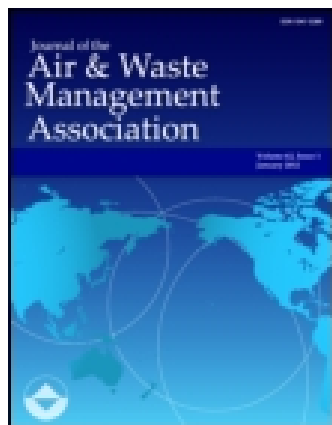


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Air & Waste

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/uawm19>

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Published online: 06 Mar 2012.

To cite this article: Viney P. Aneja (1993) Organic Compounds in Cloud Water and their Deposition at a Remote Continental Site, *Air & Waste*, 43:9, 1239-1244, DOI: [10.1080/1073161X.1993.10467201](https://doi.org/10.1080/1073161X.1993.10467201)

To link to this article: <http://dx.doi.org/10.1080/1073161X.1993.10467201>

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Organic Compounds in Cloud Water and their Deposition at a Remote Continental Site

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Some organic compounds (alkylbenzene, chlorinated hydrocarbons and polycyclic aromatic hydrocarbons) in clouds have been determined from samples collected above the canopy of a coniferous forest. The cloud samples were collected during 1987 and 1988 at Mt. Mitchell State Park, North Carolina, a remote high elevation (~2006 m MSL) continental site. Concentrations of the organic chemicals in clouds were in the range of 0.2 to ~200 ng mL⁻¹; and their estimated deposition rates via clouds were found to range from 1.58×10^4 to 4.67×10^6 ng m⁻² yr⁻¹. Great variations in concentrations were found which can best be explained, based on 72 hour back trajectory analysis, by different source locales and moving air masses. The concentration of these chemicals exceeded their water solubility as predicted by Henry's Law, suggesting that clouds are an excellent scavenger of organic chemicals in the ambient environment.

A variety of organic compounds have been found in aerosol particles, rain and snow. The organic pollutants in the aerosol component have both natural and anthropogenic origin.¹⁻³ Organic pollutants in rain and snow have been used to identify the origin of air masses producing them.⁴⁻⁷ Among the organic compounds detected in rain and snow are n-alkanes and organic acids,^{4,5,8-13} chlorinated hydrocarbons,^{10,14,15} phenols,^{12,15,16} and polycyclic aromatic hydrocarbons.^{5,6,8,10-12,17-19} However, data on organic pollutants in cloud water are rather limited and incomplete.²⁰ Carbonyl compounds in cloud water have received more attention due to their reaction with sulfur.²¹⁻²⁴ Thus it is desirable to determine the nature and concentrations of organic pollutants in cloud water. It is particularly important in light of the wide variety of organic compounds shown to be present in rain and snow. Furthermore, the primary deposition pathway of pollutants

Implications

The transport of air toxics through the atmosphere is thought to be an important pathway in their distribution. The results from this research suggest that clouds provide a unique pathway to concentrate the organic chemicals; thus making it relatively easier to monitor them. Moreover, these organic chemicals can be deposited at high elevation forest ecosystems in significant quantities by cloud episodes and then become potentially detrimental to plant life. This route of organic chemical exposure to sensitive ecosystems has been ignored thus far, but it may be a possible contributor to high elevation forest decline.

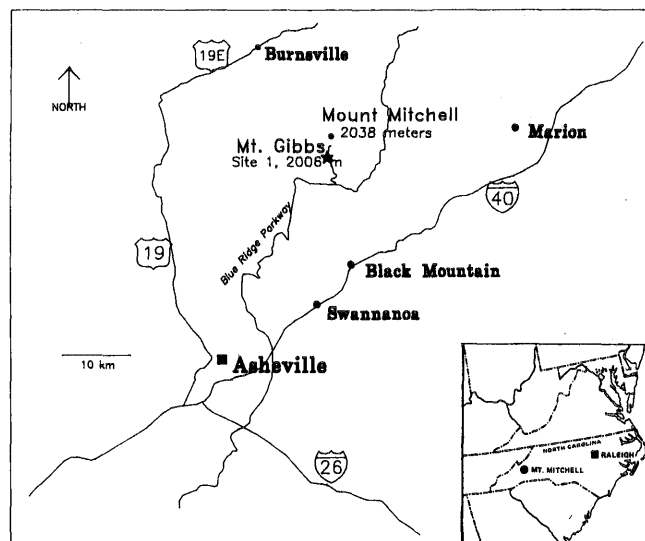


Figure 1. Map of the Mt. Mitchell State Park, NC showing the location of Mt. Gibbs (Site 1) and the adjoining towns and roads.

on high elevation forest ecosystems has been shown to be via clouds.^{25,26} It is thought that wet and dry deposition of phytotoxic organic compounds on plant surfaces contributes to the causes of forest decline.^{16,18,27}

Clouds have a natural cycling process which can typically accumulate the soluble material from a large volume of air into a small volume of cloud water. Analysis of the cloud water therefore affords an unusual opportunity to determine concentrations of pollutants as low as parts per trillion in cloud-forming air. Capel et al. (1991)²⁸ have shown that organic chemicals, particularly hydrophobic organic compounds, may be present in urban fog significantly in excess of their water solubility. Perona (1992)²⁹ has shown, based on a thermodynamic treatment, that the solubility of hydrophobic compounds dissolved in small droplets (i.e., systems with large surface-to-volume ratios) can be significantly higher than values obtained with solutions having a small surface-to-volume ratio and/or planar surface.

Here we report the preliminary results of measurements of volatile organic compounds (VOCs) in cloud water collected at Mt. Mitchell State Park (35°44'05"N, 82°17'15"W) — the highest peak (2,038 m MSL) — a remote site in the eastern U.S. These data are compared with ambient concentrations of the same

Table I. Analytical conditions for cloud water analysis using GC-FID/ECD.

Parameter	Setting
	Tekmar LSC-2
Volume	5mL
Purge flow rate	60mL/min
Purge time	10 min
Dry purge	2 min
Desorb temperature	190°C
Desorb time	4 min
Focusing	Cryotrapped in liquid nitrogen
Gas chromatograph	Perkin Elmer 3390
Column	60-m, 0.35 mm ID, 1 mm DB-1 coated fused silica capillary
Carrier gas	He, at 30cm ³ /sec
Temperature program	Subambient (N ₂)
Initial temperature	10°C
Initial time	2 min
Rate	8°C/min
Final temperature	150°C
Detectors	FID and ECD split 5 to 1
Data system	Two channel Shimadzu CR5A integrator

chemicals in air and in rain water. The possible mechanisms of air/cloud exchange are explored in an effort to examine the enhancement of Henry's Law transport process by the hydrophobic organic chemicals. Finally, the deposition of organic chemicals in clouds to the forest canopy at Mt. Mitchell State Park are discussed.

Experimental

Sampling Location/Sampling Procedures

The cloud water was collected at Gibbs Peak (~2006 m MSL) in Mt. Mitchell State Park (Figure 1). At high elevation this region has stands of red spruce and Fraser fir trees (~6 m tall). A 16.5 m tall walk-up meteorological tower at the location is equipped at the top with a passive ASRC (Atmospheric Sciences Research Center, State University of New York at Albany) cloud water collector.³⁰ In addition, meteorological instruments are located on the tower at ~16 m above ground. These instruments have the capability for measuring³¹ temperature, pressure, wind speed and direction, relative humidity, and solar radiation.

One hour integrated cloud water samples were collected manually using the ASRC cloud collector which closely simulates the collection of cloud water by coniferous trees. The pH of the samples was determined within 15 minutes of collection. Additional samples were stored in sealed bottles (60 ml) in a refrigerator for subsequent anions and cations analyses utilizing ion chromatography; and VOCs utilizing GC-MS (gas chromatograph – mass spectrometer), and GC-FID/ECD (gas chromatograph – flame ionization detector/electron capture detector).

Ambient gas phase pollutant concentrations of ozone (O₃), sulfur dioxide (SO₂), nitrogen oxides (NO, NO₂, and NO_x), and hydrogen peroxide (H₂O₂) were measured continuously at the site.³²⁻³⁵

Analysis Procedures

The cloud water samples were initially analyzed for VOC content utilizing gas chromatography/mass spectrometry (GC/MS) as follows: helium (He) was bubbled through a cloud water

sample (5 ml) contained in a specifically designed purging chamber at ambient temperature to efficiently transfer the VOCs from the aqueous phase to the vapor phase. The vapor was swept through a sorbent column (Tenax) to trap the VOCs. After purging was complete the sorbent column was heated (190 °C) and backflushed with He to desorb the VOCs onto a gas chromatographic column (30 meters long, 0.3 mm o.d. coated with D85). The flow rate through the column was 3 ml/min of He. The gas chromatograph was temperature programmed (10 °C for three minutes program to 31 °C at 3 °C/minute, changed to 8 °C/min. to a maximum of 200°C) to separate the VOCs, which were then detected with a mass spectrometer. VOCs in reagent water blanks were found to be insignificant. If necessary, an aliquot of the sample was diluted with reagent water.

The cloud water samples were analyzed additionally for six selected VOCs [methylene chloride (stationary source), chloroform (stationary source), mesitylene, i.e., 1,3,5-trimethyl benzene (stationary and/or mobile source), toluene (stationary and/or mobile source), ethylbenzene (mobile source), and o-xylene (mobile source)] using a purge and trap concentration (as discussed previously) and gas chromatography (GC) with FID/ECD. The six compounds were selected to cover both stationary and mobile sources³⁶ on the basis of GC/MS confirmatory analysis. The source in parentheses is expected to be the major source. Table I lists the experimental conditions used during this analysis of cloud water samples. Calibration was performed using two standards containing each of the six compounds prepared in water at concentrations of 1 ng/ml and 10 ng/ml. Response factors for the two standards were averaged and used to calculate the sample concentrations. Distilled water used to prepare the standards was analyzed each day. It was found to contain nondetectable amounts of these compounds.

Results and Discussion

The experiments were made to characterize, and attempt to locate the origin of, organic pollutants present in cloud water collected in Mt. Mitchell State Park, North Carolina. Seventy-two hour back trajectory analyses at 850 mb were performed for the cloud events of interest. The site elevation (2006 m MSL) is such that 850 mb back trajectories are representative of air flow responsible for cloud events.

The preliminary results reported here are for cloud water samples collected for several days between May and October 1987; and May and July 1988. Tables II and III list concentrations of the organic compounds present in the cloud water samples, air, and rain. The concentrations of the organic chemicals in clouds were in the range of 0.2 to ~200 ng mL⁻¹. Table IV lists the field pH, total anion and cation concentrations, and the wind direction during sample collection. The total inorganic ion concentrations are higher in spring and summer (>500 µequ/L) than in fall (<300 µequ/L).

The presence of organic chemicals, particularly hydrophobic organic compounds (Tables II and III), are observed consistently in clouds. This seems to suggest that clouds are an efficient scavenger and/or inclusion media of organic chemicals from the atmosphere.^{28,37} There are at least four main pathways by which these transport processes may occur, and each of these is discussed.

First, the Henry's Law exchange mechanism proposes that the organic chemicals in gas and dissolved phases, and the transport between the two phases follows Henry's Law. It relates the air concentration of a species to its aqueous concentration in an equilibrium environment. The justification of the use of Henry's Law equilibrium in the case of cloud droplets is that the relatively long atmospheric lifetime of cloud droplets (~ several hours)²⁵ allows the droplets to reach at least a significant portion of their equilibrium state with the ambient environment.

Table II. Physical/chemical constants (at 25°C) and cloud water concentrations of organic chemicals.

Compound	Molecular Weight (g mol ⁻¹)	Water Solubility (ng mL ⁻¹)	Vapor Pressure (20°C) (Pa)	Henry's Law Constant (20°C) ^a (atm m ³ mol ⁻¹)	Calculated Dimensionless Henry's Law Constant (α) at 20°C (RT/H)	Average Cloud Water Conc. (ng/mL)	Range of Cloud Water Conc. (ng/mL)
Acetone	58	6.03 E8 ^a	1.87 E4 ^c	0.00002	N/A	0.46	0-41
Chloroform	119	8.00 E6 ^b	2.11 E4 ^c	0.00332	7.2	2.41	0-10
Ethyl-benzene	106	1.52 E5 ^b	9.44 E2 ^d	0.00601	4.0	0.17	0-0.45
Hexane	84	9.50 E3 ^b	5.05 E1 ^d	0.883	0.03	1.56	0-14
Mesitylene	120	7.50 E4 ^b	2.31 E2 ^d	0.00571	4.2	0.03	0-0.23
Methylene Chloride	85	7.00 E6 ^b	4.74 E4 ^c	0.00244	9.8	8.88	0-200
Methyl Furan	82	1.52 E6 ^a	1.87 E3 ^c	0.00100	24.1	0.22	0-2
o-Xylene	106	1.75 E5 ^b	6.51 E2 ^d	0.00474	5.1	0.45	0-2.6
Toluene	92	5.15 E5 ^b	2.91 E3 ^c	0.00555	4.3	0.60	0-1.9
Trichloro-ethene	131	1.10 E6 ^b	3.14 E3 ^c	0.00842	2.9	1.38	0-6.7
Trimethyl-benzenes	120	7.50 E4 ^b	2.31 E2 ^d	0.00571	4.2	0.34	0-1.7
2-butanone	72	1.71 E8 ^a	9.33 E2 ^c	0.00019	126	13.9	0-78

^acalculated from octanol/water partition coefficients.

^bMackay and Shiu, (1981)⁴⁶

^cMellan, I., (1968)⁴⁷

^dcalculated per Wilhoit, (1971)⁴⁸

^ecalculated per Boublik, (1984)⁴⁹

^fAshworth, et al., (1988)⁵⁰ calculated $\alpha = RT/H$, temperature = 293°K. H is the Henry's Law Constant.

The effectiveness of Henry's Law exchange is regularly gaged by comparing the dimensionless Henry's Law constant, α ($= RT/H$, H is the Henry's Law Constant), with the overall washout ratio, W (cloud or rain concentration/air concentration). The washout ratio for cloud water, W_{cloud} , is thus calculated as the concentration of a chemical in the cloud water divided by the concentration of the chemical in the gas phase in the air. If the organics found in the cloud water were present due only to Henry's Law exchange then α should equal W_{cloud} .^{7,28} As shown in Tables II and III, W_{cloud} was consistently larger than α by a factor of one to two orders of magnitude and sometimes higher. The only exception was acetone which can be explained by the exceptionally high value of α which reflects its relatively high water solubility. The gas-phase concentrations of these compounds were not measured during the time of cloud collection. However, the gas-phase concentrations of these compounds were ascertained from the literature for typical urban environment. Thus these washout ratios are underestimates for clouds. The enrichment, as compared to simple gas-water exchange, of the hydrophobic organic chemicals in the cloud droplet is similar to results reported also for hydrophobic organic chemicals by Capel et al. (1991)²⁸ for urban fog; by Glotfelty et al. (1987)³⁸ for pesticides; and by Glotfelty et al. (1990)³⁹ for insecticides in fog. The high values for W_{cloud} lead to the conclusion that Henry's Law exchange alone cannot account for the observed concentration of hydrophobic organics in cloud water.

Bearing in mind that Henry's Law relates aqueous concentration to vapor pressure it is clear that as temperature increases the ratio of atmospheric to aqueous concentration must increase as well. Since the dimensionless constant α is generally 1 to 2 orders of magnitude lower than the cloud washout ratio, the Henry's Law constant must be reduced to cause α to match W_{cloud} . Henry's Law constant is reduced for the majority of the compounds when the temperature drops. It would require a significantly larger drop in

temperature, say 50 to 75 degrees, than is likely in order to bring α and W_{cloud} into parity.

A second possible pathway for the incorporation of organic compounds into cloud water considered was particle scavenging. A cloud water droplet can nucleate directly on organics in the form of aerosols in the atmosphere. There are two likely methods for such a nucleation onto a hydrophobic organic. If the organic is in an acidic environment, say in a low pH event due to the presence of sulfuric or nitric acid formed in the atmosphere, the organic can become coated with a film of very hydrophilic acid and then serve as an efficient nucleation site for cloud droplets. Alternatively, a "bubble" of acid can form on the exterior of the organic droplet and serve as a site for the nucleation of cloud water on the organic droplet.⁴⁰

Such scenarios require the presence of sulfuric or nitric acid in the atmosphere to provide the acidic coating or bubble site necessary to cause nucleation on the hydrophobic organic aerosol. The Mt. Mitchell site seems to provide just such an environment. The pH measurements of the 15 cloud samples of events collected (Table IV) range from a low of 2.78 to a high of 4.02 with a mean of 3.63. Such low pHs, particularly when coupled with the fact that most of the winds blew out of the industrial Ohio River Valley area, make the acid environment credible.

Further evidence that low pH may play a role in the levels of organics in cloud water may be found in the concentration data for individual events. Three of the organics were detected only during the event which had the lowest pH reading, 2.78. Those chemicals were acetone, hexane, and methyl furan. Hexane and methyl furan are especially convincing because both are rather hydrophobic organics. Additionally, methylene chloride was detected at extremely high concentrations of 200 ng/L on 6/3/88, the 2.78 pH day. And finally, there seems to be some positive correlation in the concentration of o-xylene, chloroform, and ethyl benzene and low pH.

Table III. Comparison of concentrations of organic chemicals in cloud, air, and rain; and atmospheric washout ratios in rain and cloud; and estimated deposition via clouds.

Compound	Average Cloud Water Conc. (ng/L)	Average Air Conc. (ng/L)	Average Rain Conc. (ng/L)	Overall Washout Ratios		Estimated ^a Deposition via Clouds (ng m ⁻² yr ⁻¹)
				W_{rain}	W_{cloud}	
Acetone	460	14.72 ^d	0.05 ^c	0.0034	31.25	2.42*10 ⁶
Chloroform	2410	1.19 ^a	241 ^a	202.5	2025	1.27*10 ⁶
Ethyl-benzene	170	1.267 ^b	34 ^b	26.8	134.2	8.94*10 ⁴
Hexane	1560	6.99 ^f	156 ^a	22.3	223.2	8.20*10 ⁵
Mesitylene	30	0.490 ^b	5.1 ^b	10.4	61.2	1.58*10 ⁴
Methylene Chloride	8880	1.24 ^f	888 ^a	716	7161	4.67*10 ⁶
Methyl Furan	220	1 E-6 ^a	3 E-5 ^a	30	2.2 E8	1.16*10 ⁵
o-Xylene	450	1.286 ^b	45 ^b	35	349.9	2.37*10 ⁵
Toluene	600	3.757 ^b	88 ^b	23.4	159.7	3.15*10 ⁵
Trichloro-ethene	1380	1.537 ^b	5.6 ^b	3.6	897.9	7.25*10 ⁵
Trimethyl-benzenes	340	1.346 ^b	30 ^b	22.3	252.6	1.79*10 ⁵
2-butanone	1390	2.40 ^d	139 ^a	57.9	579.2	7.31*10 ⁵

^a Czuczwa, et al, (1989)⁷^b Ligocki, et al, (1985)^{10,11}^c Grosjean and Wright, (1983)²²^d Buckholtz and Crow, (1990)⁵¹^e Rice, et al, (1990)⁵²^f Warneck, (1988)⁵³^g calculated value. For values not found in literature an average volumetric increase from a cloud droplet to a raindrop of 10 was assumed.^h calculated by cloud concentration (ng/L) x hours of cloud per year x 0.2 mm/hr. $W_{\text{rain}} = (\text{rain concentration (ng/L)}/\text{air concentration (ng/L)})$ $W_{\text{cloud}} = (\text{cloud concentration (ng/L)}/\text{air concentration (ng/L)})$

A third mechanism that may be at work is the enhancement of Henry's Law exchange by the association of dissolved organics with entrained particulate organics in a cloud droplet.²⁸ As organic material is dissolved into the cloud droplet it may then become associated with any particulate matter in the droplet, thus reducing the actual dissolved concentration of the organic. Such a mechanism could serve to increase the flux of gas phase organic in the atmosphere into the droplet due to Henry's Law exchange.

A fourth mechanism is suggested by Capel et al. (1990).³⁷ It was shown that dissolved and/or colloidal organic carbon could reduce the surface tension of the cloud droplet, thus implying that some hydrophobic organics are surfactants. Surface active organics could form an organic film around the cloud droplet which would then enhance the scavenging of organic compounds.²⁰ The resulting organic vapor/film equilibrium could be significantly more efficient in scavenging organic vapor than Henry's Law. However, the relative contribution of these pathways to incorporate organic chemicals in clouds is not known at this time.

The relative distribution of more than one C_8 (e.g., ethyl benzene, xylene, etc.), in the case of 1987 samples, is very similar to those observed in urban air.⁴¹ Therefore, it is likely that the source of these compounds is reasonably close to the mountain collection site. In fact, the city of Asheville, North Carolina, is about 30 km southwest of the site; Burnsville, North Carolina, is about 15 km northwest of the site; and the town of Black Mountain, North Carolina is only about 15 km south (Figure 1). It is quite conceivable that vehicular exhaust from these areas (see Figure 1) and from Interstate Highway 40 (~ 20 km south) contributed to the presence of aromatic hydrocarbons in cloud water. This is further supported by the wind direction during most of the sampling period and its coupling with back trajectory analysis (Figure 2). Wind direction dependent rainwater organic

compound compositions have been observed by Kawamura and Kaplan (1986b).⁶ Furthermore, it has been shown that anthropogenic sources in urban areas significantly contribute organic compounds to rainwater^{5,7,12} and snow.⁷

Table IV. Wind direction, pH and inorganic ion concentrations in the cloud samples collected.

	Wind Direction	pH	$\mu\text{equ./L}$	
			Total Anions	Total Cations
5/18/87	SW	3.31	1065	1097
5/21/87	Variable	3.23	915	956
5/22/87	WNW	3.44	629	562
8/13/87	ESE	3.44	698	604
8/19/87	WNW	3.17	787	908
8/19/87	WNW	3.14	885	973
10/6/87	NE→SE	4.02	257	309
10/12/87	Variable	3.92	215	227
10/12/87	Variable	3.92	148	165
5/25/88	WNW	3.83	392	367
6/3/88	WNW	2.78	2390	2252
6/9/88	WNW	3.85	121	136
7/12/88	WNW	2.98	1262	1226
7/20/88	WNW	3.30	796	808
7/20/88	WNW	3.44	644	647

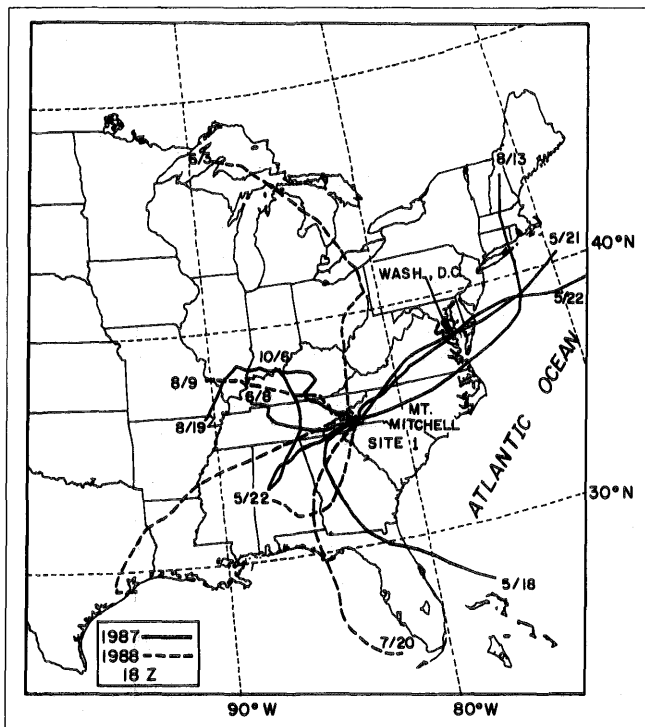


Figure 2. The 72-hour back trajectories based on 850 mb level for the 1987 and 1988 cloud samples.

The 1988 data suggests that there are large variations in the composition and concentration of cloud water organic compounds. For example, the sample collected on June 3, 1988 (Figure 3) contained a very high concentration of methylene chloride. Also, the number of different organic compounds detected was higher than for the other 1988 samples. Methylene chloride is emitted into the atmosphere during chemical manufacture and from its use as a solvent.^{42,43} It is primarily of anthropogenic origin⁴⁴ and has a moderate lifetime ($\sim 1/2$ yr).⁴⁵ A further inspection of the June 3, 1988 data indicates a relatively low field pH value (i.e., high acidity) and high anion (SO_4^{2-} , NO_3^- , Cl^-) and cation (Na^+ , K^+ , Mg^{2+} , Ca^{2+}) concentrations (Table IV). The SO_4^{2-} concentration for this particular sample was $1836 \mu\text{eq/L}$, which suggests that the relevant air mass was highly polluted. A high

concentration in combination with a low pH value indicates that the origin of the air mass may be in the industrialized areas of the Ohio Valley and the Great Lakes region. Indeed a 72 hour back trajectory analysis performed for this event (Figure 2) provides this corroboration.

The significance of the high concentrations of hydrophobic organic chemicals in cloud water is especially great with respect to deposition of the organics to the forest canopy of this ecosystem. It has been shown that high levels of organic chemicals can be detrimental to plant life.^{16,18,27} The clouds at Mt. Mitchell come into direct contact with the plant life on the mountain, particularly the high elevation (<1500 m MSL) forest canopy. When these clouds contact the forest canopy, a certain amount of the cloud water is deposited onto the plant life. The deposition rate of cloud water to forest canopy at Mt. Mitchell has been calculated to be between 0.14 and 0.27 mm/hr²⁵ at the 10 meter height above the forest canopy. Mt. Mitchell has been shown to be in clouds about 30 percent of the time.⁴⁵ This amount of cloud contact represents a major opportunity for deposition of whatever chemicals may be residing in the cloud water. Thus, estimated deposition rates via clouds for the 12 organic chemicals were found to range from 1.58×10^4 to $4.67 \times 10^6 \text{ ng m}^{-2}\text{yr}^{-1}$ (Table III), which is similar to depositional fluxes of organic chemicals from fog in an urban environment.²⁸

The results of this investigation have clearly shown that organic chemicals can be deposited on Mt. Mitchell in significant quantities by cloud episodes. Moreover, clouds provide a unique pathway to concentrate the organic chemicals; thus making it relatively easier to monitor them. There appears to be a large variation in concentration of these organic compounds in clouds. Based on 72 hour back trajectory analysis at 850 mb, the composition of these compounds may be explained by varying emission sources and air mass movements. Admittedly this is a limited data set, but the results justify further study, especially to be able to address air toxics related issues in the 1990 Clean Air Act Amendments.

Acknowledgments

This research has been funded through a cooperative agreement with the U.S. Environmental Protection Agency (CR-815289-02) as part of the Dynamic Chemical Characterization of Montane Clouds Project. I acknowledge Dr. J. Bufalini of U.S. Environmental Protection Agency, Dr. V.K. Saxena and Dr. R. Braham of North Carolina State University and Dr. P. Capel of U.S. Geological Survey for their review of the manuscript and technical discussions; Dr. R.K.M. Jayanty, and Ms. Carol Haney for analytical support; Ms. M. Das and Mr. B. Hartsell for obtaining the physical/chemical constants data; and Mrs. P. Aneja, Ms. B. Batts and Ms. M. DeFeo in the preparation of the manuscript.

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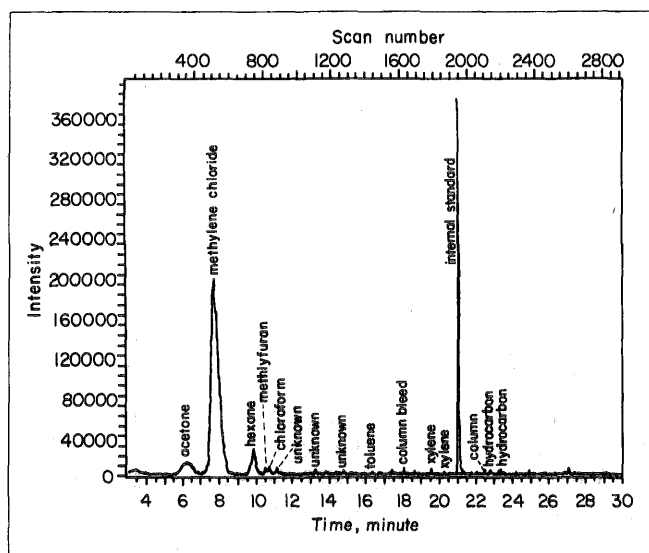


Figure 3. Gas chromatogram of the cloud sample of June 3, 1988.

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