorbate solutions of 226, 452, 791, 1130, 2260, 3390, and 4520 μg/liter TFA were equilibrated with air-dried, sieved (2 mm) soil for 24 h. A 1:10 soil-to-solution ratio was used for organic soils, and a 1:5 soil-to-solution ratio was used for mineral soils. After equilibration, the suspension was centrifuged and the centrate was filtered and analyzed for TFA by ion chromatography (15). Adsorption isotherms were plotted to evaluate the extent of TFA retention on all of the soils.

Modeling Simulation

Hypothetical calculations of the fate of atmospheric inputs of TFA on concentrations of TFA in drainage water and soil were conducted using a chemical equilibrium model. The column model couples the chemical equilibria in soils and solutions model with a one-dimensional flow model for simulation of flow through a soil column (16). Adsorption parameters calculated from the adsorption isotherms (15) were used in the column model. Scenarios of TFA concentrations were obtained from Rodriquez *et al.* (17) and Tromp *et al.* (18). Values after the year 2040 were assumed to remain constant. Calculations were conducted using site-specific information for precipitation quantity, evapotranspiration, and average bulk density for the HBEF.

RESULTS

In the upland forest, TFA was transported rapidly through the soil profile by drainage water, reaching the top of the C horizon within 1–3 weeks (Fig. 2). During the first 4 months after the application of TFA (July-October 1994), a maximum of 7–53% of the added TFA was retained in the organic Oa soil horizon (<10 cm thick), while little was retained in the deeper, more sandy Bh and Bs2 mineral horizons of this Spodosol. Concentrations of TFA were below the detection limit (<50 μg/liter) in all soil waters collected from the reference plots. The high concentrations of TFA (3 mg/liter) detected in the deeper soil horizons (30–50 cm) of the treatment plots shortly after the addition of TFA to the soil surface may indicate that TFA was transported rapidly through soil macropores.

It is likely that TFA, which was added at relatively high amounts (as in this study), will be leached from the soil during a couple of years or until the TFA concentration in soil returns to the prevailing ambient level. Cycling through the vegetation probably would take much longer. Inputs of TFA accumulated in foliage of trees on the upland plots, but the fate of the TFA in the foliage is not known. In unirrigated plots within the upland forest during the following year, the pattern of TFA movement was similar, but a lower proportion of the added TFA moved through the soil profile (19).
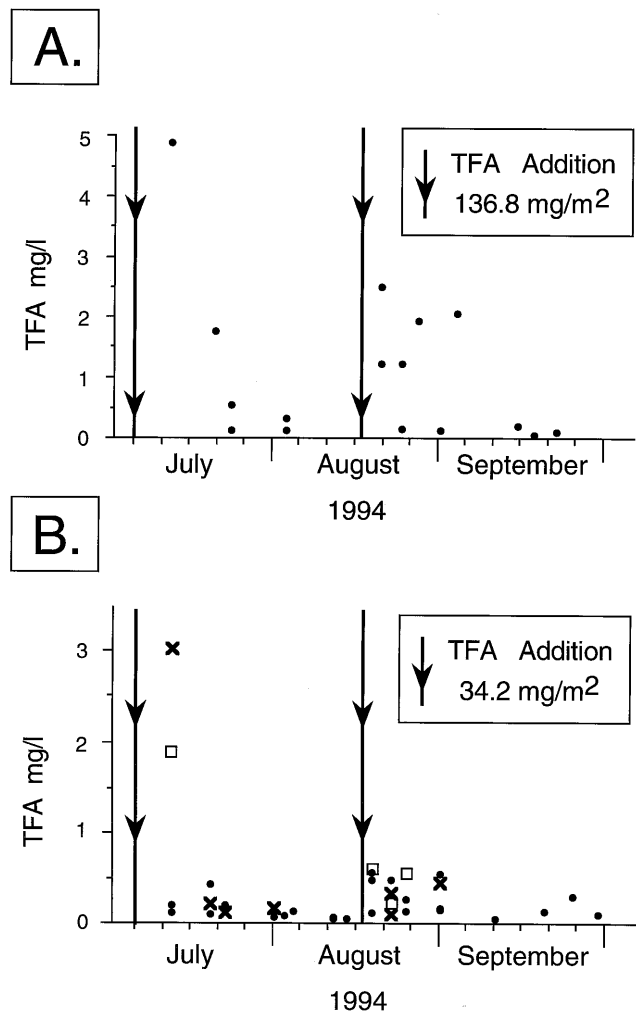

FIG. 2.   The concentration of TFA in soil water of upland forest plots in HBEF after experimental addition of TFA. (*A*) Two additions of 136.8 mg of TFA/m^2 and (*B*) two additions of 34.2 mg of TFA/m^2 were made as shown. Symbols indicate soil horizons: Oa (●, at 8 cm), Bh (□, at 28 cm), and Bs2 (X, at 48 cm). Samples (*n* = 93) with less than the ion chromatographic detection limit of 0.05 mg/liter TFA are not shown.

When TFA was applied experimentally to a small forest wetland at HBEF, the concentration of TFA decreased rapidly to <50 μg/liter in the soil water and surface water, but less than 0.2% of the added TFA was exported over the weir in the outflow stream of the wetland during June-October 1994 (Fig. 3). Based on the rate of disappearance of TFA from the soil water and the hydrology of this small wetland (13), conservative transport of added TFA should have resulted in TFA concentrations of 1–3 mg/liter in the outflow stream. The TFA concentrations in stream water samples (*n* = 28), collected June-October 1994 during the experimental manipulation were comparable to the background concentration of TFA in stream water before the addition of TFA, except for two samples (maximum TFA 0.4 μg/liter), which represented negligible outflow of TFA in stream water from the wetland area. Twice during the summer, stream flow ceased and the surface of the wetland dried, but we never detected an increase in the concentration of TFA in surface water attributable to evaporative concentration (18). Thus, the added TFA was either retained within the vegetation and soil of the wetland or transformed into other compounds.

Added TFA was retained by storage in vegetation (Table 1). The maximum concentration (79.80 ± 15.8 μg/g) of TFA
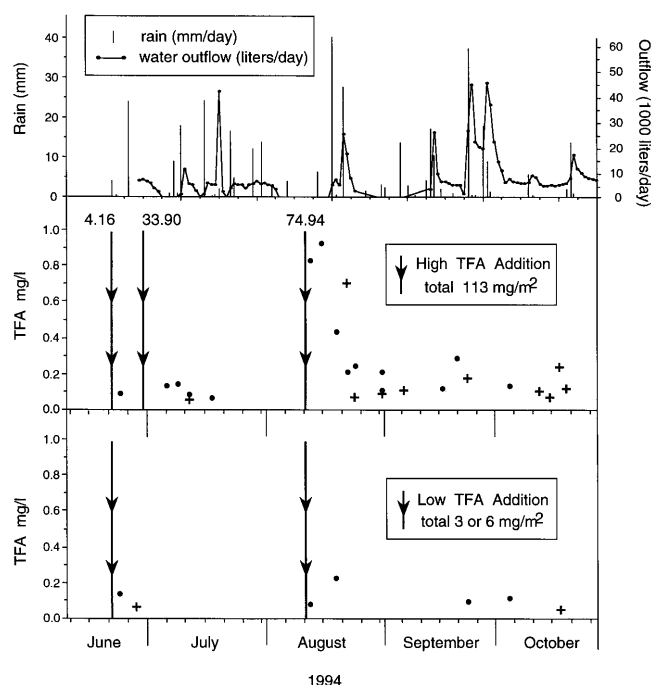
FIG. 3. The concentration of TFA in water after experimental additions of TFA to a forest wetland in HBEF. Symbols indicate surface water (●) or soil water (+). Samples ($n = 268$) with TFA concentrations less than the chromatographic detection limit of 0.05 mg/liter are not shown.

measured in vegetation occurred in leaves of one *Acer pensylvanicum* tree in the wetland, which received an additional 500 mg/m^2 TFA applied to the soil at its base. Vascular plants can take up TFA in the transpiration stream and may accumulate TFA in leaves (20, 21). In one laboratory study, plants accumulated only 60% of the TFA expected, based on passive uptake of TFA in transpiration (20). At HBEF, transpiration is ≈28% of the annual precipitation (9). Of the added TFA, <50% was retained by storage in tree leaves of the wetland. TFA probably is not metabolized by plants (21), so it likely will be redeposited on the soil surface in leaf litter. The fate of TFA in decomposing litter on the forest floor is presently unknown.

Some of the added TFA was retained in the soil (Table 1). In one laboratory study of soil adsorption, <3% of the added TFA was retained by three agricultural soils (unpublished report). However, we observed that the organic surface soil of the wetland in this study (Fig. 4) retained up to 63% of the added TFA (21 mg/kg dry soil). The surface, organic horizon of the upland forest soil retained ≈20% of the added TFA. In contrast, soils from the lower, mineral horizons of the upland forest retained only 4–8% of the added TFA. Overall, TFA retained in upland forest and wetland soil horizons closely matched retention results obtained in the laboratory (Fig. 4).

The potential for microbial degradation of TFA remains unclear. No significant microbial breakdown of TFA was detected in laboratory studies at 0.02–1140 mg/liter TFA (22, 23). In contrast, substantial, rapid breakdown of TFA at <0.1 mg/liter was observed in laboratory studies of lake and salt marsh sediments, under both aerobic and anaerobic conditions (24). Decomposition in anoxic environments is of particular concern because one of the observed intermediates was monofluoroacetate, sold commercially as the poison "1080," which is highly toxic to microorganisms (25) and mammals (26). In anoxic laboratory incubations, our wetland soil was methanogenic, but microbial degradation of TFA was slight, <1% of the added TFA (27). Whether microbial storage and/or degradation of TFA occurs in the complex, variable environment outside laboratory conditions is unknown but is vitally important for predicting the environmental impact of TFA.

At HBEF, ambient stream water concentrations are ≈10 times greater than precipitation (Table 1). Using soil adsorption and hydrologic data from the HBEF to parameterize the soil column model (16), we predicted TFA concentrations in soil and drainage water given TFA deposition scenarios until the year 2040 (18) and constant deposition thereafter. Concentrations of TFA in precipitation at HBEF were ≈6 times and 65 times less than modeled values for 1993 and 2040, respectively. However, concentrations of TFA in stream water at HBEF were ≈400 times and 5 times greater than modeled values for 1993 and 2040, respectively. Our model calculations of TFA retention in soil at HBEF suggested a severalfold increase in concentrations in response to projected increases in deposition. Clearly, more information is needed to establish both ambient and background levels of TFA in the environment.

DISCUSSION

The transport and potential environmental impact of TFA apparently varies across landscapes. Conservative transport of TFA seems most likely to occur through well drained, aerobic soils whereas nonconservative transport is more likely to occur through organic soils. Movement of TFA in the upland forest soils of the HBEF was controlled primarily by hydrologic processes. More than 70% of the added TFA was exported

Table 1. Concentrations of TFA in various ecosystem components of the HBEF

| TFA added, mg/m^2	Location	Sample	Mean TFA ± SD, μg/g ($n = 3$)	Biological concentration factor
0	Forest wetland	Precipitation	$75 \times 10^{-7} \pm 5 \times 10^{-7}$*	
0	Forest wetland	Stream water	$88 \times 10^{-6} \pm 5 \times 10^{-6}$†	
112	Forest wetland	*Acer saccharum*	2.110 ± 0.200	8
112	Forest wetland	*Acer pensylvanicum*	12.800 ± 2.000	32
112	Forest wetland	Surface soil	0.335 ± 0.418	
0	Upland forest	*Fagus grandifolia*	0.018 ± 0.003	
274	Upland forest	*Fagus grandifolia*	1.570 ± 0.150	10
274	Upland forest	Soil Oe horizon	0.082	
274	Upland forest	Soil Bh horizon	0.062	
274	Upland forest	Soil Bs horizon	0.023 ± 0.003	
68	Upland forest	Soil Oa horizon	0.197	
68	Upland forest	Soil Bh horizon	0.024 ± 0.003	
68	Upland forest	Soil Bs horizon	0.005	

*7.5 ± 0.5 ng/liter.
†88 ± 5 ng/liter.
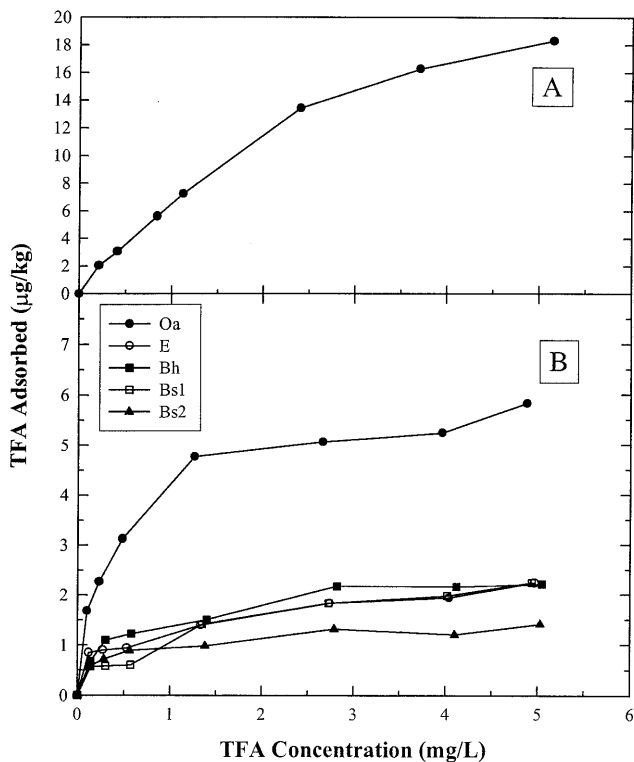
FIG. 4.   TFA retained as a function of solution TFA concentration for the wetland soil (*A*) and upland forest soil horizons (*B*).

from the upland forest in drainage water (July-November) while the remainder was retained in the surface organic soil (≈ 10–20%) and vegetation (≈ 5–20%). In contrast, probably <5% of the added TFA flowed out of the forest wetland in drainage water. Considerable TFA was retained (June-November) in the forest wetland soil (20–60%) and vegetation (20–50%).

The average global concentration of TFA in rainfall is predicted to be 160 ng/liter by 2010 (18), but precipitation in central Europe currently has elevated concentrations of TFA (≈ 100 ng/liter, range 30–240 ng/liter) (7). The concentration of TFA in precipitation (7.5 ng/liter) at HBEF (Table 1) is lower than reported elsewhere. Similarly, the ambient concentration of TFA in stream water at HBEF (88 ng/liter) is roughly equivalent to the lowest values reported for rivers of central Europe (mean ≈ 170–220 ng/liter, range 60–630 ng/liter) (7). The ambient concentration of TFA in vegetation at HBEF (18 ng/g) is lower than reported for Germany (100–200 ng/g). The generally higher concentrations of TFA in Europe may be a result of unidentified industrial or commercial sources of TFA or TFA precursors.

The toxicity of TFA to plants (EC_{50} usually < 1000 mg/liter) (20, 28), animals (rat LD_{50} = 200–400 mg of TFA as acid per kilogram) (29, 30), and humans (31) is relatively low. However, the growth of one freshwater alga, *Selenastrum capricornutum* Reinsch, was inhibited by 360 μg/liter of TFA (20), which is within the range of TFA concentrations measured in surface and soil water during this study. We applied 3–274 mg/m^2 TFA, ≈ 10–100 times the predicted rainfall deposition of TFA at HBEF (18) (0.21 mg/m^2/year). Clearly, further research is needed to assess the potential environmental impact of atmospherically deposited TFA, especially in ecosystems in which TFA accumulates.

Human-accelerated environmental change (32) occurs at numerous spatial and temporal scales, and its components, including stratospheric ozone depletion, are complexly linked. Our results do not justify delaying the planned phase out of
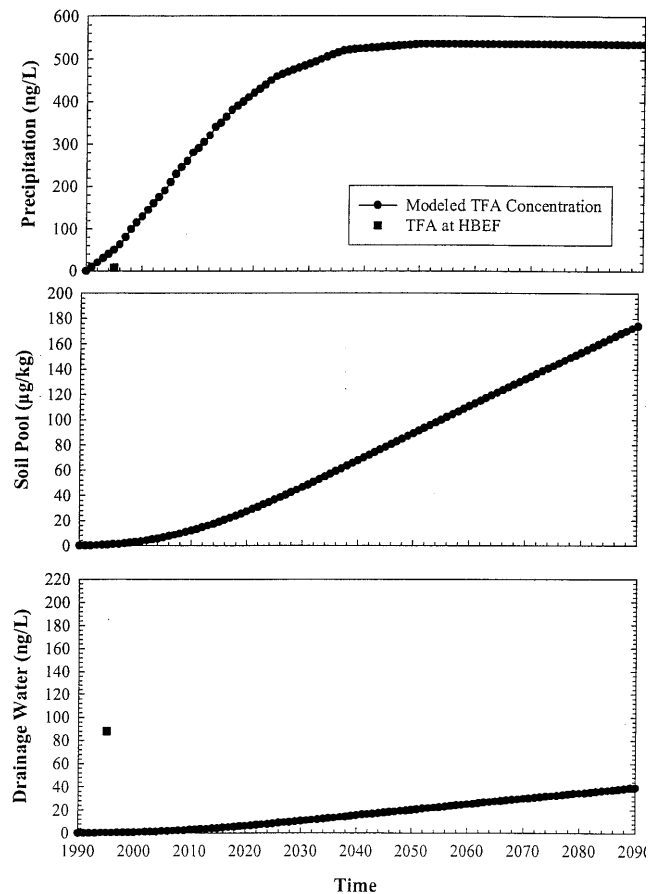

FIG. 5.   Results of modeling simulations for TFA concentration in the soil pool and drainage waters of HBEF.

CFCs but do demonstrate the folly of piecemeal environmental problem solving.

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