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The composition and deposition of organic carbon in precipitation[1]

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ABSTRACT

Wet-only precipitation was collected at Hubbard Brook, New Hampshire and Ithaca, New York from June 1976 through May 1977. Samples were analyzed for dissolved organic carbon (DOC), particulate organic carbon (POC), carboxylic acids, aldehydes, carbohydrates, tannin/lignin, primary amines and phenols. DOC was partitioned into molecular weight ranges via ultrafiltration at nominal cut-off values of 1000; 5000; 20,000; 50,000 and 100,000 daltons. Annual total organic carbon (TOC) concentrations and depositions were 1.28 mg l^{-1} and 14.0 kg ha^{-1} at Hubbard Brook, and 2.37 mg l^{-1} and 24.2 kg ha^{-1} at Ithaca. DOC comprised 84% and 80% of these totals, respectively. The majority of annual deposition occurred in summer (June–September), when both concentrations and rainfall amounts were higher. Although volume-weighted, annual mean TOC concentrations at Ithaca were more than 1.8 times higher than at Hubbard Brook; the physical/chemical profiles were similar at both sites. Particulate plus dissolved macromolecular (> 1000 MW) organics accounted for 51% and 63% of TOC at Hubbard Brook and Ithaca, respectively. Carboxylic acids, aldehydes, carbohydrates (chiefly polysaccharides) and tannin/lignin comprised most of the remaining carbon, and were present in similar amounts (as % of TOC). It is suggested that a major fraction of TOC in precipitation at these two sites in the northeastern U.S. was derived from airborne particulate matter, such as soil dust and plant material.

1. Introduction

Rain and snow falling on the landscape contain a diverse assemblage of inorganic and organic materials in both dissolved and particulate form. The inorganic constituents have received and will continue to receive considerable attention relative to concentration, deposition, temporal and spatial trends, etc. (e.g., Junge, 1963; Lodge et al., 1968; Likens et al., 1977). In comparison, the organic components in precipitation have received relatively little study (see Galloway et al., 1982).

Efforts to characterize the organic compounds in rain and snow have been few and of limited scope. Generally these compounds have been investigated or differentiated in one of two ways: in terms of total organic carbon (TOC; e.g., Skopintsev et al., 1971), total organic material (e.g., Viro, 1953), and/or dissolved organic carbon (DOC; e.g., Neumann et al., 1959); or in terms of a single class of carbon compounds such as amino acids (Fonselius, 1954; Sidle, 1967), pesticides and PCB's (Abbott et al., 1965; Wheatley and Hardman, 1965; Weibel et al., 1966; Tarrant and Tatton, 1968; Woodwell et al., 1971; Peakall, 1976; Lunde et al., 1977), hydrocarbons (Lunde et al., 1977), vitamins (Parker and Wachtel, 1971) and carboxy-

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lic acids (Galloway et al., 1976). The former approach demonstrated that organic carbon is abundant and ubiquitous in rain and snow, while the latter has shown that precipitation contains an extremely complex assemblage of organic compounds at low concentrations.

In our study, we incorporated both of these analytical approaches in an attempt to quantitatively evaluate the physical spectrum (i.e., molecular weight) of organic carbon in precipitation, to evaluate the functional-group composition of low molecular weight organics (i.e., < 1000 daltons) in precipitation, and to measure the deposition of these materials at two locations in the northeastern United States.

2. Study sites and collection procedures

Samples of precipitation for organic carbon analysis were collected at two locations in the northeastern United States: Hubbard Brook Experimental Forest, New Hampshire and Ithaca, New York. These sites, the methods of collection and periods of rainfall are described below. Data on amount of precipitation were obtained from the climatological stations at each site.

2.1. *Hubbard Brook Experimental Forest, New Hampshire*

The Hubbard Brook Experimental Forest is located near West Thornton, New Hampshire, within the White Mountain National Forest. Although the Atlantic Ocean is only about 116 km to the southeast, the climate and inorganic chemistry of precipitation are dominated by continental conditions (Likens et al., 1977). This rural area is entirely forested by northern hardwood species, predominantly sugar maple, American beech and yellow birch. Wet-only rain and snow samples were obtained (on an event basis; samples were taken on the morning following the cessation of precipitation) with a modified Health and Safety Laboratory wet/dry collector (see Galloway and Likens, 1976, 1978) located in a large clearing within the forest. There was no overhead obstruction above an angle of 45° from the opening of the collector, and collection techniques followed the recommendations of Galloway and Likens (1976).

The rainfall collector was modified to avoid contamination with organic matter. The standard polyethylene collection vessels were replaced with glass receptacles of similar size; the plastic underliner on the collector cover was removed; and the collector cover was adjusted vertically to maintain a tight collector–receptacle seal. Thus the precipitation samples came into contact with glass or metal surfaces only, and interaction with the atmosphere following collection was minimized.

Forty-eight precipitation events were sampled at Hubbard Brook during 8 June 1976 to 31 May 1977. The total precipitation collected was 91.2 cm or 84% of the 109.2 cm that fell during the year. The remaining 16% was lost due to malfunction of the sampler (icing) and sample spillage in transit to the laboratory. Sampled precipitation events ranged in size from 0.41 cm to 5.79 cm and averaged 1.90 cm. The average precipitation at Hubbard Brook is about 130 cm yr^{-1} (Likens et al., 1977).

2.2. *Ithaca, New York*

The Ithaca site was adjacent to the Department of Commerce (NOAA) Climatological Data Network Station, located on Cornell University's Game Farm. The area is approximately 1 km east of Ithaca (population ~30,000), on the eastern edge of the Cornell University campus. The site is surrounded by some forested land and by several hundred hectares of farmland used by the University for research in the cultivation of food and forage crops.

From 1 June 1976 to 31 May 1977, 47 precipitation events at Ithaca were sampled with a Finnish wet/dry precipitation collector, which was modified as above to avoid contamination (see Galloway and Likens, 1976, 1978 for description of original collector). The total precipitation sampled amounted to 95.0 cm, or 93% of the annual precipitation. Sampled precipitation events ranged in size from 0.38 cm to 9.97 cm, and averaged 2.02 cm. The largest storm not collected during the year was one of 0.60 cm.

3. Experimental methods — analytical procedure

Samples of precipitation were immediately acidified with sulfuric acid to a pH of approximately 2, and maintained at 2°C to 4°C until completion of all analyses (generally less than 5 days). Replicate analysis of several samples showed all parameters to be stable (within 5% to 10%) for storage periods up to 2 weeks.

The DOC was determined in triplicate by the persulfate oxidation method of Menzel and Vaccaro (1964). Analysis of particulate organic carbon (POC) was performed by filtering the entire sample through a precombusted (450° C) Reeve-Angel 984 H glass-fiber filter (a mat-type filter with nominal size cut off of 0.1 to 0.5 μm) on a precombusted all-glass Millipore vacuum filtration system. The POC on the filter was oxidized in the furnace of a Coleman Model 13 carbon–hydrogen analyzer, and subsequently detected with a Beckman Model 865 infrared analyzer.

The DOC was partitioned into functional groups using the following methods: carboxylic acids (Bethge and Lindstrom, 1974); aldehydes and formaldehyde (Afghan et al., 1974a); phenols (Afghan et al., 1974b); monosaccharides (Johnson and Sieburth, 1977); polysaccharides (Burney and Sieburth, 1977); primary amines (Udenfriend et al., 1972); and tannin/lignin (American Public Health Association et al., 1965). Tannin/lignin, aldehyde and polysaccharide analyses were performed on unfiltered (UM-2) sample aliquots; carboxylic acids, formaldehyde, monosaccharides, primary amines and phenols were analysed without previous ultrafiltration.

Physical separation of DOC into molecular weight ranges was done in a pressurized (3.5 atm. N_2) Amicon Model 202 ultrafiltration cell, with the following Diaflo membrane ultrafilters: XM-100A (100,000); XM-50 (50,000); UM-20 (20,000); PM-5 (5000); UM-2 (1000). Numbers in parentheses refer to the nominal molecular weight cut off of each filter (in daltons), as stated by the manufacturer. The DOC concentration of the sample filtrates was analyzed as above, to determine the amount of organic carbon in the various size intervals. Approximately 250 ml of double-distilled water was passed through each ultrafilter prior to use to remove traces of leachable organic carbon.

All storage vessels and analytical apparatus, with the exception of the ultrafiltration cell, were of borosilicate glass. Removal of organic contaminants from glassware surfaces was achieved by heating in a muffle furnace (475° C) for 8 h prior to use.

In the event that precipitation volume was insufficient to permit a complete analysis, DOC and POC were analyzed first, followed by the functional group analysis, then by ultrafiltration in order of increasing molecular weight.

4. Results and discussion

4.1. *Carbon concentration and deposition*

The concentration of TOC in precipitation at Ithaca ranged from 0.45 mg l^{-1} to 4.87 mg l^{-1}, and

Table 1. *Monthly organic carbon in precipitation at Ithaca, New York and Hubbard Brook Experimental Forest, New Hampshire during 1976–77*

	Volume-weighted mean concentration (mg l^{-1})						Deposition (g ha^{-1})					
	TOC*		DOC†		POC‡		TOC		DOC		POC	
Month	Ithaca	HB§	Ithaca	HB	Ithaca	HB	Ithaca	HB	Ithaca	HB	Ithaca	HB
June	2.67	0.99	1.91	0.95	0.76	0.04	3027	758	2168	728	858	31
July	3·09	2.05	2.42	1.99	0.67	0.06	6620	2115	5183	2050	1437	66
August	3.48	1.66	2.59	1.48	0.89	0.18	3233	2463	2409	2195	824	269
September	2·93	1.26	2.44	0.99	0.49	0.27	2508	1220	2092	956	417	264
October	2.09	1.27	1.85	1.12	0.24	0.15	3143	2398	2775	2107	368	292
November	0.59	1.87	0.25	1.41	0.34	0.46	244	611	139	461	104	151
December	1.06	0.50	0.77	0.35	0.29	0.15	475	464	345	328	130	136
January	0.81	1.13	0.66	0.98	0.15	0.15	280	532	229	459	51	73
February	1.13	1.59	0.94	1.26	0.19	0.33	523	892	437	705	86	187
March	1.69	0.88	1.32	0.59	0.37	0.29	1411	1066	1099	715	312	350
April	2.55	1.01	2.32	0.73	0.23	0.28	1505	975	1368	704	137	271
May	2.29	1.67	1.71	1.39	0.59	0.28	1263	536	940	446	323	90
Annual	2·37	1.28	1.88	1.09	0.49	0.20	24230	14031	19184	11854	5046	2180

* Total organic carbon. † Dissolved organic carbon. ‡ Particulate organic carbon. § Hubbard Brook.

had an annual volume-weighted mean of 2.37 mg l^{-1} (Table 1). Monthly volume-weighted mean concentrations exhibited a strong seasonal pattern. Concentrations were consistently high throughout the summer months (June–September), abruptly declined in the autumn (October–November), remained low during the winter (December–February) and then increased in the spring (March–May). Overall, the average summertime TOC concentration at Ithaca (3.04 mg l^{-1}) was three times greater than in winter (1.00 mg l^{-1}).

The concentration of TOC at Hubbard Brook was appreciably lower than that at Ithaca (Table 1). Concentrations ranged from 0.10 mg l^{-1} to 3.23 mg l^{-1} and averaged 1.28 mg l^{-1}. Also there was somewhat less variation between monthly means during the year than at Ithaca; nevertheless, the summertime mean (1.49 mg l^{-1}) was 1.4 times greater than the winter mean (1.07 mg l^{-1}).

Annual deposition of organic carbon (concentration in g l^{-1} times 1 ha^{-1} of precipitation) at Ithaca and Hubbard Brook (Table 1) was 24.2 kg ha^{-1} and 14.0 kg ha^{-1}, respectively. Major inputs of organic carbon occurred during summer at both sites, as a result of higher concentrations and somewhat greater amounts of precipitation. At Ithaca, 15.4 kg ha^{-1} (64% of the annual total) was deposited from June through September, with 27% deposited during July alone, when nearly 21% of the annual precipitation occurred. Summertime loadings at Hubbard Brook were 6.6 kg C ha^{-1} (47% of the annual total). The monthly pattern of input at Hubbard Brook was similar to that at Ithaca, although deposition at Hubbard Brook was lower than Ithaca during March–October and equal or somewhat higher during November–February (Table 1). The more similar inputs at these two sites during the winter may reflect spatially uniform conditions of soil and plant surfaces (i.e., likely organic carbon sources) imposed by the winter climate. There was no statistical relationship between the concentration of DOC or POC and the amount of precipitation for individual storms at either site.

The annual deposition of organic carbon in precipitation at Hubbard Brook is 1.68 times greater than the annual streamwater loss of DOC and 1.14 times greater than the total annual export of DOC and POC by streams draining the Hubbard Brook Experimental Forest (Likens et al., 1977).

4.2. *Physical characterization of TOC*

Analyses for POC indicated that the majority of organic carbon in precipitation was in the dissolved form. Annual volume-weighted mean concentrations of POC at Hubbard Brook and Ithaca were 0.20 mg C l^{-1} and 0.49 mg C l^{-1}, or 16% and 20% of TOC, respectively (Table 1). On a monthly basis, POC at Hubbard Brook ranged from 0.04 mg C l^{-1} (4% of TOC) in June to 0.46 mg C l^{-1} (25% of TOC) in November. The contribution of POC to the TOC deposition exceeded 30% only during March, the month of lowest TOC concentration, and the correlation between POC and TOC was poor ($r^2 = 0.05$). Monthly POC at Ithaca ranged from 0·15 mg C l^{-1} (19% of TOC) in January to 0·89 mg l^{-1} (26% of TOC) in August, and the correlation between POC and TOC ($r^2 = 0{\cdot}58$) was significantly higher than at Hubbard Brook.

There were marked seasonal patterns of concentration and deposition for DOC and POC at the two sites. At Hubbard Brook, 62% of the annual DOC input occurred during July through October. The maximum POC input occurred in March 1977 (350 g ha^{-1}) and the minimum (31 g ha^{-1}) occurred during June (Table 1). At Ithaca, 65% of the annual deposition of DOC occurred during July through October, and similarly to Hubbard Brook, November through January were months of low DOC input. Maximum POC input occurred during July in Ithaca (28% of the annual total) with a minimum in January and February (Table 1). The reduction and convergence of POC inputs at the two sites during the winter months suggest that sources for POC from semi-urban and agricultural Ithaca and from rural-forested Hubbard Brook were moderated because of minimal biological activity and presence of snow cover. Conversely, the two sites are more easily distinguished during the summer, when agricultural activity and forest growth are maximal.

The molecular weight profiles for DOC in precipitation from Ithaca and Hubbard Brook were similar (Fig. 1). The Ithaca distribution, however, was skewed somewhat toward larger molecules, whereas the Hubbard Brook distribution was toward smaller molecular sizes. The smallest size class (i.e., < 1000 daltons) was predominant at both sites, representing 49% and 37% of the TOC at Hubbard Brook and Ithaca, respectively. Also, the fraction of TOC in each class generally decreased

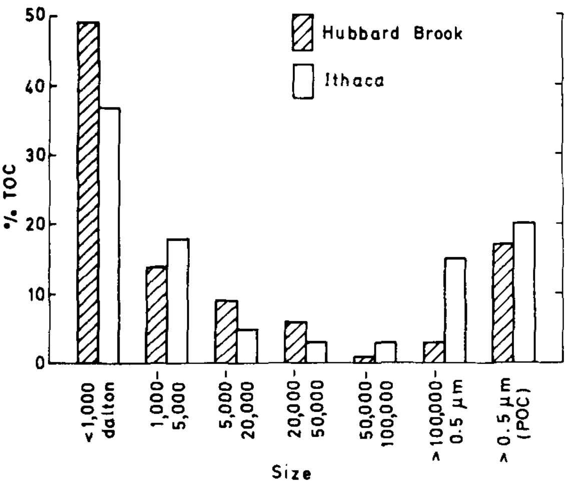

Fig. 1. Size distribution of total organic carbon in wet-only precipitation from Ithaca and Hubbard Brook.

with increasing molecular weight at both sites. The only exception to this trend was observed in the >100,000 dalton–0.5 µm interval, particularly in Ithaca. However, because small particles can pass the 0.5-µm pores of the glass fiber filter, the separation between DOC and POC is somewhat ambiguous. Thus, our method of partitioning POC and DOC may have led to an underestimate of POC, particularly at Ithaca. Some 51% of the TOC at Hubbard Brook and 63% at Ithaca was composed of high molecular weight DOC (>1000 daltons) plus POC (Table 2).

Although we made no concerted effort to chemically characterize the macromolecular organic fractions, a number of incidental analyses yield some insight into their composition. Total carbohydrate and tannin/lignin analyses of three Hubbard Brook samples, before and after ultrafiltration, showed that these compounds could account for as much as 50% of the high molecular weight (>1000 daltons) carbon. Hydrolyzable protein analysis of the same samples indicated that only a small portion (<10%) of macromolecular carbon was proteinaceous, but that nearly all of the organic nitrogen content of these samples was associated with macromolecular organics. Finally, microscopic examination of particulate matter from several rain events showed the presence of large amounts of debris similar in appearance to bits of chaff. The observed particles appeared to be larger and more abundant in Ithaca samples.

These findings suggest that structural tissue of plants contributes to the POC content of precipitation. By implication, the degradation and dissolution of this material (both in the atmosphere and in the rain sample) will influence the composition of high and low molecular weight DOC.

5. Speciation of low molecular weight DOC (LMW-DOC)

Functional group analyses of the LMW-DOC (<1000 daltons) revealed significant concentrations of carboxylic acids, aldehydes, carbo-

Table 2. *Organic carbon compounds in wet-only precipitation from Ithaca, New York and Hubbard Brook Experimental Forest, New Hampshire*

	Concentration range (mg l^{-1})		Mean concentration (mg l^{-1})		% of TOC*	
Organic species	Ithaca	HB	Ithaca	HB	Ithaca	HB
TOC	0.45–4.87	0.10–3.23	2.37	1.28	100	100
POC	0.02–1.83	0.03–0.98	0.49	0.20	20	16
DOC	0.30–3.10	0.07–2.92	1.88	1.09	80	84
<1000 MW organics	0.25–1.10	0.01–2.03	0.88	0.63	37	49
carboxylic acids	0.03–1.04	<0.02–0.68	0.46	0.30	11	14
aldehydes	<0.01–1.03	<0.01–0.55	0.40	0.35	7	11
carbohydrates	<0.05–1.35	<0.05–0.82	0.31	0.27	5	8
tannin/lignin	<0.04–1.21	<0.04–0.38	0.35	0.18	8	8
primary amines	<0.001–0.032	0.001–0.019	0.006	0.006	<1	<1
phenols	<0.001–0.024	<0.001–0.017	0.004	0.003	<1	<1
unresolved carbon	—	—	0.13	0.11	6	9
>1000 MW organics	<0.05–2.00	0.06–0.89	1.02	0.45	43	35

* Based on weighted mean concentration of organic carbon in component and weighted mean TOC concentration.

hydrates and tannin/lignin at the two sites (Table 2). Together, these compounds accounted for 41% and 31% of the TOC, 82% and 84% of the LMW-DOC, at Hubbard Brook and Ithaca, respectively. Overall, the relative abundance of these substances was similar at both sites; however, the concentrations were higher at Ithaca, particularly tannin/lignin compounds. No significant correlation was found between concentrations of any of the above species and DOC or TOC concentrations; however, concentrations, in general, rose and fell in accordance with seasonal TOC values. Primary amines and phenols were detected at the ppb level in all samples, and constituted a persistent but extremely minor fraction of the TOC in precipitation. Unlike the major constituents, amines and phenols occurred at similar concentrations in both Ithaca and Hubbard Brook samples, and they showed no seasonal trends in concentrations.

Carboxylic acids accounted for the largest share of LMW-DOC (11% to 14% of TOC; Table 2) at both locations, and with few exceptions the acids identified appear to be of natural origin. The C_1–C_5 acids, as well as lactic, glycolic, caproic, succinic and citric were observed frequently while others appeared occasionally or uniquely (Table 3). In general, a greater number of acids were identified at Hubbard Brook, but the total acid concentration was higher at Ithaca (7.2 vs 4.4 μmol). Formic acid was the most common and abundant organic acid in Ithaca precipitation, where it was found in 85% of the samples and with a volume-weighted mean concentration of 2.4 μmol. At Hubbard Brook, acetic acid predominated (88% of samples; 2.8 μmol), while formic acid appeared infrequently (26%) and as a minor constituent (0·2 μmol). Citric acid occurred more commonly at Ithaca than at Hubbard Brook and caproic acid occurred more commonly at Hubbard Brook.

Although present in virtually every sample, carboxylic acids did not contribute significantly (i.e., < 5%) to the free proton concentration at either site, and only rarely supplied more than 10% of the total acidity. At Hubbard Brook, for example, the volume-weighted, mean concentration of hydrogen ion was 64 μmol during our study. Based on the ionization constants of the organic acids in Table 3, their total contribution of free protons was no more than 1.3 μmol, or only 2% of the free acidity.

Table 3. *Summary of organic acids identified in precipitation from Ithaca, New York and the Hubbard Brook Experimental Forest, New Hampshire (HB)*

	Volume-weighted mean concentration (μmol)		Frequency of occurrence (%)	
Acid	Ithaca*	HB†	Ithaca*	HB†
Formic	2.4	0.2	85	26
Acetic	1.1	2.8	66	88
Propionic	0.8	0.3	37	29
Butyric	1.4	0.4	66	53
Valeric	0.1	0.1	20	24
Iso-Valeric	<0.1	—	2	0
Caproic	<0.1	0.1	2	18
Capric	—	<0.1	0	3
Benzoic	—	<0.1	0	9
OH-Benzoic	—	<0.1	0	3
Lactic	0.3	0.3	34	29
Glycolic	0.1	0.1	20	24
Malic	<0.1	<0.1	2	6
Fumaric	<0.1	<0.1	2	3
Oxalic	—	<0.1	0	3
Succinic	0.1	0.1	15	15
Phthalic	—	<0.1	0	3
Citric	0.9	<0.1	34	9
Iso-Citric	<0.1	—	7	0
Caprylic	—	<0.1	0	3

* Based on 41 samples, 94.5 cm of precipitation, 1976–77.
† Based on 34 samples, 75.4 cm of precipitation, 1976–77.

Low molecular weight carboxylic acids also have been observed in precipitation in southern California (Liljestrand and Morgan, 1979), and a variety of aliphatic and aromatic organic acids have been reported in rain and snow in Norway (Lunde et al., 1977). In neither case, however, were these acids present in sufficient concentrations to significantly affect the pH of rainfall. Hoffman et al. (1980a and b) recently reported the absence of carboxylic acids in rainfall from Walker Branch, Tennessee. The authors noted, however, that the more volatile species, such as formic and acetic acid, may have been lost during their extraction-concentration procedure. In any event, our results support the conclusions of Galloway et al. (1976) that organic acids play a negligible role in the formation of acid rain in the northeastern U.S.

Formaldehyde was the principal aldehyde at Ithaca and Hubbard Brook, where it accounted for

75 mol % and 57 mol %, respectively, of the total aldehyde constituent. Mean concentrations were nearly identical at Hubbard Brook (0·26 mg l^{-1}) and Ithaca (0.24 mg l^{-1}) and were similar to values for Asian precipitation cited by Junge (1963). Formaldehyde is a ubiquitous atmospheric species; it may be emitted directly from incomplete combustion processes, or formed in the atmosphere from a variety of reactions, including photochemical oxidation and ozonolysis of atmospheric organics (e.g., CH_4) (cf. Cleveland et al., 1977), all presumably contributing to formaldehyde in rainfall.

Carbohydrates and tannin/lignin each represented 13% to 21% of the LMW-DOC at Ithaca and Hubbard Brook. Polysaccharides were the principal carbohydrates, while free sugars only rarely exceeded the detection limit of 20 μg/l. Due to the general nature of the analytical technique, it is not possible to state whether the species classified as tannin/lignin is actually tannin or lignin. Both classes of compounds are produced abundantly in nature and likely enter precipitation via suspended plant and soil particles.

Unidentified low molecular weight organics represented 9% and 6% of the TOC, or 17% and 16%, of the LMW-DOC at Hubbard Brook and Ithaca, respectively. A number of uncertainties, including analytical error, contribute to the "unresolved" organic carbon component in Table 2. Conversion of analytical results to equivalent carbon concentrations may have introduced some error. With the exception of the carboxylic acid analyses, our analytical scheme was generic, rather than specific; that is, we determined the molar concentrations of each functional group, not the structure of the parent molecule. To determine carbon concentrations, it was necessary to assume an average carbon content for each group. For carbohydrates and tannin/lignin, the error involved is probably small; however, the elemental composition (i.e., wt % carbon) of aldehydes is relatively sensitive to C-chain length. Because we computed aldehyde carbon on the basis of formaldehyde, our estimate of aldehydic carbon is low, despite the dominance of formaldehyde.

The most important uncertainty arises simply because we did not attempt to analyze all possible constituents; nor were the analyses universally sensitive to all compounds of a particular group. Recent investigations (Grob and Grob, 1974; Duce and Duursma, 1977; Lunde et al., 1977) have shown that precipitation bears an extremely complex mixture of hydrocarbons, pesticides and PCB's at μg l^{-1} and ng l^{-1} concentrations. Trace amounts of DDT and related compounds have been found in Ithaca rainfall (Peakall, 1976); however, the concentrations observed were far too small, 10^{-6}% of TOC, to warrant inclusion in our survey. Lunde et al. (1977) also have demonstrated the presence of carboxylic acids in precipitation that would not have been detected with our analytical scheme. The relative contribution of these various uncertainties to the 100 to 150 μg/l of unresolved carbon is unknown.

6. Summary and conclusions

Atmospheric deposition may supply considerable amounts of DOC to the landscape. Annual TOC concentrations and depositions were 1.28 mg l^{-1} and 14.0 kg ha^{-1} at Hubbard Brook and 2.37 mg l^{-1} and 24.2 kg ha^{-1} at Ithaca during 1976–77; more than 80% of this organic carbon was DOC. The deposition of TOC at Hubbard Brook represents about 114% of the total annual export of organic carbon from terrestrial watersheds.

Seasonal trends in concentration and precipitation amount, at both sites, produced high inputs during summer months and lower inputs during winter. Concentrations of TOC were similar at Ithaca and Hubbard Brook during the winter, but were highly dissimilar during the summer. Contrasting summertime results probably reflect different levels of suspended POC in the atmosphere over rural-forested and agricultural landscapes. Convergent wintertime results, on the other hand, may result from a more uniform snowcover and absence of metabolically-active foliage on the deciduous vegetation in both areas.

Approximately 91% to 94% of the TOC in precipitation at Hubbard Brook and Ithaca was accounted for by our chemical and physical scheme of analysis and differentiation. Relatively large concentrations of carboxylic acids, aldehydes, carbohydrates and tannin/lignin were found in the precipitation. Carboxylic acids were richer in variety at the forested Hubbard Brook site, but except for acetic acid were generally appreciably higher in concentration at the semi-urban, agricultural Ithaca site. Formic was the most frequently occurring organic acid at Ithaca; however, it was relatively rare at Hubbard Brook, where acetic acid was the most common. The concentrations of aldehyde, carbohydrate and tannin/lignin were higher in Ithaca, particularly tannin/lignin. Smaller but similar amounts of primary amines and phenols were found at both sites.

The overall physical–chemical characteristics of TOC at Hubbard Brook and Ithaca were remarkably similar. With the exception of formaldehyde and a variety of carboxylic acids, the TOC content of precipitation is comprised of relatively high molecular weight species and particulate matter. Since these organics are essentially nonvolatile, they must originate either from autogenic processes (e.g., by photochemical conversion of gas to particle) or from ground-level emission. The first pathway may account for a portion of the TOC, but it is unlikely to explain the presence of carbohydrates and tannin/lignin in precipitation, or the high TOC level at Ithaca, relative to Hubbard Brook. Cultivation of fields near Ithaca may have enhanced TOC levels and marginally shifted the molecular weight distribution, but left the relative organic composition of precipitation essentially intact. Crutzen et al. (1979) have suggested that natural and man-set fires may contribute significantly to the composition of gases in the atmosphere. Such gases and particulate matter from fires include organic carbon and, therefore, may be a source of carbon found in precipitation. However, on the basis of our data it is not possible to differentiate clearly between natural and anthropogenic sources of the various organic substances found in precipitation.

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