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Determination of Trifluoroacetic Acid in 1996−1997 Precipitation and Surface Waters in California and Nevada

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The atmospheric degradation of three chlorofluorocarbon (CFC) replacement compounds, namely HFC-134a, HCFC-123, and HCFC-124, results in the formation of trifluoroacetic acid (TFA). Concentrations of TFA were determined in precipitation and surface water samples collected in California and Nevada during 1996−1997. Terminal lake systems were found to have concentrations 4−13 times higher than their calculated yearly inputs, providing evidence for accumulation. The results support dry deposition as the primary contributor of TFA to surface waters in arid and semiarid environments. Precipitation samples obtained from three different locations contained 20.7−1530 ng/L with significantly higher concentrations in fogwater (median = 689 ng/L) over rainwater (median = 63.7 ng/L). Elevated levels of TFA were observed for rainwater collected in Nevada (median = 136 ng/L) over those collected in California (median = 49.5 ng/L), indicating continual uptake and concentration as clouds move from a semiarid to arid climate. Thus several mechanisms exist, including evaporative concentration, vapor−liquid phase partitioning, lowered washout volumes of atmospheric deposition water, and dry deposition, which may lead to elevated concentrations of TFA in atmospheric and surface waters above levels expected from usual rainfall washout.

Introduction

The chlorofluorocarbon (CFC) replacement compounds, HFC-134a (CH_2FCF_3), HCFC-123 ($CHCl_2CF_3$), and HCFC-124 ($CHClFCF_3$), break down in the atmosphere to form trifluoroacetic acid (TFA) (*1*, *2*). The Henry's Law constant and high water solubility of TFA indicate that wet deposition (i.e. rain, snow, and fog) will be a primary atmospheric removal process (*3*). Upon partitioning into water, TFA dissociates (pK_a 0.47) to form the trifluoroacetate anion which remains in the aqueous phase due to its enhanced water solubility. The affinity of TFA for the aqueous phase, coupled with its high stability and virtual resistance to chemical and biological degradation (*4*, *5*), creates the potential for accumulation in surface water systems, such as vernal pools, playa type lakes, saline lakes, and other systems that are characterized by high evaporation and little or no out-flow (*6*, *7*). Since TFA is mildly phytotoxic (*8*, *9*), there is concern that continual accumulation in such systems over several years could negatively impact aquatic ecosystems.

There are limited studies on levels of TFA in the environment. Precipitation and surface water samples collected by Frank et al. (*10*) in Germany, Israel, and Switzerland during 1995 had TFA levels of 25−280 ng/L in rainwater and 60−6400 ng/L in surface waters. Fog and rainwater collected in California during 1994 were from 300 to 3,000 ng/L, with selected surface waters from those areas ranging from 100 to 3000 ng/L (*11*). A more recent study of TFA in California surface waters collected in 1994−1996 showed 55−5400 ng/L (*12*). Rain and fogwater collected in California and Nevada during this period ranged from 31 to 3800 ng/L, with elevated levels occurring in fogwater.

The objective of this study was to determine conditions under which TFA might reach concentrations in the environment above levels typically found in atmospheric precipitation. TFA concentrations were measured in precipitation from three different locations in California and Nevada to determine differences between arid and semiarid regions and estimate wet deposition inputs of TFA into surface water systems. The concentration of TFA was traced from the headwaters of two river systems to their terminal endpoints in the Great Basin. Finally, estimated annual inputs from dry deposition were used to calculate the overall yearly inputs of TFA to two terminal Great Basin lakes.

Experimental Methods

Sampling Locations. Rainwater samples were collected at Rohnert Park and Selma, CA and Reno, NV from 12/96 to 9/97 (Figure 1). Fog events occurring during this period were sampled at both California sites but not in Reno due to the lack of fog. Surface waters from the Sierra Nevada Range in both California and Nevada (Figure 1) were collected during 1996−1997. The Truckee River and Carson River systems were sampled from their headwaters in the Sierra Nevada to their terminal endpoints in the Great Basin. The Truckee River system sampling began with a tributary stream to Lake Tahoe near Eagle Falls, CA in the Sierra Nevadas, through Lake Tahoe to the lower Truckee River and Pyramid Lake, its terminal endpoint. The Carson River system sampling began in the high Sierra Nevada mountains to Carson City, NV, through Lahontan Reservoir, and ending at the Stillwater National Wildlife Refuge (Stillwater NWR). In addition to the Truckee/Pyramid and Carson/SNWR terminal systems, Mono Lake, CA, was examined along with one of its tributaries, Rush Creek, which flows from the Sierra Nevada mountains in the vicinity of Yosemite National Park.

Sampling Methods. *Fogwater Sampling.* Fogwater was collected in duplicate by two portable high-volume fog sampling units placed side-by-side. These devices, of the type reported by Jacob et. al. (*13*), were obtained on loan from the California Department of Pesticide Regulation. Each unit contains a fan that draws the foggy air past a four layer screen of 0.28 mm diameter Teflon filaments. The water coalesces on this screen and runs into a small reservoir and finally to a collection device. The entire apparatus, including the separate Teflon screens, was rinsed thoroughly with methanol and reagent water before each collection period to remove any TFA from surfaces. Several rinse blanks showed that no detectable TFA was leached (*14*) from the Teflon screens. Samples were collected in 500 mL amber vials and sealed with aluminum foil lined lids (*14*). Depending upon the sampling period 100−500 mL of fogwater was collected. All fogwater samples were frozen until the time of extraction and analysis.

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FIGURE 1. Map showing sampling sites in California and Nevada. Precipitation samples collected from Rohnert Park and Selma, CA, and Reno, NV are presented on the California−Nevada map as 1, 2, and 3, respectively.

Rain Sampling. Rain samples were collected in 500 mL amber bottles using 25 cm diameter polyethylene funnels. Each rain event was sampled in duplicate with 100−800 mL volumes typically collected per event. Funnels were rinsed with acetone (reagent grade), reagent water, and finally HPLC grade acetone between sampling efforts. All bottle caps were lined with aluminum foil before sealing. Rainwater samples were either frozen or refrigerated at 5 °C until analysis.

Surface Water Sampling. Water was sampled in duplicate from lakes and rivers by submerging two 1000 mL amber bottles at various shore locations. Bottles were rinsed three times with water from the site before sample collection. All samples within a river system were collected within 2 days. After collection, foil-sealed samples were refrigerated at 5 °C until analysis.

Extraction/Analytical Protocol. *Sample Preparation.* Concentrations of TFA in fog-, rain-, and surface waters were determined using the method of Wujcik et al. (*14*). The aqueous environmental samples were vacuum filtered at 5 °C through a 90-mm diameter GF/F filter (Whatman International LTD, Maidstone, England). Conductivity and pH measurements were made immediately before resealing the sample. Filtration and pH and conductivity measurements were preformed as quickly as possible to limit exposure to room air.

Direct Anion Exchange Extraction. Aqueous samples with conductivities less than 500 μS/cm were directly extracted with a conditioned 47 mm diameter anion exchange-SR Empore disk (3M Corp, Minneapolis, MN). The conditioning protocol involves wetting the disk with acetone to ensure a proper seal within the extraction apparatus, followed by the sequential addition of methanol, reagent water, 1 M sodium hydroxide, and reagent water again with 15 mL volumes of each solution. Reagent water used for the conditioning process and preparation of NaOH solutions was of 18 Ohm-cm specific resistance (Barnstead Nanopure System, Dubuque, IA). After the last reagent water step, the sample was pulled under vacuum through the disk at the rate of 35−45 mL/min. A series of three 15 mL methanol rinses of the extraction reservoir followed the aqueous sample. The disk was then dried under vacuum, cut into small pieces, and placed in a 22 mL headspace vial with 4.0 mL of 10% sulfuric acid (18M) in methanol. The vial was then capped and vortexed for 30 s before derivatization and analysis by headspace gas chromatography.

Liquid−Liquid Extraction. Environmental samples with conductivities above 500 μS/cm were processed by a liquid−liquid extraction before passing through the anion exchange disk. TFA recovery from the anion exchange Empore disk was previously found to diminish with increasing sample salinity, a result of competition with chloride, sulfate, and other anions (*14*). The liquid−liquid extraction procedure involved acidifying 200 mL (or less) of aqueous sample in a separatory funnel with 1 mL of sulfuric acid (18 M) for every 10 mL of sample. Cold diethyl ether (100 mL) was added followed by saturation of the aqueous phase with sodium sulfate. In a second separatory funnel, 100 mL of reagent water and 20 mL of 1 M NaOH were added along with the ether layer from the first separatory funnel. This diethyl ether extraction was conducted a total of three times with the initial aqueous sample, with each of the subsequent ether layers added to the second separatory funnel. After vigorously agitating the second funnel containing the alkaline water and ether, the aqueous layer and 2−3 mL of the ether layer were dispensed into a clean bottle. This solution, containing the TFA from the original sample, was then passed through the Empore disk as described above.

Analytical Technique. A Perkin-Elmer HS40 headspace sampler and Perkin-Elmer Autosystem GC with an electron capture detector (ECD) were used for derivatization and sample analysis (*11*, *14*). All headspace samples were thermostated at 50 °C for 1 h before injection to promote the quantitative derivatization of TFA to its volatile methyl ester, methyl trifluoroacetate (MTFA), and partitioning of MTFA to the vapor phase. The analytical column was a 25 m × 0.32 mm i.d. Poraplot Q (Chrompack, Raritan, NJ) with a 10 μm stationary phase. The carrier and makeup gases were ultrahigh purity nitrogen with flows of 3.2 mL/min at 110 °C and 32 mL/min, respectively. The injection, pressurization, and withdraw time were 0.1, 0.5, and 0.2 min, respectively. The ECD was equilibrated for 15 min at 110 °C prior to the sample analysis. The sample was also run at 110 °C for 10 min followed by an increase to 210 °C at a rate of 20 °C/min, where it remained an additional 5 min.

Sample Confirmation. Several environmental samples, including Pyramid Lake, NV, Mono, Lake, CA, Stillwater National Wildlife Refuge, NV, and rain from Reno, NV (6/19/97), were confirmed by a Hewlett-Packard 5970A GC-MS in the selected ion monitoring mode. Ion 69 *m*/*z*, which corresponds to CF_3^+ fragment, was scanned to obtain optimal sensitivity and selectivity (*14*).

Statistical calculations were conducted by Minitab software version 10.2 (Minitab Inc, State College, PA). The data sets were tested for normal distribution using an Anderson−Darling normality plot ($P < 0.05$). Since the majority of the data sets were nonnormal in distribution, a median and range are reported. Comparisons between two groups of nonnormally distributed data were conducted using a Mann−Whitney test with $\alpha = 0.05$.

Results

Method Performance. The limit of quantitation (LOQ) of the analytical technique was estimated to be 36 ng/L for a 400 mL sample (*14*). The LOQ was determined by the average analytical blank plus six times the standard deviation of the analytical blanks. While it is possible to detect TFA concentrations below 36 ng/L, the quantification is less reliable. Recoveries for spiked (579 and 1160 ng/L) environmental samples passed directly though the anion exchange Empore disk were 94−105%. Environmental samples requiring liquid−liquid extraction (i.e., those with conductivities > 500 μS/cm) gave 89−104% recovery. Relative standard deviations

TABLE 1. Concentrations of TFA (ng/L) in Precipitation Samples Collected from November 1996−September 1997

rain and fogwater samples	no. of samples	median TFA concn	range of sample concns
Rohnert Park, Sonoma County, CA			
rainwater	31	46.6[a]	25.1−158
fogwater	6	723	86.6−809
Selma, Fresno County, CA			
rainwater	23	63.9[b]	20.7−463
fogwater	21	689	101−1390
Reno, Washoe County, NV			
rainwater	6	136	108−763

[a] Ten samples fell below LOQ. [b] Five samples fell below LOQ.

TABLE 2. Concentrations of TFA (ng/L) in the Truckee River, Carson River, and Mono Lake Systems

location	no. of samples	median TFA concn	range of sample concns
Truckee River System			
upstream of Reno, NV	19	(28.9)[a]	12.8−47.7
downstream of Reno, NV	8	50.8[b]	31.0−66.5
Pyramid Lake, NV	7	79.0	77.1−95.1
Carson River System			
upstream of Carson City, NV	6	45.3	36.6−60.5
downstream of Carson City, NV	8	84.2	76.9−154
Stillwater NWR, NV	6	432.5	314−472
Mono Lake System			
Rush Creek, CA	2	51.0	50.1−52.0
Mono Lake, CA	10	192	186−227

[a] Seventeen of the 19 samples in this section were below the LOQ of 36 ng/L, thus the accuracy of this data is uncertain. [b] Only one data point fell below the LOQ.

(RSDs) for all spike-recovery samples fell in the range of 0.7−7.9%, demonstrating the consistency of the method.

Fog/Rain Results. The median and ranges for TFA determined in rain and fogwater collected during the winter of 1996/1997 in Rohnert Park, CA, Selma, CA, and Reno, NV are presented in Table 1. Concentrations in fogwater from both Rohnert Park and Selma were compared to rainwater collected from the same sites. Fogwater samples exhibited higher TFA concentration than rainwater at both sites (Mann−Whitney Tests, $P < 0.001$). The median TFA concentrations for fogwater are 15 times higher for Rohnert Park and 10 times higher in Selma than corresponding rainwater (Table 1), demonstrating the potential for TFA accumulation during single fog events.

There were no significant differences between fogwater from Rohnert Park and Selma (Mann−Whitney test $P > 0.1$). Rainwater samples also showed consistent concentrations between the two sites (Mann−Whitney test $P > 0.1$). In both cases, the median TFA concentrations in the precipitation samples between the two sites were similar (Table 1). The similar medians combined with a high degree of variability in the data sets caused the lack of statistical differences between the two sites. However, rainwater collected at Reno, NV, which is in the rain shadow of the Sierra Nevada Mountain range, showed significantly higher concentrations of TFA than the other two sites (Mann−Whitney test $P < 0.001$). The median TFA concentration in Reno rainfall was over twice as high as the other two sites (Table 1).

River/Lake System Results. A series of river samples collected upstream of Reno on the Truckee River and Carson City on the Carson River was compared to a series of downstream samples from those same sites, to test for additional inputs from the cities. Since Lake Tahoe has a large volume and complex mixing behaviors, the "upstream" segment of the Truckee River was defined as the distance from the Truckee River outflow from Lake Tahoe to Reno; it does not include any Lake Tahoe samples or tributaries to Lake Tahoe. In both cases, samples taken downstream from the cities trended toward higher TFA concentrations than upstream samples (Mann−Whitney tests, $P < 0.001$ Truckee River, $P < 0.001$ Carson River). However, this is a tenuous calculation for the Truckee River system because some of the measured values are near or below the method's limit of quantification (36 ng/L). Measured values that fell below the limit of quantification were still used for the statistical calculations because they represent the best estimate of the sample concentration. The Carson River system consistently had concentrations above the LOQ, lending more confidence to the statistical calculations. The median and ranges of TFA concentrations are presented in Table 2. In addition, concentrations of TFA in three terminal surface water systems, including Pyramid Lake, Stillwater NWR, and Mono Lake, the terminals for rivers flowing east from the Sierra Nevada mountains, were compared to the concentrations of their river sources. In all three cases, the terminals were found to have significantly higher concentrations of TFA than their source rivers (Mann−Whitney Tests, $P < 0.001$ for Pyramid Lake and Stillwater NWR and $P = 0.04$ for Mono Lake).

Discussion

Precipitation Study. Predictions of the average global concentration of TFA in rainwater by Kotamarthi et al. (*15*) show concentrations reaching 160 ng/L by the year 2010. Current concentrations of TFA in fog and rainwater in California and Nevada (Table 1) are nearing, and in many cases are above these predicted values. Although concentrations of TFA in precipitation determined in this study appear to be high, additional factors such as local enrichment occurring at the selected sites may be partially responsible. Elevated concentrations of precursor HFCs and HCFCs and photochemical oxidants such as hydroxyl radical ($OH^{\bullet}$) occurring in urban areas (*16*−*18*) could further enhance local TFA production. These locations should therefore have higher concentrations of TFA in precipitation and nearby surface water systems.

Rain and fog samples collected from two sites in California approximately 370 km apart were not statistically different from each other. The similarity in concentrations of TFA found in rain and fog at Selma and Rohnert Park may result from similar local TFA production due to population sizes and precursor use, transport of both the precursor HFCs and HCFCs and TFA from California's San Francisco Bay area, and/or a similar region-wide ambient level of TFA not connected with specific local sources.

Reno, NV, had two to three times higher rainwater concentrations of TFA than the two California sites. As an arid environment in the rainshadow of the Sierra Nevada mountain range, Reno is expected to have lower rain frequencies and lower rain volumes due to water losses from rainfall and cloudwater evaporation during transport. The effective washout of TFA from the ambient air by a lower volume of rainwater may result in an overall higher rainwater concentration. Build-up of TFA in cloudwater could also occur from continual vapor phase partitioning along its transport route and cloudwater evaporation. TFA transferred to the vapor phase during the evaporation process is expected to be rapidly repartitioned to the bulk cloud mass as a result of its low Henry's Law constant. The complete evaporation of cloudwater containing TFA could elevate ambient atmospheric concentrations as is proven for both formic and acetic acids measured in air in the southwestern United States (*19*).

Build-up of ambient TFA between rain events resulting from local production and complete cloud and rainwater evaporation, in addition to the potential accumulation of TFA in cloudwater during transport, could explain elevated TFA concentrations in Reno rain. Concentrations of TFA 2−4 times greater in precipitation than the global average have been predicted by Tromp et al. (*20*) for arid and semiarid regions. While both California sites are technically classified as semiarid environments, the drier climate of the Reno area provides the means for enhancing evaporation of cloudwater and, consequently, elevating TFA concentration in precipitation and air.

Fogwater has the potential to reach elevated concentrations of TFA in comparison to rainwater during a single event due to its high surface area-to-volume ratio (drop size 1−30 μm, density 0.05−0.1 g/m^3), low overall volume, and ability to remain suspended for long periods of time. Significantly higher concentrations of TFA in fog were observed at both sites in California (Figure 1), where fog concentrations were approximately seven times higher than rainwater. Fog may therefore provide a means of delivering elevated levels of TFA to local vegetation, given the importance of fogwater as an "occult precipitation" source to the water budget of vegetation in some parts of California (*21*).

River Systems. TFA concentration in both the Truckee and Carson River systems increased as the rivers passed through Reno and Carson City. The results (Table 2) indicate nearly a doubling of the median concentration for both river systems downstream from the cities. When represented graphically, the increase in concentration appears to be more gradual for both systems (Figures 1 and 2). The more erratic concentrations determined from the Truckee River may be a result of several surface water inputs along its path, including tributary streams, such as the Little Truckee River and Prosser Creek and their outfalls at Boca Reservoir. These inputs can lead to both dilution or augmentation of the river concentration. Also, the Truckee River samples gave results near the limit of quantification for the analytical method. The Carson River system, which has fewer large volume inputs, demonstrates a more even increase in TFA concentrations along its course. If substantial TFA inputs from the city effluent were present, a more pronounced increase in TFA concentration should be observed from just upstream to just downstream of the cities. While the river concentrations tended to increase downstream of the cities, the rise was not pronounced and thus was inconclusive as an indication of alternate sources of TFA. Several factors including evaporative concentration of TFA within the rivers, agricultural return, and vapor phase partitioning in areas of elevated TFA are possible explanations for the gradual increase. The lack of measurements and viable estimates of river evaporation for both the Truckee and Carson Rivers prevented a quantitative determination of the effect of river water evaporation on TFA concentration. Withdraw and return of water used in local agriculture occurs periodically along both the Truckee and Carson Rivers, with greater frequency at the lower halves of both systems. Water removed from both rivers for agricultural uses is typically spread out over large surface areas, allowing for enhanced water evaporation and vapor phase partitioning. Return water from these areas may provide substantial inputs of TFA that can increase the observed river concentrations. Finally, additional enrichment of TFA in the ambient air within and below Reno and Carson City could also be contributing by partitioning to the rivers.

Accumulation of TFA in Terminal Lakes. Our results indicate that TFA concentrations in terminal water bodies are significantly higher (Mann−Whitney tests, $P < 0.001$ for Stillwater NWR, $P < 0.001$ for Pyramid Lake, $P = 0.04$ for Mono Lake) than their average inputs, thus demonstrating that TFA is accumulating in terminal water bodies such as Mono and Pyramid Lakes (Table 3). The Mono Lake system showed less statistical confidence simply because only two samples were collected to determine stream input into the lake. Since we have measured TFA concentrations in rain and in-flowing rivers and can estimate dry deposition into these lakes, it is possible to calculate the approximate time, at current input rates, it would take for these lakes to accumulate to the observed TFA concentrations.

TABLE 3. Estimated TFA Inputs into Terminal Lakes and Estimated Time, in Current Input Rates, for the Lakes to Accumulate Observed TFA Concentrations

	scenario no. 1[a]	scenario no. 2[a]
Mono Lake		
total TFA in the lake	677 kg	677 kg
TFA input in streams	8.4 kg/yr	8.4 kg/yr
TFA wet deposition onto lake	6.9 kg/yr	6.9 kg/yr
TFA dry deposition	146.2 kg/yr	79.4 kg/yr
total yearly TFA inputs	161.5 kg/yr	94.7 kg/yr
estimated time to accumulate obsd TFA concns	4.2 yr	7.2 yr
Pyramid Lake		
total TFA in the lake	2478 kg	2478 kg
TFA input in streams	24.0 kg/yr	24.0 kg/yr
TFA wet deposition onto lake	13.3 kg/yr	13.3 kg/yr
TFA dry deposition	365.8 kg/yr	153.0 kg/yr
total yearly TFA inputs	403.1 kg/yr	190.3 kg/yr
estimated time to accumulate obsd TFA concns	6.2 yr	13.0 yr

[a] Scenario no. 1 uses dry deposition rates determined from an open reservoir flux experiment conducted by Zehavi and Seiber (*22*). Scenario no. 2 uses dry deposition estimated from Grosjean (*23*).

The assumptions for these calculations were the following. (1) TFA is only deposited into the lake through streams, wet deposition, and dry deposition. (2) No TFA is removed from the lake by degradation, volatilization, or binding to soil (*4*−*7*). (3) The volumes of Pyramid and Mono Lakes are maintained at their same level from year to year due to water evaporation. (4) The lake is evenly mixed so our samples are representative of the entire lake. (5) TFA inputs do not vary during a year, hence our input samples are representative of the entire year. (6) TFA vapor and particulate deposition inputs can be estimated from rough flux measurements by Zehavi and Seiber (*22*) or by applying the 92% dry deposition estimate for formic and acetic acid (*23*) to TFA. (7) TFA inputs are constant between years, which is not the case due to the increase in usage rates of HFCs (*24*). Therefore, this model will overestimate the overall quantity of TFA input to these lake systems during the introduction of the HCFCs and HFCs. (8) The TFA concentration in rainfall at the lakes is the same as in Reno, NV where our rainfall samples were taken. The volume, surface area, surface water inputs, and rainfall rates for Pyramid Lake and Mono Lake are known (*25*, *26*). Since the volume and surface area of Stillwater NWR could not be determined, its accumulation rate was not calculated.

The results show that observed concentration of TFA in Mono Lake could be reached in 4.2 and 7.2 years of current input and Pyramid Lake would have reached its observed concentrations in 6.2 and 13.0 years of current input (Table 3) depending upon the dry deposition flux estimation used. The HFCs and HCFCs were introduced in 1990, which is seven years prior to our sampling effort. Therefore, the estimated accumulation time for TFA in both Pyramid and Mono Lake correspond generally to the introduction of the CFC replacement compounds.

Although wet deposition may be the primary removal and transfer mechanism for TFA in the atmosphere in more temperate climates, dry deposition (vapor and particulate)

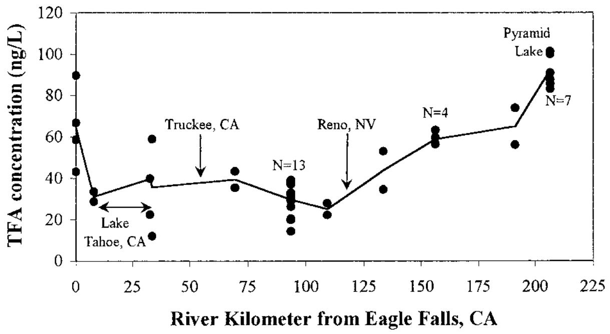

FIGURE 2. TFA concentration along the Truckee River system. Lines are drawn through the median concentrations determined at each sampling location.

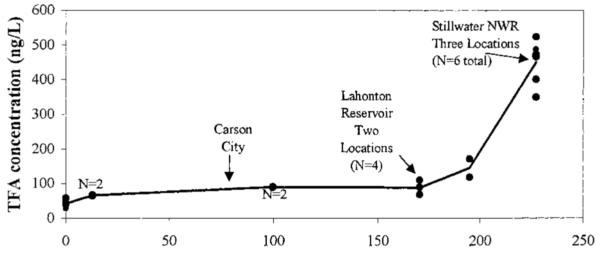

FIGURE 3. TFA concentrations along the Carson River system. Lines are drawn through the median concentrations determined at each sampling location.

appears to be the dominant pathway in arid and semiarid environments (Figure 3). Limited open reservoir studies by Zehavi and Seiber (*22*) give an average flux (particulate-vapor to water solution) value of 91.6 ng/m^2·h for TFA in Reno, NV, an arid climate. This flux value was a combination of both vapor and particulate deposition into an open reservoir during the summer months. The Henry's Law constant of $8.95 \pm 2 \times 10^3$ mol/kg·atm (at 298.15 K) determined by Bowden et al. (*3*) reinforces the fact that vapor phase TFA will partition immediately into water when present. Since arid climates receive little annual rainfall, and practically none from May to October, vapor partitioning could contribute appreciable quantities of TFA to surface water systems. Particulate deposition, which can contain small quantities of water, may also serve as a significant transport medium during the drier months. Grosjean (*23*) has determined that up to 92% of the overall flux of formic and acetic acids to the Sierra Nevada mountain range occurs via dry deposition. In both cases, vapor phase formic and acetic acid dominated the gas-particle distribution of the overall measured dry deposition totals at 94 and 88%, respectively (*23*). Since TFA has similar physical-chemical properties to these acids, it should behave like and be transported by similar mechanisms. Assuming that TFA in the environment is derived from the HFCs and HCFCs and no alternate sources, dry deposition should be the major contributor of TFA into arid and semiarid environments.

Overall, several mechanisms may exist, including water evaporation, vapor-phase uptake, lower washout volumes of atmospheric deposition waters, and the input of dry deposition, whereby the concentrations of TFA in both atmospheric and surface waters can reach concentrations well above those typically observed in rain. The evidence for operation of these mechanisms in California and Nevada, as presented here, suggest the need for additional study with collection of more complete data sets. While current concentrations of TFA are at least 3 orders of magnitude less than the EC_{50} for phytotoxicity (*8*), the stability of TFA suggests that continual build-up by the mechanisms described herein may provide a means for eventually reaching detrimental levels.

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