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Chloroacetic Acids in Rainwater

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From 1993 to 1995, chloroacetic acids have been determined in rainwater collected near the center of Zürich and in a rural area of Switzerland (Alpthal). The chloroacetic acids have been enriched either by evaporation or by anion exchanger, derivatized to their respective propyl esters, and determined by gas chromatography (GC) with electron capture detection (ECD), by coupled-column GC-ECD (GC-GC-ECD), or by GC/mass spectrometry (MS). Monochloroacetic acid is most abundant, followed by dichloro- and trichloroacetic acid. Concentrations range from 0.01 up to 9 µg/L; the dependence on meteorological conditions and sampling site is discussed.

Introduction

Chloroacetic acids (monochloroacetic acid, MCA; dichloroacetic acid, DCA; trichloroacetic acid, TCA) are widely used industrial chemicals. MCA, for instance, is produced at a rate of more than 300 000 t annually (1) as intermediate in the production of carboxymethylcellulose, of some herbicides, and of other chemicals. Chloroacetic acids have been found in the atmosphere and in precipitation (2-4). Their origin is largely unknown. 1,1,1-Trichloroethane, trichloroethene, and tetrachloroethene, presently produced at global annual rates of about 700 000 t (5, 6), are mostly released to the atmosphere. There are indications that a part of them is degraded to chloroacetaldehydes and chloroacetyl chlorides (7-11), which could further react to chloroacetic acids.

Haloacetic acids are toxic to many plants, in particular to algae (12). TCA has been used for the control of perennial weeds since the late 1940s, while the monochloroacetyl moiety constitutes the toxicogenic principle in the herbicides alachlor, propachlor, metolachlor, and metazachlor (13). Haloacetic acids have also been used as preservatives for beverages (14) because of their exquisite fungicidal and bactericidal properties. Chloroacetic acids are widespread

in the environment, which renders studies on their ecotoxicological relevance important (2).

Most published methods for trace analysis of environmental haloacetic acids are based on liquid-liquid partitioning (15-17). Alternatively, an ion chromatographic method has been used (3). EPA Method 552.1 (18) involves an anion exchanger and analyzes the methyl esters by GC-ECD. We compared enrichment by evaporation (19) in the presence of base with anion exchange of the deprotonated acids. Acids were esterified with propanol/sulfuric acid. MCA was detected by GC-GC-ECD.

Experimental Section

Materials. GC analyses were performed on a gas chromatograph 5300 from Fisons/CE Instruments (Italy) equipped with on-column injector, autosampler (AS 800), and ECD (Model 80/800), using hydrogen as the carrier gas. Pentane extracts (10-25 µL) were injected on-column onto a 7.5 m × 0.32 mm i.d. uncoated fused silica precolumn (Polymicro Technologies, Phoenix, AZ). For one-dimensional GC, a 30 m × 0.25 mm i.d. column coated with 0.5 µm of OV-1701-vinyl was used (prepared by static coating of untreated fused silica). Samples are injected at a 45 °C oven temperature (6 min), followed by a temperature program of 10 deg/min to 95 °C, of 3 deg/min to 116 °C, and of 20 deg/min to 200 °C. For GC-GC, a 30 m × 0.25 mm i.d. column coated with 0.2 µm of OV-1701-vinyl was combined with a 30 m × 0.25 mm i.d. column coated with 0.5 µm BAP-100 (a copolymer, similar to OV-330, of polyethyleneglycol and dimethyl polysiloxane, obtained from W. Blum, Ciba-Geigy, Basel). The initial oven temperature was 50 °C (6 min), followed by a program of 1.5 deg/min to 73 °C and of 20 deg/min to 200 °C. The coupled-column system resembled that described by Ibañez (20), where the direction of the carrier gas flow in the interface between the two columns was controlled by auxiliary hydrogen fed into the interface. The GC/MS analyses were performed on a Finnigan SSQ 7000 mass spectrometer in the positive-ion chemical ionization (CI) mode with helium as the carrier gas and methane as the reagent gas.

Sampling. Rainwater samples were collected daily on the roof of the building of the Official Food Control Authority, located near the center of Zürich (Switzerland), 450 m above sea level, and weekly in a rural valley about 40 km southeast of Zürich, 10 km south of Einsiedeln, 1000 m above sea level (Alpthal). At the latter site, samples were collected both in the open field and as canopy runoff in the nearby forest. They were stabilized by spiking each sampling bottle with an aqueous formaldehyde solution corresponding to at least 1% of the rainwater expected. Samples were kept frozen (-24 °C) prior to analysis.

Sample Preparation 1: Evaporation Method. Rainwater (5 mL) was filled into a 10-mL glass vial (20 × 35 mm), to which 0.5 mL of an aqueous solution of 500 mg/L of sodium bicarbonate and 10 µL of aqueous 1 mg/L 2,2-dichloropropionic acid (DCPA) were added as internal standard. The sample was evaporated to dryness, and the residue redissolved in 0.5 mL of 1-propanol containing 25 µL of concentrated sulfuric acid. The vial was closed and heated to 70 °C for 2 h. After cooling, 0.5 mL of pentane and 10 mL of a solution of sodium chloride (10%) in demineralized

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water were added. After shaking, the pentane layer was transferred to a 1-mL glass vial by means of a Pasteur pipet and analyzed by GC.

Sample Preparation 2: Ion Exchange Method. Cartridges packed with 360 mg of a strong anion exchanger (Sep-pak, Accell QMA, Millipore, USA) were flushed by means of a syringe pump and conditioned with 5 mL of an aqueous solution of sodium chloride (10%). Rainwater (20 mL) was spiked with 10 μ L of a solution of 1 mg/L DCPA as internal standard and passed through the anion-exchanger cartridge at a flow rate of 1 mL/min, followed by 3 mL of 1-propanol. Acids were eluted with 2 mL of 1-propanol acidified with 12.5 μ L/mL concentrated sulfuric acid. Furthermore, 190 μ L of concentrated sulfuric acid was added to perform esterification as described above. Esters were extracted twice with 0.5 mL of pentane after admixture of 18 mL of 20% sodium chloride in demineralized water. Pentane phases were back-washed with 9 mL of 20% sodium chloride and analyzed by GC.

Results and Discussion

Evaluation of the Methods. Evaporation of water was performed at 60 $^{\circ}$ C, because higher temperatures could have decarboxylated TCA, and took about 3 h for a 5-mL sample (which limited the sample volume). Sodium bicarbonate was added to rainwater in order to maintain the acids in the ionized form. Sample preparation took about 5 h. Eight samples were handled in parallel.

Propyl esters were preferred to methyl esters in order to achieve full solvent trapping during on-column injection and to increase elution temperatures, facilitating GC-GC analysis in a single oven system. However, when using 1-propanol, elution of the acids from the ion exchanger proposed by EPA Method 552.1 proved to be incomplete, presumably because the acids were trapped in the shrinking resin. The silica-based surface-bonded anion exchanger avoided this problem. Preparation in parallel of four samples took about 3 h.

The capacity of the ion exchanger must be sufficient to avoid that, e.g., carbonate and sulfate displace organic acids, which limits the sensitivity of the method. For rainwater with around 300 μ equiv/L anions (21), about 100 mL could be handled.

Blanks levels of the three acids were determined using demineralized water as a sample and were in the range of 10–40 ng/L. This is about one-tenth of the concentration found in most rainwaters. On-column injection with the retention gap technique was used in order to introduce large sample volumes (10–25 μ L) without losing volatile analytes (solvent trapping).

A typical chromatogram of a rainwater sample prepared by the ion exchange method and analyzed by GC-GC-ECD is presented in Figure 1. Although single-column GC was sufficient in many instances, some samples contained compounds interfering with MCA. GC-GC-ECD separated them from MCA. Furthermore, owing to a more stable baseline, chromatograms from the second column could be run at 10 times lower attenuation. GC/MS with positive ion CI of six rainwaters confirmed the data obtained by GC-(GC)-ECD.

Recoveries and relative standard deviations obtained with the two methods was compared: 10 ng of each chloroacetic acid were added to samples of blank demineralized water (5–50 mL) and directly to the esterification medium. Peak areas were normalized relative to the

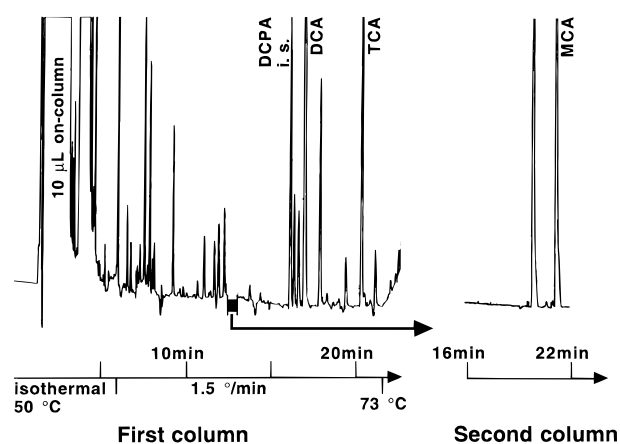


FIGURE 1. GC-GC-ECD chromatograms of a rainwater sample prepared by ion exchange.

TABLE 1

Recoveries (%) of MCA, DCA, and TCA from Demineralized Water by Evaporation (evap) or Ion Exchange (ion ex)

	MCA	DCA	TCA
5 mL evap ($n = 6$)	78 \pm 4.2	97 \pm 2.5	86 \pm 4.0
5 mL ion ex ($n = 5$)	103 \pm 7.6	103 \pm 3.0	93 \pm 2.4
10 mL ion ex ($n = 1$)	97	84	98
50 mL ion ex ($n = 1$)	106	103	109

TABLE 2

Comparison of Results Obtained through Enrichment by Ion Exchange or Evaporation of Rainwater Samples (ng/L)

	sample 1		sample 2	
	ion exchange	evaporation	ion exchange	evaporation
MCA	2990	3270	1570	1600
DCA	630	710	720	740
TCA	210	230	410	400

internal standard (DCPA) added to the samples prior to esterification. As shown in Table 1, both methods gave recoveries close to 100% (up to a sample size of 50 mL for the ion exchange method); standard deviations were similar. Results for rainwater samples obtained with the two methods agreed satisfactorily (Table 2).

Concentrations of Chloroacetic Acids in Rainwater. Rainwater samples from 1993 were analyzed by the evaporation method; those of 1994 and 1995 were analyzed by anion exchange and GC-GC-ECD. Figure 2 shows the concentrations found in Zürich rainwaters in the summer of 1993. Concentrations of TCA varied between 44 and 710 ng/L. In nearly all samples, MCA exceeded 500 ng/L, i.e., the threshold for algal toxicity (1).

Monthly mean concentrations of the chloroacetic acids in precipitation from August 1994 to September 1995 and respective monthly wet depositions are shown in Figure 3. In summer, concentrations of all three acids were substantially higher than in winter. For MCA, the average concentration in summer 1994 exceeded 2 μ g/L. These results are in agreement with previous determinations of MCA (300–4300 ng/L), DCA (0–4400 ng/L), and TCA in Germany and Austria (2–4). For TCA, the same annual fluctuation in concentrations has been observed in Austria.

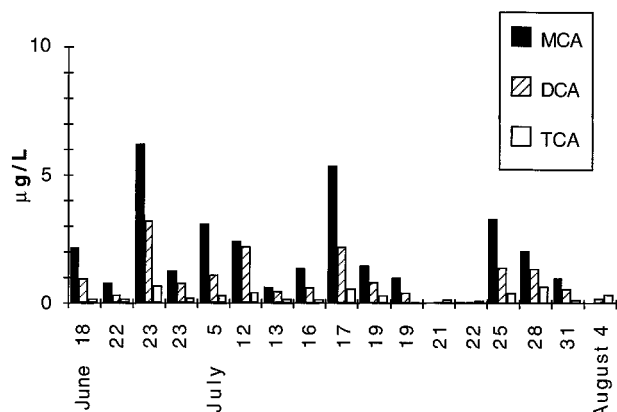


FIGURE 2. Concentrations of MCA, DCA, and TCA in rain collected in 1993 in Zürich.

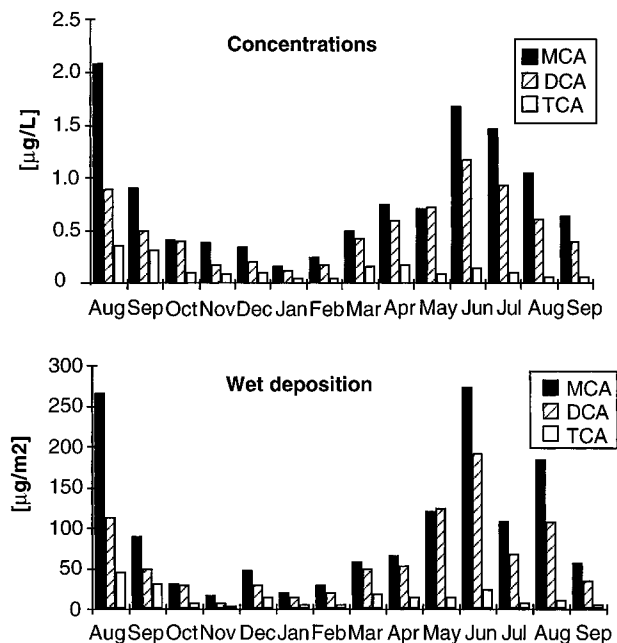


FIGURE 3. Monthly mean concentrations in rainwaters and wet deposition of MCA, DCA, and TCA in Zürich (August 1994–September 1995).

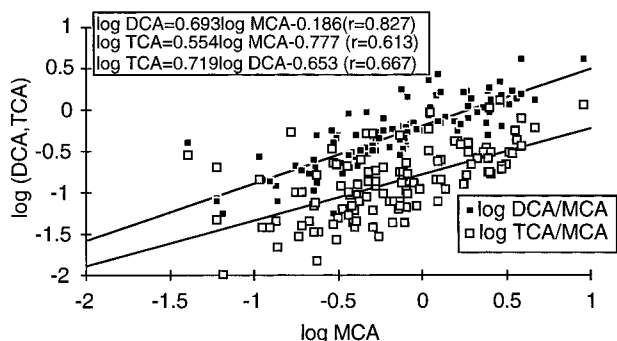


FIGURE 4. Comparison of the logarithmic concentrations of MCA, DCA, and TCA in Zürich rainwater samples (August 1994–September 1995).

MCA concentrations exceeded those of DCA about 2-fold and those of TCA about 10-fold. In air, MCA concentrations were about 10-fold higher than those of TCA (2). Correlation coefficients (r) of the logarithmic concentrations of the three acids (Figure 4) indicate fairly constant ratios of MCA, DCA, and TCA, although actual concentrations varied up to 100-fold. This suggests either a precursor common to all three

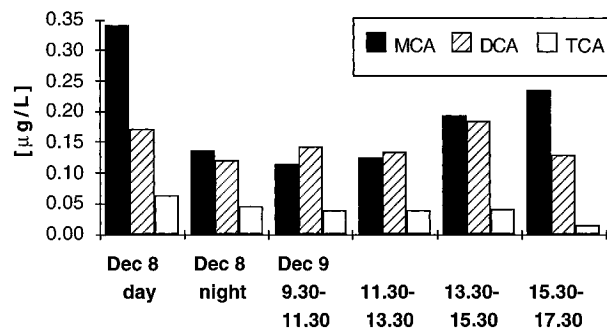


FIGURE 5. Concentrations of the acids in Zürich rainwater samples collected during 2 days of nearly continuous rainfall (December 1994).

TABLE 3

Correlation Coefficients (r) of Meteorological Conditions and Concentrations of Acids in Rainwater (Data of Zürich, August 1994–September 1995)

	MCA	DCA	TCA
(i) vol of given rain event	0.018	-0.106	-0.164
(ii) previous days without rain	0.260	0.361	0.262
(iii) vol of rain of last 3 days	-0.273	-0.191	-0.113
(iv) mean temp of last 3 days	0.402	0.392	0.081
(v) mean solar radiation of last 3 days	0.578	0.645	0.356

acids or different atmospheric precursors in fairly constant ratios.

Correlation with Meteorological Data. Correlation coefficients (r) were calculated (Table 3) for the concentrations of the acids in rainwater with the following data: (i) the volume of rain during the respective event, (ii) the number of previous days without rain, (iii) the volume of rainwater determined during the previous 3 days, (iv) the mean of the total solar radiation during each of the 3 days prior to the rain event, and (v) the mean of the average daily temperatures during the 3 days prior to the rain event.

The volume of the rain, the duration of the previous dry period, and the amount of previous rainfall do not seem to correlate with the concentrations determined. This was supported by the observation that MCA and DCA concentrations did not decrease during 2 days of almost continuous rainfall with southwest wind in December 1994 (Figure 5). The acids were either constantly formed or continuously brought in by wind transport. TCA concentrations, on the other hand, declined slightly.

Correlation coefficients of concentrations of MCA and DCA with temperature were around 0.4 and could be explained by faster evaporation of the acids at increased temperatures. However, the best correlation was found for previous solar radiation (0.6), which supports the view that chloroacetic acids are formed in the atmosphere by a direct or indirect photochemical reaction as the rate-limiting step. This also explains the significantly lower concentrations found in winter as compared to summer.

In the period from 1993 to 1995, DCA concentrations in rainwater were fairly constant, whereas those of MCA and TCA decreased. The June and July data of MCA decreased by 10% each year, while TCA was approximately constant over the first year but declined by 64% between 1994 and 1995 (Figure 6). It was interesting to note that in Dübendorf

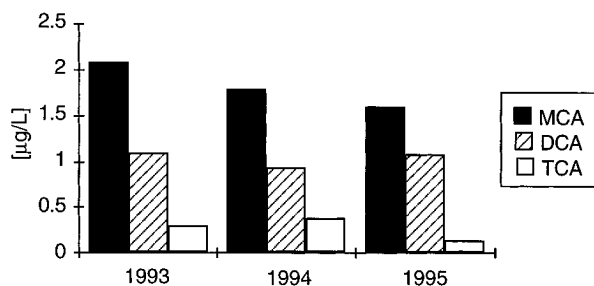


FIGURE 6. Mean concentrations of the chloroacetic acids in Zürich rainwater of June and July of 1993–1995.

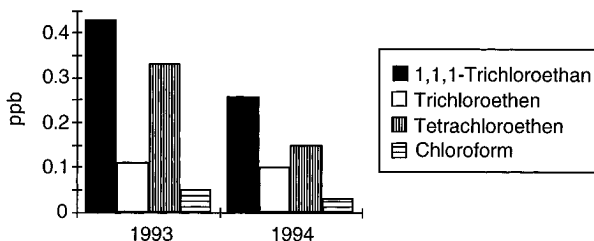


FIGURE 7. Mean concentrations of some chlorohydrocarbons in the air at Dübendorf in 1993 and 1994 (22, 23).

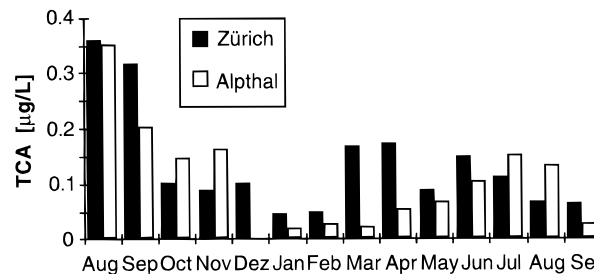
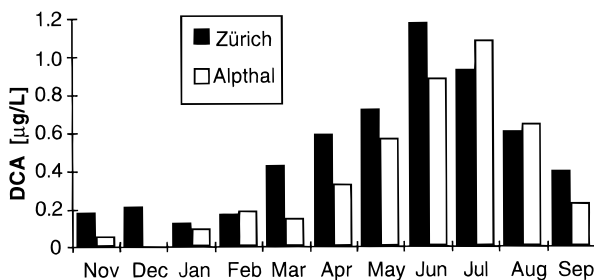
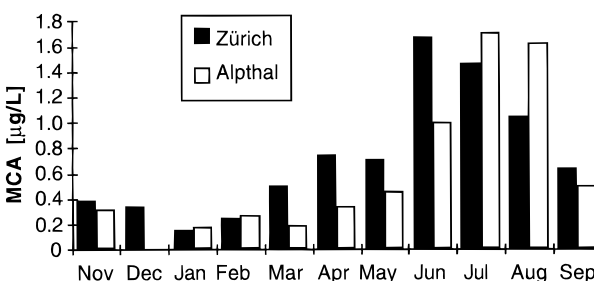


FIGURE 8. Comparison of monthly mean concentrations of MCA, DCA, and TCA in rainwater of Zürich and Alpthal; November 1994–September 1995 for MCA and DCA and August 1994–September 1995 for TCA.

(about 5 km north of the rain sampling site) the concentrations of some chlorohydrocarbons also decreased considerably from 1993 to 1994 (Figure 7; 22, 23), supporting the view that they could be precursors of the chloroacetic acids.

Wet Deposition. In Alpthal, concentrations found in rainwaters are mostly lower than in Zürich (Figure 8), perhaps because the total volume of rain is about twice that of Zürich. Total wet deposition ($\mu\text{g}/\text{m}^2$) in Alpthal is,

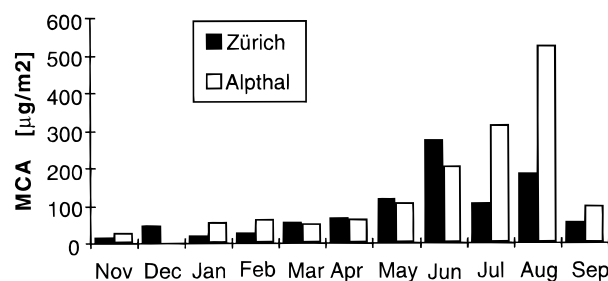


FIGURE 9. Comparison of the monthly mean wet deposition of MCA ($\mu\text{g}/\text{m}^2$) in Zürich and Alpthal (November 1994–September 1995).

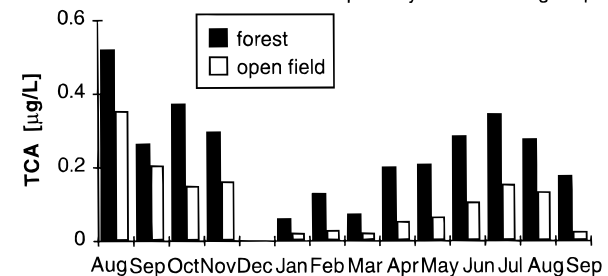
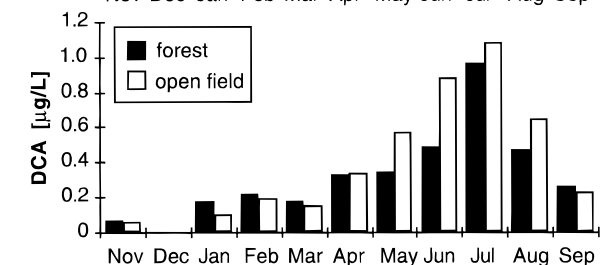
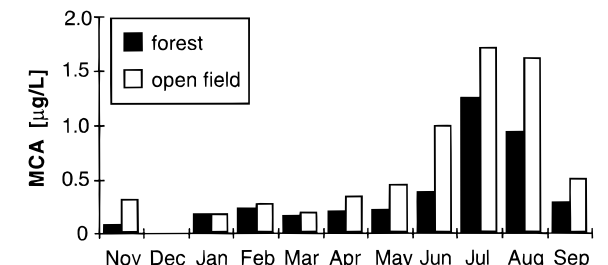


FIGURE 10. Monthly mean concentrations of MCA, DCA, and TCA in open-field precipitation and forest-canopy runoff; November 1994–September 1995 for MCA and DCA and August 1994–September 1995 for TCA.

TABLE 4

Annual Wet Deposition of Chloroacetic Acids in Switzerland, Calculated from deposition in Zürich with Annual Rainfall of $1500 \text{ L m}^{-2} \text{ yr}^{-1}$ (24) in Switzerland

precipitation ($\text{L m}^{-2} \text{ yr}^{-1}$)	MCA ($\mu\text{g m}^{-2} \text{ yr}^{-1}$)	DCA ($\mu\text{g m}^{-2} \text{ yr}^{-1}$)	TCA ($\mu\text{g m}^{-2} \text{ yr}^{-1}$)
Zürich	1367	730	137
Switzerland	1500	801	150
annual wet deposition in Switzerland (41 293 km^2)	46 t	33 t	6 t

in fact, equal to slightly higher than in town (for MCA shown in Figure 9).

An annual wet deposition in Zürich of $1 \text{ mg}/\text{m}^2$ of MCA and about $140 \mu\text{g}/\text{m}^2$ of TCA is calculated (Table 4) based on the data between September 1994 and September 1995. Extrapolated for the territory of Switzerland, this amounts to an annual deposition of 46 t of MCA and 6 t of TCA.

In Alpthal, deposition of TCA by canopy runoff from the trees was larger than by rain in the open field (Figure 10), as already reported (25, 26). This may be explained by dry deposition onto trees with subsequent rinsing. On the other hand, for MCA and DCA, the concentrations in the canopy runoff were smaller. These acids are probably taken up by vegetation because of their lower acidity and polarity.

Conclusions. Two methods have been used for the determination of chloroacetic acids in rainwater; concentrations of about 1 $\mu\text{g/L}$ have been found. In view of the high phytotoxicity, particularly of MCA, and the occurrence of all three acids in precipitation and terrestrial vegetation (2), including those of nutritional importance (27), further investigations are required to identify the main sources. Studies should be initiated that allow the differentiation between natural and anthropogenic contributions in order to assess the potential for reduction of the environmental burden of chloroacetic acids.

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