Chemometric Studies of Cloudwater and Wet Deposition

by

Xudong Huang

M.S., Chemistry
Tufts University, May 1990, U. S. A.
B.S., Radiation Chemistry
University of Science & Technology of China, July 1987, China.

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Massachusetts Institute of Technology, September 1995

Signature of Author...
Department of Nuclear Engineering
July 28, 1995

Certified by...
Dr. Ilhan Olmez, Principal Research Scientist
Nuclear Reactor Laboratory
Department of Nuclear Engineering
Thesis Supervisor

Certified by...
Professor Mario J. Molina
Department of Earth, Atmospheric, and Planetary Sciences
Department of Chemistry
Thesis Reader

Accepted by...
Professor Jeffrey P. Freidberg
Department of Nuclear Engineering
Chairman, Department Committee on Graduate Students

CHEMOMETRIC STUDIES OF CLOUDWATER AND WET DEPOSITION

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ABSTRACT

This thesis consists of two independent studies employing chemometrics and instrumental neutron activation analysis (INAA): cloudwater and rainwater studies at Mt. Washington, New Hampshire and wet deposition studies at Moss Lake and Willsboro in the Adirondack region, New York.

Three major factors (a background, an acidity, and a crustal factor) were identified by principal component factor analysis (PCFA) and explain 77.8% of the total variance of trace inorganic species concentrations in fifty-three cloudwater samples. The association of both V and Mn with the acidity factor and other evidence indicate that V and Mn can act respectively as an oxidant and a catalyst in the aqueous oxidation of S(IV) species. An estimation of solar radiation absorption by 0.5 km fair-weather cumulus clouds indicates a difference between solar absorption by pure cloudwater and by cloudwater together with transition metals and their complexes under an extreme condition that cloudwater droplet growth is only by water vapor condensation mechanism. Dilution and washout effects may be responsible for the observed concentration changes of various inorganic species from cloudwater to rainwater.

The comparison of annual wet deposition fluxes and site background concentrations for various inorganic species indicates that there are anthropogenic influences on wet deposition although similar background concentrations. And median concentration ranges found at both sites are comparable to remote locations. Willsboro was affected by a local urban influence. Wet deposition fluxes of SO_4^{2-} and NO_3^- at both sites are typical of those over the northern U. S. and eastern Canada. The Moss Lake site has higher fluxes because of its higher precipitation volume. The concentration levels for some potential toxic species in wet deposition pose no immediate threat to human and aquatic organisms. Washout ratios for some trace elements determined at the Moss Lake site show that snow generally has higher wet removal efficiency than rain.

Thesis Supervisor: Dr. Ilhan Olmez
Title: Principal Research Scientist

Thesis Reader: Dr. Mario J. Molina
Title: Martin Professor of Atmospheric Chemistry

BIOGRAPHICAL SKETCH

Name: Xudong Huang

Date of Birth: January 31, 1965

Place of Birth: Fuzhou, Fujian Province, China

Education:

Doctor of Philosophy, Massachusetts Institute of Technology, Cambridge, MA, September 1995
Thesis Title: Chemometric Studies of Cloudwater and Wet Deposition

Master of Science in Chemistry, Tufts University, May 1990.

Bachelor of Science in Radiation Chemistry, University of Science & Technology of China, Hefei, China, July 1987
Thesis Title: Synthesis of Gamma Radiation-induced Cement-polymer Complex Material

Secondary Education, Fuzhou Railway High School, Fuzhou, China, July 1982

Experiences:

Nuclear Reactor Laboratory, M. I. T., Cambridge, MA, September 1990 - July 1995
Graduate research assistant

Department of Chemistry, Tufts University, Medford, MA, January 1988 - July 1990
Teaching assistant

Affiations:

Phi Lambda Upsilon Honorary Chemical Society, member since 1990
American Chemical Society, student member since 1989
American Nuclear Society, student member 1990
Health Physics Society, student member since 1994

Publications, Conference Proceedings, and Technical Report:

Aras, N. K., Huang, X., Olmez, I., and Gordon, G. E. (1995). “Composition and Sources of Atmospheric Particulate Matter at an Industrialized Urban Air Shed,” *Tr. J. Of Engineering and Environmental Sciences*, **19**, 1-13.

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Introduction

1.1. Motivation of This Thesis Study

As an integral part of their biogeochemical cycling, trace inorganic and organic species are common constituents in cloudwater, fogwater and wet depositions (Zuo and Hoigne, 1993). Examples of these species, are dissolved transition metal ions (TMI), iron (Fe), manganese (Mn), vanadium (V), etc.; acidity-related cations and anions such as sulfate (SO_4^{2-}), nitrate (NO_3^-), hydronium (H_3O^+), and ammonium (NH_4^+); and organic ligands as oxalic ($C_2O_4^{2-}$), pyruvic ($C_3H_3O_3^-$), and glyoxalic ($C_2HO_3^-$) anions. Their physical and chemical roles, especially for TMIs and their complexes with organic ligands found in cloudwater, are poorly understood except for a few ions. For example, the absorption of solar radiation by cloudwater has been revisited recently because measurements exceed theoretical estimates. Although recent experiments have reconfirmed the existence of this problem, there has been no satisfactory answer to date. A possible resolution to the problem may be related to light-absorbing species in cloudwater, such as complex ions of transition metals forming with organic ligands. Recent studies have also confirmed that Fe(III)-organo complex is involved in the aqueous photo-oxidation of S(IV) in cloudwater (Zuo and Hoigne, 1993; Faust *et al.*, 1993). However, there is a likelihood that transition metal ions or complexes can also serve either as oxidants or catalysts for aqueous photo-oxidation of S(IV) in cloudwater similar to the Fe(III)-organo complex. These are fundamental questions and are strongly associated with the global energy budget and acid rain problem. Furthermore, the health risk and stress of an ecosystem incurred by some excessive toxic trace elements, such as arsenic (As), antimony (Sb), etc., and acidity from wet deposition are also not well-defined due to the lack of information regarding long-term background concentrations and annual wet deposition fluxes of these species. Knowledge of these two parameters is essential to any risk model that attempts to assess an ecological system under any toxic element stress. Moreover, some toxic elements contained in wet depositions have large bioconcentration factors and may eventually be incorporated into human food chains. It is expected that the regulation of these wet deposition-borne toxic elements will eventually become an indispensable part of future environmental regulation. The following sections provide a summary and background information relevant to the aforementioned problems which are investigated in this thesis study.

1.1.1. Atmospheric Cycling of Trace Elements

Mankind has a long history of systematically employing natural raw materials for its well-being. As industrialization progressed, the scale of anthropogenic elemental cycling due to the mining, processing and utilization of raw materials has reached or exceeded the scale of its natural cycling. Information on annual consumption, reserves, and potential resources for 25 elements is tabulated in **Table 1.1**. Consumption of some toxic elements such as chromium (Cr), As, cadmium (Cd), mercury (Hg), and lead (Pb) is significant. For example, annual consumption of Hg and Pb ranges from about six thousand metric tons of Hg to six million metric tons of Pb. The dilemma is that, on one hand, these toxic elements pose a potential threat to human health, while on the other hand, they are major by-products of necessary anthropogenic processes employed for the improvement of human welfare.

Table 1.2 presents natural and anthropogenic sources of atmospheric emissions for some elements (Morgan and Stumm, 1991). Emissions from each source may exist in either gaseous or particulate form. Typical anthropogenic sources are fossil fuel combustion, smelters, and cement production, whereas natural emissions occur as continental dust, volcanic eruptions, etc. Anthropogenic emissions for some elements sometimes exceed their natural emissions into the atmosphere (Wedepohl, 1991). For example, Hg, a cumulative toxin, is emitted naturally at a rate of forty metric tons per year, while eleven thousand metric tons are emitted from anthropogenic sources per year. It is no wonder that increasing environmental Hg concentration is of concern. Following dioxin, the environmental release of Hg and its compounds is the most highly regulated by the U. S. Environmental Protection Agency (EPA). Their toxicity lies in the fact that they are highly bioavailable and detrimental to most members of the biosphere (Goyer, 1991).

Tropospheric aerosols, which bear elements from both natural and anthropogenic sources, pass through an initial mixing process in the lower region of the troposphere. Their dispersion in the atmosphere represents the combination of many physicochemical partitioning processes. The presence of various trace elements in cloudwater is explained if one considers the following process: First, uplifted air with moisture expands adiabatically due to the continuous decrease of atmospheric pressures at higher altitudes. Concurrently, relative humidity (RH) increases because of the drop in atmospheric temperature resulting in air that is saturated with water vapor (i.e., RH=100%). The RH at a certain atmospheric temperature is defined as the ratio of the actual partial pressure of water vapor in the atmosphere to the ideal partial pressure of water vapor that would exist

Table 1.1. Annual World Consumption, Reserves, and Potential Resources for 25 Elements in Metric Tons (Merian, 1991).

	Be	Mg	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As
Annual consumption	$>1.3\times10^4$	3.3×10^5	3.8×10^6	2.9×10^4	2.5×10^6	2.2×10^7	6.3×10^8	2.3×10^4	7.8×10^5	8.2×10^6	6.5×10^6	4.0×10^4
Reserves in ore deposits		large	1.6×10^8	2.2×10^7	7.8×10^8	1.8×10^9	9.3×10^{10}	5.1×10^6	5.4×10^7	6.0×10^8	1.6×10^8	1.3×10^7
Potential resources					6.0×10^9	1.1×10^9	1.4×10^{11}		1.0×10^8	1.8×10^9	4.0×10^9	

	Se	Zr	Mo	Ag	Cd	Sn	Te	Pt	Au	Hg	Tl	Pb	Bi
Annual consumption	1.6×10^3	5.2×10^4	6.2×10^4	1.3×10^4	2.0×10^4	2.2×10^5	2.0×10^2	1.0×10^2	1.4×10^3	5.8×10^3	35	5.4×10^6	4.8×10^3
Reserves in ore deposits	1.1×10^5	3.7×10^7	8.8×10^6	2.0×10^5	2.2×10^5	1.0×10^7	2.2×10^4	6.5×10^3	3.0×10^4	2.5×10^5	1.4×10^3	1.9×10^8	1.0×10^5
Potential resources				2.0×10^6		2.7×10^7		1.6×10^4		4.0×10^5		1.3×10^9	

Table 1.2. Natural and Anthropogenic Elemental Emission Fluxes into the Atmosphere in 10^8g Per Year (Merian, 1991).

Element	Continental Dust Flux	Volcanic Dust Flux	Volcanic Gas Flux	Industrial Particulate Emissions	Fossil Fuel Flux	Total Emissions, Industrial Plus Fossil Fuel
Al	356500	132750	8.4	40000	32000	72000
Ti	23000	12000	–	3600	1600	5200
Sm	32	9	–	7	5	12
Fe	190000	87750	3.7	75000	32000	107000
Mn	4250	1800	2.1	3000	160	3160
Co	40	30	0.04	24	20	44
Cr	500	84	0.005	650	290	940
V	500	150	0.05	1000	1100	2100
Ni	200	83	0.0009	600	380	980
Sn	50	2.4	0.005	400	30	430
Cu	100	93	0.012	2200	430	2630
Cd	2.5	0.4	0.001	40	15	55
Zn	250	108	0.14	7000	1400	8400
As	25	3	0.1	620	160	780
Se	3	1	0.13	50	90	140
Sb	9.5	0.3	0.013	200	180	380
Mo	10	1.4	0.02	100	410	510
Ag	0.5	0.1	0.0006	40	10	50
Hg	0.3	0.1	0.001	50	60	110
Pb	50	8.7	0.012	16000	4300	20300

in the air (Hemond and Fechner, 1994). The excessive supersaturated water vapor, which is produced by further cooling, condenses on suspended cloud condensation nuclei (CCN) to form cloudwater droplets. Thus, clouds are the collection of these floating cloudwater droplets of certain size.

Early laboratory experiments, conducted by Coulier (1875) and Aitken (1880, 1881, and 1923), indicated that cloudwater droplets were formed in aerosol-free air through homogeneous nucleation only if supersaturation reaches several hundred percent. In reality, cloudwater droplets are formed by a heterogeneous nucleation mechanism in the presence of those CCN, with a required supersaturation of 2% or less (Hobbs, 1993). The CCN are, in fact, tropospheric aerosols with a certain size range from both natural and anthropogenic sources, such as continental crust, ocean, volcanic eruption, fossil fuel combustion, and biomass burning, etc. **Figure 1.1** presents the aerosol size distribution of heavily polluted atmosphere over land. As seen in **Figure 1.1**, categorization usually adopted in aerosol science is based on the aerosol radii. The categorization is as follows:

(1) Aitken nuclei ($5\times10^{-7}cm-10^{-5}cm$ or $0.005\mu m-0.1\mu m$);
(2) Large nuclei ($10^{-5}cm-10^{-4}cm$ or $0.1\mu m-1\mu m$);
(3) Giant nuclei ($>10^{-4}cm$ or $>1\mu m$).

Most large and giant nuclei actively serve as CCN to form cloud droplets while Aitken nuclei are removed mainly through attachment to cloud droplets initiated by Brownian motion. The cloud droplets pass through cycles of evaporation and condensation leaving behind cloud droplets with a concentrated mix of chemical substances, including various trace elements (Mason, 1971). The modern understanding of cloudwater droplet structure is shown in **Figure 1.2**. It is made of an insoluble or partially soluble center surrounded with water. The core contains mixed hygroscopic and non-hygroscopic chemical substances including trace elements. The trace elements, which include some TMIs, are concentrated and distributed between the core and the remaining volume of the droplet. In the aqueous portion of the droplet, dissolved TMIs form TMI complexes with dissolved organic materials (DOM). This structure can be extended to other form of atmospheric water droplets such as fogwater droplets.

Eventually, the chemical substances in the atmosphere are removed by both dry and wet deposition processes. **Figure 1.3** summarizes the major partitioning steps of atmospheric elemental cycling from emission to deposition (Schroeder and Lane, 1988). Depending upon their atmospheric residence times, aged tropospheric aerosols, which can be transported over local, urban, regional or even global scales and are known to carry marker elements originating from many sources. In contrast to their organic counterparts, these robust marker elements can resist physicochemical transformations during their

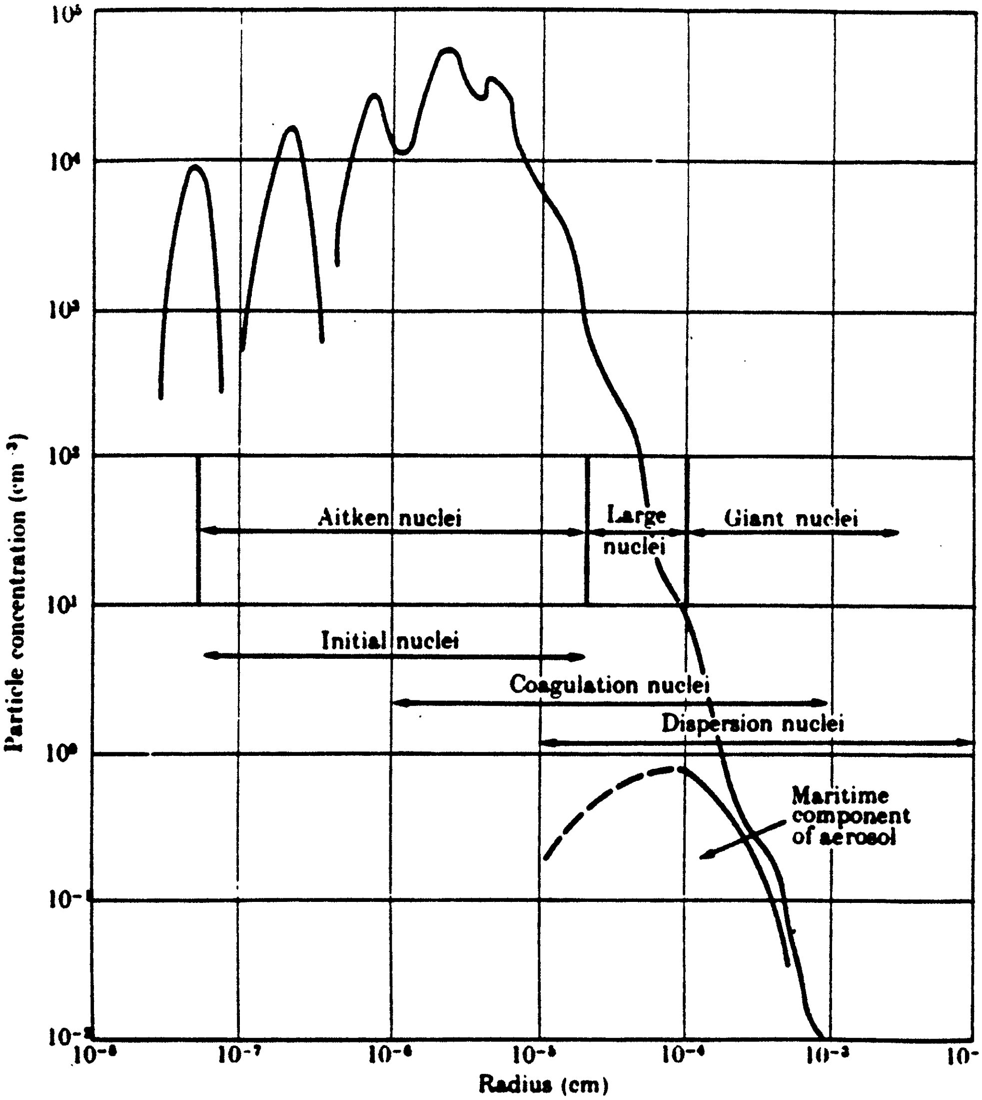

Figure 1.1. Aerosol Size Distribution of Heavily Polluted Atmosphere over Land (Mason, 1971).

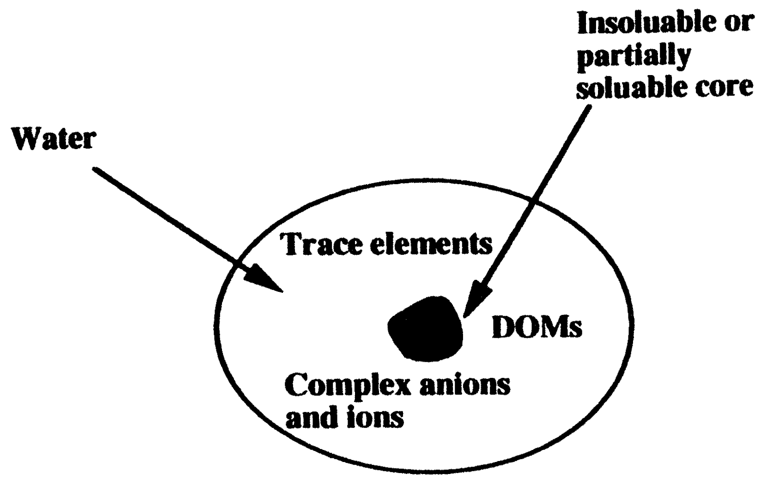

Figure 1.2. Schematic Structure of Cloudwater Droplet (not to scale).

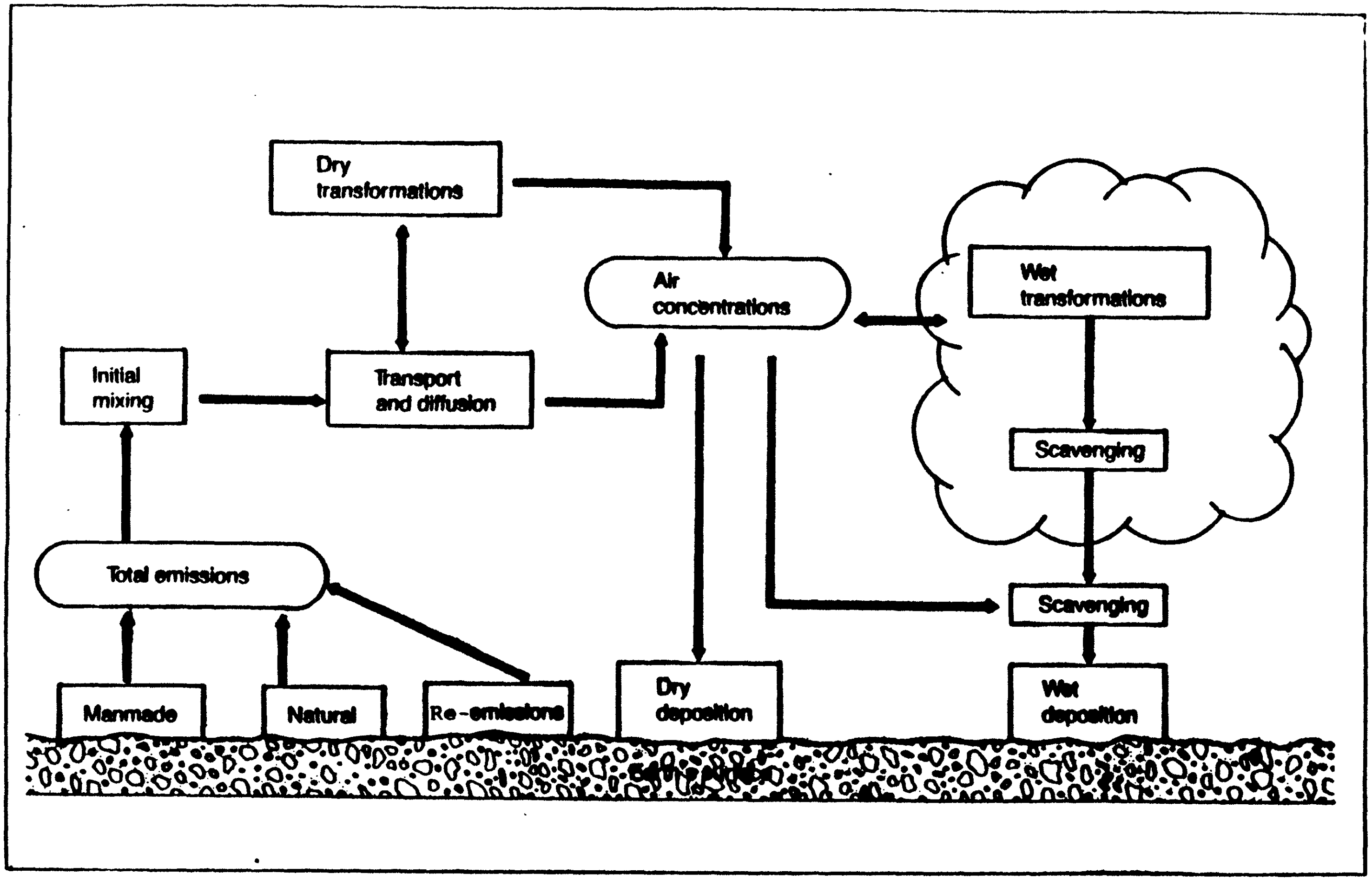

Figure 1.3. Major Partitioning Steps of Atmospheric Elemental Cycling (Modified from Schroeder and Lane, 1988).

transportation (Olmez and Gordon, 1985). Since these inorganic tracers play important roles in receptor modeling, there has been an intensive effort to identify and categorize them over past years. A list of marker elements whose origins have been identified is summarized in **Table 1.3**. This table is the result of the endeavors of many receptor modeling scientists, and by no means is this the final version. Update may be required because of changing emission characteristics of old sources and the identification of new ones. One notable example of this is the change of marker elements for motor vehicle emissions from Pb and bromine (Br) to Br, zinc (Zn), and Sb (Huang, *et al.*, 1994).

1.1.2. Role of Trace Elements in Cloudwater Physics and Chemistry

The external energy source of the earth and its atmosphere is mainly solar energy. Variations in the delicate energy balance between the earth (including lithosphere, hydrosphere, and biosphere) and its atmosphere can influence the world's climate and weather on regional and global scales. Solar energy absorption is a prime factor in this influence. Incident solar ultra-violet (UV) radiation with wavelengths shorter than 290 nm is absorbed by ozone (O_3), oxygen (O_2), water (H_2O) vapor, and carbon dioxide (CO_2) are mainly responsible for absorption of solar radiation of wavelengths longer than 800 nm. However, no strong absorbers for the visible and near-visible part of solar radiation exist. The solar radiation in the "window" between 300 nm and 800 nm in the absorption spectrum for the atmosphere is the so-called short-wave (SW) radiation. The absorptivity of the atmosphere from 100 nm to 30,000 nm is shown in **Figure 1.4**. **Figure 1.5** also details the energy balance of the earth between incident, absorbed, reflected, and re-emitted solar radiation. For simplicity, the incoming solar energy budget was summarized qualitatively in **Table 1.4** (Seinfeld, 1986). Current estimates indicate that approximately 20% of the incident solar energy are absorbed by the atmosphere, including about 2% by clouds. Many measurements of cloud solar absorption show the existence of the cloud solar absorption anomaly in which very experimental results exceed that of theoretical calculations (Stephens and Tsay, 1990). A series of more recent cloud forcing measurements reconfirm the excessive absorption of solar SW radiation by clouds, indicating an inadequate understanding of cloud interaction with solar radiation (R. D. Cess *et al.*, 1995; Ramanathan, *et al.*, 1995; Pilewskie and Valero, 1995). The consequences are large in terms of tropical atmospheric dynamics and marine heat transfer, since the 20% absorbed incident solar energy helps drive the atmospheric circulation and even oceanic heat transport. Excessive absorption of solar SW radiation by clouds would result in a reduction in the required heat transferred from

Table 1.3. Marker Elements and Their Sources

Source	Marker Element
Aluminum plant	Al
Chlor-alkali plant	Cl, Hg
Coal combustion	As, Se, Hg
Continental crust	Al, Sc, Mn, Fe, REEs*, Th, U
Incinerator	Na, K, Cl, In, Hg
Industrial urban area	V, Zn, As, Se, Br, Sb
Iron/steel work	Fe, Zn, Se, Mo, Sb
Marine aerosols	Na, Cl
Motor vehicle	Br, Zn, Sb
Oil combustion	Mg, V, Sb, REEs*, La/Sm ratio
Precious metal work	Co, Zn, Au
Refineries	REEs*
Regional transport	Fine aerosol mass, As, Se, Hg
Smelter	Zn, As, Se, Cd, In, Sb, Hg, Au, As/Se ratio
Wood burning	K

*Rare earth elements: La, Ce, Sm, *etc.*

This table is established based on several research findings such as: Olmez and Gordon, 1985; Olmez *et al.*, 1988; Rahn and Lowenthal, 1984; Small *et al.*, 1981; and Huang *et al.*, 1994, *etc.*

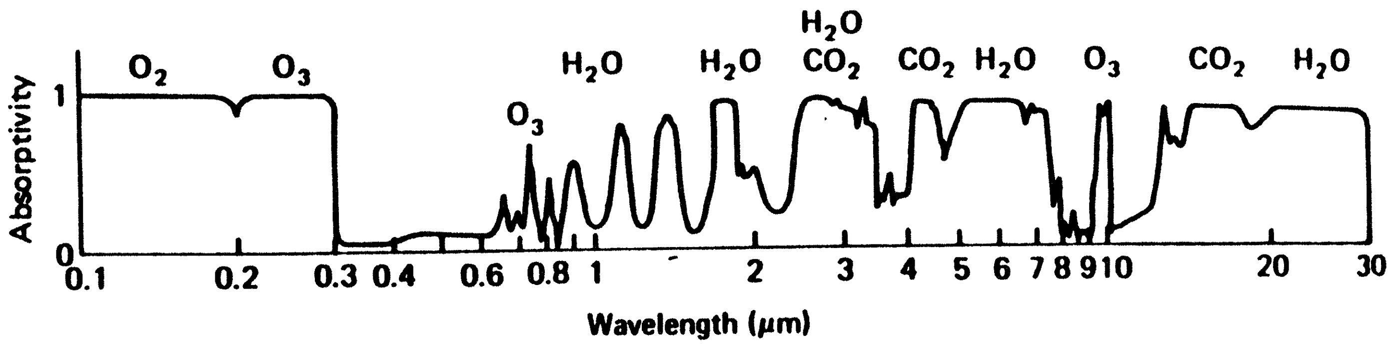

Figure 1.4. Absorption Spectrum for the Atmosphere (Seinfeld, 1986).

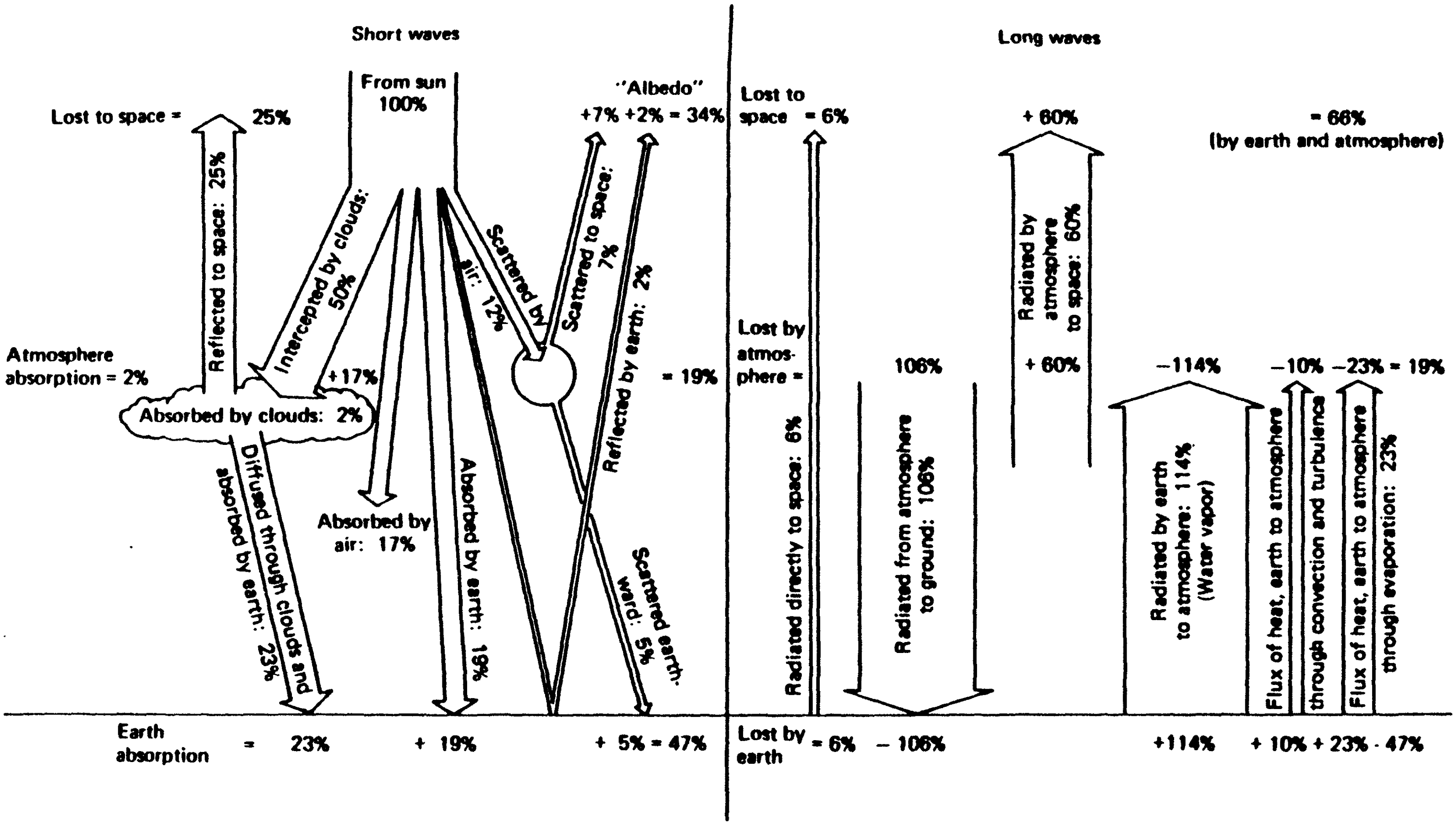

Figure 1.5. Earth's Energy Balance (Seinfeld, 1986).

Table 1.4. Incoming Solar Energy Budget (Seinfeld, 1986).

Percentage Attenuation	Attenuating Medium
50%	Intercepted by clouds (25% back to space, 23% to earth, 2% absorbed by clouds)
17%	Absorbed by atmospheric gaseous and particulate substances
12%	Scattered by the air
19%	Absorbed by the earth
2%	Reflected by the earth back to space
100%	Total

the tropic to the extra-tropics both in the atmosphere and the oceans (Ramanathan, *et al.*, 1995; Pilewskie and Valero, 1995). This leads to the question: "What is the missing absorber in clouds?" Or more specifically, "Is the presence of some trace elements, which are commonly present in atmospheric aerosols, waters, and especially in cloudwater, related to the anomalous cloud solar absorption?".

There is a considerable amount of evidence indicating that some TMIs or their complexes may serve as oxidants or catalysts in redox reactions in atmospheric water under certain circumstances (Weschler, *et al.*, 1986; Graedel, *et al.*, 1986). For example, modeling studies of nonlinear source-receptor behavior in the removal of sulfur dioxide (SO_2) emitted by urban sources indicate that the oxidation process of S(IV) in both gaseous and aqueous phases is important (Hales, 1991). There are some major chemical reactions leading to the transformation of S(IV) to S(VI). In the gas phase, the oxidation of SO_2 by hydroxyl radical (OH·) is the dominant process, but about 40 to 80% SO_2 aqueous-phase oxidation occurs in clouds. Aqueous oxidizing species consist of such as hydrogen peroxide (H_2O_2), O_3, and O_2. The oxidation of SO_2 by O_2 requires the presence of Fe and/or Mn catalysts (Martin and Hill, 1987a, 1987b; Seigneur, 1991). More recent studies show that Fe(III)-organo complex is responsible for the aqueous-phase photochemical formation of H_2O_2. The H_2O_2 then oxidizes SO_2 in fog and cloud waters (Zuo and Hoigne, 1993; Faust *et al.*, 1993). Furthermore, laboratory experiments indicate that higher concentrations of DOM inhibit the Fe-catalyzed S(IV) oxidation by O_2 (Kotronarou and Sigg, 1993). **Figure 1.6** shows the major aqueous-phase photochemical reactions involving major oxidants and free radicals in atmospheric water droplets and gas-to-droplet partitioning of gas-phase photoreactants. As discussed by Faust, photo-oxidation of S(IV) in cloudwater forms post cloud SO_4^{2-} aerosols that are larger and more efficient in scattering solar radiation than counterparts of the same mass concentration formed from the gas-phase S(IV) oxidation. These are mainly responsible for the global cooling effects of man-made SO_4^{2-} aerosols (Faust, 1994). Although Mn is not mentioned in **Figure 1.6**, previous studies suggest that its catalytic role in atmospheric water cannot be ignored. In the combined Fe(III)-Mn(II) system, Martin found the SO_4^{2-} formation rate to be 3-10 times more rapid than expected from the sum of their independent rates (Martin, 1984). Olmez also found this association between Mn and SO_4^{2-} concentrations (Olmez, 1988). Previous laboratory studies further confirm the catalytic synergism between Mn(II) and Fe(III) in S(IV) oxidation (Ibusuki and Takeuchi, 1987; Grgic *et al.*, 1992). In the final analysis, however, proof is needed that this catalytic synergism between Mn(II) and Fe(III) or even catalytic function of the Mn(II) itself in S(IV) oxidation really does exist in authentic atmospheric waters.

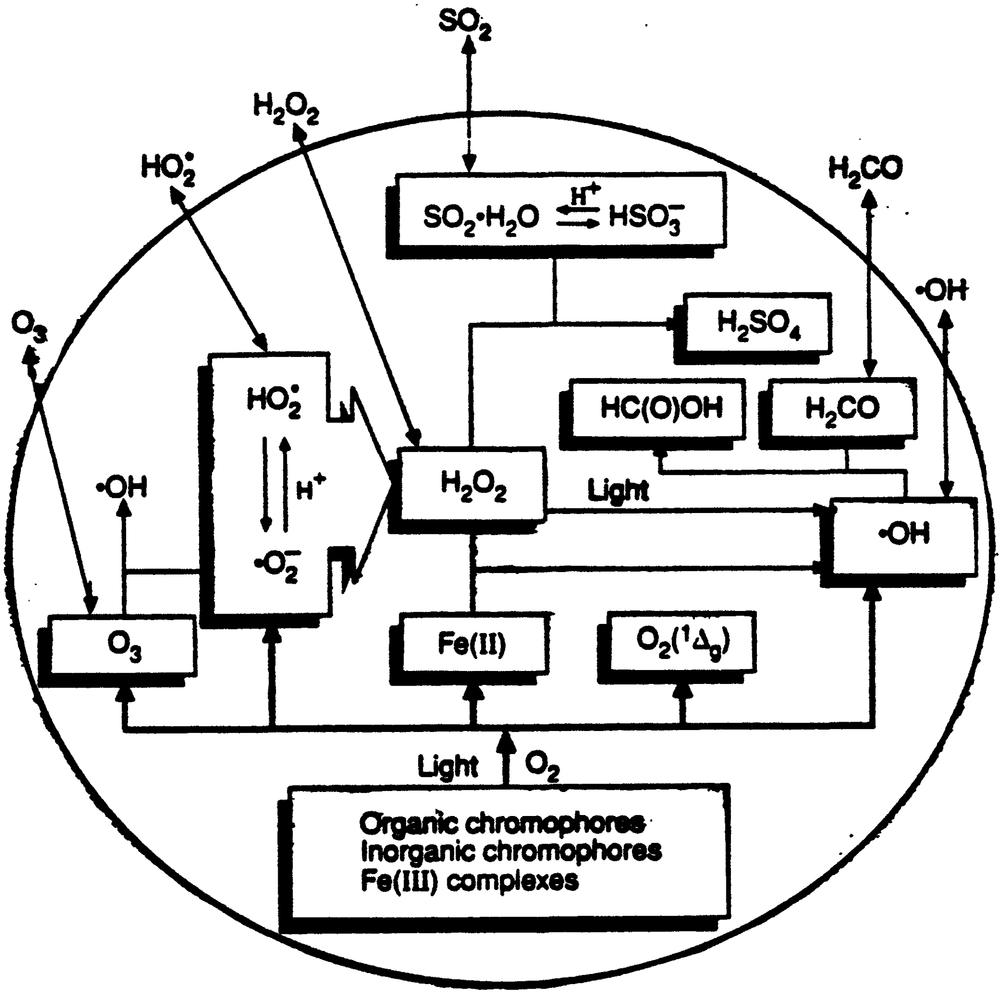

Figure 1.6. Major Aqueous-phase Photochemical Reactions in Atmospheric Water Droplet (Faust, 1994).

To understand the roles of trace elements in cloudwater physics and chemistry, cloudwater and rainwater samples were concurrently collected at Mt. Washington, N. H., at elevations of 1536 m and 610 m, respectively. The concentrations of trace inorganic species (trace elements, SO_4^{2-}, NO_3^-, H_3O^+, and NH_4^+) in the samples were determined. These data may be used to chemometrically examine grouping behavior of measured trace elements, to identify their roles in the aqueous-phase S(IV) oxidation chemistry, and to investigate their functions in anomalous cloud solar absorption. Furthermore, concentration changes between the cloudwater, the rainwater at the high elevation, and the rainwater at the low elevation were investigated based on these data. There is only one earlier report in the literature relating concentration changes of trace elements in cloudwater and rainwater as a function of elevation (Bogen, 1974).

1.1.3. Wet Deposition of Trace Inorganic Species

Wet deposition of inorganic species is an integral part of their biogeochemical cycling, and evidence indicates that increased anthropogenic and/or natural emissions of inorganic species have caused an increased loading to the ecosystem through wet depositions (Galloway *et al.*, 1982) which have produced some unfavorable environmental effects. The corrosion of building materials, depletion of acid neutralizing capacity (ANC) of lakes, leaching out of soil and plant nutrients as potassium (K), calcium (Ca), magnesium (Mg) ions, and increase of bioavailability of toxic elements are all results of excessive deposition of the acidic species, NH_4^+, H_3O^+, SO_4^{2-}, and NO_3^- (Baker and Gherini, 1990; Sullivan *et al.*, 1988; Merian, 1994). For example, excessive NH_4^+ or ammonia (NH_3) deposition on a forest ecosystem, will lower the pH of soil through the following oxidation reaction that occurs in soil microorganism:

$$NH_4^+ + 2O_2 + H_2O \rightarrow NO_3^- + 2H_3O^+$$

Further, high NH_4^+/K and NH_4^+/Mg ratios damage the roots of trees and disturb biological cycles within the ecosystem (Chemical & Engineering News, May 1, 1995). Wet depositions containing potentially toxic elements such as Cr, As, Sb, etc. also endanger human health and the welfare of other organisms. On the positive side, wet deposition provides some essential soil nutrients such as Ca, K, Mg, phosphates (PO_4^{3-}), and NH_4^+. There are, however, increasing concerns for the destruction of ecosystem, the contamination of the food chain, and the threat to human health due to acid rain and excessive atmospheric deposition of toxic elements. In the past decades, many different scales of atmospheric deposition monitoring programs have been established in the North America. A summary of atmospheric deposition monitoring programs implemented in Canada and the U. S. was provided by Voldner and Alvo and is quoted as follows (Voldner and Alvo, 1989):

> "In response to the Great Lakes Water Quality Agreement (GLWQ Agreement) of 1972 and Annex 11 of the 1978 Agreement, the U.S. and Canada established networks, situated along their respective shorelines of the lakes. The objectives of these networks were to determine deposition to the lakes of selected contaminants and to establish trends in deposition. In 1981, the U.S. network was upgraded to the Great Lakes Atmospheric Deposition (GLAD) and by 1982, 36 sites were in operation. All of these sites were equipped with wet-only samplers, while 18 had additional bulk samplers. The wet-only samplers were to provide information on nutrients, major ions, and selected metals in precipitation. The bulk samplers were to provide information on both wet and dry depositions to the same species as well as information on toxic chemical deposition. In 1986, the network closed its 18 sites and abandoned the bulk samplers in response to criticism of its operation. The Canadian network operated a few bulk samplers until 1979, when the Great Lakes Precipitation (GLP) network was established. Bulk sampling was discontinued, and 16 sites with wet-only collectors were used to collect selected metals, major ions, and nutrients. In addition to the GLAD and GLP networks, there are five major networks with samplers in or adjacent to the Great Lakes basins. Two of the networks are located in Canada and three in the U.S. These major networks deploy primarily inland monitors, which are generally situated in a rural setting. They were established as part of the U.S. and Canadian acid deposition programs and measure concentrations of major ions in precipitation. They will aid in the determination of deposition of major ions to the Great Lakes and their basins. In 1978, the National Atmospheric Deposition Program (NADP) was established in the U.S. by the Association of State Agricultural Experiment Stations. In 1982, it merged with the National Trend Network (NTN) which is federally supported and became the NADP/NTN. The Multi State Atmospheric Power Production Pollution Study (MAP3S) was created in 1976 to develop a data base for the evaluation of regional transport and deposition models. Samples from nine sites located in northern United States are collected on a precipitation event basis. The Utility Acid Precipitation Study Program (UAPSP) was created for the similar purpose as MAP3P and collects daily samples. There are similar networks in Canada. From 1980 to 1983, the Canadian Air and Precipitation Network (APN) collected daily samples while the Canadian Network for Sampling Acid Precipitation (CANSAP) collected monthly integrated samples. The Acid Precipitation in Ontario Study (APIOS) daily and cumulative networks were established in 1980 by the Province of Ontario in order to determine deposition patterns in Ontario. It deploys 36 sites located primarily in southern Ontario. The cumulative sampling period is 28 days. The Canadian Air and Precipitating Monitoring Network (CAPMoN) are created in 1983 to measure temporal and spatial variations as well as long-term trends in precipitation and air chemistry. It is the present upgrade and amalgamation of APN and CANSAP. It includes 18 sites in eastern Canada and collects daily samples."

1.1.4. Wet Deposition in the Adirondacks

Title III of the Clean Air Act Amendments (CAAA) passed by the U. S. Congress in 1990 calls for the control of eleven toxic elements among the 189 hazardous air pollutants (HAP) (U. S. Congress, 1990). Like other toxic airborne pollutants (TAP), these trace elements, which have both natural and anthropogenic sources, can be removed from the atmosphere by wet and dry deposition mechanisms (Schroeder and Lane, 1988). Accurate determination of trace element composition in wet depositions can provide a better understanding of atmospheric trace element cycling and their impact on the ecosystem within the sampled region.

The Adirondack Region is located in northern New York State. It has drawn national attention because of the effects of acidic deposition on its surface water and fish communities. Many research efforts have been directed at a better understanding of the chemical and biological status of the Adirondack ecological zone (Baker and Gherini, 1990). As part of the research program to characterize trace-elements in atmospheric particulate materials, two wet deposition sampling sites in this region were selected by the Management Committee of the Adirondack Lakes Survey Corporation (ALSC) for this study. The primary goal of this monitoring program was to obtain a long-term background concentration for trace elements from wet deposition and estimates of their annual wet deposition fluxes at these sampling sites. These two sites had been previously used by the MAP3S and the UAPSP for wet deposition sampling during late 1970s and early 1980s (Voldner and Alvo, 1989). It is probable that their results may be obsolete because of the introduction of more stringent emission-controls by utilities in the past decade. Furthermore, except for major anions and cations, the measured species in their study did not include trace elements of anthropogenic origin. The resulting data from this new sampling program, along with ambient aerosol data from these two sites and three others within or near the Adirondacks, provides a present baseline that may be used to track any future trends in the atmospheric elemental loading over the region. This information also measures the current impact of atmospheric wet deposition to the watersheds within the region.

1.2. Thesis' Objectives and Outline

In this thesis study, the following objectives are expected to be achieved:

(1) Characterization of trace inorganic species in cloudwater. This includes their concentration frequency distributions, origins, and major factors that strongly influence the inorganic species observed concentration patterns in cloudwater.

(2) Identification of trace transition metal species involved in aqueous-phase oxidation of S(IV) species in cloudwater.

(3) Investigation of the relationship between trace transition metal species and their organo-complexes and the solar short-wave absorption anomaly of clouds.

(4) Examination of factors causing concentration changes of trace inorganic species between concurrently collected cloudwater and rainwater.

(5) Characterization of trace inorganic species in wet deposition. This includes their concentration frequency distributions, and the relationship between the weekly precipitation volume and inorganic species concentrations.

(6) Acquisition and comparison of background concentrations and annual wet deposition fluxes for selected inorganic species determined at two sampling sites.

(7) Investigation of anthropogenic influences on wet depositions.

(8) Risk assessment of measured concentration levels for some trace inorganic species in wet depositions.

(9) Washout ratios for selected trace elements determined in the Moss Lake site.

The outline of this thesis is as follows:

Chapter 1: Motivation and background information of this thesis.

Chapter 2: Detailed experimental methodologies employed in this study. This includes sampling site descriptions and sampling procedures, plus a detailed description of the cloudwater and wet deposition samplers. Description of analytical techniques employed, including instrumental neutron activation analysis (INAA), suppressed Ion Chromatography (IC), and quality assurance and quality control (QA/QC) procedures.

Chapter 3: Description of essential chemometric methods applied to this study such as log-normal distributional analysis, principal component factor analysis (PCFA), and regression and correlation analysis.

Chapter 4: Results and discussion for cloudwater and rainwater studies.

Chapter 5: Results and discussion for wet deposition studies

Chapter 6: Summary and recommendations for further investigations.

Appendix A: Concentration data set of inorganic species measured in cloudwater and rainwater

Appendices B1 and B2: Concentration data set of inorganic species determined in wet deposition.

Chapter 2
Experimental Methodology

2.1. Sampling Sites and Sample Collections in the Thesis Study

Performing representative sampling is a critical part of many environmental analyses (Keith, 1991). Thus, the discussion of the sampling step relevant to the thesis begins in the following sections. They include the cloudwater, rainwater, and wet deposition sampling site descriptions and procedures, and unique features of the cloudwater, rainwater, and wet deposition samplers.

2.1.1. Sampling Site and Collection of Cloudwater and Rainwater

Mt. Washington Observatory (1917 m) on top of Mt. Washington is located in the White Mountains National Forest of New Hampshire, 71°19' W, 44°16' N (**Figure 2.1**). Its daily weather records date back to 1933. Its ongoing research activities and facilities provide much valuable information about in-situ cloud physics and chemistry. Simultaneous collection of cloudwater and rainwater samples from individual precipitating clouds was performed at the Lakes of the Clouds Facility of the Appalachian Mountain Club (AMC). The facility is located 1536 m above sea level on the southern slope of the summit cone of Mt. Washington. Concurrent rainwater samples at a lower elevation site were collected at the AMC's Pinkham Notch Mountain Resource Center at 610 m on the eastern slopes of Mt. Washington. These cloudwater and rainwater samples were collected over summers of 1988, 1989, and 1990.

In this study, the ground-level cloudwater collector that was used is the AMC/WPI (Appalachian Mountain Club/Worcester Polytechnic Institute) Passive Cloud Water Collector (**Figures 2.2** and **2.3**). It is made of acrylic plastic and prevents rainwater contamination. The collection principle and collector structure are discussed by Daube *et al.* and quoted as follows (Daube *et al.*, 1987):

> "It utilizes the wind to deliver cloud droplets to a bank of Teflon strands for collection. The cloudwater droplets are collected principally by the mechanism of inertial impaction on Teflon® strings. Both empirical and theoretical approaches were used to selected the optimum strand diameter, with the understanding that an infinite number of combinations of wind speed, droplet diameters and moisture content of cloud events exists under field conditions. The selected optimum strand diameter is 0.78 mm. The Teflon® strands are strung in removable cartridges to facilitate the cleaning and replacement of collecting surfaces. The cloud droplets collected on the strands coalesce and flow down the strands into small holes in the lower acrylic cartridge support. The

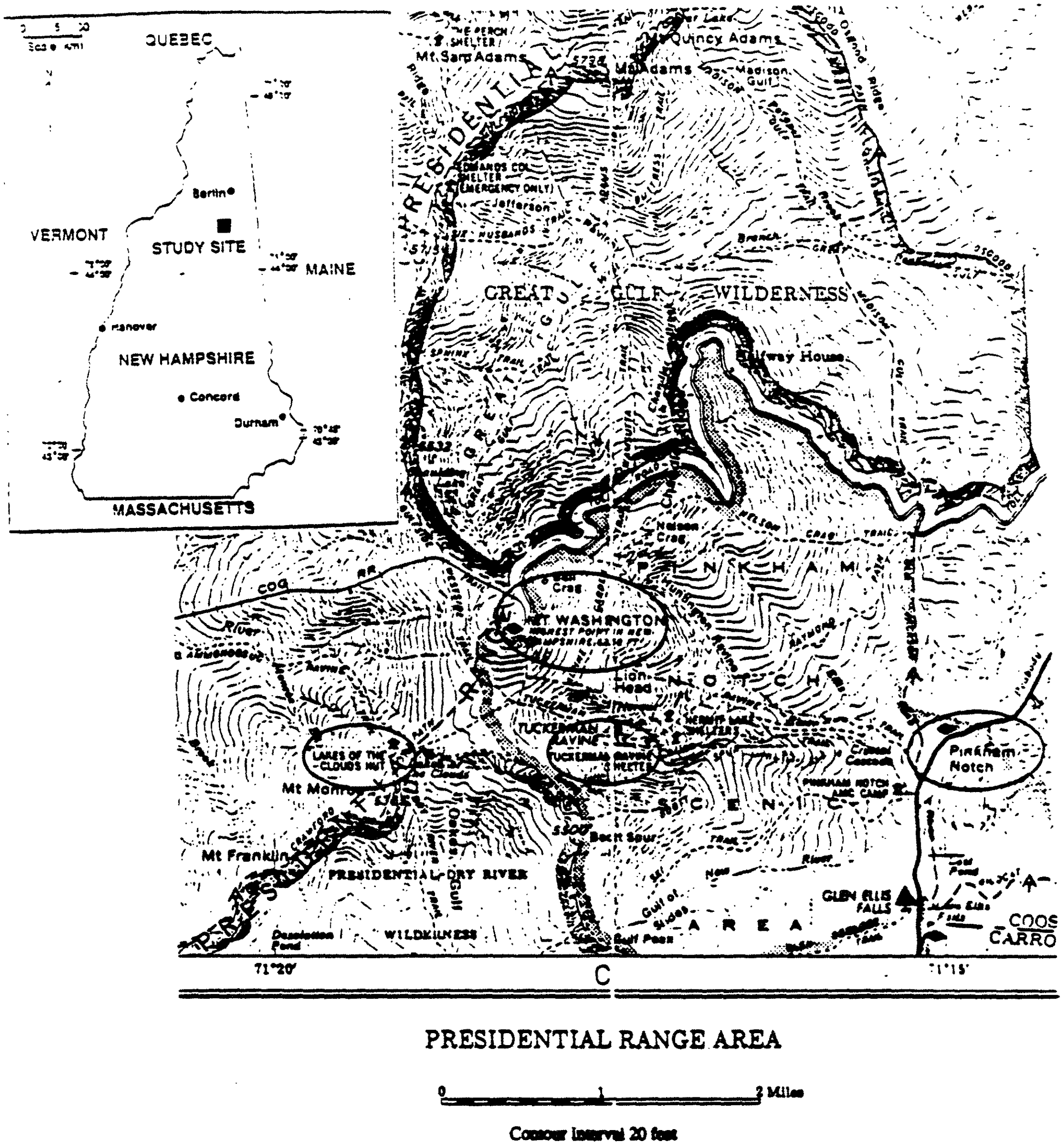

Figure 2.1. Cloudwater and Rainwater Collection Sites at Mt. Washington.

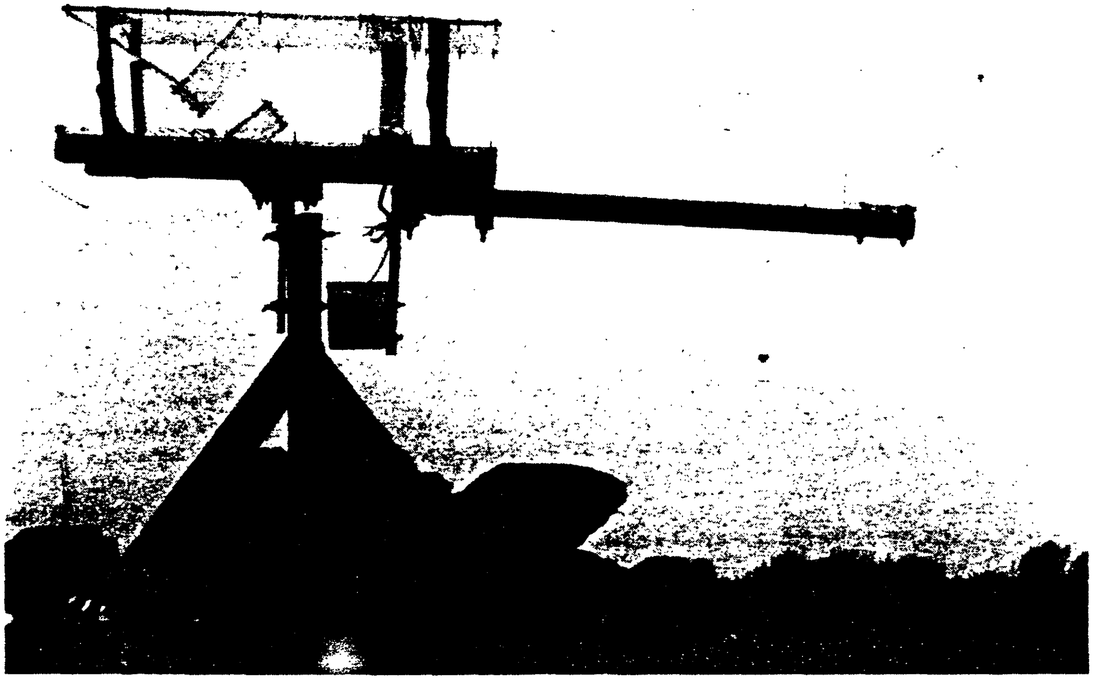

Figure 2.2. AMC/WPI Passive Cloudwater Collector (Daube *et al.*, 1987).

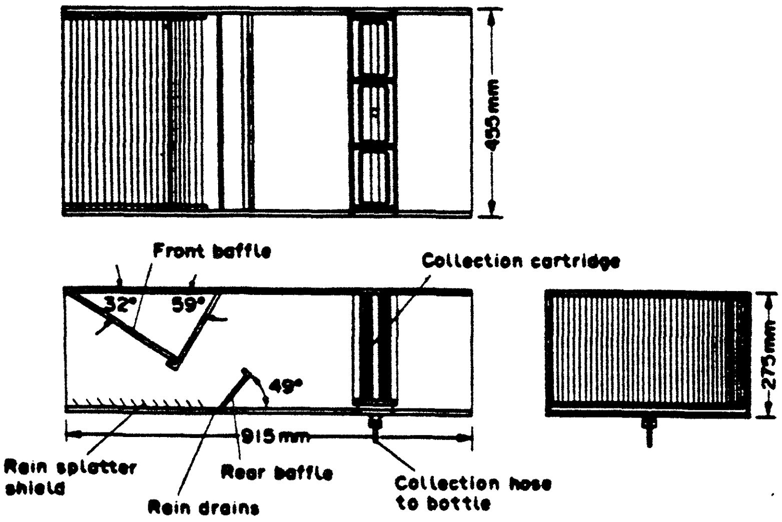

Figure 2.3. Dimensional Scheme for AMC/WPI Passive Cloudwater Collector (Daube *et al.*, 1987).

collected water then drips into an enclosed acrylic trough, which funnels the sample through a polypropylene hose fitting and into a polypropylene tube that connects to a sample bottle. The collector is covered between sampling periods to prevent contamination by dry deposition.

The collector stand consists of a wooden frame built from 50 by 100 mm boards. The upper portion is supported on a bearing assembly about which the collector rotates. The upper assembly is a flat board to which the collector is strapped. The inlet is kept pointed into the wind by a vane located 1 m behind the collector. The base is secured to the ground with rocks.

Exclusion of the heavier rain droplets is accomplished by both the placement of the collection strands deep within the collection box and by a baffle system. The air flowing through the baffles is restricted and forced to turn, causing it to accelerate. The rain droplets, with their greater inertia, overcome the viscous drag effect of the air stream and pass out of it, impacting on the lower baffle. A drain below the baffle permits the separated rain water to leave the collector. The cartridge containing the collection strands is located behind the baffle to allow adequate expansion of the air flow to maximize utilization of the collection surface area. Several additional components have been incorporated to prevent contamination of the cloudwater sample by rain. Both baffles have lips to prevent the impacted rainwater from running to the edge of the baffle and from becoming re-entrained in the accelerated airflow. The upper baffle has a small reservoir where water collects prior to draining out holes drilled on the side of the collector. To prevent rain splatter on the lower surface of the collector from re-entering the airstream, a series of vanes set at 40° are positioned in front of the lower baffle. Rainwater collected by these vanes leaves the collector at the base of the lower baffle."

Rainwater samples are collected by a Hubbard Brook-type bulk precipitation collector. Its construction consists of an open polyethylene funnel, Tygon tubing, and a 2-L polyethylene container (**Figure 2.4**). The container is made inaccessible to the atmosphere by employing external water vapor barriers. Previous field tests indicated that there is no significant sample evaporation from the system during a weekly period under various environmental conditions (Likens *et al*, 1967).

2.1.2. Sampling Sites and Collection of Wet Deposition

The Adirondack region, located in northern New York State, has the general physiographic feature of the dome structure of the North American plate. It covers a 4,000 km^2 upland area that is forested and mountainous. There are approximately 2,800 lakes and ponds within the region, with most of these surface waters having low levels of ANC. These lakes and ponds fill deep valleys produced by glacial erosion during the last glacial era. The annual precipitation of the region is among 100 and 150 cm. There are two physiographic regions, the High Peaks and the Adirondack Highlands, which have surface elevation ranges 1200-1600 m and 500-700 m, respectively (Baker and Gherini, 1990).

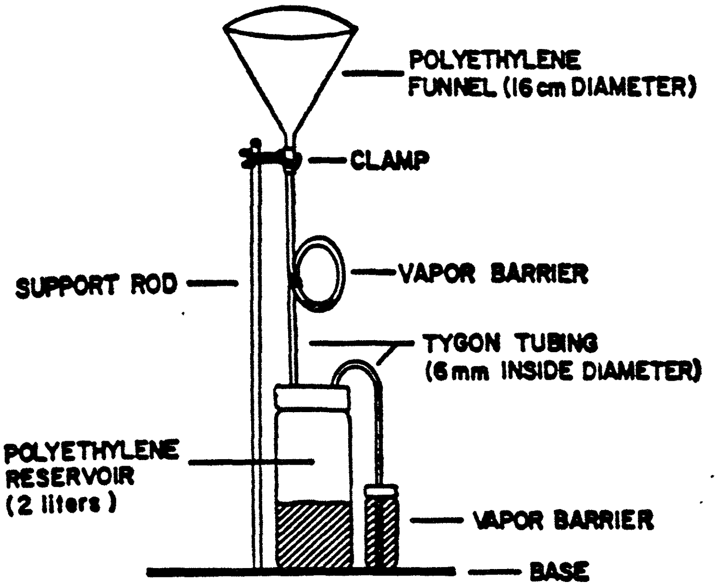

Figure 2.4. Side View of the Hubbard Brook-type Bulk Precipitation Collector (Likens *et al.*, 1967).

Two wet deposition sampling sites within the Adirondacks were selected by the Management Committee of the Adirondack Lakes Survey Corporation (ALSC). They are the Willsboro and Moss Lake sites that previously were designated as the MAP3S and the UAPSP wet deposition sampling sites during late 1970's and early 1980's (Voldner and Alvo, 1989). The Moss Lake sampling site (43° 46' N, 74° 51' W) has an elevation of 541 m and is in the Oswegatchie-Black watershed, which belongs to the less rocky Adirondack Highlands. To the east of the High Peaks, the surface elevation of the Lake Champlain area decreases drastically. Thus, the Willsboro sampling site (44° 24' N, 73° 23' W) is within the Lake Champlain watershed and has an elevation of 40 m (**Figure 2.5**). Sampling was performed between March 1992 and October 1993 at the Willsboro site, and between October 1991 and October 1994 at the Moss Lake site.

Weekly integrated wet deposition samples were collected by Model APS Acid Precipitation Samplers (Graseby Andersen, GA). The collectors are constructed of polyurethane coated, heavy gauge aluminum (**Figures 2.6** and **2.7**). The sampling was accomplished using an automatic wet event collector with a sensor, an event recorder, two large-volume wet/dry deposition containers (13.25 L each), and a movable gabled-roof cover. Wet deposition samples were collected only from the wet-side container each Tuesday. Samples were then transferred to labeled, acid-cleaned polyethylene bottles by the field operators.

These cloudwater, rainwater, and wet deposition samples were shipped to the Environmental Research & Radiochemistry (ER&R) Division of the Nuclear Reactor Laboratory (NRL) at Massachusetts Institute of Technology (MIT). The samples were stored at 4°C at the sampling sites, transferred to MIT in insulated containers, and stored at this laboratory at the same temperature.

2.2. Analytical Methodology

There have been many studies on the application of the instrumental neutron activation analysis (INAA) to various sample matrices including atmospheric waters (Tanizaki, 1990). Compared with other conventional chemical analytical techniques, some of INAA's unique features, such as freedom of matrix effects, have rendered it a useful tool in modern analytical sciences. Before performing the INAA on the cloudwater, rainwater and wet deposition samples, some preliminary steps were taken to ensure precision and accuracy of the final data. These steps are described in the following sections.

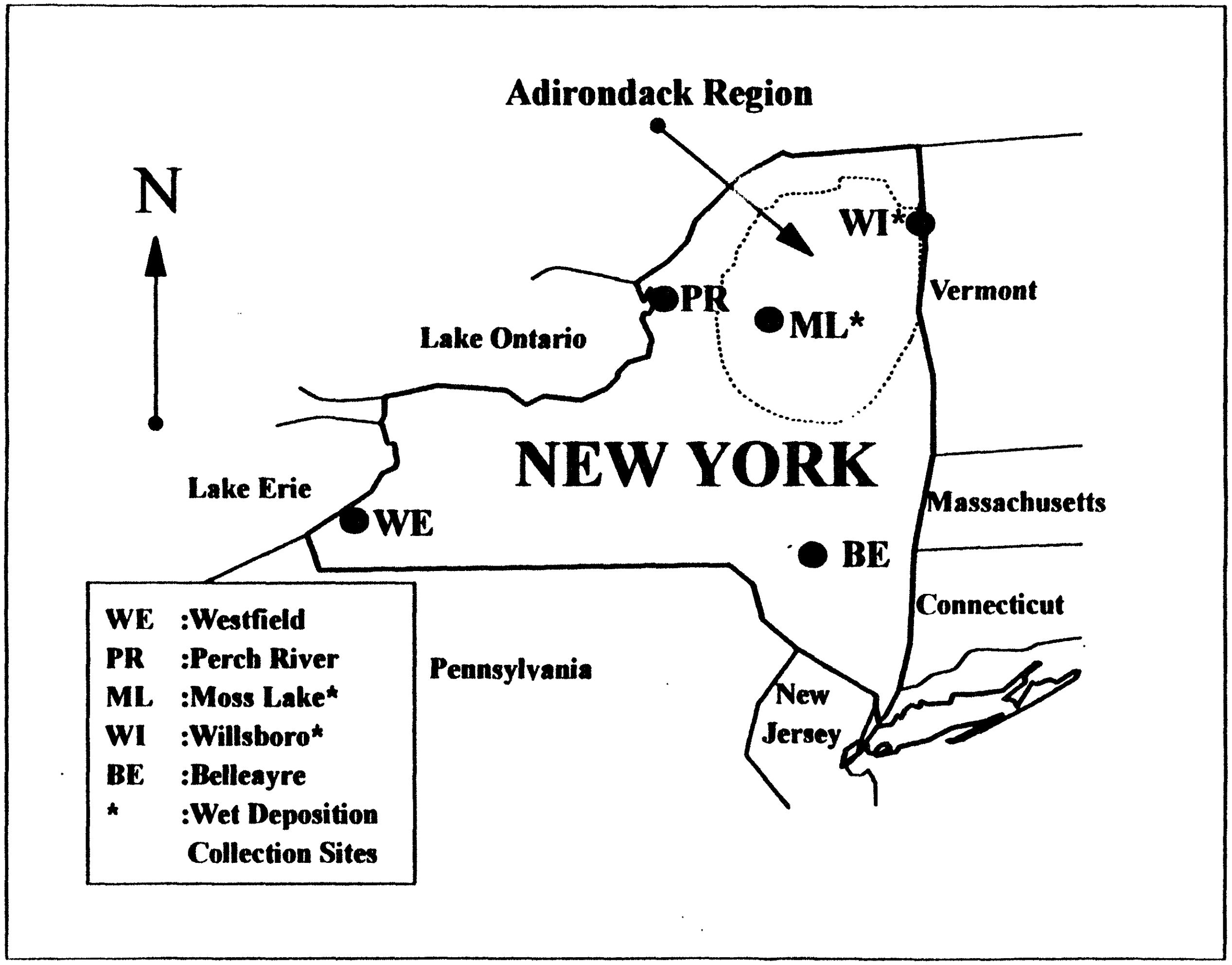

Figure 2.5. Wet Deposition Collection Sites Within the Adirondacks.

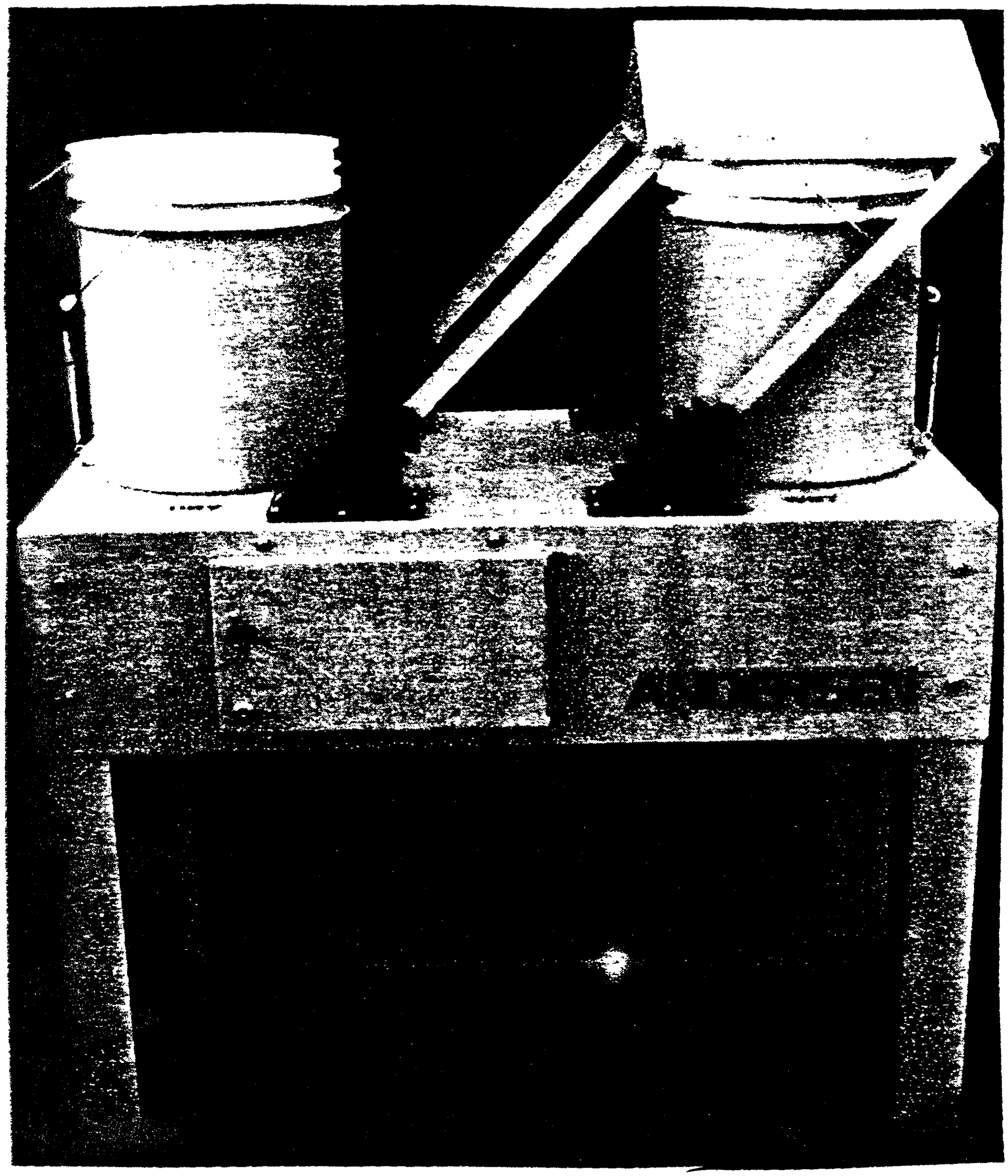

Figure 2.6. Model APS Acid Precipitation Sampler (from the marketing pamphlet of Graseby Andersen).

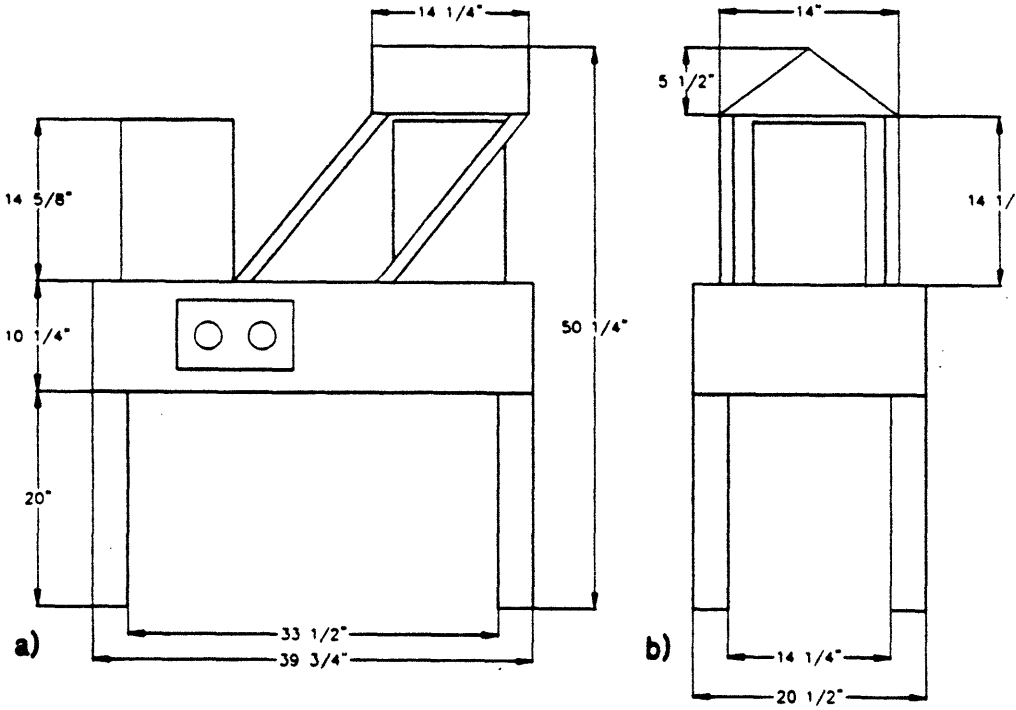

Figure 2.7. Dimensional Scheme for Model APS Acid Precipitation Sampler (from the marketing pamphlet of Graseby Andersen).

2.2.1. Sample Handling

The trace or ultra-trace elemental analysis required for atmospheric water sample contamination in the sample handling must be avoided. All sample handling at MIT was performed in a CRP laminar/flow Ultra Clean Work Station (Clean Room Products, Inc., NY) to minimize transient airborne particulate contamination. To prevent human peripheral contamination, the experimenter wore a clean laboratory coat with hood, mask, and polyethylene gloves during sample handling. All pipetting tips, sample bags, sample vials, and Teflon® tweezers were acid-cleaned prior to use. Nitric acid used for cleansing was prepared by 1:10 (v/v) dilution of concentrated nitric acid with de-ionized water. The concentrated nitric acid used was AR® grade (Mallinckrodt, KY) with a weight concentration of 70.5% HNO_3. The de-ionized water was obtained by purifying tap-water through a MEGA-PURE® System (Barnstead/Thermolyne, IA) which is composed of two ultra-high purity and high capacity cartridges. Since we are only interested in the dissolved trace inorganic species, all samples were filtered through *Acrodisc®* CR PTFE 1 μm poresize filters (Gelman Sciences, MI) to remove suspended materials from atmospheric water samples.

2.2.2. Sample Pre-concentration

The application of INAA to water sample analysis for trace elements directly is not always applicable despite the high sensitivity of the technique. Reasons for this are as follows:

(1) Some trace elements are present at part per billion (ppb) or sub-ppb levels. The direct irradiation of large volumes of water needed to attain this sensitivity is not feasible.

(2) The high concentrations of sodium (Na), chlorine (Cl), and Br, in natural waters, produce high spectral background due to Compton scattering. This causes gamma spectral interferences for many trace elements with radioisotopes of short- and medium half-lives. These two examples indicate the need for pre-concentration of trace level elements and for the elimination of interfering elements.

There are a number of pre-concentration methods available. Freeze-drying, heat evaporation, adsorption (on activated carbon, molecular sieve, etc.), coprecipitation, ion exchange, and solvent extraction are examples of available techniques. Previously, radiochemical separation has been performed following neutron irradiation to remove interfering radioisotopes (Tanizaki, 1990). In her lyophilization studies using radioactive tracers, Harrison has demonstrated that most trace elements with the exceptions of some volatile elements such as Hg, iodine (I), and Cl in water have above 90% retention yield using freeze-drying as a pre-concentration method (Harrison, 1977). Olmez and Hayes have developed a freeze-drying procedure for natural water samples, which can effectively increase analytical sensitivity, decrease blank elemental concentrations in sample bags, and reduce large volumes of water samples to their residues (Olmez and Hayes, 1989). Their procedure was employed in these studies. In this procedure, each sample was freeze-dried in a small, acid-cleaned, polyethylene bag (100 mg) by successive additions of 5 mL aliquots of sample each followed by a drying cycle. The freeze-drying unit (Freeze Dryer 3, Model 75200, LABCONCO® CO., MO) is operated at a vacuum of approximately 50 torr at a temperature of less than -50°C (**Figures 2.8** and **2.9**). This process is repeated for at least 10 or more cycles depending on the volume of samples to be pre-concentrated. The freeze-dried residues are then analyzed by INAA as described below.

2.2.3. INAA Methodology

2.2.3.1. Historical Background of INAA

Neutron activation analysis (NAA) is one of the most sensitive methods to perform quantitative and qualitative analysis of elements present in the various sample matrices. In 1936, the analytical application of INAA was discovered by Swedish chemist Georg Hevesy and his student Hilde Levi. They reported a method that was used to detect rare-earth elements (REEs) qualitatively. Based on their studies of reactions of REEs with neutron irradiation, they found that dysprosium (Dy) became highly radioactive after neutron irradiation. We now know that the ^{164}Dy (n, γ)^{165}Dy nuclear reaction occurred, emitting 94.7 keV γ-rays. At that time, the element's identification was based on their distinctive half-lives ($t_{1/2}$) rather than their characteristic γ-energy lines.

NAA remained unused until the 1950's because there were few neutron sources available for this work. During the development of NAA, other NAA techniques have appeared such as: fast neutron activation analysis (FNAA), epithermal neutron activation analysis (ENAA), thermal neutron activation analysis (TNAA), radiochemical neutron activation analysis (RNAA), cyclic neutron activation analysis (CNAA), prompt-gamma neutron activation analysis (PGNAA), etc. Rapid growth of NAA practices, especially the TNAA during 1950's and 1960's, can be a[illegible] to the increased number of an

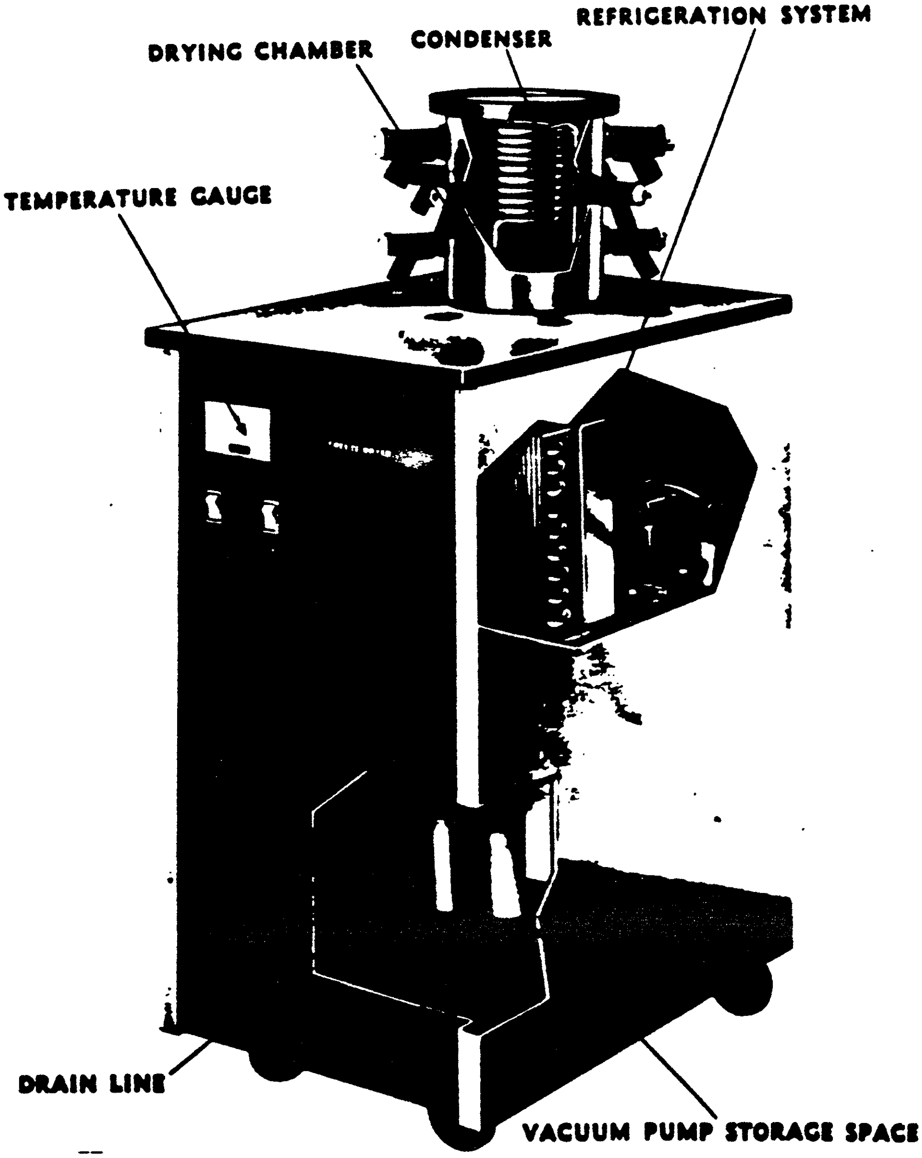

Figure 2.8. Model 75200 Freeze Dryer 3
(from the operating manual of LABCONCO®, CO.).

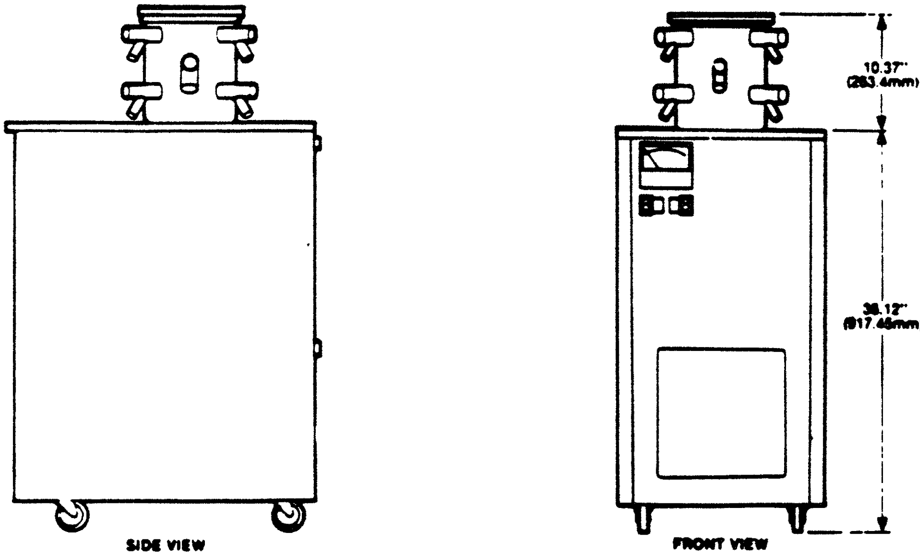

Figure 2.9. Dimensional Scheme for Model 75200 Freeze Dryer 3 (from the operating manual of LABCONCO®, CO.).

access to reactor-based neutron sources and the development of solid state γ-ray detectors with better sensitivity and energy resolution. These were the result of continuous improvements in reactor technology as well as in nuclear instrumentation. Fifty years of development of TNAA has enabled it to enter the analytical instrumentation era and it is now known as instrumental neutron activation analysis (INAA). There are numerous references describing INAA applications in many scientific disciplines such as environmental science, biology, criminology, material science, archaeology, geochemistry, and cosmochemistry. Like other physical or chemical analytical techniques, INAA has its advantages and disadvantages that are enumerated as follows (Ehmann and Vance, 1991):

Advantages:

(a) Many adjustable experimental parameters available to optimize analytical sensitivity and accuracy;

(b) Sensitive to many elements and adaptable to concurrent multi-element analysis for major, minor, trace, and ultra-trace elements;

(c) Relatively non-destructive, samples may be re-analyzed;

(d) Minimum sample preparation and using contamination-free method;

(e) Free of matrix effects.

Disavantages:

(a) Lack of information on chemical form of analyzed samples;

(b) Not sensitive in analyzing some light and heavy elements such as oxygen (O), nitrogen (N), boron (B), and Pb;

(c) Analytical times are long for elements with long half-lives;

(d) Require sophisticated neutron source and detection system.

The pioneer environmental application of INAA was done by Zoller and Gordon in 1970. They applied INAA to measure more than 20 elements in atmospheric aerosols of urban areas utilizing Ge(Li) γ-ray detectors (Zoller and Gordon, 1970). An extension of their work has been the application of INAA to the determination of trace elements in natural water samples, such as cloudwater, rainwater, snow, fogwater, lake water, river water, and groundwater. INAA is presently less widely used than in the past, even though it is an established analytical technique. It is challenged by other techniques, for example, inductively coupled plasma emission-mass spectroscopy (ICP-MS). However, in some cases, the higher limits of detection (LOD) of ICP-MS for As, Sb, and selenium (Se) has made it less competitive than INAA. Further, such competing techniques usually require digestion and pre-concentration steps that are prone to introducing contamination (Tanizaki, 1990).

The future development of INAA depends on the continuous improvement of neutron source and γ-ray spectroscopic techniques. As part of the advanced neutron source (ANS) project, the National Institute of Standard and Technology (NIST), the Oak Ridge National Laboratory (ORNL), and the Ward Laboratory of Cornell University have committed their cold neutron sources for PGNAA in material analysis research. There are further efforts to surpress backgrounds from the Compton scattering (CS) in order to improve sensitivities for some elements in γ-ray spectroscopy. Of course, continuous availability of high-flux thermal neutron sources and reasonable INAA service costs should also be taking into account.

2.2.3.2. Principle of INAA

The principle of INAA will be described generally in this section. Nuclear reactors are the main sources of high-flux thermal neutrons. Thermal neutron fluxes are typically in the range of 10^{12}-10^{14} n/cm^{2}sec. Thermal neutrons induce only (n, γ) reactions so primary interferences due to the other nuclear reactions such as (n, p), (n, n'), (n, 2n) are minimized if not totally eliminated.

When a stable naturally occurring isotope is irradiated with thermal neutrons, a radioactive isotope is sometimes produced. During the decay of the radioisotope, γ-rays are emitted with characteristic energies and relative intensities. These specific γ-rays are used to both identify and determine the concentration of an element.

Assume that an isotope of an element ^{A}X in the sample goes through an (n, γ) reaction to produce a radioisotope ^{A+1}X that emits γ-rays with energy E. The unknown mass m of the element can be determined from the following equation at its full energy peak (FEP) at E.

$$m = \frac{PA\lambda}{N_A \varepsilon(E) e a \sigma \phi [1 - \exp(-\lambda t_i)] F} \qquad (2.1)$$

where: P = net counts under the peak of the isotope ^{A+1}X;

A = atomic mass of the isotope of the element X;

λ = decay constant of the radioisotope produced;

$\varepsilon(E)$ = absolute detector efficiency at FEP at E;

e = intensity of the FEP at E;

a = abundance of isotope with atomic mass A;

σ = thermal neutron cross-section for the (n, γ) reaction (in barn, 1b = 10^{-24}cm^2);

ϕ = thermal neutron flux (n/cm^{2}sec);

N_A = Avogadro's number;

t_i = irradiation time;

$F = \exp(t_1) - \exp(t_2)$, decay factor during the counting, where t_1 = cooling time and $t_1 - t_2$ = counting time.

To eliminate the errors that arise from variations of the detector efficiency, changes of counting geometry, and fluctuations of thermal neutron flux, a comparator method is used in which a certified standard reference material with an accurately known elemental composition is irradiated simultaneously with the sample. Therefore,

$$\frac{m_u}{m_s} = \frac{P_u F_s}{P_s F_u} \qquad (2.2)$$

and then

$$m_u = \frac{m_s P_u F_s}{P_s F_u} = \frac{M_s C_s P_u F_s}{P_s F_u} \qquad (2.3)$$

where M = mass of sample; C = concentration of element X in the sample; s and u denote quantities which are related to standard and unknown samples, respectively. Thus, the final concentration C_u for one particular element can be determined if m_u is divided by the unknown sample mass M_u.

In practice, certain errors are always insignificant when compared to others. The quantities A, e and a are known very accurately for most isotopes. Also the flux ϕ and the efficiency $\varepsilon(E)$ can be determined with a known but small error. The inaccuracies in the times t_1 and t_2 are negligible and thus the decay factor F is considered to be error-free. Accordingly, from the equation 2.3, the relative error of m_u can be expressed as following:

$$\frac{s_{m_u}}{m_u} = \sqrt{\sum_{i=1}^{4} \frac{s_i^2}{T_i^2}} \qquad (2.4)$$

where T_i denotes quantities of M_s, C_s, P_u or P_s; and s_i is their respective standard error. Therefore, s_i / T_i is the relative standard error (Tsoulfanidis, 1983).

2.2.3.3. Gamma Energy Measurements and Minimum Detection Limit

In the early 1950s, the availability of Thallium (Tl)-activated sodium iodide (NaI) crystals as a scintillation detector opened the modern era of γ-ray spectroscopy. Ge(Li) detectors, constructed of germanium (Ge) crystal doped with lithium (Li) by diffusion and drifting process developed in 1960's, overcame the poor energy resolution problem inherent in NaI(Tl) detectors. Further improvement was realized in the 1980's with the availability of high purity germanium (HPGe) detectors.

The uncharged γ-photon creates no direct ionization or excitation of the Ge crystal through which it passes. The detection of γ-rays is therefore critically dependent on the γ-photon interactions with Ge crystal during which it transfers all or part of its energy to an electron in the crystal. Although many possible γ-ray's interaction mechanisms with matter are known, only three major types play a key role in γ-radiation measurements: photoelectric effect (PE), Compton scattering (CS), and pair production (PP). In a γ-spectrum, the so-called back scattering peak, Compton edge or shoulder, and the Compton continuum originates from the CS while the PP is responsible for the annihilation, double escape, and single escape peaks (Knoll, 1989). The FEP can be attributed to the PE if the process has allowed the full deposition of the incident γ-photon energy in the detector. The minimum detection limit C_m (MDL) for a specific element in INAA varies from sample to sample. The lack of uniform C_m for a specific element is due to some factors such as: non-uniformity of sample matrix, variations of counting geometry, variable sensitivity of FEP(s) located in Compton continuum, background, etc. The C_m value for a specific element present in a particular sample was obtained by the following modified equation (Olmez, 1989):

$$C_m = \frac{3.29}{S}\left(\frac{R_b}{t}\right)^{0.5} \qquad (2.5)$$

where: S= sensitivity (cps/ng);

R_b= cps of background under the FEP used;

t= counting time (s).

2.2.3.4. Elemental Identification and Quantification

Freeze-dried samples were combined with a pre-weighed standard and a control sample and placed in polyethylene sample carriers ("rabbits") for thermal neutron irradiation. The standard and control sample were Standard Reference Materials (SRM), SRM 1633 Coal Fly Ash and SRM 1571 Orchard Leaves, respectively. These are offered with certified trace element concentrations by the National Institute of Standard and Technology (NIST) (Geithersburg, MD). The irradiation facility was the 5-MW MITR-II reactor at the Massachusetts Institute of Technology (MIT, Cambridge, MA). It is a tank-type reactor fueled by 93% uranium-235 (^{235}U). The inner tank contains purified H_2O to serve as both coolant and neutron moderator while the outer tank contains D_2O used as a neutron reflector. The cross-sectional and top views of MITR-II are shown in **Figures 2.10** and **2.11**. A special feature regarding sample irradiation in the MITR-II reactor is that there is an air-flow cooling system installed in the beam port. Thus, sample irradiations are performed under ambient temperature and pressure conditions. This important feature minimizes material loss and deterioration of the sample due to irradiation heating.

The following INAA procedures are similar to those described previously with some modifications (Germani, *et al.*, 1980; Olmez, 1989). Samples were placed in the 1PH1 beam port of MITR-II reactor and subjected to two different irradiations. Initially samples were irradiated for 10 minutes. They were then allowed to "cool" or decay for 2 minutes to eliminate radioactivities from very short-lived radioisotopes such as ^{20}F ($t_{1/2}$= 11 s). Samples were counted for 6 and then 20 minutes to measure intensities of γ-rays from radioisotopes with short (2 to 10 minutes) and moderately short (0.2 to 15 hour) half-lives. A pneumatic tube facility was used here to shorten the sample transfer time between the reactor and the counting laboratory. The samples then were allowed to decay for several days so that minimal radioactivity could be present. They were then re-irradiated for 12 hours to produce long-lived radioactivities. These were allowed to decay for 3-4 days. Gamma-rays emitted from the latter samples were counted for 8-10 hours to obtain spectra of radioisotopes with moderately long (14 hours to 3 day) and long (>3 days) half-lives. All irradiations were performed with an approximate thermal neutron flux of $8 \times 10^{12} n/cm^2 sec$.

Gamma-rays emitted from the irradiated samples were observed with HPGe γ-ray detectors coupled to 8192-channel pulse-height analyzers (Canberra Industries, Inc., CT) which connected to a VAX station 3100 (Digital™ Equipment Corp., MA). Computer-directed Canberra ND 9900 Genie system programs running on the VAX

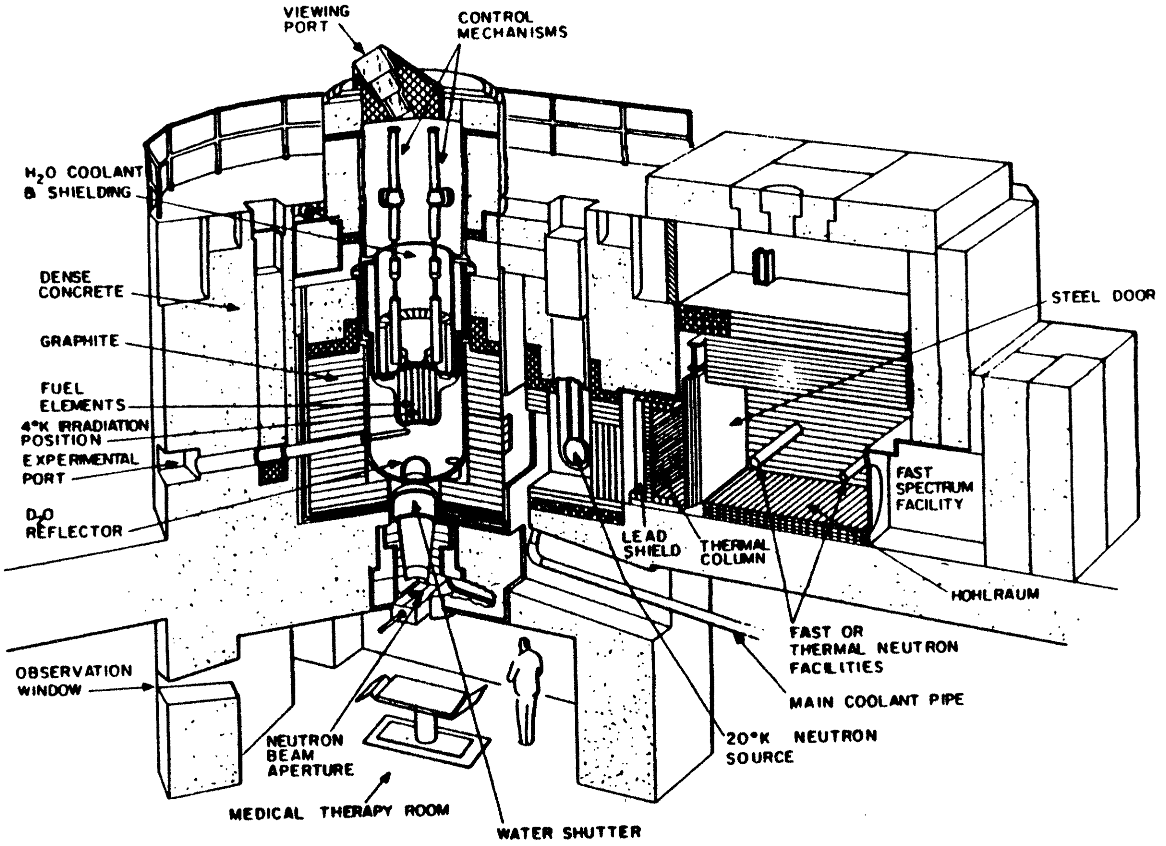

Figure 2.10. Cross-sectional View of MITR-II Research Reactor (from the introductory pamphlet of MITR-II).

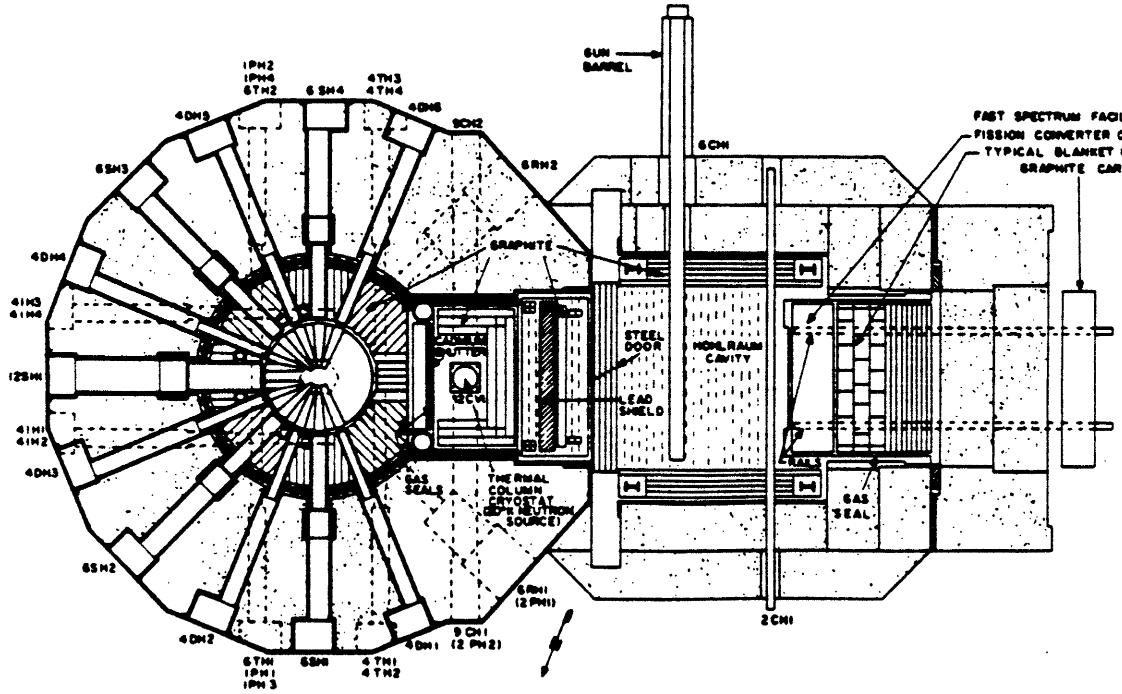

Figure 2.11. Top View of MITR-II Research Reactor (from the introductory pamphlet of MITR-II).

workstation was used to perform either automatic or interactive peak-fitting routines to search for particular best-fit FEP(s) for each isotope. Radioisotopes and their specific γ-energies used for peak-fittings are presented in **Table 2.1**. Peaks used are either interference-free or were those whose interferences are well documented. The final concentrations for different detectable elements in the sample matrix were printed out by a Digital™ on-line LA75 Companion printer.

The steps of the aforementioned experimental procedures including sampling, pre-concentration, and INAA are summarized in **Figure 2.12**. The following sections will discuss measurements of major anions and pH values in cloudwater and wet deposition samples.

2.2.4. Ion Chromatography (IC)

Ion Chromatography (IC) was introduced by Small, Stevens and Bauman in 1975, in their innovative work employing ion-exchange chromatographic separation and the conductimetric detection of the anions and cations. Coupled with modern computer techniques, IC has experienced a rapid growth because it offered, for the first time, a rapid, reliable, accurate, and simultaneous determination of many inorganic or organic anions and cations. This unique feature has led to the application of IC in many fields such as environmental, industrial, clinical, and pharmaceutical fields in only two decades.

Modern IC can be roughly classified into non-suppressed and suppressed IC groups. In this study, liquid-solid suppressed IC was employed to determine chloride (Cl^-), nitrate (NO_3^-), and sulfate (SO_4^{2-}) anions in cloud, rain, and wet deposition samples. A block diagram of the instrumental components is shown in **Figure 2.13**.

The mobile phase, or the eluent as it is called in IC, contains the competing ions and is continuously pumped through the column that hosts the solid separation phase under a specific pressure and flow-rate. The sample is introduced into the eluent through an injection port and is carried to the column. The column separates the solute anions according to their size and polarity. The separated anions are eventually detected with a flow-through detector. The function of the suppresser is to modify both the eluent and the solute so as to improve the sensitivity of the conductivity detector. The suppresser requires a regenerant solution to ensure its durability. The resulting recorded chart is the chromatogram of detected anions (**Figure 2.14**). In the chromatogram, different anions can be identified by their own separable peaks. The distances between the starting point to the peaks are proportional to characteristic retention times in the column while the peak heights or areas are proportional linearly to the concentrations of the anions

Table 2.1. Gamma Energy Line (s) for Elements Determined by INAA

Shorts1					
	Element	**Energy Line (keV)**	**Radioisotope**	**Half-life**	**Intensity (%)**
	Mg	843.8	Mg-27	9.45m	100
	Al	1779	Al-28	2.25m	100
	Ti	320.1	Ti-51	5.76m	100
	V	1434.1	V-52	3.76m	100
	Cu	1039.3	Cu-66	5.10m	100
Shorts2					
	Element	**Energy Line (keV)**	**Radioisotope**	**Half-life**	**Intensity (%)**
	Na	1368.6	Na-24	14.96h	90
	Cl	1642.4	Cl-38	37.2m	100
	K	1524.6	K-42	12.36h	100
	Mn	846.8	Mn-56	2.578h	100
	Ga	834.1	Ga-72	14.1h	100
	Sr	388.4	Sr-87m	2.80h	100
	In	417	In-116m	54.2m	35
	I	442.9	I-128	25m	100
	Ba	165.9	Ba-139	1.396h	70
	Dy	94.7	Dy-165	2.33h	100
Longs					
	Element	**Energy Line (keV)**	**Radioisotope**	**Half-life**	**Intensity (%)**
	Sc	889.3	Sc-46	83.81d	100
	Cr	320.1	Cr-51	27.7d	100
	Fe	1099.2	Fe-59	44.51d	100
	Co	1332.5, 1173.2	Co-60	5.271y	100
	Zn	1115.5	Zn-65	243.8d	100
	As	559.1	As-76	1.096d	100
	Se	264.7	Se-75	119.78d	100
	Br	554.3	Br-82	1.471d	80
	Rb	1076.7	Rb-86	18.65d	100
	Mo	140.5	Mo-99	2.7476d	100
	Cd	336.3	Cd-115	2.228d	100
	Sb	564.1	Sb-122	2.70d	100
	Cs	795.9	Cs-134	2.065y	90
	La	1596.5	La-140	1.678d	100
	Ce	145.4	Ce-141	32.5d	100
	Nd	91.1	Nd-147	10.98d	100
	Sm	103.2	Sm-153	1.929d	100
	Eu	1408	Eu-152	13.48y	90
	Tb	879.4	Tb-160	72.3d	100
	Yb	396.3	Yb-175	4.19d	100
	Lu	208.4	Lu-177	6.68d	100
	Hf	482.1	Hf-181	42.4d	100
	Ta	1221.4	Ta-182	114.43d	95
	Au	411.8	Au-198	2.694d	100
	Th	312	Pa-233	27.0d	100
	U	106.1	Np-239	2.355d	100

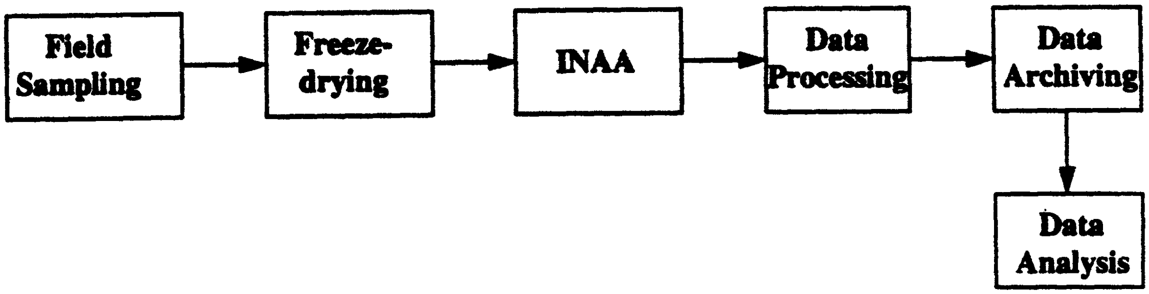

Figure 2.12. Block Diagram of Major Experimental Procedures.

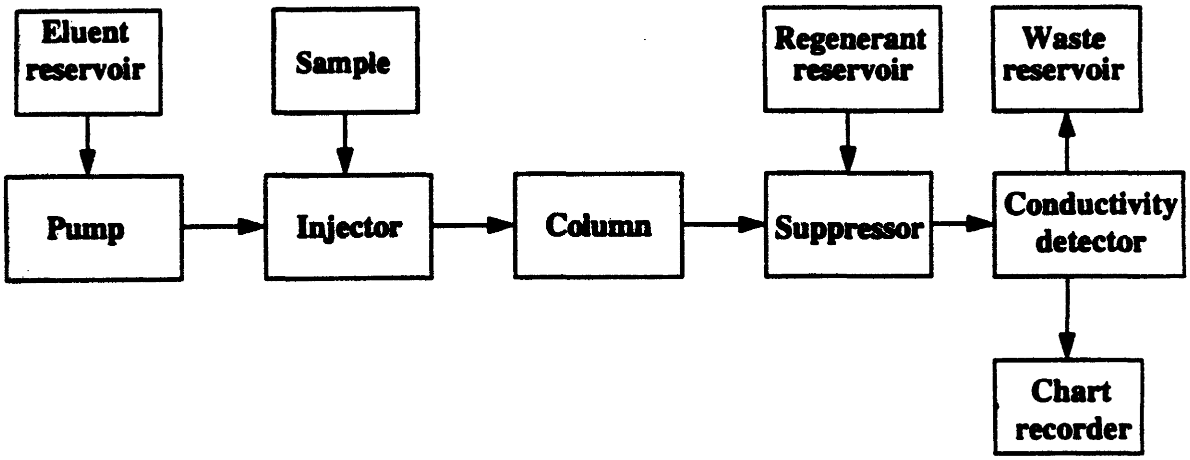

Figure 2.13. Block Diagram of Instrumental Components for Suppressed IC.

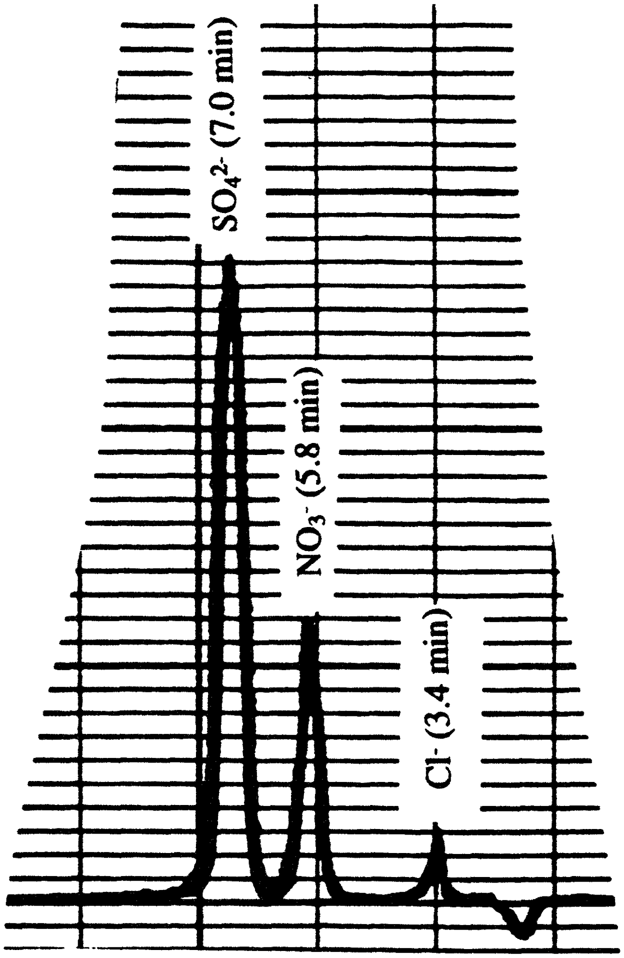

Figure 2.14. Chromatogram and Retention Times for Anions in This Study.

(Haddad and Jackson, 1990). The relevant instrumental parameters are summarized in **Table 2.2.** The concentration data of Cl^-, NO_3^-, SO_4^{2-} and NH_4^+ species in cloudwater and rain water samples were provided by Dr. Kenneth Kimball of Mt. Washington Observatory while the concentrations of Cl^-, NO_3^-, SO_4^{2-} species in wet deposition samples were determined by the thesis author.

2.2.5. Hydronium (H_3O^+) Measurement

Instead of using the Gran titration procedure (Gran, 1952), direct pH measurements were performed on cloudwater, rainwater, and wet deposition samples. Each sample was measured for pH three times and a standard deviation of the measurements was obtained. The pH meter used was a Chemcadet® 5986-50 pH meter (Cole-Parmer® Instrument Company, IL). The field pH values of cloud and rain samples were furnished by Dr. Kenneth Kimball of Mt. Washington Observatory while laboratory pH measurements were taken on wet deposition samples by the thesis author.

2.3. Quality Assurance/Quality Control (QA/QC) Procedure

The QA/QC procedures are essential in any environmental sampling and analysis program (Keith, 1991). In this thesis study, the unique design of the AMC/WPI Passive Cloud Water Collector has enabled cloud water to be collected with little or no rainwater contamination and a minimized sample evaporation problem. The design of the Hubbard Brook-type rain collector also eliminates sample evaporation problems. The wet deposition field sampling procedures were drafted based on the National Atmospheric Deposition Program (NADP) guideline. The precipitation samplers equipped with the large-volume containers and a movable, internally sealed gabled-roof cover minimizes potential sample overflow and evaporation problems. After receiving samples at MIT, all sample handling was conducted within a laminar-flow clean-hood to prevent contamination. All sample containers were acid-cleaned prior to use. The freeze-drying procedure has been proven to be effective in decreasing both the bag-blank concentrations and the required sample volume while increasing the analytical sensitivity. Particular attention was given to prevent any sample mislabeling by careful reference to field sampling log-sheets. A special feature of the sample irradiation facility in the MITR-II reactor is the air cooling system in the beam port. Its presence insures that sample irradiation is always performed under ambient temperature conditions preventing sample material loss from heating. Since a comparator method was used, the control

Table 2.2. Major Instrumental Parameters for Suppressed IC

Component	**Parameter**
Sample preparation	Filtration
Eluent	0.001M $NaHCO_3$ and 0.002M Na_2CO_3 mixed solution
Regenerant	0.025M H_2SO_4 solution
Carrier Gas	Compressed N_2 and Air
Flow-rate	1 mL/min.
Column	Waters anion column (IC-PAKtm)
Detection	Dionex conductivity detector
Recording	Chart recorder

sample insured that the analytical error for detectable elemental concentrations was within specific limits.

A review of QC procedures for nuclear analytical measurements may be found in the paper written by Seymour (Seymour *et al.*, 1993). The QA/QC procedures in this study are summarized in **Table 2.3**, which is similar to ones given by Olmez (Olmez *et al.*, 1995).

Table 2.3. Quality Assurance and Quality Control Procedures

Activity	Parameter	Procedure
Sampling	Sample evaporation Contamination	NADP sampling protocol Unique design of sampler
Sample pre-analysis handling	Contamination Bag blank Material loss during sample irradiation	Sample handling underneath laminar-flow clean hood Unique preconcentration procedure Unique feature of MITR-II
Analysis	Stability of the counting system Spectral interference	Multiple measurements of pH values Use of standard reference materials as control sample Regular gamma-energy line calibration Regular background counting Counting geometry Use of different radioactive isotopes and gamma energies Interactive peak fitting
Data processing and treatment	Random errors	Validation of computer programs Statistics

Chapter 3
Data Interpretation Methodology-Chemometrics

3.1. Chemometrics

3.1.1. Introduction

Chemometrics is defined as the computer-assisted use of statistical and mathematical techniques to analyze high-dimensional chemical data. It is an interdisciplinary subject that attempts to interpret some unique characteristics of a system from mutually independent or dependent measured variables related to the system. It began with the applications of pattern recognition techniques in the chemical field in the 1970s. It is a growing young science field and struggling to find a niche in the modern science world (Chemical & Engineering News, Dec. 12, 1994).

Two decades' growth and diversification of chemometrics have been reflected in an increase in the scientific literature. Two specialist journals have been established: the *Journal of Chemometrics* and *Chemometrics & Intelligent Laboratory Systems*. *Analytical Chemistry* has also issued fundamental reviews of chemometrics in even years since 1980. Several reference books about chemometrics have been published (Sharaf *et al.*, 1986; Massart, *et al.*, 1987; Martens and Næs, 1989; Brereton, 1990; Deming and Morgan, 1993). As the advancement of computer technology and chemical measurement techniques continues, chemometrics will find an indispensable role in the handling of explosively growing chemical data (Beebe and Pell, 1994).

3.1.2. Environmental Applications of Chemometrics: Receptor Modeling

Chemometrics has found an application in environmental fields ever since its inception. Lately, it has been applied to groundwater contamination studies (Olmez *et al.*, 1994; Gullu, *et al.*, 1994). The following paragraphs discuss why receptor models are better than dispersion models with respect to accounting for stochastic features of the atmosphere.

The atmosphere is one of the major sub-systems of a complex environmental system with unique stochastic characteristics. It is an open system that maintains delicate dynamic energy and mass-balances with the lithosphere, hydrosphere, and biosphere (**Figure 3.1**). Its variables are believed to obey some deterministic physicochemical laws. However, in 1963 Lorenz discovered chaotic behavior of the atmospheric system

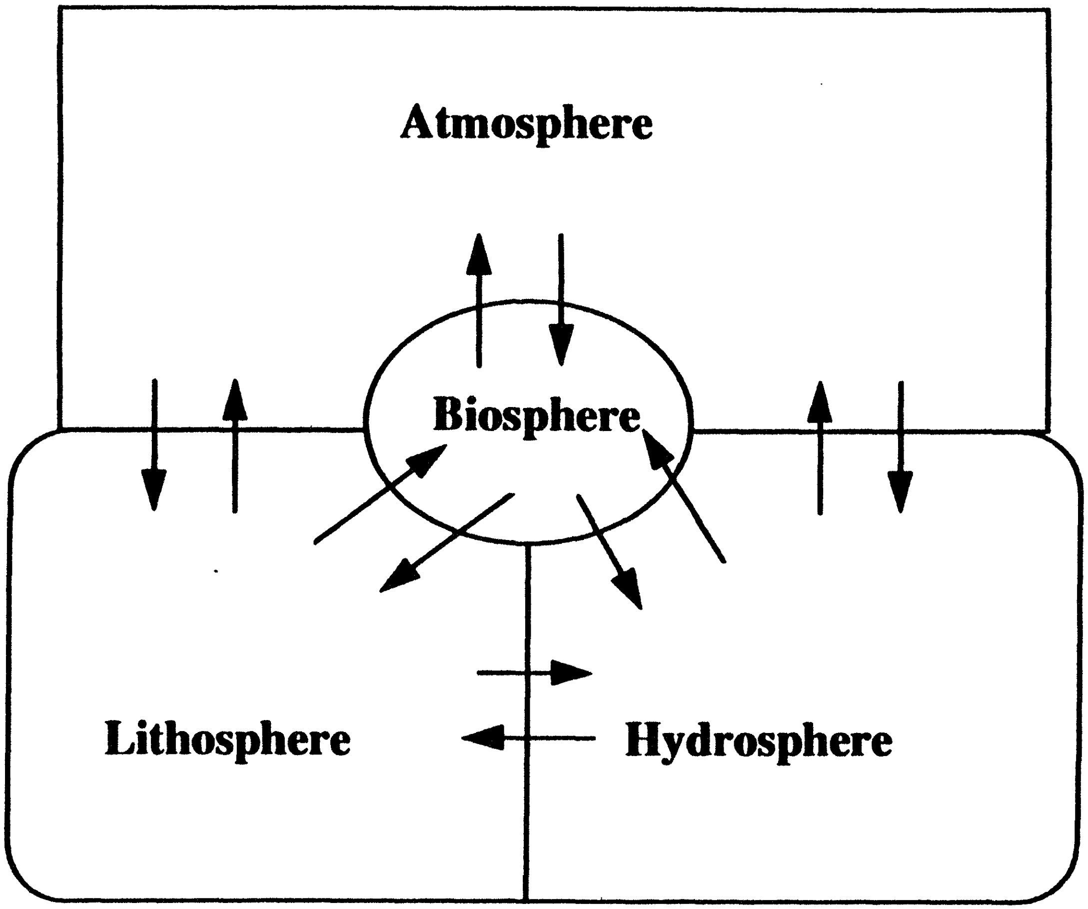

Figure 3.1. Diagram Showing Environmental System with Constant Energy and Mass Exchange Within It.

and showed that it is actually a nonlinear dynamic system whose time-history is highly dependent upon its initial conditions (Lorenz, 1963). In fact, the atmospheric pollutants, which are affected both by stochastic atmospheric characteristics and changeable pollutant emission source characteristics may have infinite variance and a stable but not normal (such as skewed or log-normal) distribution of their associated random variable(s) (such as pollutant concentration). In view of this fact, any mathematical model describing the atmospheric system will be invalid without accounting for its stochastic features. Unfortunately, this is often the case for the dispersion modeling approach, which is based on the purely deterministic view of the atmospheric system.

Central issues of characterization of the pollutant emission sources in air quality management are:

(1) The identification of the emission sources and/or associated marker species and the quantitative estimation of emission rates and patterns;

(2) The understanding of the transport of the pollutants from the emission sources to downwind locations and the associated physicochemical transformation processes that can occur during the transportation.

All this information can be the base for a mathematical model that applies to the quantitative assessment of pollutant concentration levels along with some influencing factors, such as emission rates, meteorological conditions, etc. In the dispersion model approach, various source emission inventories are used as inputs to grid, box or plume models to predict ambient concentration levels of total suspended particulate (TSP) matter, SO_2 or other air pollutants to develop optimal control strategies for air pollutants. However, due to the stochastic features of the atmosphere mentioned above, it must simplify real atmospheric processes greatly and make assumptions whenever possible in order to produce workable mathematical models. Generally, these models require extensive computing times even on the largest and fastest computers. Also, although many refinements have been made over the years in the dispersion modeling of atmospheric pollutants, there are still many cases when the models do not predict ambient pollutant concentration levels accurately and thus provide both ineffective and inefficient air quality management strategies. This is because these models have only considered the deterministic features and failed to take into account of the inherent stochastic characteristics of atmospheric system. Also, the source emission inventories, which are inputs for dispersion models, vary with time. This is especially true for emission sources equipped with pollution control devices. Furthermore, dispersion models usually ignore contributions from fugitive process emissions and dust. Finally, air quality standards have begun to require a knowledge of the size ranges of pollutant aerosols (e.g., the new PM_{10} standard) which bear certain toxic substances, or have a special role in visibility degradation or climate modification. In general, dispersion models do not account for this (Hopke, 1991).

Because of the inherent problems of dispersion models, it is necessary to have alternative modeling methods that can provide the source identification and apportionment based on observed pollutant concentrations at the point of their impact. Such methods are called receptor models since they are focused on the behavior of the measured chemical species at sampling or receptor sites. This is the opposite of the source-oriented dispersion models that focus on the whole physicochemical transformation time-history evolved from emission sources to the receptor sites. In receptor models, many chemometric tools are applied to extract information about emission sources using the data matrix collected at receptor sites. The most widely used receptor model is "chemical mass balance" (CMB). Others include pattern recognition, statistical process control (SPC), time-series analysis, hypothesis testing, distributional analysis, non-parametric statistical testing, factor analysis (FA), regression analysis, and uni- or multivariate statistical techniques. More recently, neural networking techniques were used in receptor modeling (Wienke and Hopke, 1994; Wienke *et al.*, 1994). Unlike dispersion models that are based on the deterministic features of atmospheric system, receptor models take into account of stochastic characterics of the atmosphere. Thus, it is more applicable and informative, although it depends upon the further improvement of relevant chemometric techniques.

3.2. Distributional Analysis

It is a long-standing fact that the concentration frequency distributions for measured chemical species and aerosol size distributions in environmental fields are approximate log-normal distributions (Seinfeld, 1986). In the Ott's theory of successive random dilutions, the final measured pollutant's concentration C_m is linked with its source concentration C_0 and series dilution factors F_i's (Ott, 1990):

$$\ln C_m = \ln C_0 + \sum_{i=1}^{m} \ln F_i, \quad m>0 \qquad (3.1)$$

It should be pointed out that Fi must be considered a partitioning factor instead of dilution factor since there are concentration steps involved from an emission source to a receptor site (Schroder and Lane, 1988). Therefore, Fi's follow the uniform distribution, and their probability distribution function (pdf) is :

$$f(Fi)=\frac{1}{b},\ b>0 \qquad (3.2)$$

According to the proof given by Johnson and Kotz, the pdf of the $\ln Fi$ is the standard exponential distribution:

$$f(\ln Fi)=\exp(-z),\ z\geq 0 \qquad (3.3)$$

Furthermore, the pdf of $\sum_{i=1}^{m}\ln Fi$ is a special form of γ-distribution as the following (Johnson and Kotz, 1970):

$$f(\sum_{i=1}^{m}\ln Fi)=\frac{x^{m-1}\exp(-x)}{\Gamma(m)},\ x\geq 0 \qquad (3.4)$$

where γ-function of m is defined as (Hilderbrand, 1976):

$$\Gamma(m)=\int_0^{\infty}\exp(-t)t^{m-1}dt \qquad (3.5)$$

As m goes to infinity, the pdf of $\sum_{i=1}^{m}\ln Fi$ approach standard normal distribution, i.e.,

$$f(\sum_{i=1}^{m}\ln Fi)\rightarrow\frac{\exp(-x^2/2)}{\sqrt{2\pi}} \qquad (3.6)$$

Finally, when Co is constant and m is a large number, then $\ln Cm$ will be normally distributed as indicated by equation 3.1. Therefore, Cm will follow approximately log-normal distribution. However, the strict conditions can be relaxed as long as Co's variance is much smaller than the variance of all Fi's (Ott, 1990).

If the frequency distributions of concentration or other variables of chemical species can thus be assumed to be log-normal distribution. The two-sided Kolmogorov-

Smirnov one-sample test (K-S Test) is run for goodness-of-fit at the significant level $\alpha=0.05$. For the goodness-of-fit test of at least ordinal scale data, the K-S test is preferred over χ^2-test that was designed only for use with nominal scale data. The test statistic DN is given by:

$$DN = \sup_{c} \left| F(c) - F_0(c) \right| \qquad (3.7)$$

where $F(c)$ and $F_0(c)$ are empirical and hypothesized cumulative distribution functions (cdfs), respectively. The DN is the largest difference between empirical and hypothesized cdfs. The quantile Q of the test statistic can be obtained either from **Table 3.1** or calculated approximately from the formula (Daniel, 1990):

$$Q \approx \frac{1.22}{\sqrt{n}}, \text{ for } n>40 \qquad (3.8)$$

where p-value for the test can be calculated as:

$$p = 1-\alpha \text{ for one-sided test; } p = 1-2\alpha \text{ for two-sided test} \qquad (3.9)$$

The criterion for failing K-S test is either $DN>Q$ or actual $\alpha<0.05$. The geometric mean $(\overline{C}_g)$ and the dimensionless geometric standard deviation $(s_g)$are defined followings:

$$\overline{C}_g = \sqrt[n]{\prod_{i=1}^{n} C_i} \qquad (3.10)$$

and

$$s_g = \exp\left(\sqrt{\frac{\sum_{i=1}^{n} (\ln C_i - \ln \overline{C}_g)^2}{n-1}}\right) \qquad (3.11)$$

where n is the sample size. The s_g measures the data spread around the $\overline{C}_g$ and thus reflects the magnitude of different stochastic processes influencing the chemical species (Cheng, *et al.*, 1991). To make things more complex, meteorological, physical, and chemical effects which confound each other are imbedded in the processes.

Table 3.1. Quantiles of the K-S Test Statistic (Daniel, 1990)

One-sided test	$p = 0.90$	0.95	0.975	0.99	0.995
Two-sided test	$p = 0.80$	0.90	0.95	0.98	0.99
$n = 1$	.900	.950	.975	.990	.995
2	.684	.776	.842	.900	.929
3	.565	.636	.708	.785	.829
4	.493	.565	.624	.689	.734
5	.447	.509	.563	.627	.669
6	.410	.468	.519	.577	.617
7	.381	.436	.483	.538	.576
8	.358	.410	.454	.507	.542
9	.339	.387	.430	.480	.513
10	.323	.369	.409	.457	.489
11	.308	.352	.391	.437	.468
12	.296	.338	.375	.419	.449
13	.285	.325	.361	.404	.432
14	.275	.314	.349	.390	.418
15	.266	.304	.338	.377	.404
16	.258	.295	.327	.366	.392
17	.250	.286	.318	.355	.381
18	.244	.279	.309	.346	.371
19	.237	.271	.301	.337	.361
20	.232	.265	.294	.329	.352
21	.226	.259	.287	.321	.344
22	.221	.253	.281	.314	.337
23	.216	.247	.275	.307	.330
24	.212	.242	.269	.301	.323
25	.208	.238	.264	.295	.317
26	.204	.233	.259	.290	.311
27	.200	.229	.254	.284	.305
28	.197	.225	.250	.279	.300
29	.193	.221	.246	.275	.295
30	.190	.218	.242	.270	.290
31	.187	.214	.238	.266	.285
32	.184	.211	.234	.262	.281
33	.182	.208	.231	.258	.277
34	.179	.205	.227	.254	.273
35	.177	.202	.224	.251	.269
36	.174	.199	.221	.247	.265
37	.172	.196	.218	.244	.262
38	.170	.194	.215	.241	.258
39	.168	.191	.213	.238	.255
40	.165	.189	.210	.235	.252

The closer D is to Q, the less log-normal the concentration frequency distribution is. The physical reason for this is that either a relatively large variable source term and/or fewer stages of partitioning from the source to the receptor can cause larger deviation from log-normality due to a strong local emission impact and/or lower precipitation volume. Therefore, the magnitude of D value can be an indicator of these factors causing a deviation from log-normality. **Figure 3.2** summarizes relative positions for some descriptive parameters in a histogram of an approximately log-normal concentration frequency distribution.

3.3. Factor Analysis

3.3.1. Introduction

Factor analysis (FA) is a branch of multivariate statistics. In 1904, Charles Spearman formulated the FA methodology when developing a psychological theory. Other major contributors to FA following its formulation are: Cyril Burt, Karl Pearson, Godfrey H. Thomson, J. C. Maxwell Garnett, and Karl Holzinger (Harman, 1967). There have been ever increasing applications of factor analysis to fields other than psychology, for example, sociology, meteorology, political science, medicine, geography, business, and even environmental sciences. Presently, FA has become an indispensable subject of chemometrics.

Different forms of FA which suits to various environmental conditions have been extensively used in receptor modeling studies. This has been demonstrated by the variety in the relevant literature: principal component factor analysis (PCFA) (Gatz, 1978; Henry and Hidy, 1979, 1982); factor analysis (FA) (Blifford and Meeker, 1967; Hopke *et al.*, 1976; Gaarenstroom *et al.*, 1977; Henry, 1978; Heidam, 1984; Thurston and Spengler, 1985; Keiding *et al.*, 1986; Keiding and Sorensen, 1987); target transformation factor analysis (TTFA) (Alpert and Hopke, 1980, 1981; Hopke *et al.*, 1980, 1983); factor analysis followed by multiple linear regression (FA-MLR) (Kleinmann et al., 1980a, 1980b); self-modeling curve resolution (SMCR) (Henry and Kim, 1988, 1990; Kim, 1989); and Monte Carlo based factor analysis (MCFA) (Kuik *et al.*, 1993a, 1993b).

3.3.2. Data Preparation Prior to FA

Before proceeding with FA, some precautions about data preparation must be taken. To reduce missing value bias and increase statistical significance, only chemical

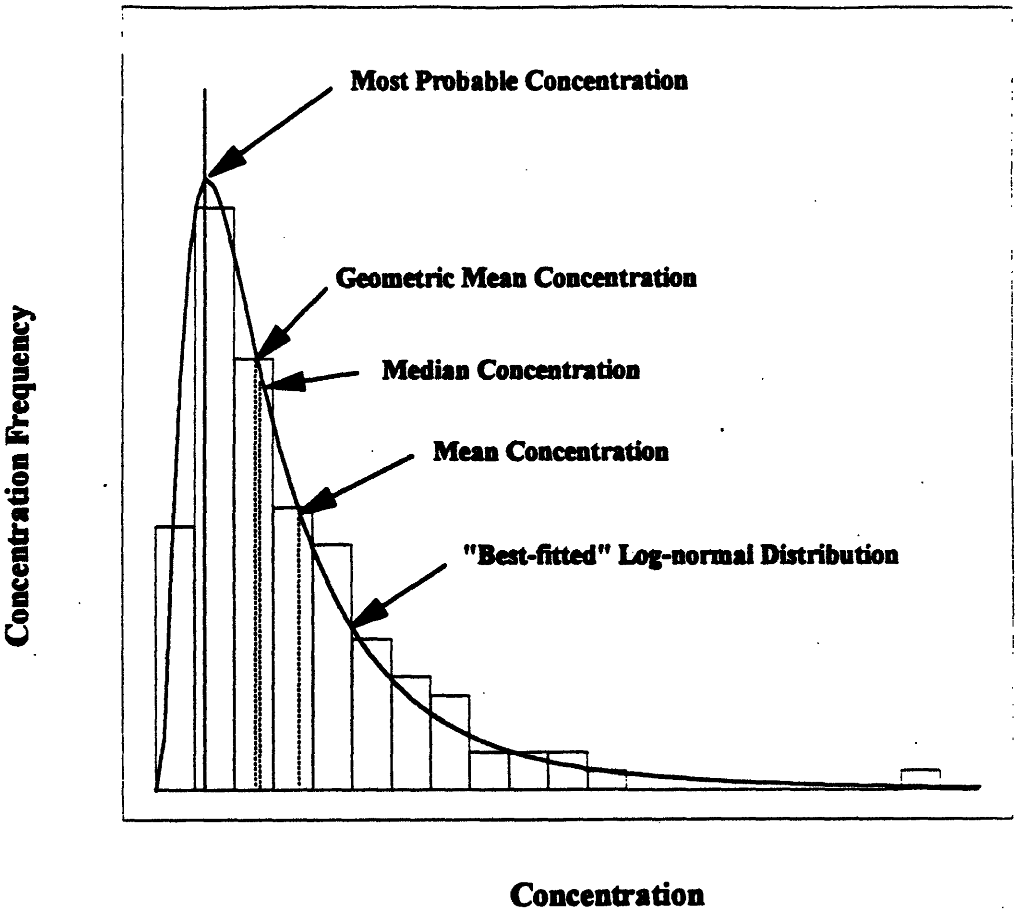

Figure 3.2. Histogram for an Approximately Log-normal Concentration Frequency Distribution.

species that have at least 0.7 observed frequency were selected as input variables in this thesis study. Also, to ensure data matrix homogeneity, they should have passed the K-S tests for concentration frequency distribution log-normality. Furthermore, to have statistically reliable FA results, the degrees of freedom (DF) should exceed at least 30 (Henry, 1991). The number of DF per chemical species in the analysis for the n samples and V chemical species that is defined empirically as:

$$DF = n - 1 - \frac{V-1}{2} \qquad (3.12)$$

However, missing values remaining in the input data matrix are still a nuisance for FA, which occur when real measured values are below analytical detection limits. Their handling lacks a unified approach and the chosen method usually depends on personal preference and the judgment of researchers. As addressed by Helsel, some widely used missing value treatments are simple substitution methods such as: substitution of one or one half of the detection limit; substitution of different values from the multiplication of detection limit by a random number among 0 and 1; and the substitution of zero (Helsel, 1990), etc. Heidam proposed a missing value handling method for the FA (Heidam, 1982). This and simple substitution methods are known to be inherently biased and statistically unjustified. Therefore, distributional methods have been adopted in this thesis study, and the missing values have been replaced with the estimated most probable values among the concentration frequency distributions for the selected chemical species . The reasons for the approach are:

(1) It is the maximum likelihood estimation (MLE) that has statistical justification;

(2) Sample size is large (>50) and concentration frequency distributions for selected chemical species fit assumed log-normal distribution at 0.05 significant level;

(3) The most probable value can be estimated precisely without too much bias.

The following estimation procedure of the most probable values is used for selected chemical species whose concentration frequency distributions are approximately log-normal:

The pdf for the 2-parameter log-normal distribution is given by:

$$f(C_i)=\frac{1}{\sqrt{2\pi}vC_i}\exp[-\frac{(\ln C_i-u)^2}{2v^2}],\ C_i>0,\ v>0 \qquad (3.13)$$

where u and v are distribution-related adjustable parameters (Miller, *et al.*, 1990). Therefore, the most probable concentration C_p can be obtained by letting $\frac{df(C_i)}{dC_i}=0$ as:

$$C_p=\exp(u-v^2) \qquad (3.14)$$

The arithmetic mean ($\overline{C}$) and standard deviation (s) for log-normal distribution is given by (Miller, *et al.*, 1990):

$$\overline{C}=\exp(u+\frac{v^2}{2}) \qquad (3.15)$$

and

$$s=\sqrt{\exp(2u+v^2)[\exp(v^2)-1]} \qquad (3.16)$$

Furthermore, the C_p can be related to $\overline{C}$ and s by eliminating u and v as:

$$C_p=\overline{C}[(\frac{s}{\overline{C}})^2+1]^{-1.5} \qquad (3.17)$$

Finally the $\overline{C}$ and s can be obtained by doing log-normal concentration distribution fitting to real concentration data, and thus the C_p can be calculated. These C_p values serve as substitutes for the relevant missing values in the input data matrix. The C_p value's relative position compared to other descriptive parameters has been shown in **Figure 3.2.**

3.3.3. Operational Procedure of PCFA

In this study, only varimax rotated PCFA was employed, leaving out uncertainty analysis. The very first step in every kind of factor analysis model is the singular value decomposition (SVD) step. The singular value decomposition theorem states that any matrix Z can be decomposed uniquely as:

$$Z = U \otimes D \otimes V^T. \qquad (3.18)$$

In receptor modeling applications, Z is a transformed data matrix of m rows of species and n samples arranged in columns. V contains the $n \times n$ eigenvectors of $Z^T \otimes Z$, U contains the $m \times m$ eigenvectors of $Z \otimes Z^T$, and D is a $m \times n$ diagonal matrix includes singular values that are the square roots of the corresponding eigenvalues. The most common transformation is so-called Z-transformation. It is a scaling step that centers the original concentration matrix C to the arithmetic mean ($\overline{C_j}$) and scale it to the standard deviation (s_j):

$$Z_{ij} = \frac{C_{ij} - \overline{C_j}}{s_j} \qquad (3.19)$$

where C_{ij} and Z_{ij} are original and transformed concentration matrix elements for the species or variable i in sample j, respectively (Henry, 1991). For the log-normal concentration frequency distribution, a natural logarithmic transformation of concentration data was applied. Thus the actual Z-transformation was produced according to the following formula (Heidam, 1982):

$$Z_{ij} = \frac{\ln(C_{ij} / \overline{C}_{ig})}{\ln s_{ig}} \qquad (3.20)$$

where $\overline{C}_{ig}$ and s_{ig} are geometric mean and geometric standard deviation for species or variable i that are defined by equations 3.9 and 3.10, respectively. The number of factor k was chosen based on the empirical criterion that its eigenvalue should be greater than unity.

Refering to equation 3.18, let $L = UD$ and $F = V^T$, then,

$$Z = L \otimes F. \qquad (3.21)$$

where L and F are called component loading and component score matrices, respectively. This approach is designated as Q-mode analysis that is usually adopted in physical sciences. In order to find physically meaningful L' and F', an orthogonal transformation matrix T has to be found and applied (Henry, 1991):

$$Z = (U \otimes T^{-1}) \otimes (T \otimes D \otimes V^T) = L' \otimes F'. \qquad (3.22)$$

3.4. Regression Analysis and Correlation Analysis

Regression analysis and correlation analysis were first invented by the English scientist Francis Galton in the nineteenth century. They originated from his research in heredity of sweet peas and human stature. Now they have become two of the most useful and powerful statistical techniques to create quantitative relationships among variables for predication or estimation purposes, and to measure the strength of the relationships among variables. Regression analysis usually involves one dependent variable say Y which regresses on one or more independent variables X. Different regression models such as: linear, exponential, reciprocal, multiplicative may be chosen depending upon the relationships among variables. However, the method's major underlying assumptions are addressed here in order to proceed with regression analysis correctly.

(1) In a classical regression model, nonrandom independent variable(s) should be identified first;

(2) The measurement of the independent variable is either error-free or has negligible error;

(3) The dependent variable should be mutually independent statistically, i.e., the frequency distribution of their values should be normal (Daniel and Terrell, 1992).

There are not many limitations due to the underlying assumptions regarding application of correlation analysis. However, precaution must be taken regarding application of regression analysis on environmental time-series' data that generally has inherent mutual dependency among themselves. This is the major reason that their frequency distributions often appear to be log-normal. Therefore, transformation of original data set has to be done before regression analysis, for example, transforming the whole data set logarithmically, and using differences or additives between consecutive data points. These transformation steps have been proven to either transform dependently non-normally distributed data to independently normally distributed ones or offset mutual dependency among the data (Box and Cox, 1964). However, stochastic models that involve extensive time-series analysis should be employed over regression models whenever possible due to the stochastic features of the atmosphere (Milionis and Davies, 1994).

Chapter 4
Results and Discussion: Cloudwater and Rainwater Studies at Mt. Washington

4.1. Inorganic Species in Cloudwater

4.1.1. General Concentration Patterns of Inorganic Species in Cloudwater

The measured concentrations of various inorganic species in cloudwater and rainwater at Mt. Washington are tabulated in *Appendix A*. As discussed in Chapter 3, only inorganic species that has at least a 0.7 observed frequency were subjected to further analysis. They are Na, Mg, Al, K, Ca, Sc, V, Cr, Mn, Fe, Zn, As, Br, Sb, La, Sm, Au, H_3O^+, NH_4^+, SO_4^{2-}, NO_3^-, and Cl^-. This was done to reduce the effect of missing value perturbations on data analyses. The mean ($\overline{C}$), median ($\overline{C}_m$), and geometric mean ($\overline{C}_g$) concentration, for each of the tabulated species was calculated. The log-normal concentration distribution fitting was also performed for each chemical species, and its most probable concentration (C_p), among the distribution was obtained following the procedure discussed in Chapter 3. **Table 4.1** summarizes the results.

The concentration frequency distributions for the tabulated inorganic species in cloudwater are all approximately log-normal ($DN < Q$, observed $\alpha > 0.05$) based on the two-sided K-S test at a significance level α=0.05. Based on magnitudes of their geometric mean concentrations, the tabulated inorganic species can be classified into three groups:

Group 1: SO_4^{2-}, NO_3^-;
Group 2: NH_4^+, Cl^-, H_3O^+, Na, Mg, Al, K, Ca, Fe;
Group 3: Zn, Mn, Sc, V, Cr, As, Br, Sb, La, Sm, and Au.

Species listed in group 1 are the major anions exist in cloudwater and are closely related to cloudwater acidity. Group 2 species are major electroneutral balancing cations and are the dominant elements in cloudwater. The Cl^- is also within the group. The last group are trace elements that have both anthropogenic and crustal origins. These results agree with findings in cloud chemistry studies at Mt. Mitchell of North Carolina (Saxena and Lin, 1990). However, only major cations and anions such as H_3O^+, NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, NO_3^-, and Cl^- were investigated by them. Unlike this study, the roles of some trace elements in physicochemical processes occurring in cloudwater could not

Table 4.1. Results of Log-normal Concentration Distribution Fitting in Cloudwater

Element	Observed Frequency	$\overline{C}$ (ng/mL)	$\overline{C}_m$ (ng/mL)	$\overline{C}_g$ (ng/mL)	*DN*	*Q*	Observed α	C_p (ng/mL)
Na	1.0	97	71	62	0.057	0.17	0.99	20
Mg	0.81	61	38	37	0.096	0.18	0.82	11
Al	0.96	93	47	49	0.12	0.17	0.45	10
K	0.93	130	94	87	0.056	0.17	0.99	27
Ca	0.81	130	50	53	0.12	0.18	0.55	7.0
Sc	0.98	1.2	0.14	0.17	0.12	0.17	0.42	0.053
V	1.0	2.1	0.91	0.77	0.087	0.17	0.82	0.18
Cr	0.94	1.6	0.42	0.47	0.066	0.17	0.98	0.13
Mn	1.0	5.8	2.8	2.6	0.051	0.17	0.99	0.49
Fe	0.87	71	51	47	0.070	0.18	0.98	18
Zn	0.98	16	10	10	0.074	0.17	0.94	3.9
As	1.0	1.8	0.43	0.45	0.062	0.17	0.99	0.070
Br	1.0	5.6	3.4	3.4	0.052	0.17	0.99	1.4
Sb	1.0	1.2	0.13	0.16	0.10	0.17	0.62	0.039
La	0.89	1.0	0.040	0.049	0.10	0.18	0.77	0.0048
Sm	0.96	0.99	0.006	0.008	0.10	0.17	0.68	0.0003
Au	0.98	0.002	0.0003	0.0004	0.079	0.17	0.90	0.00008
H_3O^+	1.0	120	54	61	0.082	0.17	0.86	13
NH_4^+	0.81	820	340	260	0.094	0.18	0.84	9.5
SO_4^{2-}	0.81	6500	2300	2300	0.12	0.18	0.54	71
NO_3^-	0.81	2500	1100	1100	0.086	0.18	0.91	57
Cl^-	0.81	280	130	100	0.14	0.18	0.37	14

be determined from their studies. To date, this thesis work is the most comprehensive cloud chemistry study completed This is especially true with respect to a broad range of trace elements included here.

4.1.2. Origins of Inorganic Species in Cloudwater

Although aerosols are precursors of inorganic species in cloudwater, their formation through gaseous and aqueous phase reactions is also important. The following reactions describe the gaseous or aqueous phase formations of, and the presence of dominant inorganic species (SO_4^{2-}, NO_3^-, NH_4^+, Cl^-) in cloudwater:

Biogenic or anthropogenic origin NH_3 can react with H_2SO_4 and HNO_3 in the atmosphere to form particulate $(NH_4)_2SO_4$ and NH_4NO_3. This is so-called gas-to-particle conversion:

$$2NH_{3(g)} + H_2SO_{4(g)} \Leftrightarrow (NH_4)_2SO_{4(s)}$$
$$NH_{3(g)} + HNO_{3(g)} \Leftrightarrow NH_4NO_{3(s)}$$

The soluble compounds dissociate in cloudwater if they are captured by cloudwater droplets according to the following reaction:

$$(NH_4)_2SO_{4(s)} \Leftrightarrow (NH_4)_2SO_{4(aq)} \rightarrow 2NH_4^{+}{}_{(aq)} + SO_4^{2-}{}_{(aq)}$$
$$NH_4NO_{3(s)} \Leftrightarrow NH_4NO_{3(aq)} \rightarrow NH_4^{+}{}_{(aq)} + NO_3^{-}{}_{(aq)}$$

Of course, gaseous NH_3, H_2SO_4, and HNO_3 can be captured by cloudwater droplets directly and dissociate to form NH_4^+, SO_4^{2-}, and NO_3^- through following reactions:

$$NH_{3(g)} + H_2O_{(l)} \Leftrightarrow NH_3 \bullet H_2O_{(aq)} \rightarrow NH_4^{+}{}_{(aq)} + OH^{-}{}_{(aq)}$$
$$H_2SO_{4(g)} \Leftrightarrow H_2SO_{4(aq)} \rightarrow H_3O^{+} + HSO_4^{-}{}_{(aq)} \rightarrow 2H_3O^{+} + SO_4^{2-}{}_{(aq)}$$
$$HNO_{3(g)} \Leftrightarrow HNO_{3(aq)} \rightarrow H_3O^{+} + NO_3^{-}{}_{(aq)}$$

Furthermore, SO_4^{2-} may originate from marine aerosols while gaseous H_2SO_4 is generally thought to be formed primarily through the following gas-phase reactions:

$$SO_2 + OH\bullet \xrightarrow[M]{} HOSO_2\bullet$$
$$HOSO_2\bullet + O_2 \rightarrow HO_2\bullet + SO_3$$
$$HO_2\bullet + NO \rightarrow NO_2 + OH\bullet$$
$$SO_3 + H_2O \rightarrow H_2SO_4$$

where M is a third body, such as suspended atmospheric particles. The three body reaction in the first step of the above reaction sequence is the rate-determination step (Seinfeld, 1986). As discussed in the Chapter 1, the aqueous-phase formation of SO_4^{2-} in cloudwater is equally important.

As shown in **Figure 4.1**, formation of gaseous HNO_3 is a part of atmospheric nitrogen chemistry. It can be generated through NO_2 and N_2O_5 pathways by radical reactions or direct addition of H_2O vapor. The following reactions are generally regarded as the aqueous-phase formation of NO_3^-:

$$2NO_{2(g)} \Leftrightarrow 2NO_{2(aq)} \Leftrightarrow N_2O_{4(aq)}$$
$$N_2O_{4(aq)} + H_2O_{(l)} \rightarrow 2H_3O^+ + NO_2^-{}_{(aq)} + NO_3^-{}_{(aq)}$$

Sea salts are generally considered to be the main source of chloride anions in cloudwater droplets. In this study, the average Cl/Na ratio is 1.2 in cloudwater, which is smaller than the ratio of 1.8 in sea water. This is an indication of the depletion of Cl occurring in marine aerosol precursors. A commonly accepted mechanism for the Cl loss is as follows (Keene *et al.*, 1986):

$$NaCl_{(s)} + H_3O^+ \rightarrow Na^+{}_{(aq)} + HCl_{(g)}\uparrow$$

However, gaseous HCl originating from some industrial processes may also be captured by cloudwater droplets and dissociated in cloudwater:

$$HCl_{(g)} \Leftrightarrow HCl_{(aq)} \rightarrow H_3O^+ + Cl^-{}_{(aq)}$$

As mentioned in Chapter 1, cloudwater serves as a temporary sink for trace elements in their biogeochemical cycling. The aerosols, which bear trace elements emitted from both natural and anthropogenic sources, are captured by cloudwater droplets and pass through cycles of condensation and evaporation. Their concentration patterns in cloudwater are actually the result of various complex atmospheric processes including

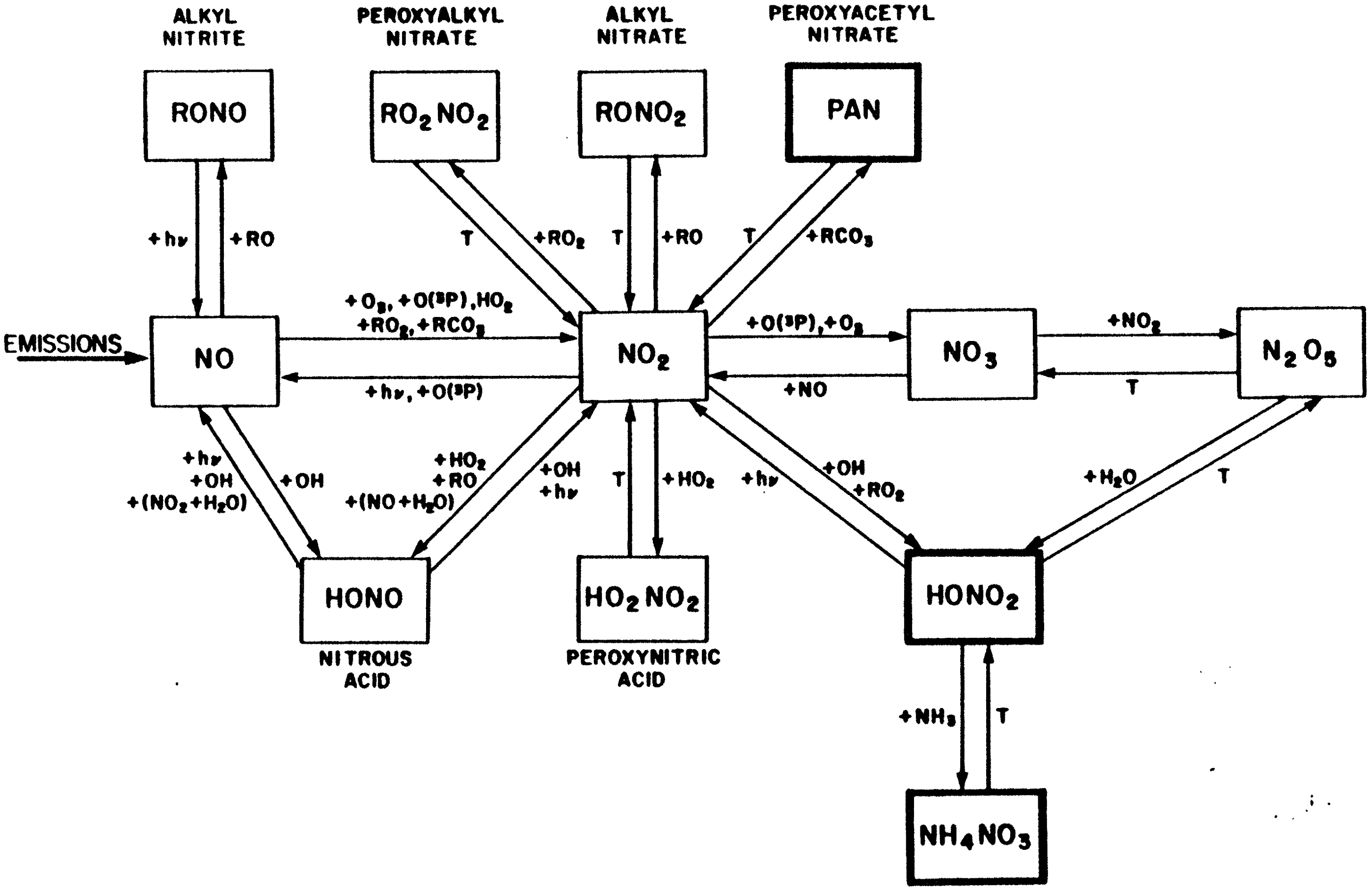

Figure 4.1. Atmospheric Nitrogen Chemistry (Seinfeld, 1986).

emission and partitioning. Therefore, those aerosols that contain different trace elements are also precursors for those trace elements observed in cloudwater.

4.2. Major Factors Responsible for Inorganic Species Concentration Patterns in Cloudwater and Their Implications

Factor analysis provides a way to sort out the major factor(s) explaining the greatest portion of the total variances within a data set. To identify major factors responsible for inorganic species concentration patterns in cloudwater, varimax-rotated PCFA was performed. The statistical package employed for PCFA is the PC version STATGRAPHICS® 7.0 (Manugistics™, Inc., MD). The relevant PCFA procedure is discussed in Chapter 3. The Z-transformation is performed employing the equation 3.20 due to the log-normal concentration frequency distributions for selected inorganic species. **Table 4.2** presents the PCFA results of fifty-three cloudwater samples. The *DF* is about 42 calculated by equation 3.12. The missing concentration values were substituted by their most probable concentrations for selected species. Three major factors were identified based on the criterion of eigenvalues larger than unity. Together, they explain 77.8% of the total variance. To identify samples that are influenced by a given factor, which represents possible sources or source groups, factor scores for each factor were calculated. As seen in **Figures 4.2, 4.3,** and **4.4**, the standardized factor scores for each sample are all within -2 to +2 range, indicating well-homogenized characteristics of cloudwater.

The first factor includes most of the inorganic species of both anthropogenic and natural origins. This single factor explains 51.3% of the total variance. It is assigned a background factor displaying an inorganic composition pattern for unperturbed and well-mixed clouds at the sampling site. As mentioned in Chapter 1, the CCN are classified as large and giant nuclei that are actively involved in the formation of cloudwater droplets. These tropospheric aerosols originate from both natural and anthropogenic sources, such as continental crust, ocean, volcanic eruption, fossil fuel combustion, and biomass burning. They evolve through cycles of evaporation and condensation leaving behind cloudwater droplets containing various concentrated chemical substances, including certain trace elements (Mason, 1971). Therefore, the cloud background factor that includes most of the inorganic species represents homogenized and mixed source groups of these species.

The second factor is designated as the acidity factor because all acidic species (SO_4^{2-}, NO_3^-, and Cl^-) and major electroneutral balancing cations (H_3O^+, NH_4^+, and

Table 4.2. Results of Principal Component Factor Analysis of Inorganic Species in Cloudwater

Element	Factor 1	Factor 2	Factor 3
Na	0.80		
Mg	0.81		
Al	0.82		0.46
K	0.83		
Ca		0.84	
Sc	0.69		0.61
V	0.75	0.35	
Cr	0.84		
Mn	0.88	0.26	
Fe	0.81		0.39
Zn	0.83		
As	0.77		
Br	0.83		
Sb	0.88		
La	0.85		0.39
Sm	0.82		0.40
Au			0.76
H_3O^+	0.61	0.45	
NH_4^+		0.91	
SO_4^{2-}		0.97	
NO_3^-		0.96	
Cl^-		0.78	
Variance Explained %	51.3	19.5	7.0

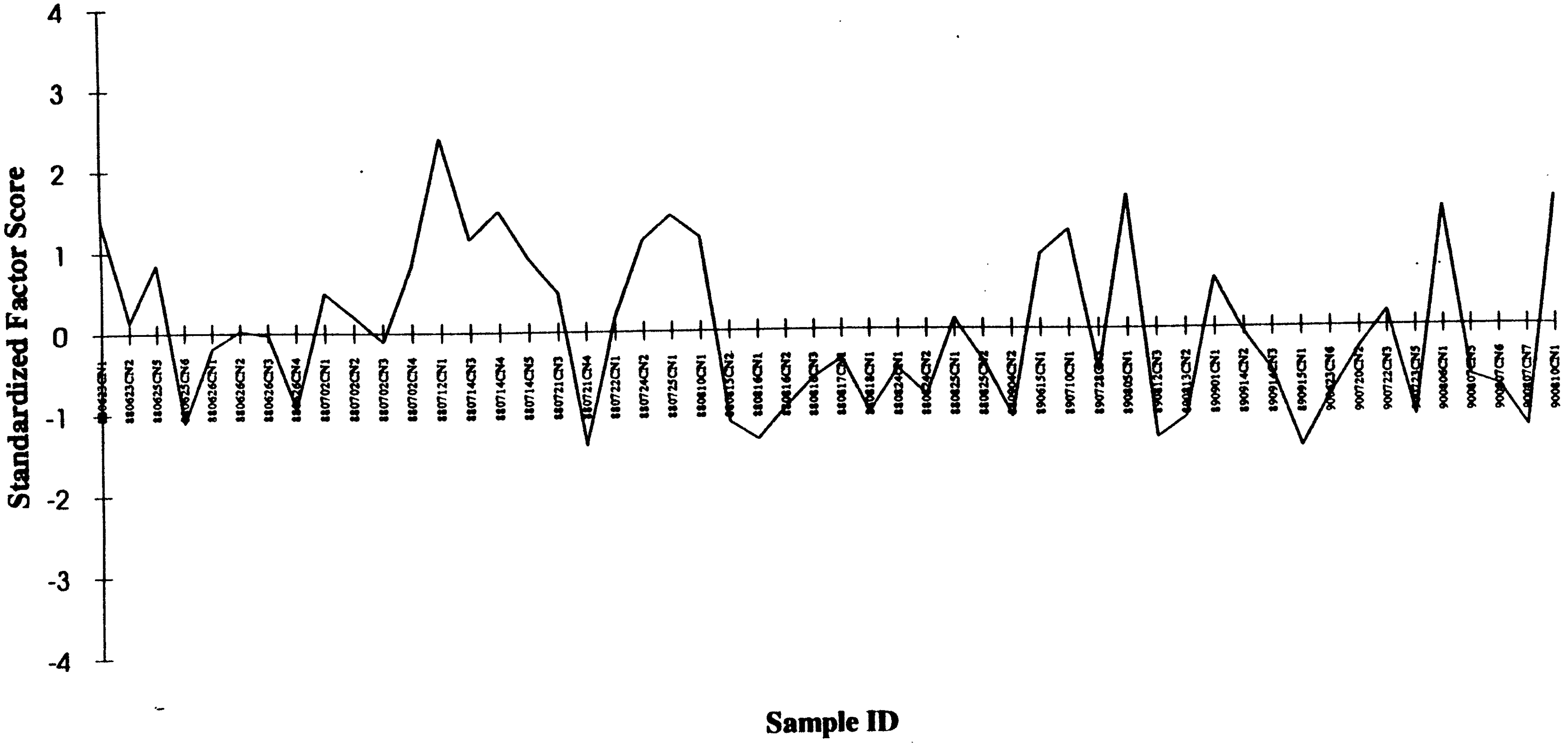

Figure 4.2. Factor 1 Score Plot.

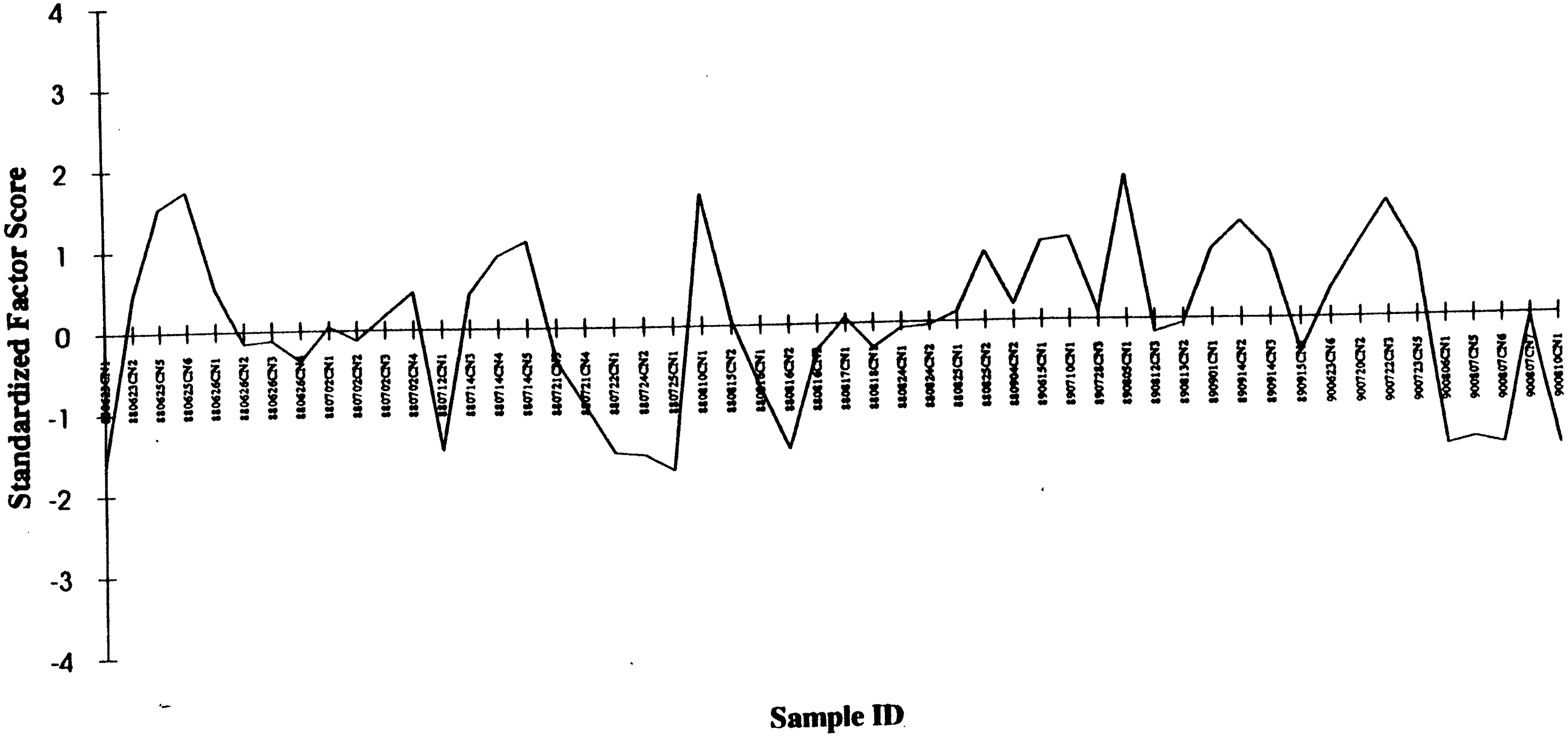

Figure 4.3. Factor 2 Score Plot.

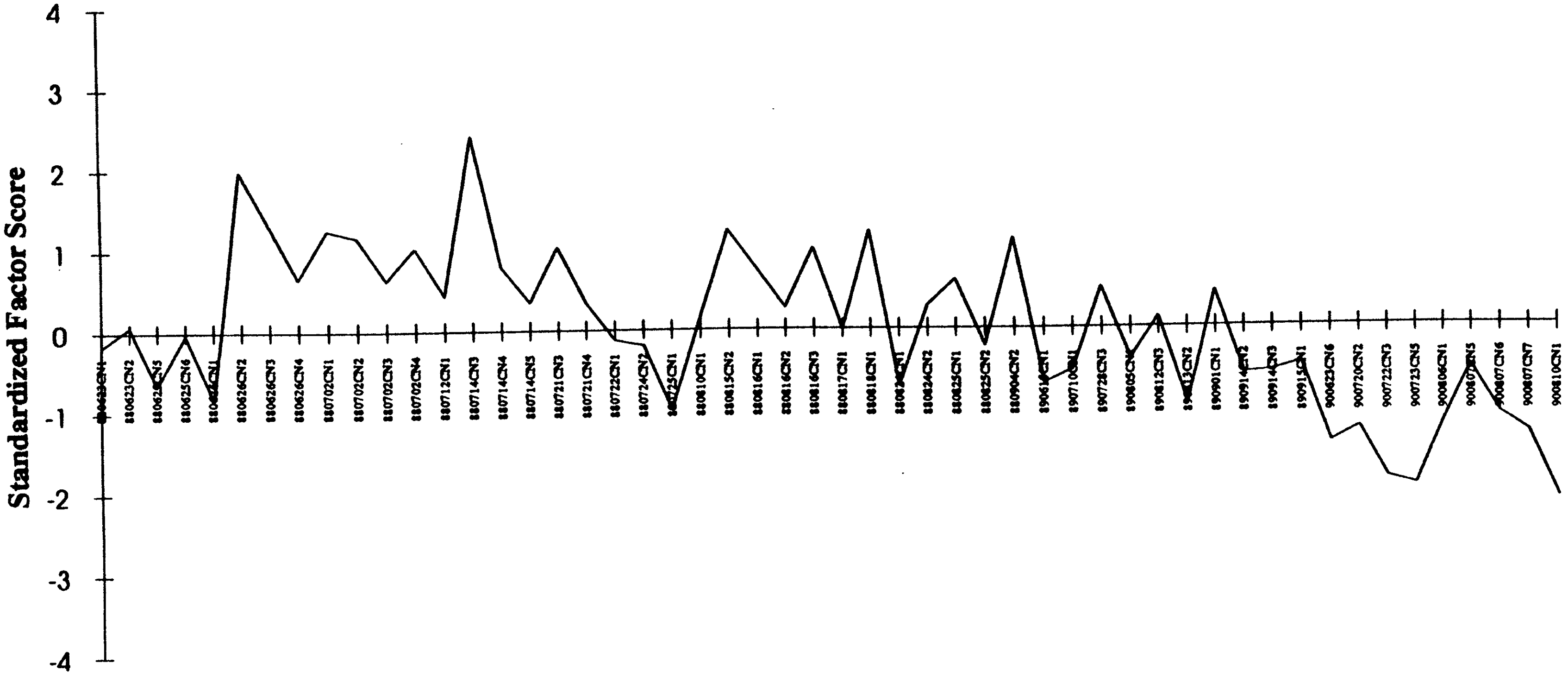

Figure 4.4. Factor 3 Score Plot.

Ca^{2+}) are strongly associated with it. Other than being emitted from various sources, these species are also the products of atmospheric reactions, such as gas-to-particle conversion, heterogeneous, and homogeneous formation. **Figure 4.3** shows nine samples that have the greatest influence on the acidity factor. Their averaged pH is 3.59, which is lower than the averaged pH=3.65 of ten samples influencing the background factor most. This is because all acidic species are associated with this factor. Although there is higher H_3O^+ loading in the background factor than in the acidity factor, the inherent basic property of other trace metals loaded in the first factor offset the acidity. The Ca and NH_4^+ have strong loading in the acidity factor since they are major electroneutral balancing species. The chemical forms in their aerosol precursors are ionic compounds, $CaSO_4$, $(NH_4)_2SO_4$, etc. Moreover, the V and Mn have non-negligible loading on the acidity factor as seen in **Table 4.2.**

As discussed in Chapter 1, the V is a major marker element for OFPP. The V (existing as V porphyrins in fuel oil) is emitted from OFPP flue gases in the form of vanadium pentoxide (V_2O_5). The V concentration in fuel oils is around 50 ppm. In flue gases of two OFPP located in Philadelphia, the averaged V concentration in fine particles is about 15800 ppm and 15500 ppm in coarse particles (Olmez, *et al.*, 1988). Previous studies indicate that the major V sources in the northeastern U. S. are OFPP and residential oil furnaces (Zoller, *et al.*, 1971; Gordon, 1988). It appears likely, therefore, that OFPP and other industrial oil combustion units are the primary sources of V-bearing aerosols. Furthermore, the correlation coefficients between V and SO_4^{2-} and NO_3^- are 0.67 and 0.72, respectively. **Figure 4.5** confirms their associations graphically. In the figure, La, although a marker element for OFPP, does not follow the general trend as closely as the V does. This is because La also originates from crustal material in addition to OFPP. The association of V with the acidity factor may be explained in two ways:

(1) Both V and the acidic species, emitted from oil burning sources are transported together from these sources to the sampling site. During transport, they were captured by water droplets and passed through cycles of condensation and evaporation in cloud as other species were.

(2) Similar to the acidic species, V is involved in a secondary chemical transformation. In fact, the V in cloudwater will not remain chemically inert since its low pH aqueous-phase redox chemistry is very active (Greenwood and Earnshaw, 1994). One possible role in which the V may play in aqueous phase, is the oxidation of S(IV) species. It is known that VO^{2+} and HSO_3^- will be the dominant V and S(IV) species in aqueous phase as indicated in **Figures 4.6** and **Figure 4.7**, respectively.

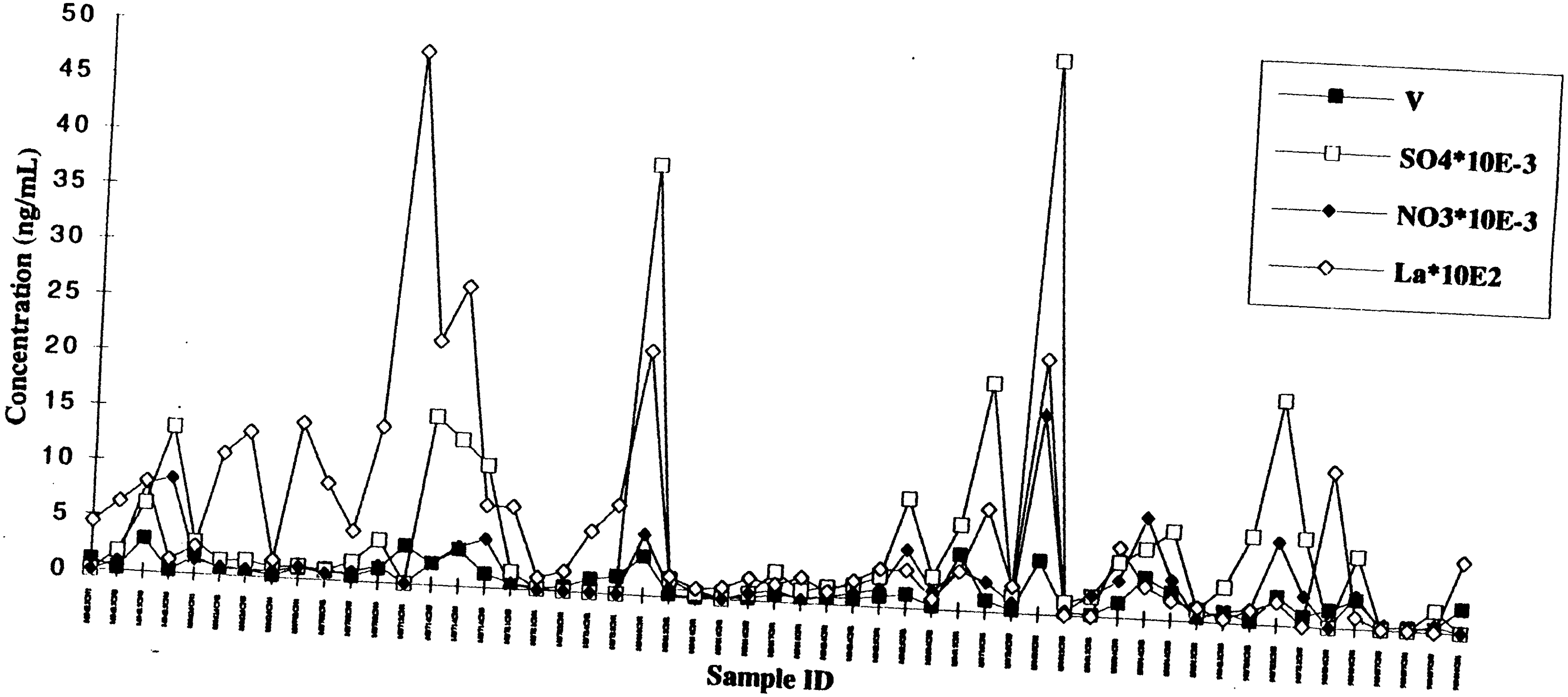

Figure 4.5. Graph Showing Associations among V, La, SO_4^{2-} and NO_3^-.

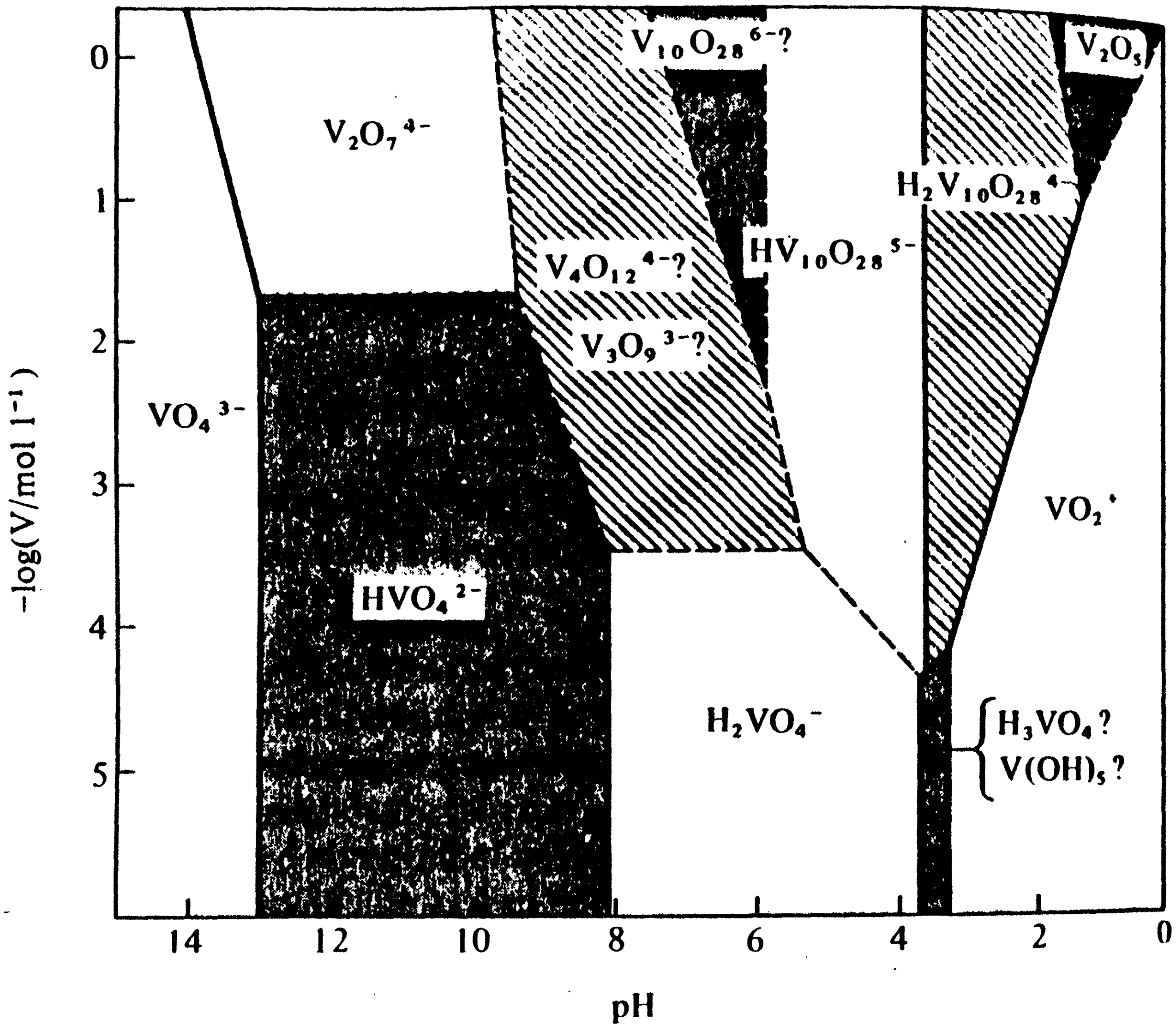

Figure 4.6. Occurrence of Various V Species as a Function of pH and Total Concentration of V (Greenwood and Earnshaw, 1994).

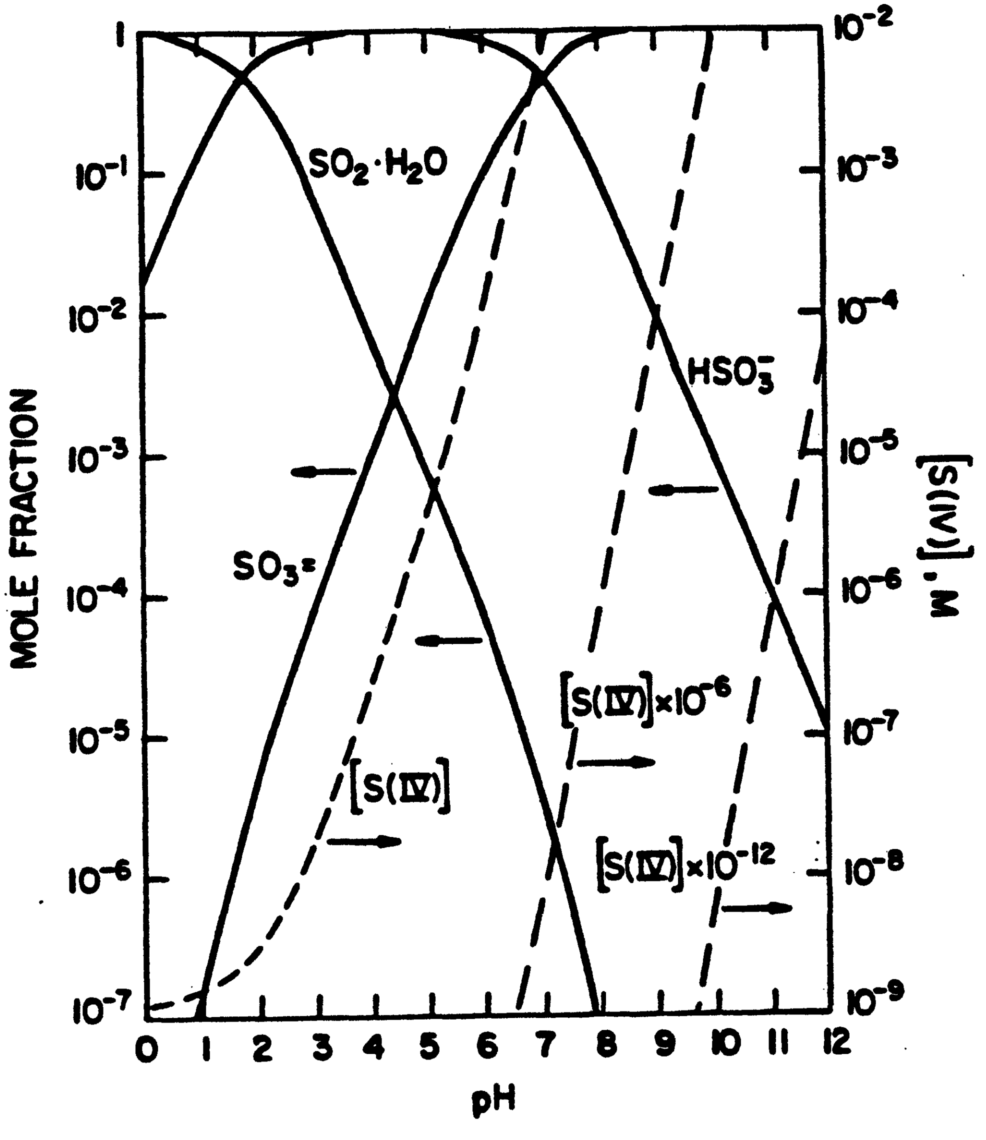

Figure 4.7. Mole Fractions and Concentrations of Dissolved S(IV) Species as a Function of pH at $T = 298K, p_{SO_2} = 10^{-9} atm$ (Seinfeld, 1986).

The equilibrium constant K for the plausible redox reaction may be calculated as following:

$$
\begin{array}{ll}
 & 2\times) VO_2^{+} + 2H_3O^{+} + e \rightarrow VO^{2+} + 3H_2O; E^{\circ} = 0.991V \\
 & 1\times) HSO_3^{-} + 4H_2O \rightarrow SO_4^{2-} + 3H_3O^{+} + 2e; E^{\circ} = -0.172V \\
+) & \\
\hdashline
 & 2VO_2^{+} + HSO_3^{-} + H_3O^{+} \rightarrow 2VO^{2+} + SO_4^{2-} + 2H_2O; \Delta E^{\circ} = 1.81V
\end{array}
$$

The Nernst equation at an electrochemical equilibrium is as follows:

$$\Delta E^{0} = \frac{RT}{nF} \ln K \qquad (4.1)$$

where ΔE^{0} (in units of V) is the equilibrium standard potential difference at $P = 1atm$, $T = 298K$ condition, $R = 8.314\ \mathrm{J{\cdot}mol^{-1}K^{-1}}$, n = mole number of electrons transferred in the redox reaction in question, and F is the Faraday constant which equals to 96500 C. The equilibrium constant, K, may then be determined by the following formulae:

$$K = \exp(nF\Delta E^{0} / RT) \qquad (4.2)$$

The constant, K, is calculated as 1.8×10^{61}. This large equilibrium constant K for the above redox reaction involving S(IV) oxidation, indicates that the reaction is thermodynamically feasible. The extent to which this reaction contributes to the total S(IV) oxidation is unknown. However, if the above reaction proves to be kinetically feasible, it will provide another possible pathway for S(IV) to S(VI) transformation.

It is interesting to observe that Mn, whose major source is wind-blown dust, is also associated with the acidity factor. The correlation coefficient between the Mn and SO_4^{2-} is 0.61. This would imply that there is some involvement of Mn in the S(IV) to S(VI) transformation. Laboratory studies have confirmed the catalytic synergism between Mn(II) and Fe(III) in S(IV) oxidation (Ibusuki and Takeuchi, 1987; Grgic *et al.*, 1992). Olmez also found good correlation between acidity and Mn in fifteen cloudwater samples collected at Whiteface mountain of New York as shown in **Figure 4.8** (Olmez, 1988). In this study, there were two continuous cloud episodes that show the similar correlation. These two cloud episodes occurred in June 26 and July 2, 1988. The

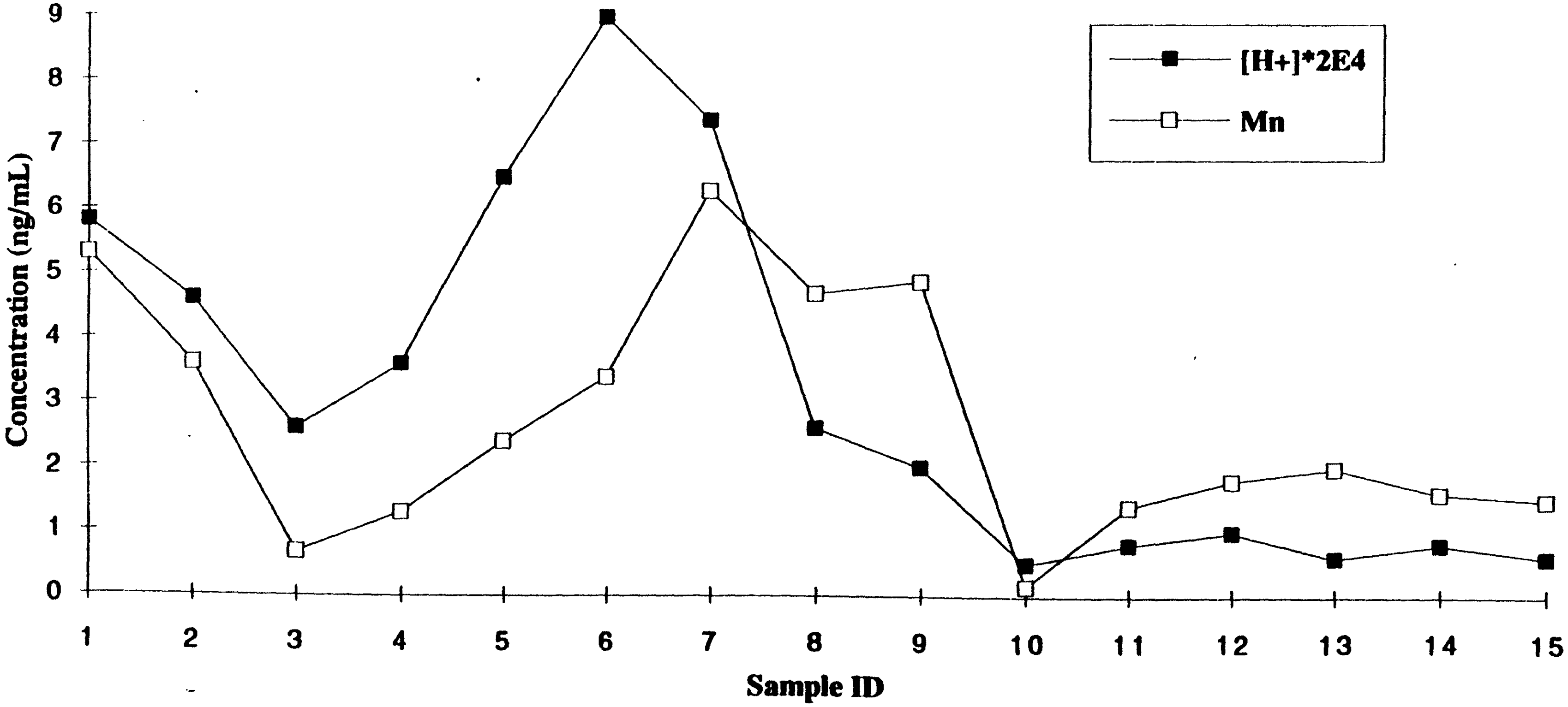

Figure 4.8. Graph Showing Correlation of Mn with Acidity in Cloudwater (Olmez, 1988).

temperatures were 279.68±1.31°K and 276.90±0.80°K, respectively, and with the same north and northwest local wind directions. The effects of these two meterological factors on the concentration changes were either negligible or evenly distributed. **Figure 4.9** clearly suggests a positive correlation between Mn concentrations, SO_4^{2-} concentration, and cloudwater acidity during these two dynamic cloud episodes. It is well known that SO_4^{2-} species are the main causes for rain acidity ($pH<5$) in northeastern United States. When the pH is less than 5, the H_2O_2 pathway is the major cause of aqueous-phase oxidation of S(IV) to S(VI) (Hales, 1991). Current studies cannot rule out the possibility of a Mn(II)-involving photochemical formation of H_2O_2, which in turn oxidizes S(IV) to S(VI) in the aqueous phase. It may play similar catalytic role as Fe(III) does. Reasons that Fe(III) and Mn(II) share many chemical properties are as follows:

(1) They are neighboring elements in the elemental periodic table;

(2) Mn(II) and Fe(III) are isoeletronic, having same ground-state electronic configuration: $1s^22s^22p^63s^23p^63d^34s^2$;

(3) Each can bind with O-containing ligands to form organo metallic complexes in which the O is the donor atom (Greenwood and Earnshaw, 1994);

(4) The difference of metal-O bond energy is small: Mn-O: 402.9±41.8 kJ mol^{-1}; Fe-O: 390.4±17.2 kJ mol^{-1} (CRC Handbook of Chemistry and Physics, 1990-1991).

In view of above discussion and supporting evidence, a mechanism may be postulated for the aqueous-phase S(IV) to S(VI) transformation by in-situ formed H_2O_2, which is catalyzed photochemically by Mn(II)-organo complex. It is similar to the mechanism involving the Fe(III)-organo complex proposed by Zuo and Hoigne (Zuo and Hoigne, 1993):

$$
\begin{aligned}
&Mn(II)-L\xrightarrow{h\nu}Mn(I)+L\bullet\\
&Mn(I)orL\bullet+O_{2(aq)}\rightarrow Mn(II)orL+O_2^-\bullet\\
&2O_2^-\bullet+2H_3O^+\rightarrow H_2O_2+O_2+2H_2O\\
&H_2O_2+HSO_3^-\rightarrow SO_4^{2-}+H_3O^+
\end{aligned}
$$

As discussed by Faust, both SO_4^{2-} wet deposition flux and solar energy flux reach their maxima during the summer in the northern hemisphere, indicating the importance of photo-oxidation of S(IV) species in cloudwater (Faust, 1994). It is important that the complexity of the above reaction mechanism be examined experimentally using authentic cloudwater.

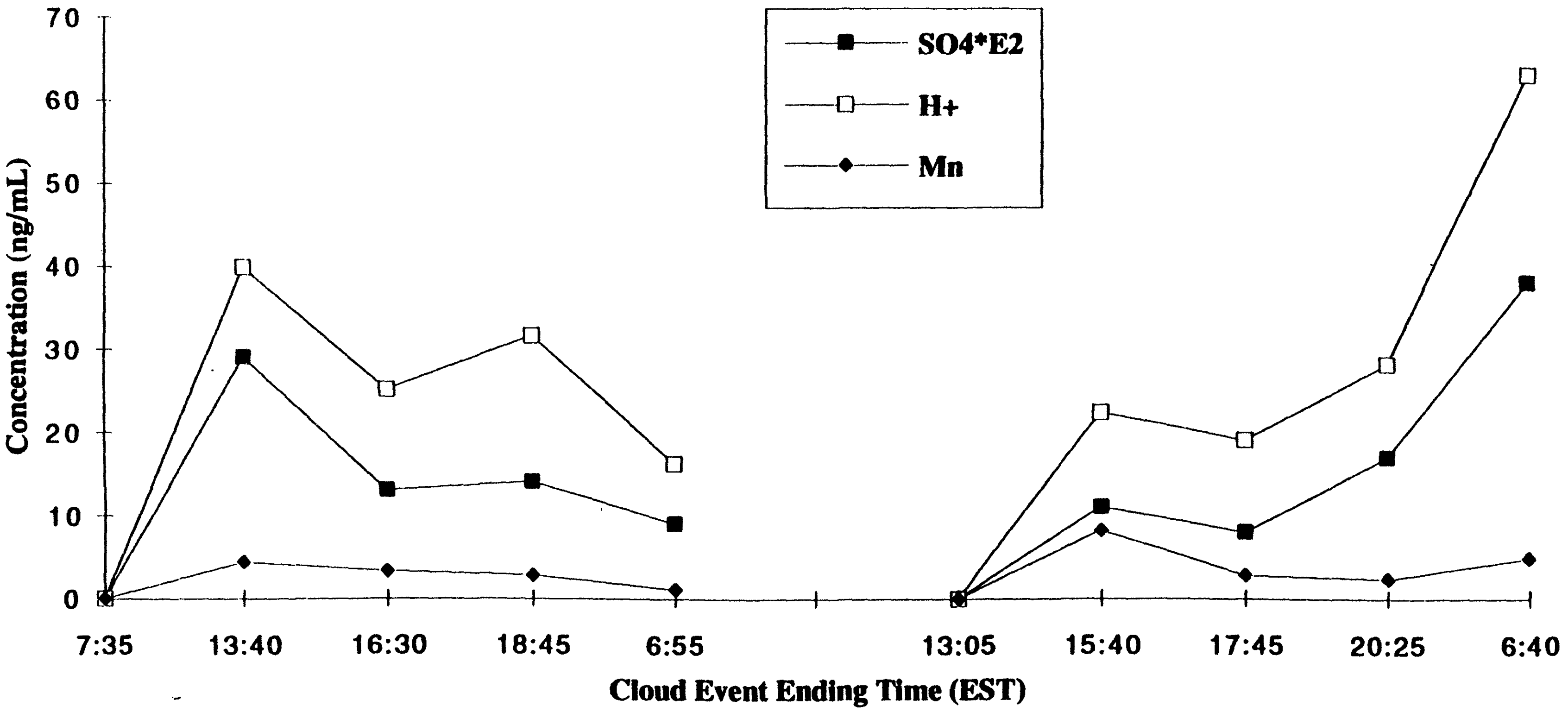

Figure 4.9. Graph Showing Correlation of Mn with SO_4^{2-} and Acidity in Cloud Episodes.

The third factor derived from the PCFA of the data is a crustal factor as indicated by some of its marker elements, i.e., Al, Sc, Fe, La, Sm. In these cloudwater samples, average La/Sm ratio is 7.1 comparing to 5.0 in natural crustal material. This marginal increase of La/Sm ratio implies those aerosol precursors of these cloudwater samples do carry an OFPP emission source signature. However, the crustal contribution to La and Sm in cloudwater dominates over OFPP contributions. As **Figure 4.4** indicates, the averaged pH value for the ten samples that influenced the crustal factor the most is 4.50. The increase of pH can be attributed to the inherently basic property of crustal materials. It is interesting to observe that Au is also associated with this factor. The reason for this is unclear. As Au concentrations are very low in cloudwater (around pg/g level) at this point, its significance to the overall data analysis may be disregarded.

4.3. Transition Metals in Cloudwater and Solar SW Radiation Absorption of Clouds

The cloud absorption anomaly described in Chapter 1 has been known for almost four decades. More recent experiments further strengthen the belief that the discrepancies between measurements and model predictions do exist. Current explanation for this is concentrate on cloud morphology such as heterogeneous instead of homogeneous clouds; uncertainties in cloud optical properties such as population densities and sizes of cloud droplets; and the distribution of foreign carbon-based aerosols in cloud droplets.

Transition metal cations and their complexes are well known for their strong absorption of visible or near-visible light spectral regions, which lie within the spectral range of solar SW radiation. This is adequately explained by the crystal field theory (CFT) of modern inorganic chemistry. The CFT suggests that energy level splitting of their unfilled *d*-orbital occurs under the influence of various ligands, such as H_2O, DOM, halogen anions (X^-), etc. (Greenwood and Earnshaw, 1994). The concentrations of first-series transition metals such as Fe, Mn, V, and Cr, which are present in cloudwater droplets (most probably as complexes with DOM), are among 10^{-5} to 10^{-8} M equivalency in this study. However, precipitating cloudwater droplet sizes are about 10 times larger than the cumulus cloudwater droplet size. Therefore, the effective concentration of transition metals in a cumulus cloudwater droplet may be reasonably assumed as 1000 times higher than measured concentration values in the precipitating cloudwater droplet. For example, 10^{-6} M concentration in precipitating cloudwater is equivalent to a 10^{-3} M concentration in cumulus cloudwater. It is plausible to argue that these may be the missing absorbers responsible for solar SW radiation absorption anomalies of clouds.

The following sections discuss two different estimations about increased solar SW radiation absorption by transition metals and/or their complexes, and present a general and conceptual approach. This was adopted without reference to any particular transition metal or associated organo-complex.

4.3.1. Estimations Based on the Beer-Lambert's Law and Mie Scattering Theory

The first estimation approach was based on the Beer-Lambert Law as shown in the following equation:

$$\lg\left(\frac{I_t}{I_0}\right) = -\varepsilon C l \qquad (4.3)$$

where I_t and I_0 are transmitted and incident light intensities respectively, ε is the molar absorption coefficient (in $M^{-1}cm^{-1}$ unit) of an absorbing chemical species at a particular wavelength, C is its concentration (in M unit), and l is the path length of the species-containing solution in which the light intensity is attenuated. The absorbed fraction of incident light $\frac{I_a}{I_0}$ can be expressed as:

$$\frac{I_a}{I_0} = 1 - 10^{-\varepsilon C l} \qquad (4.4)$$

where I_a is the absorbed light intensity.

Therefore, equation 4.4 may be applied to estimate fractional absorption of incoming solar SW radiation by possible absorbers in cloudwater droplets so long as relevant parameters are reasonably assigned. This approach to study the cloud solar absorption anomaly is as follows:

A 0.5 km fair-weather cumulus cloud column (L) with a 1 m by 1 m cross-sectional area and average 1.0 g/m^3 liquid water content (LWC) is equivalent to 500 g/m^2 liquid water path (LWP, LWP=LWC×L) (Mason, 1971). Then the effective liquid water thickness (l) within this cloud column is calculated as 0.05 cm. The ε for transition metal complexes in visible and near-visible spectral range are within 1-100 $M^{-1}cm^{-1}$. In this study, values of ε=10 and C=10^{-3} M in cumulus cloudwater were chosen. These choices are based on the actual measured concentration range for transition metals in precipitating cloudwater. Then the fractional absorption of incident light $\frac{I_a}{I_0}$ is about

0.0012 as shown in **Table 4.3**. The calculated results show that there is approximately 0.1% extra absorption by cloudwater containing transition metals or their complexes.

The second approach was a modeling approach based on the Mie Scattering Theory. This model also resolves the occurrence of multiple scattering within clouds. A Unix-based combined program called Mie-Radin was run on the Cray main frame system for these computations. The distribution of cloud droplet sizes is assumed to be a gamma distribution. This assumption is generally adopted in cloud radiative transfer modeling. The effective radius (r_e) of a cloud droplet is 5 μm, within typical 1-10 μm range for cumulus cloudwater. Further, the thickness for the cumulus cloud is given as 0.5 km. The typical wavelength for incident near-visible solar radiation was chosen as λ=375 nm. This wavelength is near the spectral region where transition metals or their complexes generally have maximum absorption. The last required input parameter is the extinction coefficient $k(\lambda)$. This consists of the imaginary parts of the spectral complex refractive index ($\hat{n}(\lambda)$):

$$\hat{n}(\lambda) = n(\lambda) - ik(\lambda) \qquad (4.5)$$

For pure cloudwater, $k(\lambda) \approx 10^{-9}$ at a wavelength of λ=375 nm. The extinction coefficient $k(\lambda)$ for cloudwater with transition metals or their complexes can be estimated from following relations:

$$k(\lambda) = \frac{\lambda \alpha(\lambda)}{4\pi} \qquad (4.6)$$

and

$$\alpha(\lambda) = 2.303\varepsilon C \qquad (4.7)$$

where $\alpha(\lambda)$ is the Lambert absorption coefficient (Hale and Querry, 1973). Using the same ε and C values as in the first approach, i.e., ε=10 and C =10^{-3} M, the $k(\lambda)$ was estimated as about 10^{-7} at λ=375 nm for cloudwater containing transition metals and/or their organo-complexes. The computations are given in **Table 4.3**. The calculations show that both the albedo and fractional transmission values do not change significantly. However, the fractional absorption value for cloudwater with transition metals or their complexes are 2.4 times larger than the value for pure cloudwater. This may indicate that total reflection and transmission of clouds are less sensitive to the minute or trace level substances present in cloudwater. Rather, they depend mainly on the overall physical properties of cloudwater droplets. These properties include droplet size distribution and optical properties. Absorption within the cloud, however, is more sensitive to the composition of chemical species in cloudwater droplets.

4.3.2. Comments on the Estimation Results

The first estimation is less accurate than the second as it treats the liquid water in the cloud as a conceptual layer of water without considering the water droplet's size distribution or their relevant optical properties. Furthermore, the Beer-Lambert's Law cannot be applied to quantify absorption of incident solar light by pure liquid water. However, these two approaches agree with each other with respect to the magnitudes of solar radiation absorption as **Table 4.3** shown.

Chapter 1 refers to the significant climatic consequences if the anomaly of solar radiation absorption by clouds holds true. Controversy will exist as long as validity of current measurements is in doubt. Uncertainty analyses must be performed to identify the effects of measurement errors on the anomaly. Also, the assumption that concentrations of transition metals and their complexes in precipitating cloudwater are approximately one thousand times lower than in cumulus cloudwater are questionable. This is because it is assuming that the cloud droplet growth is solely through water vapor condensation mechanism. In fact, the droplet growth is can be controlled by collision and coalescence mechanisms (Molina, 1995; Mason, 1971). Depending upon the LWC in clouds, the estimation in **Table 4.3** may only represent an extreme case that only water vapor condensation is responsible for cloudwater droplet growth. The current model of solar SW radiation absorption by clouds applies only to the absorption by pure liquid water, water vapor, and aerosols in clouds. However, a recent experiment indicates that the absorption and scattering properties of clouds are primarily water-like, thereby reducing the probability that the presence of carbon-based aerosols as absorbers in cloudwater (Pilewskie and Valero, 1995). Although the above estimated results indicate that the absorption by pure water alone is questionable, it is the estimation under an extreme condition. Therefore, it is too early to state that those transition metals, their complexes are responsible for the observed excess solar absorption by clouds. Until further evidence is available, the cloud absorption anomaly of solar SW radiation will continue to be debated in the scientific community.

Table 4.3. Estimation of Solar Radiation Absorption by Cloudwater

Estimation Approach and Estimated Parameters		Pure Cloudwater	Cloudwater+ Transition Metals or Complexes
Beer-Lambert's Law	Fractional Absorption	≈0	0.0012
Mie Scattering Theory	Albedo	0.6241	0.6219
	Fractional Transimission	0.3732	0.3716
	Fractional Absorption	0.0027	0.0065

4.4. Concentration Changes of Trace Inorganic Species in Concurrent Cloudwater and Rainwater

Among the cloudwater and rainwater samples, there are 14 sample pairs, which are composed of concurrent samplings of cloudwater and rainwater at 1536 m altitude, and rainwater alone at 610 m altitude. These samples were collected over the summer months of 1989 and 1990. **Table 4.4** presents both median concentration ratios of rainwater to cloudwater at 1536 m elevation and rainwater to rainwater at 610 m and 1536 m elevation, for trace inorganic species. These ratios are the first set of data, to represent dynamic concentration changes involving rainout and washout processes.

As expected the first ratios ($C_{rw(h)}/C_{cw}$) are less than one because of dilution effects which occur during the rain-drop growing process. Ratios for different species are approximately 0.5. The cloudwater concentration for each species depends upon its rainout process that can be quantified by the following equation:

$$C_{cw} = \frac{C_a \psi}{LWC} \qquad (4.8)$$

where C_{cw}, C_a, and ψ are a species' concentration in cloudwater, in aerosol, and its rainout efficiency, respectively. The rainout efficiency ψ represents an additive effect of the consumption of CCN (ψ_n); Brownian attachment of Aitken nuclei (ψ_b); and attachment of Aitken nuclei by Facy-effect due to the water vapor gradient (ψ_f) (Junge, 1963). In this study, the rainout efficiencies for different species were not obtained because measurements of C_a and LWC were not performed. The rain concentration for each species is reflected by its water-absorbing ability to sustain continuous growth from cloud droplets to rain droplets.

The second ratios ($C_{rw(l)}/C_{cw(h)}$) are all larger than unity. This is attributed to evaporation effects and the washout mechanism of falling rain droplets. The latter is a natural cleansing process for suspended aerosols beneath clouds. The final inorganic species concentration in rainwater (C_{rw}) can be quantified by the following equation:

$$C_{rw} = \xi C_0 + \Delta C \qquad (4.9)$$

where C_0 and $\xi \geq 1$ are the initial species concentration in rainwater and the rain evaporation factor, respectively. ΔC is the concentration increase due to the washout

Table 4.4. Median Concentration Ratios of Trace Inorganic Species in Cloudwater and Rainwater

Element	$C_{rw(h)}/C_{cw}$*	$C_{rw(l)}/C_{rw(h)}$**
Na	0.49	1.58
Al	0.41	1.01
Cl	0.38	1.80
Ca	0.33	1.00
Sc	0.58	1.43
V	0.30	1.63
Cr	0.40	1.28
Mn	0.29	2.18
Fe	0.41	1.28
Zn	0.55	1.65
As	0.18	1.40
Br	0.54	1.38
Sb	0.38	1.59
La	0.08	3.71
Sm	0.39	2.33
H_3O^+	0.63	1.12
NH_4^+	0.34	1.10
SO_4^{2-}	0.35	1.24
NO_3^-	0.34	1.28

*$C_{rw(h)}/C_{cw}$: median concentration ratio of rainwater to cloudwater at 1536 m elevation;
**$C_{rw(l)}/C_{rw(h)}$: median concentration ratio of rainwater at 610 m elevation to rainwater at 1536 m elevation.

effect. It can be calculated using the following equation if the rain collection efficiency $\eta \leq 1$ for aerosols of radius r and the aerosol size distribution $n(r)dr$ are known:

$$\Delta C = \frac{\pi H}{r_c} \int \eta r^3 n(r) dr \qquad (4.10)$$

H is the cloud base height above the rain sampling site and r_c is rain droplet radius (Junge, 1963). In this study, the theoretical calculations were not performed due to the lack of relevant parameters. The washout process may be dominant over the rain droplet evaporation process because of a temperature increase at lower elevations. The reason is that the actual lapse rate for the "wet" and stable atmosphere is less than 3.6 to 5.5°C/1000 m elevation change (Hemond and Fechner, 1994). This means that the maximum temperature increase is approximately 5°C due to an elevation decrease from 1536 m to 610 m. Another minor mechanism causing a surface temperature increase in rain droplets as they descend is their heat-generating friction with surrounding atmosphere.

Chapter 5

Results and Discussion: Wet Deposition Studies in the Adirondack Region

5.1. Results of Wet Deposition Studies in Willsboro and Moss Lake Sampling Sites

5.1.1. Inorganic Species Concentrations and Precipitation Volumes of Wet Deposition

The primary goal of this wet deposition study was to obtain long-term background concentrations and annual wet deposition fluxes of various inorganic species at each sampling site. Knowledge of these two parameters is essential to any risk model that attempts to assess the Adirondack ecological system stress and its relation to toxic inorganic species presence. This information also describes the current impact of atmospheric wet deposition to the watersheds within the Adirondack region.

The complete concentration data of inorganic species found in wet deposition samples collected at each site are given in *Appendices B1 and B2*. To reduce the effect of missing value perturbations on data analysis, only inorganic species that has at least a 0.7 observed frequency are considered to be significant enough to be included in the following discussions. The qualifying species are Na, Mg, Al, K, V, Cr, Mn, Co, Zn, As, Br, Sb, La, Sm, Au, SO_4^{2-}, NO_3^-, and H_3O^+ for the Moss Lake site. With the exception of Cr, Co, and La, the remaining qualifying species for the Willsboro site are Na, Mg, Al, K, V, Mn, Zn, As, Br, Sb, Sm, Au, SO_4^{2-}, NO_3^-, and H_3O^+. The calculated mean $\overline{C}$), median ($\overline{C}_m$), and geometric mean ($\overline{C}_g$) concentrations for these species are listed in Columns 3, 4, and 5 of **Tables 5.1 and 5.2** for Moss Lake and Willsboro, respectively.

K-S tests were performed for each species contained in wet depositions from each sampling site. The statistical package employed for this analysis is the PC version STATGRAPHICS® 7.0 (Manugistics™, Inc., MD). As **Tables 5.1 and 5.2** show, frequency distributions of these species concentrations and weekly integrated precipitation volumes from each site follow log-normal distributions (columns 5, 6, and 7). Inorganic species fail the K-S tests are: La ($DN=Q$) at Moss Lake and Sm ($DN>Q$ and $\alpha<0.05$) at both sites . Their concentration frequency distribution has no particular mode. Therefore, they were ignored in further analyses.

Table 5.1. Results of Log-normal Concentration Distribution Fitting for Wet Deposition Samples at Moss Lake

Element	Observed Frequency	$\overline{C}$ (ng/mL)	$\overline{C}_m$ (ng/mL)	$\overline{C}_g$ (ng/mL)	*DN*	*Q*	Observed α
Na	0.99	68	44	44	0.049	0.13	0.98
Mg	0.83	27	13	15	0.12	0.14	0.20
Al	0.93	21	16	13	0.11	0.13	0.26
K	0.95	46	32	34	0.077	0.13	0.66
V	0.95	0.17	0.14	0.14	0.076	0.13	0.69
Cr	0.90	0.42	0.32	0.31	0.099	0.13	0.37
Mn	1.0	2.1	1.2	1.4	0.11	0.13	0.23
Co	0.73	0.20	0.090	0.084	0.067	0.15	0.92
Zn	0.99	6.3	5.3	4.9	0.071	0.13	0.74
As	0.96	0.058	0.042	0.043	0.054	0.13	0.96
Br	1.0	1.1	1.0	0.88	0.071	0.13	0.74
Sb	0.99	0.048	0.040	0.039	0.089	0.13	0.46
La	0.94	0.14	0.015	0.023	0.13	0.13	0.12
Sm	0.91	0.0023	0.0020	0.0016	0.18>	0.13	<0.009
Au	0.94	0.00073	0.00037	0.00040	0.11	0.13	0.22
SO_4^{2-}	1.0	2800	2100	1800	0.093	0.13	0.39
NO_3^-	1.0	2300	1900	1700	0.074	0.13	0.68
H_3O^+	1.0	53	49	42	0.14	0.17	0.23
P-Vol.*	1.0	1400	1200	1010	0.12	0.13	0.16

* in mL.

Table 5.2. Results of Log-normal Concentration Distribution Fitting for Wet Deposition Samples at Willsboro

Element	Observed Frequency	$\overline{C}$ (ng/mL)	$\overline{C}_m$ (ng/mL)	$\overline{C}_g$ (ng/mL)	DN	Q	Observed α
Na	0.98	74	46	49	0.13	0.17	0.38
Mg	0.80	38	31	27	0.11	0.19	0.67
Al	0.93	34	14	14	0.093	0.17	0.78
K	0.87	260	88	98	0.15	0.18	0.27
V	0.94	0.43	0.25	0.26	0.13	0.17	0.34
Mn	1.0	1.3	0.84	0.87	0.071	0.17	0.95
Zn	0.98	20	8.1	10	0.16	0.17	0.12
As	1.0	0.049	0.040	0.038	0.14	0.17	0.24
Br	1.0	1.5	1.0	0.96	0.066	0.17	0.97
Sb	1.0	0.038	0.034	0.030	0.14	0.17	0.24
Sm	0.91	0.0011	0.0005	0.0007	0.29>	0.17	<0.0005
Au	1.0	0.0007	0.0003	0.0003	0.082	0.17	0.86
SO_4^{2-}	1.0	2600	1900	1700	0.093	0.17	0.74
NO_3^-	1.0	2200	1700	1700	0.088	0.17	0.79
H_3O^+	1.0	160	65	67	0.067	0.17	0.97
P-Vol.*	1.0	1100	1000	760	0.16	0.17	0.02

* in mL.

5.1.2. Relationship between Trace Inorganic Species Concentration and Precipitation Volume

The literature describes empirical relationships between concentrations of dissolved inorganic species and precipitation volumes to be either hyperbolic or inverse half-power relationship. These relationhips are given as:

$$C_i \approx a + b / P_i \qquad (5.1)$$

or

$$C_i = AP_i^{-q},\ q \approx 0.5 \qquad (5.2)$$

C_i and P_i are dissolved inorganic species concentration and precipitation volume, respectively while a, b, and A are relevant regression coefficients (Bayens *et al.*, 1990; Prado-Fiedler, 1990; Seto and Oohara, 1992). Several simultaneous processes may be responsible for their inverse relationship summarized by Prado-Fiedler (Prado-Fiedler, 1990):

(1) Rainout effect: Clouds will ingest aerosols supplied by the updraft during a precipitation event. This supply will decrease as the precipitation event proceeds;

(2) Dilution effect: Dilution occurs with time in a precipitation event;

(3) Washout effect: Particulate aerosols will be washed out during the early stage of a precipitation event resulting in a decrease of their concentrations with time;

(4) Raindrops evaporation effect: Some volatile species may evaporate as the raindrops pass through low humidity air columns.

Tests were made to determine whether the similar hypobolic or inverse half-power relationships exist in concentrations of dissolved inorganic species and precipitation volumes determined in this study. Subsequently, hyperbolic curve-fitting (columns 2 and 3) and a linear regression of $\ln C_i$ on $\ln P_i$ were performed. The results and associated standard errors (column 4) are presented in **Tables 5.3** and **5.4** for selected species. In general, the results have large standard errors. The magnitudes of errors are dependent on different inorganic species. Further, the Moss Lake site has the larger absolute q values than that of the Willsboro. This indicates that the former site has a higher wet removal efficiency for various inorganic species because of its higher

Table 5.3. Results of The Hyperbolic Curve-fitting and Linear Regression of $\ln C_i$ and $\ln P_i$ at Moss Lake

Element	a	b	q
Na	45±15	14000±5900	-0.39±0.09
Mg	21±8	4700±3200	-0.23±0.12
Al	14±3	4600±1300	-0.46±0.12
K	47±8	1400±3300	-0.10±0.09
V	0.16±0.01	9.0±6.0	-0.17±0.09
Cr	0.38±0.06	29±22	-0.27±0.09
Mn	2.4±1.0	310±410	-0.37±0.11
Co	0.10±0.12	54±44	-0.13±0.13
Zn	5.3±0.8	660±320	-0.39±0.07
As	0.043±0.006	8.8±2.6	-0.22±0.09
Br	0.93±0.09	110±37	-0.22±0.08
Sb	0.041±0.004	5.3±1.5	-0.24±0.08
Au	0.43±0.04	1.5±1.5	0.013±0.078
SO_4^{2-}	2300±310	240000±120000	-0.12±0.12
NO_3^-	1800±220	270000±8800	-0.21±0.09
H_3O^+	110±64	450±220	0.10±0.14

Table 5.4. Results of The Hyperbolic Curve-fitting and Linear Regression of $\ln C_i$ and $\ln P_i$ at Willsboro

Element	a	b	q
Na	56±14	7800±4300	-0.32±0.12
Mg	32±7	2600±2100	-0.23±0.12
Al	30±12	2000±3800	-0.23±0.19
K	300±140	-17000±40000	-0.19±0.17
V	0.28±0.17	73±56	-0.26±0.13
Mn	1.2±0.3	65±95	-0.21±0.12
Zn	18±5	990±1600	-0.20±0.16
As	0.049±0.007	-0.25±2.2	-0.07±0.11
Br	1.4±0.3	21±93	-0.10±0.13
Sb	0.037±0.005	0.3±1.4	-0.07±0.12
Au	0.0006±0.0002	0.043±0.050	0.21±0.17
SO_4^{2-}	2600±510	-2900±150000	0.01±0.14
NO_3^-	1800±300	190000±91000	-0.21±0.10
H_3O^+	140±38	6200±12000	0.08±0.21

precipitation volume than the Willsboro's. H_3O^+ has small positive q values at each site indicating that its concentration increases slightly as the precipitation volume increases. This is due to the high acidity (pH around 3 to 5) of the precipitation prevailing over northeastern part of the United States. Au exhibits a similar behavior. It is possible that strong Au source(s) in or around Adirondack regions maintains stable Au-enriched aerosol supplies even during precipitation events. None of these q values are close to 0.5 except Al at the Moss Lake site. It appears that these simple empirical formulae do not adequately describe the relationship between C_i and P_i values determined at the two sites because of complicated processes together with spatial and temporal variations. Consequently, the real quantitative connection between C_i and P_i needs further investigation.

5.1.3. Annual Wet Deposition Fluxes of Trace Inorganic Species

One of the commonly accepted methods for the estimation of the wet deposition flux, D_j, for a measured species, j, in wet deposition samples is the following:

$$D_j = \overline{C}_j \bullet P_T \qquad (5.3)$$

where

$$\overline{C}_j = \sum_{i=1}^{m} C_{ij} P_i \,/\, \sum_{i=1}^{m} P_i \qquad (5.4)$$

and

$$P_T = \sum_{i=1}^{n} P_i . \qquad (5.5)$$

$\overline{C}_j$ and P_T are estimators of the true precipitation-weighted mean concentration and the total precipitation volume for the period T, respectively. The subscripts, i and j denote the sample and a measured species in the sample, respectively. Generally, the number of sampling periods, n, is larger than the number of samples, m, due to missing concentration values for measured species in samples. However, this approach ignores the contributions from the sampling periods with missing C_i values. The effects of missing data can be significant if not properly addressed (Sirois, 1990).

In view of the inadequacy of this approach, an innovative linear-regression method was employed to estimate the annual wet deposition flux for measured species at the sampling sites. The dependent variables are their cumulative weekly wet deposition flux within the whole sampling period, while independent variables are the corresponding sampling weeks. In this approach, the estimations are not compromised by missing C_i values. The sampling periods with missing concentration values are equally treated as points in a regression line as ones without missing values. The linear regression results, and annual wet deposition fluxes are summarized in the **Tables 5.5** and **5.6** for selected species. As examples, acquisition of annual wet deposition fluxes of Zn and V at the Willsboro site regression results are shown in **Figures 5.1** and **5.2**. In these figures, the weekly wet deposition flux and cumulative wet deposition flux are shown together. The annual wet deposition flux is the product of the linear regression slope and fifty-two, i.e., one full year.

For comparison, the fluxes determined by the precipitation-weighted method are also tabulated in columns 5 of **Tables 5.5** and **5.6**. The average flux differences due to each method are 14% and -10% at the Moss Lake and the Willsboro sites, respectively. Therefore, the wet deposition fluxes calculated by precipitation-weighted method may be overestimated or underestimated because of missing concentration value perturbations and precipitation volume differences. Based on the magnitudes of the linear slopes and the wet deposition fluxes, the listed species may be divided into four groups in decending orders:

(1) SO_4^{2-} and NO_3^- (acidic anions);
(2) Na, Mg, Al, K, and H_3O^+;
(3) Mn, Zn and Br;
(4) V, Cr, Co, As, Sb, La, Sm, and Au.

These results indicate that acidic anions and electroneutral balancing cations are still the dominant species in wet deposition as they are in cloudwater. Although not determined in the wet deposition, Ca^{2+} and NH_4^+ would also be included in this group. The elements listed in group 3 and 4 elements originate mainly from anthropogenic sources and have non-negligible wet deposition concentrations. Elemental grouping pattern is similar at both sampling sites. Also, similar grouping pattern can be obtained if based on species concentration magnitudes as shown **Tables 5.1** and **5.2**. Therefore, the slopes are no more than indicators of relative concentration magnitudes of various inorganic species. Furthermore, this similar grouping pattern was also observed in cloudwater as discussed in Chapter 4. This implies that washout processes are not efficient enough to change the dissolved inorganic species concentration pattern formed by rainout, condensation, and evaporation processes that occur in clouds even though their concentrations decrease from clouds to wet deposition. Further, with a few exceptions, the high degree of linearity ($r^2>0.9$) of the regression lines implies the following relationships:

Table 5.5. Linear Regression Results and Annul Wet Deposition Flux (kg/ha·yr) at Moss Lake

Element	Slope	r^2	Flux*	Flux**
Na	0.0091	0.98	0.47	0.52
Mg	0.0030	0.98	0.16	0.17
Al	0.0030	0.75	0.16	0.15
K	0.0079	0.94	0.41	0.47
V	0.000030	0.86	0.0016	0.0016
Cr	0.000051	0.94	0.0026	0.0034
Mn	0.00031	0.97	0.016	0.019
Co	0.000018	0.97	0.00094	0.00093
Zn	0.00099	0.91	0.052	0.054
As	0.0000095	0.98	0.00049	0.00053
Br	0.00019	0.98	0.0097	0.011
Sb	0.0000083	0.98	0.00043	0.00048
La	0.0000069	0.90	0.00036	0.00047
Sm	0.00000031	0.95	0.000016	0.000016
Au	0.0000016	0.94	0.000085	0.000095
SO_4^{2-}	0.41	0.95	21	29
NO_3^-	0.31	0.96	16	22
H_3O^+	0.0098	0.92	0.51	0.66

* calculated by linear regression method;
** calculated by precipitation-weighted method.

Table 5.6. Linear Regression Results and Annul Wet Deposition Flux (kg/ha·yr) at Willsboro

Element	Slope	r^2	Flux*	Flux**
Na	0.0070	0.99	0.37	0.31
Mg	0.0034	0.98	0.17	0.13
Al	0.0033	0.94	0.17	0.14
K	0.030	0.85	1.6	1.2
V	0.000035	0.99	0.0018	0.0015
Mn	0.00012	0.96	0.0065	0.0061
Zn	0.0027	0.94	0.14	0.12
As	0.0000057	0.94	0.00030	0.00026
Br	0.000014	0.99	0.0072	0.0070
Sb	0.0000049	0.97	0.00021	0.00019
Sm	0.00000013	0.86	0.0000069	0.0000058
Au	0.000073	0.93	0.0000038	0.0000033
SO_4^{2-}	0.30	0.94	16	14
NO_3^-	0.25	0.98	13	10
H_3O^+	0.0097	0.67	0.50	0.86

* calculated by linear regression method;
** calculated by precipitation-weighted method.

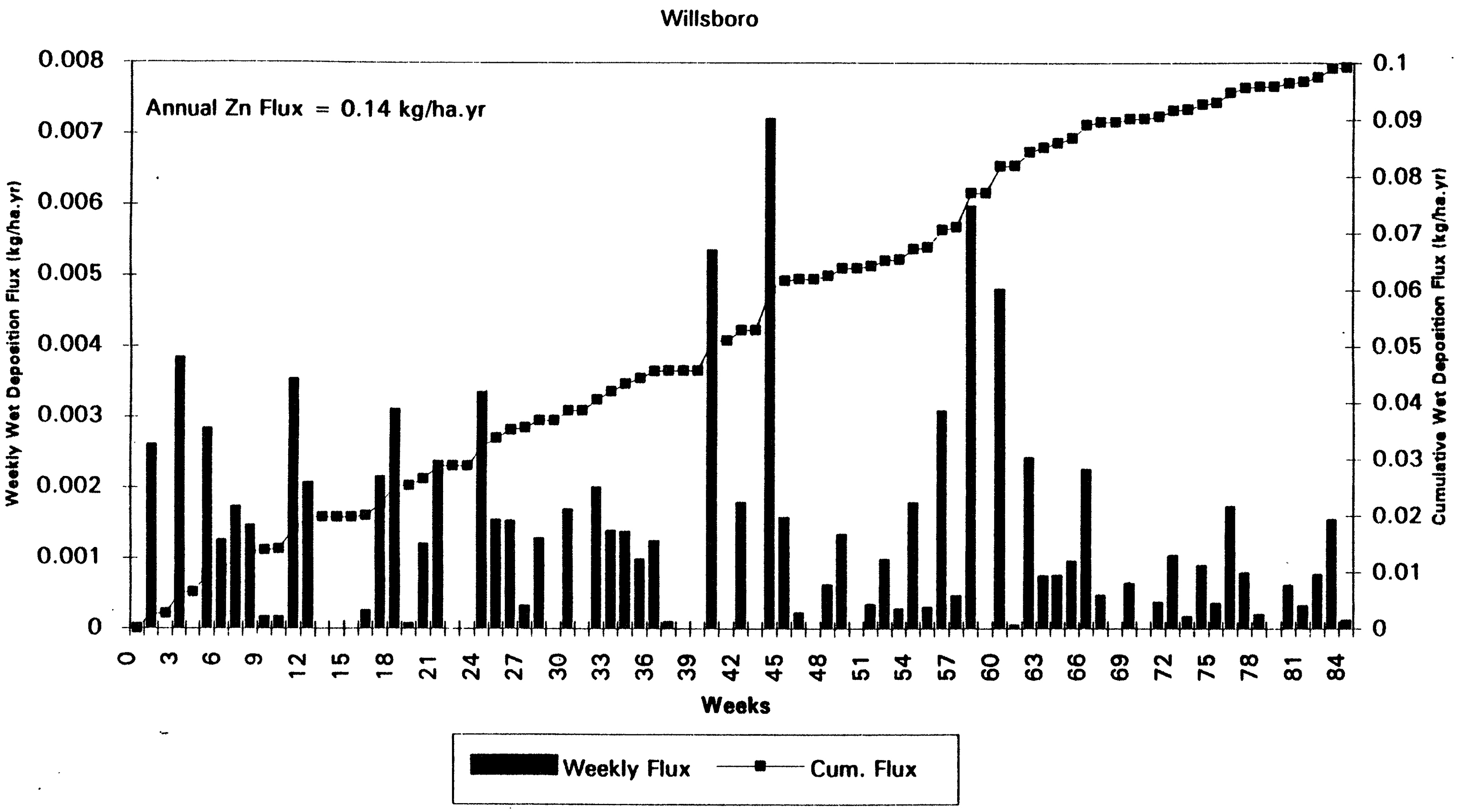

Figure 5.1. Wet Deposition Flux of Zn at the Willsboro Site.

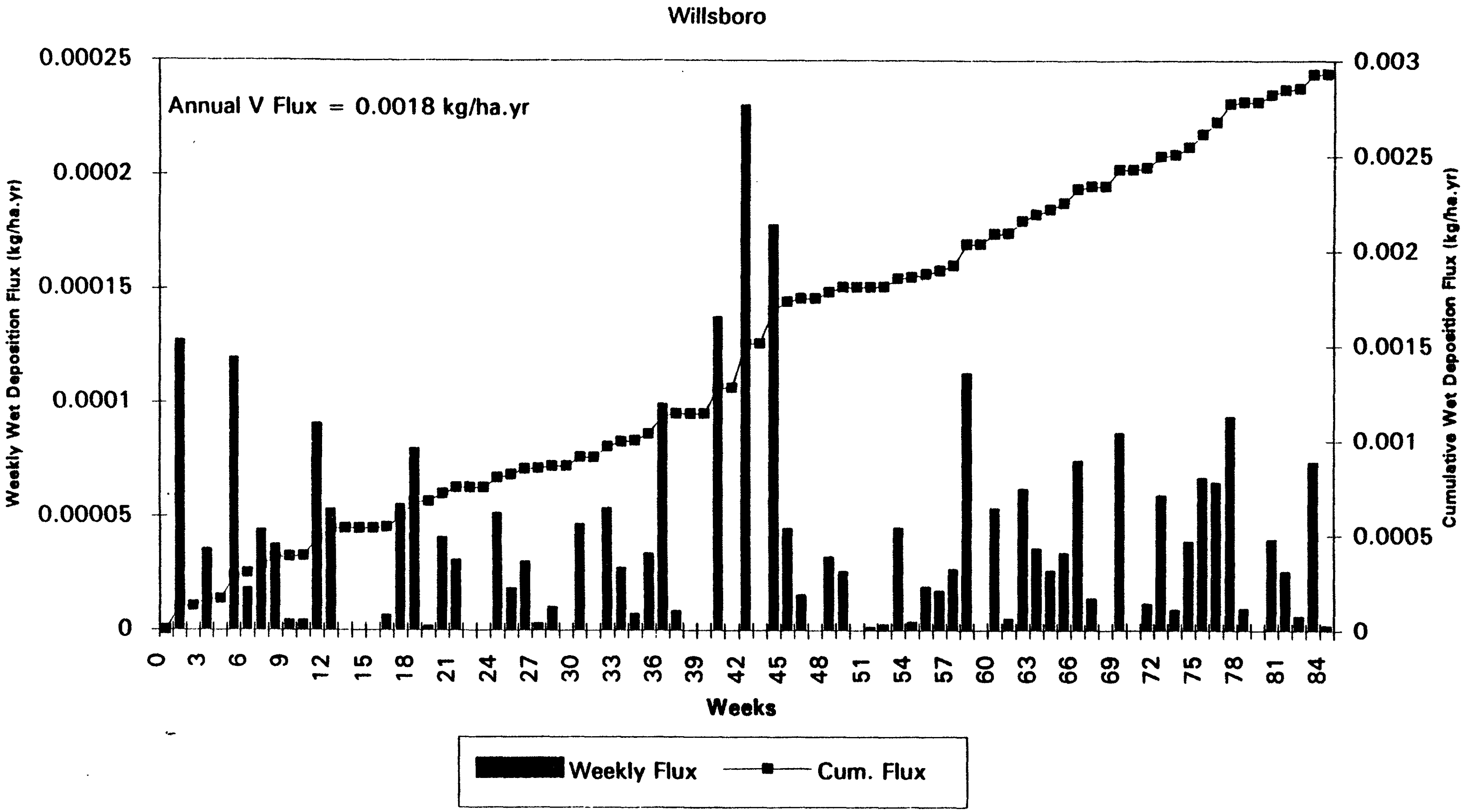

Figure 5.2. Wet Deposition Flux of V at the Willsboro Site.

(1) On average, the weekly wet deposition flux over the whole sampling period could be constant even though there are variations. This is because of influences from meterological, physicochemical and even variable source factors.;

(2) The constant wet deposition flux also indicates that variations of P_i and C_i cause their values cancel each other because of their inverse relationship.

These further imply that although deposition characteristics are frequently affected by rainout and washout processes, weekly total loadling of various dissolved inorganic species are evenly distributed over long periods of time.

5.2. Anthropogenic Influences and Wet Depositions

5.2.1. Comparison of Background Concentrations in Wet Deposition and in Antarctic Ice Core Samples

An objective of this study is to obtain the background concentrations for trace inorganic species in wet depositions in the Adirondack region. The background wet deposition concentrations are actually "site background concentrations" at a sampling site. They reflect the natural inorganic species loading from wet deposition as distinguished from anthropogenic source impact. Variable source impacts cause deviations from the background concentrations. Therefore, the most probable concentration, C_p, for a species as it appears in its measured concentration frequency distribution should be defined operationally as its "site background concentration" for the sampling site. The procedure for estimating the background concentration may be found in Chapter 3.

The C_p values tabulated in **Table 5.7** are background concentrations for listed species at the two sites during the sampling period. For comparison, the background concentrations of some trace elements in the Antarctic ice core samples are presented in columns 4 and 5 of **Table 5.7** (Keskin, 1995). As the table shows, the background concentrations of trace elements with anthropogenic origins, such as V, Zn, and As associated with the post-industrial era, are approximately two folds higher in concentration than those associated with the pre-industrial era. Background concentrations in wet deposition at both sites are comparable to or greater than those in the Antarctic ice core samples. This is a clear indication of anthropogenic influences. Elements such as Na, Al, and Cr, have lower background concentrations in wet

Table 5.7. Comparison of Background Concentrations of Trace Elements in Wet Deposition and Antarctic Ice Core Samples (ng/mL)

Element	Moss Lake	Willsboro	Pre-industry*	Post-industry**
Na	22	22	23	26
Mg	6.2	14	2.4	3.4
Al	4.8	3.3	4.4	7.7
K	18	26	2.2	0.91
V	0.080	0.13	0.010	0.019
Cr	0.17	-	0.23	0.42
Mn	0.48	0.42	0.055	0.095
Zn	2.9	2.9	0.55	0.86
As	0.023	0.022	0.001	0.004
Br	0.54	0.42	0.009	0.052
Sb	0.024	0.016	0.019	0.021

-: data are not available;
*between the beginning of 16th century to 20th century;
**between the beginning of 20th century to 1989 A.D.

depositions than in the Antarctic ice core samples. The reason for this is that both total dissolved and particulate elemental concentrations were contained in ice core samples, while only dissolved elemental concentrations were determined in wet depositions. Therefore, suspended mineral contributions to the elemental concentrations are excluded in wet depositions but not in ice core samples. Further, background elemental concentrations at both sites are similar to each other as shown in columns 2 and 3 of **Table 5.7**. This is because that the two sites are all in remote areas, although the Willsboro site is close to an urban area - Burlington, VT. Excluding local urban source influences, the site background concentrations for various trace elements in wet deposition are, therefore, expected to be similar.

5.2.2. Comparison of Median Concentrations and Annual Wet Deposition Fluxes

As mentioned, the Moss Lake and Willsoboro sampling sites are located in remote areas though the latter is relatively close to Burlington, Vermont. A comparison of median concentrations for several anthropogenic trace elements is listed in **Table 5.8**. Although median concentrations of some elements such as Zn, are rather high at both sampling sites, concentrations for most other elements with anthropogenic origins fall well within the remote concentration scale. Since the median concentrations in the table were compiled more than one decade ago (Galloway *et al.*, 1982), this may indicate that there has been an increase in atmospheric loading during this period for some trace elements originating from anthropogenic emissions. In addition, Zn and V have higher median concentrations in Willsboro than in Moss Lake. Referring to **Figure 5.3**, the annual wet deposition fluxes of marker elements (V, Zn, As, Br, Sb) for urban area emissions are given for the two sites. The annual wet deposition flux of Zn at Willsboro is almost three times greater than at Moss Lake. Furthermore, the annual wet deposition flux for V at Willsboro (0.0018 kg/ha.yr) is also slightly higher than at Moss Lake (0.0016 kg/ha.yr). This also indicates that the Willsboro site, which is near to the Burlington metropolitan area, receives a higher source impact from Zn and V emissions. This result agrees with other aerosol studies in which the Willsboro site was found to be under an urban influence since it is in a vicinity of metropolitan Burlington area (Garabedian and Poirot, 1994; Olmez, 1994). In fact, aerosol precursors bearing Zn and V, which are emitted from high temperature combustion sources (HTCS), are also found in wet deposition. These sources include municipal incinerators, motor vehicles, residential oil furnaces and OFPP. Although the Willsboro site receives less precipitation than the Moss Lake site, the strong local source impact of Zn and V at Willsboro site

Table 5.8. Comparison of Median Concentrations of Trace Elements in Wet Deposition (ng/mL)

Element	Urban*	Rural*	Remote*	Moss Lake	Willsboro
V	42	9	0.16	0.14	0.25
Mn	23	5.7	0.19	1.2	0.84
Zn	34	36	0.22	5.3	8.1
As	5.8	0.29	0.019	0.042	0.040
Sb	-	-	0.034	0.040	0.034

*: data are from Galloway, J. N., *et al.*, (1982);
-: data are not available.

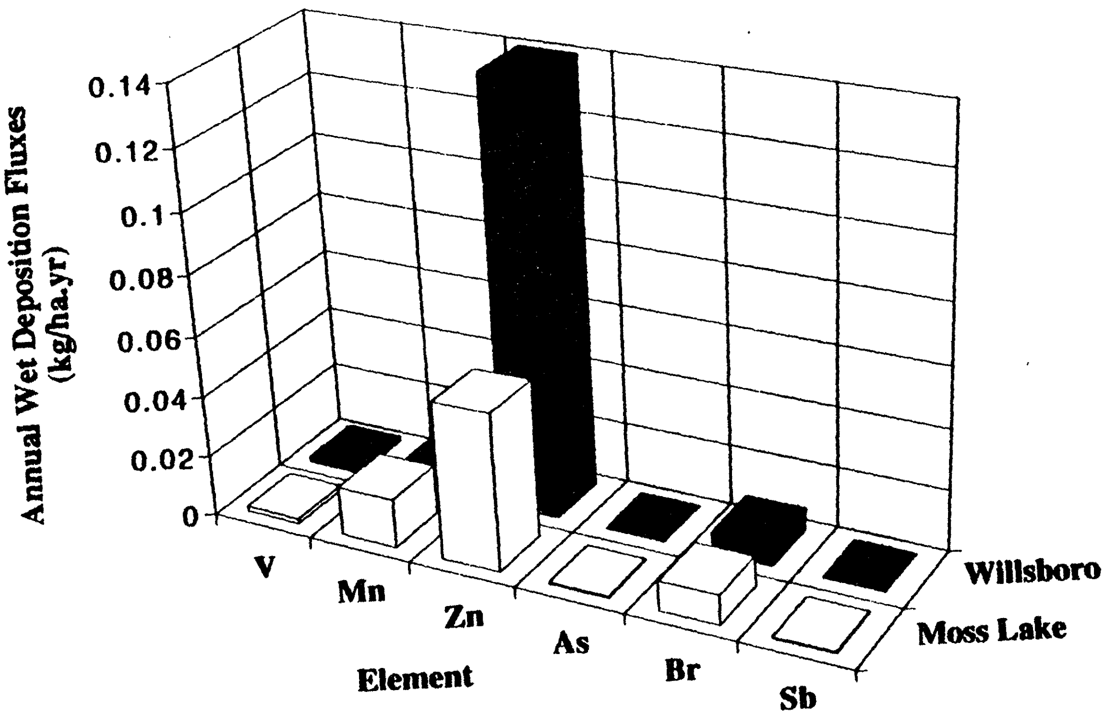

Figure 5.3. Comparison of Annual Wet Deposition Fluxes of Some Trace Elements at the Moss Lake and the Willsboro Sites.

causes their higher loading from wet deposition as compared with the more remote and wetter Moss Lake site. The local source impacts of other elements (As, Br, and Sb) are not as strong as Zn and V. Their sources are more regional, and lower precipitation in Willsboro site may actually reduce their contributions to the wet deposition there.

There have been numerous studies on SO_4^{2-} and NO_3^- content in atmospheric depositions. **Table 5.9** gives ranges of SO_4^{2-} and NO_3^- annual wet deposition fluxes from different studies (Atteia, 1994; Zemba, *et al.*, 1988). The geological distribution of these studies includes mid- or northern Europe, northeastern U. S., and eastern Canada. These industrial areas are considered to have serious acid rain problems, though the sampling sites are all in remote areas. The annual deposition fluxes of SO_4^{2-} and NO_3^- determined in Moss Lake and Willsboro sites are also tabulated for comparison. As the table indicates, Moss Lake has higher annual wet deposition fluxes of SO_4^{2-} and NO_3^- than Willsboro. The annual wet deposition fluxes of SO_4^{2-} and NO_3^- at the Moss Lake site are within the deposition flux range of northeastern U. S., and eastern Canada. Fluxes at the Willsboro site are below the lower limits of these regional deposition ranges. This can be attributed to the higher precipitation volumes at Moss Lake. Annual wet deposition fluxes of SO_4^{2-} at both sites are comparable to those in France East, Germany (Hesse), and Holland. These sites are known to be heavily influenced by emissions from coal burning utilities and industries in those regions. The annual wet deposition fluxes of NO_3^- at both sites are higher than at most European sites. The cause of this may be the additional loading originating from oil-burning emissions that are prevalent over northeastern U. S. As previous studies indicate, the origins of SO_4^{2-} and NO_3^- found in two sites can be generally traced back to distance sources, such as air masses originating from the south or southwest and west or northwest, i.e., highly industrial regions in Ohio River valley of the U. S. and Ontario province of Canada. In-cloud formation of these species over the region is very important when the meteorological conditions are suitable, especially for SO_4^{2-} (Johnson, *et al.*, 1987; Faust *et al.*, 1993).

5.3. Is There Any Present Danger of Inorganic Species Found In Wet Deposition to Human or Other Organisms' Welfare?

As stated in Chapter 1, a goal of this study is to investigate the current impact of atmospheric wet deposition on watersheds within the Adirondacks. To understand whether the concentration levels for specific inorganic species in wet deposition exceed recommended safety limits for both drinking water and freshwater aquatic organisms, the background and maximum concentrations for some relevant species determined at both

Table 5.9. Comparison of Annual Wet Deposition Fluxes (kg/ha·yr) of SO_4^{2-} and NO_3^- in This Study with Other Studies

Study Site	SO_4^{2-}	NO_3^-
Western Switzerland*	4.6-8.6	4.4-7.5
France West*	4.8-6.4	0.8-2.4
France East*	18-24	3.8-6.2
Austria*	7-15	3-7
Germany (Hesse)*	12.3-21.9	4.5-7.7
Holland*	6-70	5.6-34
Finland*	3-10	1-3
Northeastern U. S. and Eastern Canada**	20-30	15-20
Moss Lake	21	16
Willsboro	16	13

* Data are from Atteia, O. (1991).
** Data are from Zemba, *et al.* (1988).

sites were compiled in the **Table 5.10**. The EPA's National Ambient Water Quality Criteria (AWQC) for freshwater and EPA's National Primary Drinking Water Standards are listed in columns 6 and 7 for comparison. The background and maximum concentration levels in the wet deposition samples are all well below the established EPA limits for both drinking water and freshwater except one high Zn value in the Willsboro site. This is because that the Willsboro site receives strong local Zn source impact as aforementioned. The amounts of these potentially toxic inorganic species found in wet depositions are probably not directly harmful to man or other organisms. However, their cumulative toxic effects must be assessed based on risk analysis models.

5.4. Washout Ratios at the Moss Lake Site

At the Moss Lake sampling site, five wet deposition episodes (two snow events and three rain events) were singled out for washout effect analysis. These episodes all occurred in one day during a sampling week. Their daily elemental concentrations in $PM_{2.5}$ aerosols were also available. The relevant information about these five wet deposition episodes is summarized in **Table 5.11**. Only seven trace elements measured have both concentrations in $PM_{2.5}$ aerosols and wet deposition; they are Na, Al, Mn, Zn, As, Br, and La. The dimensionless washout ratio (W), is based on the following definition:

$$W = \frac{C_w \rho}{C_a} \qquad (5.6)$$

where C_w and C_a are elemental concentrations in wet deposition and in $PM_{2.5}$ aerosol, respectively. For estimation simplicity, air density ρ is chosen as $1161 g/m^3$ at an atmospheric pressure of 1 atm and a temperature of 300 K condition.

The calculated W values for these elements are given in **Figure 5.4**. These values may not be real washout ratios since the wet deposition and aerosol concentrations are not the total wet deposition and suspended particulate concentrations. As interpreted by Peirson et al., a large W value for an element generally indicates its higher concentration at the altitude where rain first forms (Peirson *et al.*, 1973). The W values for the elements in snow are generally higher than in rain as **Figure 5.4** indicates. This is because the snow rimming process in which the supercooled CCN captured by snow crystals, enhances the enrichment of various species in snow crystals. Also, snow crystals have a porous surface morphology and usually have higher capture efficiency for suspended aerosols than rain droplets (Collett, *et al.*, 1991).

Table 5.10. Comparision of Background and Maximum Concentrations of Trace Inorganic Species in Wet Deposition with EPA's National AWQC and MCLG (ng/mL)

Element	Moss Lake		Willsboro		Drinking Water*	Fresh Water**
	Background	Maximum	Background	Maximum		
Cr	0.17	3.2	-	-	100	1716/221
Zn	2.9	53	2.9	150	-	120/110
As	0.023	0.26	0.022	0.22	50	360/190
Sb	0.024	0.12	0.016	0.13	6	-
SO_4^{2-}	620	9920	670	17000	400000	-
NO_3^-	970	8990	1000	8500	10000	-

-: data are not available;
*Maximum Contaminant Level Goal (MCLG) tabulated in EPA National Primary Drinking Water Standards (February 1994);
**Criterion Maximum Concentration (CMC)/Criterion Continuous Concentration (CCC) listed in 40 CFR Part 131, EPA's numerical criteria for priority toxic pollutants in fresh water (July 1994). The detailed definition of the CMC and CCC can be found in the same document.

Table 5.11. Sampling Information of Five Wet Deposition Episodes at Moss Lake

Sampling Date	10/27/1991	12/29/1991	01/04/1992	09/03/1992	07/02/1993
Wet Deposition Episode Lasting Time (hour)	2	14	8	12	2
Deposition Type	rain	snow	snow	rain	rain
Deposition Volume (mL)	301.4	737.5	227.4	3907.1	140.1
Back Wind Trajectory	SW	W	S, SE	SW	SE
Daily $PM_{2.5}$ Elemental Concentration Data	available	available	available	available	available

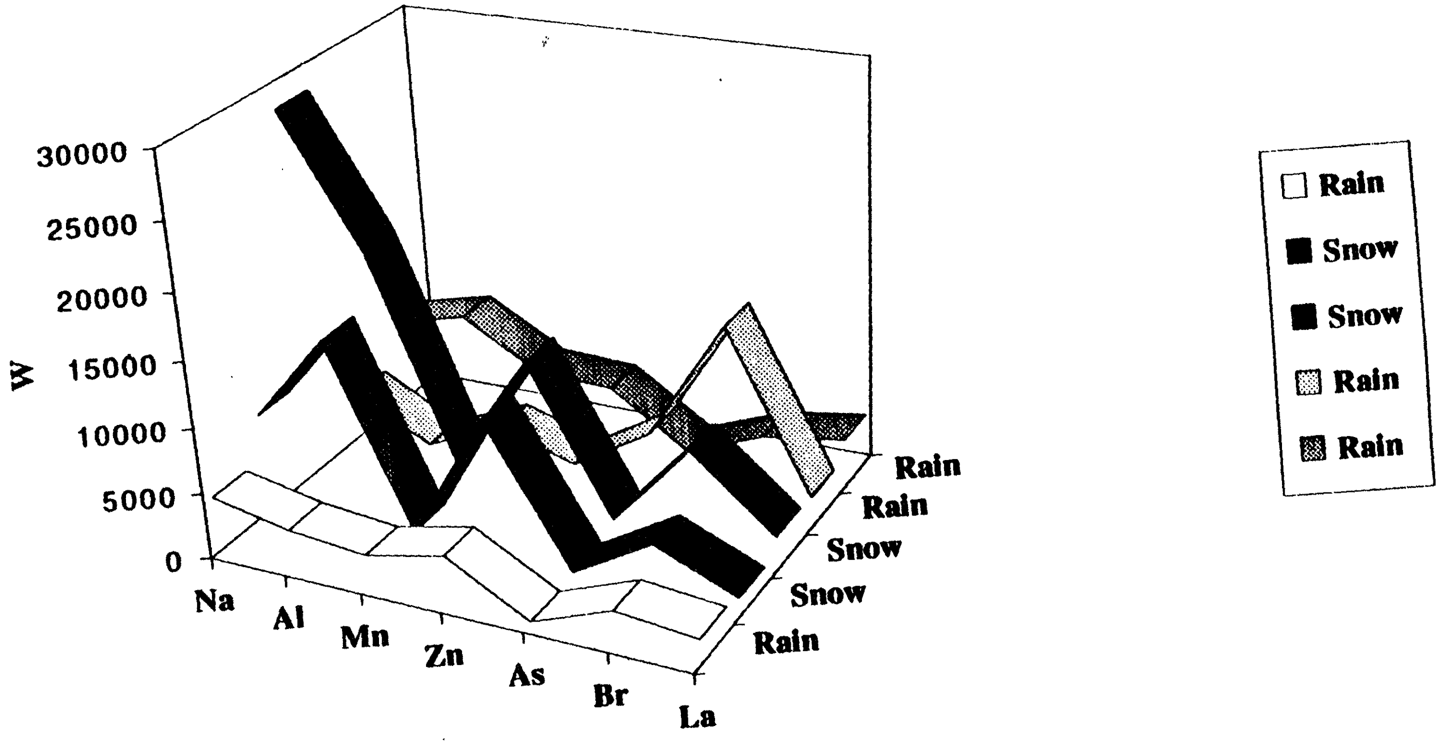

Figure 5.4. Comparison of Washout Ratios at the Moss Lake Site.

Chapter 6
Summary and Future Studies

6.1. General Summary

This thesis consists of two independent studies that are both related to biogeochemical cycling of trace inorganic species: cloudwater and rainwater studies at Mt. Washington, New Hampshire and wet deposition studies in the Adirondack region, New York. They focus on the roles that some trace metal ions and their complexes play in the solar radiation absorption of clouds and the aqueous oxidation of S(IV) species. Wet deposition characteristics such as background concentrations and annual wet deposition fluxes of various trace inorganic species in the Adirondack region were also determined to relate any anthropogenic influence.

To accomplish these objectives, simultaneous collections of cloudwater and rainwater samples from different precipitating clouds were performed at the Lakes of Clouds Facility of the Appalachian Mountain Club (AMC), located 1536 m above sea level on the southern slope of the summit cone of Mt. Washington (1917 m), New Hampshire, over the summers of 1988, 1989, and 1990 using the AMC/WPI (Appalachian Mountain Club/Worcester Polytechnic Institute) Passive Cloud Water Collector. Concurrent rainwater samples were collected at AMC's Pinkham Notch Mountain Resource Center at 610 m on the eastern slopes of Mt. Washington by a Hubbard Brook-type bulk precipitation collector. The wet deposition sampling sites in the Adirondack were at Moss Lake and Willsboro. Weekly integrated wet deposition samples were collected from October 1991 to October 1994 at the Moss Lake site, and from March 1992 to October 1993 at the Willsboro site employing Model APS Acid Precipitation Samplers (Graseby Andersen, GA). These cloudwater, rainwater, and wet deposition samples were sent to the Environmental Research & Radiochemistry (ER&R) Division of the Nuclear Reactor Laboratory (NRL) at Massachusetts Institute of Technology (MIT) for analyses. Instrumental Neutron Activation Analysis (INAA) coupled with a freeze-drying pre-concentration technique and ion chromatography (IC) analytical methodologies together with the use of chemometrics proved to be effective for the determination and characterization of dissolved trace inorganic species in cloudwater and wet deposition. The following sections summarize the major study results and recommendations and suggestions for further research.

6.2. Major Results from Cloudwater and Rainwater Studies at Mt. Washington and Recommendations for Future Research

The concentration frequency distributions for the inorganic species in cloudwater are found to be approximately log-normal ($DN < Q$, observed $\alpha > 0.05$) based on the two-sided K-S test at a significant level of α=0.05. Based on the magnitudes of their geometric mean concentrations, the inorganic species can be classified into three groups:

Group 1: SO_4^{2-}, NO_3^-;
Group 2: NH_4^+, Cl^-, H_3O^+, Na, Mg, Al, K, Ca, Fe;
Group 3: Zn, Mn, Sc, V, Cr, As, Br, Sb, La, Sm, and Au.

Species listed in group 1 are the dominant anions that exist in cloudwater and are closely related to cloudwater acidity. Group 2 species are major electroneutral balancing cations and are the dominant elements in cloudwater. The Cl^- is also within the group. The third group contains trace elements of both anthropogenic and crustal origins. These results agree with findings in cloud chemistry studies at the Mt. Mitchell, North Carolina (Saxena and Lin, 1990), which covered only major cations and anions such as H_3O^+, NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, NO_3^-, and Cl^-. Some trace elements that occur in cloudwater and may have roles in some physicochemical processes could not be determined from their studies. To date, this thesis work is the most comprehensive cloud chemistry study, especially with respect to the broad range of trace elements covered. These inorganic species are either from their aerosol precursors or products of gaseous and aqueous phase reactions in the atmosphere.

Principal component factor analysis (PCFA) was applied to the inorganic species concentration data set of fifty-three cloudwater samples to identify major factors responsible for concentration patterns in cloudwater. Three major factors were identified, which together explain 77.8% of the total variance of inorganic species concentrations in fifty-three cloudwater samples. They are a background factor, an acidity factor, and a crustal factor. Interestingly, both V and Mn have non-negligible loading on the acidity factor.

The correlation coefficients between V and SO_4^{2-}, and V and NO_3^- are 0.67 and 0.72, respectively. The association of V with the acidity factor may indicate its involvement in the following thermodynamically feasible redox reaction:

$$2VO_2^+ + HSO_3^- + H_3O^+ \rightarrow 2VO^{2+} + SO_4^{2-} + 2H_2O$$

The extent to which this reaction accounts for total S(IV) oxidation is unknown. However, if the above reaction proves to be kinetically feasible, it will provide another possible pathway of S(IV) to S(VI) transformation.

It is also interesting to observe that the Mn, whose major source is wind-blown dust, is also associated with the acidity factor. The correlation coefficient between the Mn and SO_4^{2-} is 0.61 in this study. There is also a positive correlation between Mn concentration, SO_4^{2-} concentration, and cloudwater acidity during two dynamic cloud episodes. Although it needs to be proved kinetically, previous studies and proper reasoning may infer an involvement of Mn in the S(IV) to S(VI) transformation through the following mechanism:

$$
\begin{aligned}
&Mn(II)-L \xrightarrow{h\nu} Mn(I)+L\bullet \\
&Mn(I) or L\bullet + O_{2(aq)} \rightarrow Mn(II) or L + O_2^- \bullet \\
&2O_2^- \bullet + 2H_3O^+ \rightarrow H_2O_2 + O_2 + 2H_2O \\
&H_2O_2 + HSO_3^- \rightarrow SO_4^{2-} + H_3O^+
\end{aligned}
$$

The effect of transition metals and their organo-complexes on solar radiation absorption by a 0.5 km fair-weather cumulus cloud was estimated based on the Beer-Lambert Law and the more sophisticated Mie Scattering Theory. The results indicate a difference between solar absorption by pure cloudwater and by cloudwater containing transition metals along with their complexes. However, it may only represent an extreme case that only water vapor condensation is responsible for cloudwater droplet growth. Therefore, it is too early to state that transition metals along with their complexes are responsible for the observed excess solar absorption by clouds. Until further evidence is available, the cloud absorption anomaly of solar SW radiation will continue to be debated in the scientific community. Finally, the dilution and washout effect may be responsible for the observed concentration changes of various inorganic species from cloudwater to rainwater.

The future study with respect to the involvement of V and Mn in in-cloud oxidation of S(IV) species should be examined kinetically. For relevant experimental procedures, one may refer to the experiments performed by Zuo and Hoigne, and Faust et al. (Zuo and Hoigne, 1993; Faust, et al., 1993). These experiments are related to the catalytic role of Fe(III)-organo complex in S(IV) oxidation in cloudwater and fogwater. The role that transition metal ions and their complexes play in excessive solar radiation absorption by clouds also needs to be further examined. A suggestion for a future experiment is the measurement of direct spectral absorption by cloudwater droplets for incident solar radiation at different wavelengths. Although previous spectral studies on the absorption and scattering features of clouds in the tropical atmosphere suggest that it is water-like (Pilewskie and Valero, 1995), the spectral absorption differences between pure liquid water and cloudwater have not been extensively examined. Finally, the concurrent sampling of cloudwater and rainwater should be extended. These include measurements of the concentrations of various inorganic species in aerosols at same altitude together with the determination of aerosol and cloudwater droplet size distribution.

6.3. Major Results from Wet Deposition Studies in the Adirondack Region and Suggestions for Future Wet Deposition Studies

K-S tests were performed for each species determined in wet depositions from each sampling site. The frequency distributions of their concentrations and the weekly integrated precipitation volumes from each site followed log-normal distributions. Lanthanum (La) ($DN=Q$) at Moss Lake and samarium (Sm) ($DN>Q$ and $\alpha<0.05$) at both sites failed the K-S tests. There is an inverse relationship between trace inorganic species concentration and precipitation except for Au and H_3O^+, but it is neither an exactly hyperbolic nor an exactly inverse half-power relationship. The annual wet deposition fluxes for various inorganic species were calculated empolying a linear regression method (cumulative weekly wet deposition flux versus sampling week) since the fluxes calculated by a precipitation-weighted method deviated approximately by ±12% from the former method due to missing concentration value perturbation. The slopes of the regression lines for various inorganic species become indicators of their relative magnitudes in wet deposition. Moreover, a similar trace inorganic grouping behavior was observed in wet deposition when compared with cloudwater. This implies that washout processes are not efficient enough to change the pattern of the dissolved inorganic species concentrations formed by rainout, condensation, and evaporation processes occur in clouds, although their concentrations decrease from clouds to wet deposition. The high degree of linearity ($r^2>0.9$) of the regression lines implies that weekly total loading of various dissolved inorganic species is evenly distributed even though deposition characteristics are frequently affected by the variability of emission sources, rainout, and washout processes.

The site background concentrations of selected inorganic species were calculated and found to be similar at both sites. They do show, however, anthropogenic influences when compared to background concentrations of various inorganic species as measured in Antarctic ice core samples. Still, median concentrations for some trace elements with anthropogenic origins do fall well within the range of remote concentrations. Wet deposition fluxes of Zn and V are higher at the Willsboro site than at the Moss Lake site. This is attributed to a local urban influence on the Willsboro from the nearby metropolitan Burlington area. Compared to SO_4^{2-} and NO_3^- wet deposition fluxes in European sites, the Moss Lake and Willsboro have high SO_4^{2-} and NO_3^- wet deposition fluxes that are typical of those occurring in the northern U. S. and eastern Canada. The Moss Lake site has even higher fluxes because of its higher precipitation volume. Concentrations of some potentially toxic species in wet depositions are well below recommended safety limits for both drinking water and freshwater aquatic organisms, indicating no immediate threat to human or aquatic organisms. Finally, washout ratios for some trace elements were determined from five wet deposition episodes at the Moss Lake with respect to their dissolved concentrations in wet deposition and their and $PM_{2.5}$ aerosol concentrations. Results show that snow generally has higher washout ratios than rain due to its surface morphology, indicating higher wet removal efficiency.

Current wet deposition studies world-wide lack unified sampling, measurement, and data interpretation methodologies. Durst *et al.* have outlined recommended procedures for sampling and described procedures for ion chromatographic determination of major anions (Durst, *et al.*, 1991). Electrometric determination of pH in atmospheric wet deposition was also prescribed (Durst, *et al.*, 1994). The procedures that are recommended by International Union of Pure and Applied Chemistry (IUPAC), should be used as guidelines for any future wet deposition studies. The innovative method of calculating annual wet deposition flux using linear regression applied here is recommended for future wet deposition studies. Also, relevant risk models should be developed to assess the cumulative effects of some potentially toxic elements and the impact of their atmospheric wet depositions.

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Appendix A:

Trace Elemental Concentrations (ng/mL), Major Anion and Cation Concentrations (ng/mL), and pH Values in Cloudwater and Rainwater Collected at the Mt. Washington, New Hampshire

* The concentration of Au is in pg/mL;

** Example samples: 890914CN2, 890914RN2, 890914RN2P

89: Year

09: Month

14: Day

C: Cloudwater

R: Rainwater

N2: Cloud Event Number

P: Rainwater collected at the AMC's Pinkham Notch Mountain Resource Center (610 m elevation)

Element	880617RN1	+/-	880623CN1	+/-	880623CN2	+/-
Na	260	20	160	13	74	7
Mg	24	13	230	51	44	21
Al	7.7	2.7	120	8	92	7
Cl	94	52	45	36	48	31
K	360	67	410	58	120	50
Sc	0.1	0.01	0.18	0.01	0.14	0.01
Ti			9.3	8.9	17	7
V	0.18	0.04	0.94	0.11	0.23	0.06
Cr	0.62	0.07	0.89	0.07	0.41	0.06
Mn	6.3	0.1	23	0.3	4	0.1
Fe	42	10	71	10	42	9
Co	0.056	0.022	0.21	0.03		
Zn	200	19	35	3	12	1
As	0.45	0.07	1.2	0.1	0.41	0.07
Se			0.51	0.12		
Br	10	3	7.8	2.5	12	4
Rb	0.16	0.12	1.9	0.2	0.34	0.13
Sr	7.3	3.3	4.7	2.8		
Mo			0.097	0.058		
Cd	1.3	0.9				
In						
Sb	0.12	0.01	0.4	0.03	0.11	0.01
Cs						
Ba	3.9	2.1	11	2	2.1	1.4
La			0.044	0.006	0.063	0.006
Ce			0.066	0.037	0.074	0.032
Nd					0.12	0.08
Sm	0.004	0.001	0.012	0.001	0.007	0.001
Au	0.41	0.05	0.55	0.1	0.19	0.03
Th			0.022	0.007	0.32	0.02
U						
Ca					100	
NH4					310	
SO4					1800	
NO3					850	
pH	3.90		4.25		4.32	

Element	880625CN5	+/-	880625CN6	+/-	880625RN2	+/-
Na	130	11	34	5	620	43
Mg	110	43			270	49
Al	140	9	23	4	590	27
Cl	28	19			57	45
K	160	41			370	79
Sc	0.19	0.01	0.091	0.007	0.96	0.06
Ti					16	8
V	3	0.2	0.21	0.05	6.9	0.4
Cr	0.36	0.06	0.15	0.06	2.1	0.1
Mn	7.3	0.1	1.6	0.04	32	0.5
Fe	66	9	26	9	390	21
Co	0.11	0.02			0.36	0.04
Zn	12	1	9.3	0.9	38	4
As	0.52	0.07	0.094	0.029	1.9	0.2
Se	0.14	0.1			1.1	0.2
Br	8.3	2.6	2.1	0.7	18	6
Rb	0.43	0.13			1.4	0.3
Sr						
Mo	0.068	0.048			0.3	0.1
Cd	0.063	0.05				
In	0.005	0.004				
Sb	0.59	0.04	0.037	0.004	0.82	0.06
Cs					0.043	0.029
Ba	4.2	1.7			7.3	3.1
La	0.082	0.008	0.012	0.003	0.45	0.03
Ce	0.14	0.03			0.99	0.07
Nd					0.16	0.09
Sm	0.012	0.001	0.003	0.001	0.068	0.006
Au	0.2	0.04	0.14	0.03	0.7	0.12
Th	0.009	0.006			0.084	0.011
U					0.035	0.012
Ca	300		900			
NH4	1400		3300			
SO4	6200		13200			
NO3	8020		8560			
pH	3.88		3.90		4.26	

Element	880625RN3	+/-	880625RN4	+/-	880626CN1	+/-
Na	31	5	92	9	46	5
Mg			93	34	48	26
Al	24	4	160	9	31	3
Cl			31	20		
K	80	18	190	49	62	28
Sc	0.079	0.007	0.27	0.02	0.11	0.01
Ti						
V	0.066	0.037	0.39	0.07	1.5	0.1
Cr	0.17	0.06	0.26	0.06	0.14	0.06
Mn	0.59	0.02	5.5	0.1	4.4	0.1
Fe	30	9	79	9	19	9
Co			0.059	0.022		
Zn	3.5	0.4	5.4	0.5	6	1
As	0.033	0.009	0.23	0.04	0.41	0.05
Se					0.095	0.094
Br	1.4	0.5	6.9	2.1	3.4	1.2
Rb			0.48	0.1	0.11	0.07
Sr						
Mo						
Cd			0.016	0.03		
In						
Sb	0.045	0.004	0.15	0.01	0.12	0.01
Cs						
Ba			4.5	2		
La	0.012	0.003	0.13	0.01	0.025	0.003
Ce			0.24	0.04		
Nd	0.15	0.05				
Sm	0.003	0.0001	0.018	0.002	0.004	0.001
Au	0.25	0.04	0.095	0.025	0.058	0.017
Th			0.017	0.006		
U						
Ca					170	
NH4					630	
SO4					2900	
NO3					1280	
pH	4.50		4.38		4.40	

Element	880626CN2	+/-	880626CN3	+/-	880626CN4	+/-
Na	55	6	36	5	22	4
Mg	24	11	26	9	12	7
Al	120	7	190	10	28	3
Cl						
K	160	43	92	28	34	19
Sc	0.25	0.02	0.39	0.03	0.11	0.01
Ti	16	5	12	4	8.6	3.7
V	0.6	0.06	0.57	0.06	0.14	0.04
Cr	0.52	0.06	0.5	0.06	0.22	0.06
Mn	3.3	0.1	2.8	0.1	1.1	0.03
Fe	90	10	120	10	29	9
Co	0.006	0.021				
Zn	15	1	4.4	0.4	9.4	0.9
As	0.56	0.07	0.77	0.09	0.3	0.04
Se						
Br	4.1	1.4	2	0.7	2.5	0.8
Rb	0.45	0.13	0.38	0.11		
Sr						
Mo	0.06	0.05	0.054	0.039		
Cd						
In						
Sb	0.097	0.009	0.083	0.007	0.065	0.006
Cs						
Ba			1.3	1.1	2.7	1.7
La	0.11	0.01	0.13	0.01	0.015	0.003
Ce	0.13	0.04	0.18	0.03		
Nd						
Sm	0.017	0.002	0.017	0.002	0.004	0.001
Au	2.1	0.3	0.17	0.03	0.2	0.03
Th	0.018	0.006	0.062	0.007		
U						
Ca	70		50		20	
NH4	200		280		160	
SO4	1300		1400		900	
NO3	700		620		510	
pH	4.60		4.50		4.79	

Element	880630RN1	+/-	880702CN1	+/-	880702CN2	+/-
Na	28	4	69	7	89	8
Mg	22	19	73	21	23	8
Al	31	4	230	11	200	10
Cl	6.8	5.7	18	16	8.1	7.2
K	87	23	180	49	190	44
Sc	0.092	0.008	0.42	0.03	0.34	0.02
Ti	7.6	3.3	16	6	14	5
V	0.44	0.05	0.91	0.08	0.99	0.08
Cr	0.13	0.06	0.57	0.07	0.8	0.07
Mn	1.1	0.03	8.2	0.1	2.8	0.1
Fe	32	9	130	11	100	11
Co			0.059	0.023		
Zn	5.4	0.6	8.5	0.9	5.4	0.5
As	0.17	0.03	0.34	0.05	0.23	0.03
Se						
Br	4	1	6.6	2.1	4.4	1.5
Rb	0.19	0.08	0.97	0.16	0.68	0.2
Sr						
Mo			0.069	0.047	0.036	0.035
Cd						
In						
Sb	0.04	0.004	0.13	0.01	0.15	0.01
Cs						
Ba					2	1.4
La	0.03	0.004	0.14	0.01	0.087	0.007
Ce			0.29	0.04	0.14	0.03
Nd			0.12	0.08	0.25	0.06
Sm	0.004	0.001	0.026	0.002	0.014	0.001
Au	0.2	0.03	0.24	0.06	0.39	0.05
Th			0.03	0.007	0.05	0.01
U			0.02	0.01		
Ca	50		150		50	
NH4	180		100		220	
SO4	1200		1100		800	
NO3	800		1010		560	
pH	4.25		4.65		4.72	

Element	880702CN3	+/-	880702CN4	+/-	880712CN1	+/-
Na	54	6	190	15	260	20
Mg	80	26	120	34	260	49
Al	98	6	290	15	520	26
Cl	6.7	6	22	14		
K	150	35	95	33	460	92
Sc	0.16	0.01	0.39	0.03	0.56	0.04
Ti	8.8	4.5			36	14
V	0.43	0.06	1.2	0.1	3.4	0.2
Cr	0.29	0.06	1.1	0.1	2.1	0.1
Mn	2.4	0.05	4.8	0.1	43	1
Fe	51	9	110	11	280	15
Co	0.045	0.022	0.04	0.02	0.45	0.03
Zn	8	0.8	18	2	49	5
As	0.18	0.03	0.96	0.1	1.3	0.1
Se			0.13	0.11	1.7	0.2
Br	4	1	6.6	2.1	20	6
Rb	0.35	0.12	0.64	0.21	1.7	0.2
Sr						
Mo			0.041	0.039	0.13	0.03
Cd						
In					0.013	0.009
Sb	0.12	0.01	0.28	0.02	0.82	0.06
Cs					0.078	0.025
Ba			3	2	9	3
La	0.045	0.005	0.14	0.01	0.48	0.03
Ce			0.2	0.04	0.82	0.06
Nd			0.17	0.06	0.74	0.13
Sm	0.008	0.001	0.022	0.002	0.07	0.01
Au	0.3	0.04	0.55	0.06	1.1	0.2
Th	0.008	0.006	0.021	0.007	0.31	0.02
U						
Ca	50		70			
NH4	440		960			
SO4	1700		3800			
NO3	820		1450			
pH	4.55		4.20		3.40	

Element	880714CN3	+/-	880714CN4	+/-	880714CN5	+/-
Na	260	24	120	15	93	9
Mg	110	67	200	100	91	29
Al	450	27	290	21	97	6
Cl					15	10
K	250	87	200	120	88	40
Sc	0.56	0.04	0.52	0.04	0.16	0.01
Ti	32	16	62	31		
V	1.9	0.2	3.3	0.3	1.2	0.1
Cr	1.5	0.2	1.2	0.2	3.7	0.1
Mn	9.1	0.2	15	0.2	9.1	0.1
Fe	460	33	220	28	53	10
Co	0.18	0.07	0.12	0.06	0.06	0.02
Zn	100	10	32	3	29	3
As	0.5	0.12	1.2	0.1	9	0.9
Se			1.3	0.3	0.52	0.12
Br	5.8	2.1	18	6	10	3
Rb	0.55	0.31	1.3	0.3	0.27	0.14
Sr						
Mo	0.16	0.11				
Cd						
In					0.014	0.01
Sb	0.21	0.02	0.53	0.04	0.26	0.02
Cs						
Ba			6.4	4.7	1.7	1.5
La	0.22	0.02	0.27	0.02	0.074	0.007
Ce	0.31	0.09	0.34	0.09	0.12	0.03
Nd			0.32	0.2	0.11	0.08
Sm	0.035	0.004	0.042	0.004	0.013	0.001
Au	7.3	0.8	0.45	0.08	1	0.1
Th						
U						
Ca	10		130		320	
NH4	1690		2020		2700	
SO4	15200		13200		11000	
NO3	1910		3550		4340	
pH	3.80		3.72		3.90	

Element	880714RN2	+/-	880721CN3	+/-	880721CN4	+/-
Na	47	8	72	7	15	3
Mg	48	18	29	10	12	12
Al	140	10	120	7	32	3
Cl			8.6	7.4		
K	180	44	54	46	48	19
Sc	0.32	0.02	0.25	0.02	0.11	0.01
Ti			11	5	4.3	3.2
V	0.42	0.07	0.51	0.07	0.15	0.04
Cr	0.76	0.11	1.2	0.1	0.091	0.059
Mn	3.7	0.1	4.8	0.1	0.48	0.02
Fe	96	16	78	10	21	9
Co			0.083	0.024		
Zn	7.7	0.8	13	1	3	0.3
As	0.2	0.05	2.8	0.3	0.017	0.008
Se	0.3	0.2				
Br	6.2	2.1	9.3	3.1	1	0.4
Rb			0.46	0.13	0.1	0.09
Sr						
Mo	0.12	0.08				
Cd			0.095	0.055		
In						
Sb	0.11	0.01	0.33	0.03	0.051	0.005
Cs						
Ba	2.9	1.8	3.9	1.6	1.4	1.2
La	0.067	0.008	0.074	0.007	0.011	0.002
Ce			0.088	0.032		
Nd						
Sm	0.013	0.002	0.011	0.001	0.004	0.001
Au	1.4	0.2	0.76	0.09	0.13	0.02
Th	0.025	0.012	0.034	0.007	0.007	0.006
U						
Ca	60		80		10	
NH4	710		30		20	
SO4	6000		1500		100	
NO3	1750		460		20	
pH	3.94		4.55		5.00	

Element	880721RN2	+/-	880721RN3	+/-	880721RN4	+/-
Na	76	7	22	4	16	4
Mg	46	20	53	17		
Al	29	3	120	8	5.4	2
Cl	7.5	6.1				
K	64	25			23	17
Sc	0.1	0.01	0.11	0.01	0.06	0.01
Ti						
V	0.36	0.04	1.3	0.1	0.044	0.027
Cr	0.21	0.06	0.33	0.06	0.12	0.06
Mn	1.2	0.03	0.46	0.03	0.12	0.01
Fe	40	9	19	9	9.9	8.3
Co						
Zn	14	1	4.6	0.5	2.8	0.3
As	0.098	0.019	0.027	0.011	0.011	0.006
Se						
Br	3.7	1.2	1.5	0.5	0.91	0.36
Rb	0.21	0.09			0.15	0.05
Sr						
Mo					0.032	0.029
Cd						
In	0.004	0.003				
Sb	0.17	0.01	0.041	0.004	0.015	0.002
Cs						
Ba						
La	0.004	0.002	0.022	0.003		
Ce						
Nd						
Sm			0.003	0.001	0.0006	0.0001
Au	0.76	0.08	0.21	0.05	0.33	0.04
Th						
U						
Ca	110		10		10	
NH4	60		20		10	
SO4	900		200		300	
NO3	460		30		160	
pH	4.46		5.12		5.00	

Element	880721RN5	+/-	880722CN1	+/-	880724CN2	+/-
Na	8.6	3	81	8	200	16
Mg			27	19	50	17
Al	3.1	1.9	68	6	110	8
Cl			8.8	6.8		
K	36	15	120	38	220	55
Sc	0.05	0.005	0.2	0.01	0.21	0.02
Ti	3	0.7	4.4	4		
V			0.39	0.06	1.2	0.1
Cr	0.067	0.058	0.39	0.07	0.72	0.08
Mn	0.57	0.02	2	0.04	7.1	0.1
Fe			51	9	64	12
Co					0.11	0.03
Zn	2.2	0.3	10	1	37	4
As	0.014	0.01	0.24	0.04	0.87	0.11
Se					0.17	0.13
Br	1.6	0.5	4	1.3	7.2	2.4
Rb					0.93	0.17
Sr					3.6	2.4
Mo						
Cd						
In						
Sb			0.18	0.02	0.29	0.02
Cs						
Ba			1.8	1.2	4.6	1.9
La	0.006	0.002	0.018	0.004	0.055	0.007
Ce					0.088	0.043
Nd						
Sm			0.005	0.001	0.016	0.002
Au	0.2	0.03	0.18	0.03	0.41	0.09
Th			0.007	0.006	0.013	0.009
U						
Ca	10					
NH4	20					
SO4	500					
NO3	820					
pH	4.70		4.40		4.12	

Element	880724RN2	+/-	880725CN1	+/-	880810CN1	+/-
Na	47	6	510	37	92	9
Mg	71	19	72	27	100	41
Al	330	16	67	7	210	12
Cl			11	9	23	14
K	110	33	510	85	83	37
Sc	0.89	0.06	0.15	0.01	0.26	0.02
Ti	19	7			7.8	7.6
V	0.31	0.06	1.6	0.1	3.5	0.2
Cr	0.43	0.06	1.9	0.1	0.71	0.09
Mn	1.4	0.03	3.1	0.1	12	0.1
Fe	160	11	74	14	150	16
Co	0.035	0.022	0.11	0.03	0.15	0.03
Zn	5.1	0.5	28	3	25	3
As	0.052	0.026	0.51	0.08	1.1	0.1
Se					1.4	0.2
Br	8.6	2.8	11	3	12	3
Rb	0.5	0.1	1	0.2	0.76	0.3
Sr						
Mo					0.12	0.05
Cd					0.075	0.055
In					0.006	0.005
Sb	0.054	0.005	0.22	0.02	0.49	0.04
Cs					0.054	0.029
Ba	1.6	1.2			7.1	2.2
La	0.14	0.01	0.08	0.01	0.22	0.02
Ce	0.17	0.03	0.056	0.048	0.39	0.05
Nd					0.14	0.07
Sm	0.016	0.002	0.01	0.001	0.033	0.003
Au	0.24	0.04	0.18	0.04	0.3	0.05
Th	0.052	0.007	0.24	0.02		
U						
Ca					450	
NH4					7100	
SO4					38800	
NO3					5490	
pH	4.90		4.10		3.30	

Element	880815CN2	+/-	880815RN1	+/-	880816CN1	+/-
Na	28	4	28	4	28	4
Mg	7.5	6.6	11	9.7		
Al	19	4	41	5	18	3
Cl	17	16	6.7	6.4		
K	53	24	69	33	21	15
Sc	0.098	0.009	8.5	0.6	0.082	0.007
Ti	6.2	4.1				
V	0.21	0.05	0.41	0.06	0.053	0.044
Cr	0.089	0.065	28	2	0.21	0.06
Mn	1.7	0.04	1.9	0.04	0.68	0.02
Fe	33	10			17	9
Co			5.1	0.6		
Zn	5.9	0.7	410	41	15	1
As	0.09	0.01	7.2	1.1	0.36	0.04
Se			9.9	2.4		
Br	2.3	0.8	240	77	0.86	0.32
Rb	0.27	0.19	34	7.7		
Sr						
Mo			3.8	1.3		
Cd			1.2	0.7		
In						
Sb	0.12	0.01	4.3	0.4	0.044	0.004
Cs			0.56	0.42		
Ba	1.6	1.5				
La	0.018	0.003	2.4	0.2	0.008	0.002
Ce			8	1		
Nd	0.2	0.06	9.4	1.8		
Sm	0.004	0.001	0.47	0.04	0.002	0.0001
Au	1.2	0.2	25	3	0.27	0.04
Th			1	0.2	0.009	0.006
U						
Ca	60				10	
NH4	350				20	
SO4	1600				400	
NO3	720				730	
pH	4.70		4.55		5.10	

Element	880816CN2	+/-	880816CN3	+/-	880816RN1	+/-
Na	18	4	76	7	16	4
Mg						
Al	19	3	39	4	6.9	2.2
Cl	5.3	3.6				
K	90	13			24	21
Sc	0.094	0.008	0.12	0.01	0.097	0.016
Ti						
V	0.17	0.04	0.21	0.04	0.088	0.027
Cr	0.31	0.06	0.52	0.07	0.14	0.09
Mn	0.46	0.02	1.5	0.04	0.26	0.01
Fe	22	9	22	9		
Co					0.055	0.045
Zn	6.4	0.7	19	2	9.2	1.6
As	0.053	0.009	1.7	0.2	0.03	0.01
Se						
Br	0.74	0.27	2.1	0.8	0.5	0.2
Rb	0.087	0.057				
Sr						
Mo						
Cd						
In						
Sb	0.19	0.02	0.094	0.008	0.044	0.004
Cs						
Ba						
La	0.01	0.002	0.02	0.003	0.007	0.003
Ce						
Nd						
Sm	0.003	0.0001	0.004	0.001	0.002	0.0001
Au	0.23	0.05	1.1	0.2	0.5	0.1
Th						
U	0.011	0.005				
Ca			20		10	
NH4			140		10	
SO4			600		400	
NO3			630		60	
pH	5.01		4.91		5.00	

Element	880816RN2	+/-	880816RN3	+/-	880817CN1	+/-
Na	24	4	47	6	48	6
Mg			15	8	17	15
Al	8.6	2.1	18	3	23	3
Cl						
K	45	19			66	23
Sc	0.07	0.01	0.085	0.011	0.089	0.015
Ti					6.9	3.5
V	0.091	0.031	0.13	0.04	0.66	0.06
Cr			0.17	0.07	0.3	0.1
Mn	0.38	0.02	0.8	0.02	2.7	0.1
Fe	21	10			15	16
Co			0.04	0.03		
Zn	4.4	0.5	15	2	13	2
As	0.03	0.01	0.036	0.005	0.71	0.07
Se						
Br	0.66	0.23	0.45	0.17	2.6	0.9
Rb	0.18	0.11	0.37	0.25		
Sr					1.6	1.3
Mo						
Cd						
In						
Sb	0.012	0.002	0.059	0.005	0.16	0.01
Cs						
Ba			1.5	0.8	1.4	1.2
La	0.005	0.002	0.003	0.002	0.015	0.003
Ce					0.056	0.052
Nd					0.26	0.1
Sm					0.004	0.001
Au	0.32	0.04	1.6	0.2	0.55	0.12
Th					0.02	0.01
U						
Ca	40		20		30	
NH4	30		80		560	
SO4	300		400		2700	
NO3	220		240		1090	
pH	5.10		5.10		4.35	

Element	**880818CN1**	**+/-**	**880824CN1**	**+/-**	**880824CN2**	**+/-**
Na	65	7	92	8	49	6
Mg			19	8	38	22
Al	16	3	30	3	26	4
Cl						
K	63	21	89	25	79	24
Sc	0.13	0.02			0.092	0.008
Ti						
V	0.46	0.05	0.67	0.06	0.65	0.07
Cr	0.24	0.09	0.22	0.07	0.26	0.08
Mn	1	0.03	1.4	0.03	0.9	0.03
Fe					21	11
Co	0.25	0.07			0.052	0.027
Zn	6.6	1.9			4.4	0.5
As	0.13	0.02	0.47	0.05	0.077	0.018
Se						
Br	1.2	0.4	2.2	0.6	0.98	0.33
Rb					0.2	0.12
Sr	1.3	1				
Mo	0.065	0.042				
Cd						
In					0.005	0.004
Sb	0.052	0.005	0.098	0.008	0.053	0.005
Cs						
Ba			2.2	1.3		
La	0.023	0.003	0.011	0.002	0.022	0.004
Ce						
Nd						
Sm	0.003	0.001	0.002	0.0001	0.002	0.001
Au	1.6	0.3	0.33	0.04	0.94	0.09
Th			0.02	0.01		
U						
Ca	30		40		20	
NH4	290		90		40	
SO4	1100		1500		1800	
NO3	300		650		1130	
pH	4.85		4.49		4.29	

Element	880824RN1	+/-	880824RN2	+/-	880825CN1	+/-
Na	220	26	56	6	150	13
Mg					24	15
Al	43	16	6.7	2.9	150	8
Cl					7.8	6.6
K					140	32
Sc	0.47	0.06	0.099	0.009	0.22	0.02
Ti					16	7
V	0.65	0.19	0.12	0.04	0.92	0.09
Cr			0.4	0.07	0.56	0.09
Mn	2.2	0.1	0.49	0.02	1.8	0.04
Fe	77	53	32	10	69	16
Co			0.082	0.026		
Zn	19	3.2	9.5	1	14	2
As			0.043	0.009	0.69	0.07
Se						
Br	3	1.3	0.84	0.3	1.8	0.5
Rb						
Sr						
Mo	0.18	0.14				
Cd						
In						
Sb	0.06	0.01	0.043	0.004	0.11	0.01
Cs						
Ba						
La	0.012	0.009	0.016	0.003	0.034	0.004
Ce			0.072	0.035		
Nd	0.72	0.26	0.19	0.06		
Sm	0.005	0.002	0.0026	0.0001	0.005	0.001
Au	1.3	0.3	0.86	0.14	0.84	0.08
Th					0.02	0.01
U						
Ca	10		10		40	
NH4	40		170		70	
SO4	600		800		2700	
NO3	270		460		1600	
pH	4.75		4.70		4.20	

Element	880825CN2	+/-	880904CN2	+/-	880905RN1	+/-
Na	54	6	18	4	9.9	3.2
Mg	30	25				
Al	50	5	22	4	36	4
Cl						
K	40	20				
Sc	0.097	0.012	0.11	0.01	0.1	0.01
Ti	5.6	4.7				
V	1.2	0.1	0.28	0.05	0.17	0.05
Cr			0.22	0.07	0.13	0.07
Mn	2.2	0.05	1.4	0.04	0.54	0.02
Fe	49	12	31	11	24	10
Co						
Zn	7.4	0.9	7.9	0.9	11	1
As	0.22	0.02	0.16	0.02	0.038	0.007
Se	0.14	0.11				
Br	0.83	0.28	1.3	0.5	0.39	0.17
Rb						
Sr						
Mo						
Cd						
In						
Sb	0.12	0.01	0.11	0.01	0.068	0.006
Cs						
Ba						
La	0.034	0.004	0.009	0.002	0.011	0.003
Ce	0.09	0.03				
Nd						
Sm	0.006	0.001	0.0026	0.0001	0.0026	0.0001
Au	0.33	0.04	2.3	0.4	0.22	0.05
Th						
U						
Ca	50		10		10	
NH4	160		640		80	
SO4	9800		2900		300	
NO3	5220		1620		120	
pH	3.68		4.03		4.80	

Element	880907RN1	+/-	890615CN1	+/-	890615RN1P	+/-
Na	44	5	110	13	27	4
Mg	20	10	69	42		
Al	21	4	100	12	12	4
Cl						
K	39	19	170	44		
Sc	0.078	0.008	0.22	0.02	0.09	0.01
Ti						
V	0.24	0.04	5	0.3	0.18	0.05
Cr	0.16	0.07	0.52	0.14	0.28	0.06
Mn	1.3	0.03	5.3	0.1	0.61	0.03
Fe	14	9	68	19	19	9
Co			0.056	0.048	0.052	0.021
Zn	7.8	0.9	29	3	2.3	0.3
As	0.19	0.02	1.1	0.1	0.045	0.013
Se						
Br	1.9	0.6	6	2	1.6	0.6
Rb	0.21	0.2	0.48	0.2	0.21	0.11
Sr						
Mo						
Cd						
In	0.005	0.004			0.003	0.002
Sb	0.062	0.005	0.32	0.03	0.06	0.005
Cs						
Ba						
La	0.016	0.003	0.035	0.008	0.025	0.003
Ce						
Nd						
Sm	0.0016	0.0001	0.009	0.002	0.0026	0.0001
Au	0.23	0.03	0.23	0.06	0.34	0.06
Th						
U						
Ca			190		10	
NH4			830		40	
SO4			7700		750	
NO3			3550		490	
pH	4.72		3.64		4.58	

Element	890710CN1	+/-	890710RN1	+/-	890710RN1P	+/-
Na	120	11	24	4	120	10
Mg	160	39			19	13
Al	120	7	17	3	20	3
Cl	370	39	73	9	270	29
K	400	62			230	40
Sc	0.14	0.03	0.076	0.008	0.14	0.02
Ti						
V	1	0.1	0.14	0.04	0.084	0.038
Cr	0.78	0.16	0.32	0.07	0.77	0.13
Mn	18	0.3	1.2	0.03	2.9	0.1
Fe	52	27	15	10	67	17
Co	0.22	0.06			0.072	0.036
Zn	32	4	7.2	0.8	46	5
As	1.8	0.2	0.08	0.01	0.15	0.02
Se	1	0.3				
Br	6.9	1.9	1.7	0.6	2.6	0.8
Rb						
Sr	7	0.4				
Mo	0.08	0.06				
Cd	0.18	0.11				
In						
Sb	0.56	0.04	0.071	0.006	0.22	0.02
Cs						
Ba	3.1	1.8	2	1	1.6	1.1
La	0.092	0.008	0.006	0.002	0.044	0.005
Ce	0.12	0.06			0.12	0.05
Nd	1.3	0.2			0.23	0.09
Sm	0.022	0.002	0.002	0.0001	0.01	0.001
Au	0.32	0.06	1.1	0.2	0.53	0.1
Th	0.05	0.02			0.02	0.01
U					0.009	0.008
Ca	710		60		160	
NH4	330		220		230	
SO4	20600		1540		1370	
NO3	2650		600		760	
pH	3.60		4.20		4.06	

Element	890728CN3	+/-	890728RN3	+/-	890728RN3P	+/-
Na	36	5	44	5	54	7
Mg	21	16	19	15	32	14
Al	41	4	17	3	70	6
Cl	96	11	130	15	190	24
K	110	21	160	23	120	30
Sc	0.14	0.01	0.081	0.007	0.17	0.02
Ti	5.4	3.2			11	5
V	0.25	0.04	0.075	0.031	0.23	0.05
Cr	0.28	0.07	0.14	0.06	0.56	0.1
Mn	1.6	0.04	0.85	0.02	2.5	0.1
Fe	22	11	16	9	69	14
Co			0.014	0.022		
Zn	7.1	0.9	13	1	7.7	0.9
As	0.59	0.06	0.15	0.02	0.083	0.012
Se						
Br	1.8	0.5	1.2	0.4	2.5	0.9
Rb	0.41	0.3	0.21	0.11		
Sr						
Mo						
Cd						
In						
Sb	0.093	0.007	0.055	0.005	0.13	0.01
Cs						
Ba	2.1	1			3.6	1.9
La	0.024	0.003	0.007	0.003	0.052	0.005
Ce						
Nd						
Sm	0.004	0.001	0.002	0.0001	0.008	0.001
Au	0.6	0.1	0.14	0.03	0.56	0.12
Th						
U						
Ca	30		40		90	
NH4	380		130		90	
SO4	1440		780		970	
NO3	900		570		510	
pH	4.31		4.46		4.78	

Element	890805CN1	+/-	890805RN1	+/-	890805RN1P	+/-
Na	420	30	38	5	14	3
Mg	97	27				
Al	150	9	12	2	13	2
Cl	970	100	59	8	43	6
K	230	55	53	17	24	1
Sc	0.31	0.04	0.066	0.005	0.084	0.011
Ti	20	7				
V	4.8	0.3	0.28	0.04	0.28	0.04
Cr	1.5	0.2	0.089	0.059	0.071	0.064
Mn	10	0.2	0.36	0.02	0.37	0.01
Fe	140	31	9.9	8.4		
Co	0.31	0.08			0.12	0.03
Zn	39	5	3.5	0.4	3.3	0.7
As	1.5	0.2	0.041	0.019	0.039	0.005
Se	2.9	0.6				
Br	11	3	0.7	0.2	0.57	0.2
Rb						
Sr	3.4	3.2				
Mo						
Cd	0.17	0.11				
In	0.004	0.003				
Sb	0.69	0.05	0.045	0.004	0.043	0.004
Cs						
Ba	7.9	2.2				
La	0.23	0.02	0.007	0.002	0.026	0.003
Ce	0.57	0.09				
Nd	1.6	0.3				
Sm	0.034	0.003	0.0006	0.0001	0.0016	0.0001
Au	0.44	0.1	1	0.1	0.19	0.03
Th						
U	0.03	0.02				
Ca	460		20		10	
NH4	4000		200		160	
SO4	50000		1980		1990	
NO3	17900		950		780	
pH	3.05				4.33	

Element	890812CN3	+/-	890812RN3	+/-	890812RN3P	+/-
Na	77	7	52	6	58	6
Mg	11	7	19	7	19	12
Al	11	2	4.8	2.1	32	3
Cl	170	19	110	13	150	16
K	33	13	16	12	31	18
Sc	0.077	0.012	0.094	0.014	0.078	0.009
Ti	4.8	3.3				
V	0.31	0.04	0.047	0.029	0.13	0.03
Cr			0.11	0.08	0.25	0.07
Mn	0.5	0.02	0.26	0.01	0.58	0.02
Fe						
Co	0.25	0.04	0.096	0.038	0.063	0.028
Zn	2	1	16	2	4.7	0.8
As	0.04	0.01	0.053	0.008	0.035	0.006
Se						
Br	3.6	1.3	1.6	0.5	3	0.8
Rb			0.63	0.5		
Sr					1.5	1.3
Mo			0.039	0.038		
Cd						
In						
Sb	0.024	0.003	0.021	0.003	0.036	0.004
Cs						
Ba						
La			0.004	0.003	0.008	0.003
Ce						
Nd					0.12	0.07
Sm	0.002	0.0001	0.0006	0.0001	0.002	0.0001
Au	0.53	0.11	0.14	0.04	0.62	0.06
Th						
U						
Ca	20		30		10	
NH4	80		10		20	
SO4	1190		560		790	
NO3	390		290		410	
pH	4.65		5.09		4.68	

Element	890813CN2	+/-	890813RN2	+/-	890813RN2P	+/-
Na	150	12	66	10	61	11
Mg	37	14	23	16	1	11
Al	5.5	2.2	23	6	17	7
Cl	230	32	120	15	200	23
K	43	14	180	31	97	44
Sc	0.06	0.01	0.21	0.03	0.3	0.03
Ti	3.2	2.7			7.4	6.2
V	0.14	0.03	0.15	0.07	0.16	0.09
Cr	0.067	0.067	0.67	0.17	0.76	0.23
Mn	0.61	0.02	0.41	0.03	0.6	0.05
Fe			39	27	50	32
Co	0.21	0.03	0.39	0.08		
Zn	3.2	0.6	7.9	1.8	18	2
As	0.08	0.01	0.058	0.012	0.1	0.02
Se						
Br	2.7	0.8	3.8	1.4	3.3	1.1
Rb						
Sr	1.4	1.3				
Mo						
Cd						
In						
Sb	0.034	0.004	0.047	0.006	0.13	0.01
Cs						
Ba						
La						0.028	0.008
Ce						
Nd						
Sm	0.0006	0.0001	0.002	0.001	0.007	0.001
Au	0.31	0.04	0.76	0.17	3	0.5
Th						
U						
Ca	20		10		10	
NH4	10		10		20	
SO4	1760		930		1130	
NO3	1890		1320		1480	
pH	4.20		4.40		4.30	

Element	890901CN1	+/-	890901RN1	+/-	890901RN1P	+/-
Na	130	14	13	3	51	6
Mg	110	53			8.7	5.6
Al	99	8	9.7	2.2	25	3
Cl	390	41	87	10	170	19
K	190	70	22	12	60	24
Sc	0.27	0.02	0.081	0.007	0.1	0.01
Ti					2.8	2.4
V	1.3	0.1	0.4	0.04	0.43	0.04
Cr	0.46	0.13	0.18	0.06	0.23	0.07
Mn	11	0.2	0.94	0.02	2.4	0.05
Fe	70	19	20	9	13	10
Co						
Zn	17	2	6.3	0.7		
As	0.56	0.08	0.17	0.02	0.1	0.02
Se			0.05	0.1		
Br	5.1	1.5	2.7	1	3.7	1.3
Rb					0.38	0.16
Sr						
Mo						
Cd						
In						
Sb	0.21	0.02	0.08	0.01	0.1	0.01
Cs						
Ba						
La	0.063	0.012	0.007	0.003	0.039	0.004
Ce					0.047	0.032
Nd	0.22	0.11				
Sm	0.009	0.001	0.003	0.0001	0.007	0.001
Au	0.67	0.1	0.62	0.13	0.36	0.08
Th						
U			0.008	0.006	0.022	0.009
Ca	260		40		40	
NH4	740		300		310	
SO4	4960		2560		3350	
NO3	3280		1480		2110	
pH	3.89		4.08		4.00	

Element	890914CN2	+/-	890914RN2	+/-	890914RN2P	+/-
Na	28	4	49	6	94	11
Mg	17	6.5			48	16
Al	31	3	22	4	80	8
Cl	220	23	210	23	550	58
K	30	25	88	24	150	50
Sc	0.11	0.01	0.068	0.008	0.16	0.02
Ti			7.9	3.5		
V	3.7	0.2	1.5	0.1	3.6	0.2
Cr	0.38	0.08	0.18	0.07	0.4	0.2
Mn	3.1	0.1	1.8	0.04	10	0.2
Fe	49	12	43	11	83	23
Co	0.28	0.03	0.067	0.024	0.15	0.05
Zn	12	1	22	3	30	4
As	0.43	0.04	0.2	0.02	0.16	0.02
Se	0.25	0.12			0.39	0.23
Br	3.3	1	2.6	0.8	4.9	1.5
Rb					1.4	0.6
Sr			2.9	1.8	6.2	3.9
Mo	0.043	0.039			0.081	0.072
Cd			0.048	0.039		
In					0.008	0.007
Sb	0.34	0.03	0.15	0.01	0.31	0.03
Cs						
Ba	1.1	1	1.7	0.9		
La	0.029	0.004	0.005	0.002	0.048	0.007
Ce	0.055	0.038			0.15	0.07
Nd	0.24	0.08			0.23	0.15
Sm	0.002	0.0001	0.0015	0.0001	0.009	0.001
Au	0.41	0.08	0.27	0.03	0.83	0.08
Th			0.035	0.007		
U						
Ca	100					
NH4	1000					
SO4	6300					
NO3	9100					
pH	3.61		3.69		3.44	

Element	890914CN3	+/-	890914RN3	+/-	890914RN3P	+/-
Na	15	3	15	4	14	3
Mg	20	13			12	10
Al	24	3	5.4	2.6	4.3	2.5
Cl	120	15	71	9	58	8
K	17	15	60	21	32	22
Sc	0.076	0.011	0.065	0.008	0.13	0.01
Ti	5.7	4.7			3	2.8
V	2.5	0.1	0.33	0.04	0.73	0.06
Cr	0.26	0.07	0.17	0.06	0.17	0.06
Mn	1.4	0.03	0.31	0.02	0.58	0.02
Fe	41	12	29	11	27	9
Co	0.037	0.028			0.029	0.021
Zn	6.2	0.9	3.6	0.6	9.4	1.2
As	0.35	0.04	0.062	0.008	0.053	0.027
Se	0.16	0.13				
Br	1.1	0.3	0.72	0.26	0.93	0.32
Rb	0.39	0.3				
Sr						
Mo					0.047	0.042
Cd						
In						
Sb	0.23	0.02	0.066	0.006	0.059	0.005
Cs						
Ba	2.4	1			1.6	1.3
La	0.017	0.003				
Ce						
Nd						
Sm	0.0026	0.0001	0.0006	0.0001	0.001	0.0001
Au	0.37	0.04	0.081	0.019	0.17	0.04
Th						
U						
Ca	20		10		10	
NH4	400		100		110	
SO4	8000		2780		2580	
NO3	3590		1210		1550	
pH	3.68		4.08		4.39	

Element	890915CN1	+/-	890915RN1P	+/-	900623CN6	+/-
Na	5	3	20	9	26	4
Mg						
Al						
Cl						
K	19	18			45	15
Sc	0.072	0.007	0.19	0.02	0.082	0.011
Ti	14	9				
V	0.34	0.11			0.99	0.14
Cr			0.55	0.17	0.16	0.07
Mn	0.2	0.01	0.34	0.04	0.7	0.02
Fe	29	10	32	26		
Co						
Zn	1.3	0.3	4.4	0.8	3.9	0.7
As	0.13	0.02	0.026	0.013	0.12	0.01
Se						
Br	1.1	0.3			2.5	0.8
Rb	0.26	0.12				
Sr						
Mo						
Cd						
In						
Sb	0.051	0.005	0.1	0.01	0.086	0.007
Cs						
Ba						
La	0.012	0.003			0.003	0.002
Ce						
Nd					0.14	0.07
Sm	0.002	0.0001	0.003	0.001	0.002	0.0001
Au			0.76	0.08	0.058	0.017
Th						
U						
Ca	10				20	
NH4	10				340	
SO4	1010				3200	
NO3	250				980	
pH	4.55		4.46		4.10	

Element	900623RN6	+/-	900720CN2	+/-	900720RN2	+/-
Na	43	5	58	6	24	4
Mg			100	24		
Al	35	29	31	3	10	2
Cl	120	66				
K			110	27		
Sc	0.13	0.01	0.064	0.006	0.057	0.006
Ti			24	5	6	3
V	0.38	0.15	0.27	0.04	0.11	0.03
Cr	0.22	0.06	0.18	0.06		
Mn	1.1	0.04	4.6	0.1	0.35	0.02
Fe	24	9	14	9		
Co			0.038	0.022		
Zn	5.9	0.7	9.8	1.2		
As	0.1	0.04	0.21	0.02	0.028	0.009
Se			0.13	0.1		
Br	1.2	0.4	1.5	0.5	0.64	0.24
Rb			0.23	0.13	0.27	0.14
Sr			2.8	1.8		
Mo						
Cd	0.07	0.06				
In						
Sb	0.084	0.007	0.11	0.01	0.024	0.003
Cs						
Ba			3.4	1.6	1.6	1
La			0.012	0.002		
Ce						
Nd						
Sm	0.002	0.001	0.005	0.001	0.0006	0.0001
Au	0.2	0.05	0.038	0.015	0.063	0.016
Th						
U						
Ca	20		390		20	
NH4	150		1200		130	
SO4	1500		7900		1500	
NO3	630		1320		230	
pH	4.40		4.00		4.50	

Element	900722CN3	+/-	900722RN3	+/-	900723CN5	+/-
Na	72	7	44	5	38	5
Mg	8.5	6.4				
Al	37	3			9.7	2.1
Cl						
K	120	37	49	18	36	18
Sc	0.056	0.007	0.13	0.01	0.046	0.005
Ti			33	2		
V	2.6	0.1	0.21	0.04	0.9	0.1
Cr	0.14	0.06	0.3	0.1	0.1	0.06
Mn	4.7	0.1	0.4	0.02	0.6	0.02
Fe	49	11	27	9	12	9
Co	0.041	0.024				
Zn	10.	1	8	1	3.2	0.4
As	0.43	0.05	0.09	0.03	0.21	0.03
Se	0.41	0.12				
Br	3.4	1	0.97	0.33	0.6	0.2
Rb						
Sr						
Mo						
Cd						
In						
Sb	0.24	0.02	0.043	0.004	0.053	0.005
Cs					0.024	0.017
Ba	1.6	1.3				
La	0.021	0.003				
Ce						
Nd						
Sm	0.006	0.001	0.0006	0.0001		
Au	0.055	0.019	0.25	0.05	0.069	0.018
Th						
U			0.013	0.009		
Ca	140		20		20	
NH4	2280		190		530	
SO4	20300		2100		7900	
NO3	7500		960		2660	
pH	3.40		4.20		3.70	

Element	900723RN5	+/-	900806CN1	+/-	900806RN1	+/-
Na	41	5	260	19	17	4
Mg			49	13		
Al	7.9	2.1	110	6		
Cl			1060	110	110	13
K	28	13	290	54	38	15
Sc	0.063	0.012	0.13	0.01	0.053	0.006
Ti			11	5		
V	0.5	0.05	1.6	0.1	0.21	0.03
Cr	0.11	0.07	1.1	0.1		
Mn	0.34	0.02	4.6	0.1	0.24	0.01
Fe			58	10		
Co			0.025	0.022		
Zn	5	1	16	2	1.4	0.3
As	0.059	0.008	3.5	0.3	0.034	0.013
Se						
Br	1.1	0.4	3.9	1.1	1.6	0.5
Rb	0.6	0.4	0.41	0.22		
Sr						
Mo						
Cd						
In						
Sb	0.041	0.004	0.4	0.03	0.11	0.01
Cs					0.034	0.02
Ba						
La	0.003	0.002	0.14	0.01	0.011	0.002
Ce			0.2	0.04		
Nd			0.08	0.07		
Sm	0.0006	0.0001	0.023	0.002		
Au	0.095	0.018	0.17	0.03	2.5	0.2
Th			0.037	0.008		
U						
Ca	10				10	
NH4	220				190	
SO4	2300				1400	
NO3	920				520	
pH	4.15		3.70		4.40	

Element	900806RN1P	+/-	900806RN2	+/-	900806RN2P	+/-
Na	43	5	28	4	45	5
Mg					9.2	6.3
Al	9.5	2.5	3.9	2.1	2.4	2
Cl	700	72			29	18
K			23	20		
Sc	0.067	0.008	0.051	0.005	0.077	0.006
Ti	3	2.9				
V	0.4	0.05	0.37	0.04	0.19	0.04
Cr	0.65	0.07				
Mn	0.96	0.03	0.33	0.02	0.47	0.02
Fe	22	10			9.9	8.4
Co	1.4	0.1				
Zn	12	2	1.5	0.3	4.3	0.5
As	0.11	0.02	0.03	0.01		
Se						
Br	2.2	0.7	1.2	0.4	1.1	0.4
Rb						
Sr						
Mo						
Cd						
In						
Sb	0.1	0.01	0.033	0.003	0.022	0.003
Cs						
Ba						
La						
Ce						
Nd						
Sm	0.0016	0.0001				
Au	0.082	0.023	0.14	0.02	0.036	0.019
Th						
U						
Ca	30		10		10	
NH4	150		140		100	
SO4	1800		1700		1200	
NO3	820		710		840	
pH	4.20		4.40		4.20	

Element	900806RN3	+/-	900806RN3P	+/-	900806CN4	+/-
Na	15	3	110	10	140	12
Mg	13	10	20	12	13	10
Al	7.1	2	12	2	6.1	2
Cl			11	9	480	49
K	22	8	77	26	42	22
Sc	0.06	0.01	0.07	0.01	0.11	0.01
Ti	2.7	1.9			3.9	3
V	0.2	0.03	0.33	0.04	2.6	0.1
Cr			0.24	0.07	0.36	0.06
Mn	0.4	0.02	0.82	0.03	0.93	0.03
Fe			21	11	34	9
Co	0.051	0.032	0.6	0.04	0.074	0.022
Zn	2.4	0.6	9.3	1.3	8	1
As	0.041	0.006	0.066	0.009	0.57	0.07
Se					0.22	0.11
Br	1.5	0.5	2.3	0.7	3	1
Rb			0.6	0.3	0.14	0.09
Sr						
Mo						
Cd						
In						
Sb	0.025	0.003	0.16	0.01	0.097	0.008
Cs						
Ba					1.5	1.1
La	0.003	0.002	0.004	0.002	0.01	0.003
Ce						
Nd			0.11	0.07		
Sm	0.0006	0.0001	0.002	0.0001	0.002	0.0001
Au	0.098	0.022	0.087	0.017	0.086	0.024
Th						
U						
Ca	10		40		30	
NH4	100		140		610	
SO4	1000		1500		6500	
NO3	640		1020		2960	
pH	4.40		4.35		3.70	

Element	900806RN4	+/-	900806RN4P	+/-	900807CN5	+/-
Na	40	5	98	9	54	8
Mg					17	16
Al	3.6	1.9	3.4	1.9	17	4
Cl	150	17	270	29	880	91
K	26	16	71	27		
Sc	0.06	0.01	0.1	0.01	0.16	0.02
Ti					4.3	3.8
V	0.27	0.04	0.56	0.05	0.22	0.06
Cr					0.42	0.14
Mn	0.25	0.02	0.42	0.02	0.34	0.02
Fe	14	9	20	9	37	23
Co			0.08	0.02		
Zn	1.9	0.3	5.1	0.7	5.6	1.2
As	0.062	0.014	0.1	0.03	0.35	0.04
Se						
Br	1.7	0.5	3.1	0.9	3.6	1.1
Rb	0.17	0.13	0.12	0.07		
Sr			1.3	1.2		
Mo						
Cd						
In					0.007	0.005
Sb	0.034	0.004	0.047	0.005	0.067	0.008
Cs						
Ba						
La						
Ce						
Nd						
Sm						
Au	0.17	0.03			0.18	0.04
Th						
U						
Ca	10		20			
NH4	130		210			
SO4	1300		1600			
NO3	770		950			
pH	4.30		4.32		4.35	

Element	900807RN5	+/-	900807RN5P	+/-	900807CN6	+/-
Na	41	5	140	11	79	8
Mg	9.8	7.4	48	18	6.2	4.7
Al	6.2	2.4	3.7	1.9	13	3
Cl	110	13	560	58	240	26
K			69	26	120	28
Sc	0.1	0.01	0.059	0.008	0.06	0.01
Ti			5.9	3.1		
V	0.16	0.03	0.28	0.04	0.33	0.04
Cr	0.1	0.06	0.6	0.1	0.18	0.07
Mn	0.21	0.02	0.79	0.02	0.29	0.02
Fe	15	8				
Co	0.032	0.021	0.26	0.03	0.31	0.04
Zn	3.1	0.4	4.7	0.7	2.7	0.6
As	0.1	0.02	0.14	0.02	0.26	0.03
Se						
Br	1.6	0.5	4.1	1.2	2.8	0.9
Rb						
Sr			1.5	1.4		
Mo						
Cd						
In	0.0001	0.0014				
Sb	0.029	0.003	0.046	0.005	0.056	0.005
Cs						
Ba						
La	0.004	0.002	0.003	0.002		
Ce						
Nd					0.35	0.09
Sm	0.0006	0.0001	0.0006	0.0001	0.0006	0.0001
Au	0.053	0.014	0.14	0.03	0.21	0.02
Th						
U						
Ca	10		60			
NH4	120		240			
SO4	1300		2200			
NO3	830		1250			
pH	4.20		4.20		4.50	

Element	900807RN6	+/-	900807RN6P	+/-	900807CN7	+/-
Na	44	5	42	5	32	5
Mg						
Al	11	2	6.7	2	2.4	2.1
Cl	700	72	180	20	120	15
K			31	22	18	15
Sc	0.066	0.007	0.054	0.006	0.053	0.006
Ti					3.3	2.9
V	0.18	0.04	0.22	0.04	0.31	0.04
Cr	0.29	0.07	0.074	0.061	0.45	0.06
Mn	0.22	0.02	0.44	0.02	0.26	0.01
Fe	12	9	14	10		
Co	0.044	0.021				
Zn	2.1	0.3	2.9	0.5	2.2	0.4
As	0.038	0.011	0.054	0.007	0.18	0.02
Se						
Br	1.5	0.5	2	0.6	2	0.6
Rb						
Sr					0.96	0.91
Mo						
Cd						
In						
Sb	0.025	0.003	0.043	0.004	0.039	0.004
Cs						
Ba						
La						
Ce						
Nd						
Sm	0.0006	0.0001	0.0006	0.0001	0.0006	0.0001
Au	0.091	0.018	0.041	0.015	0.09	0.02
Th						
U						
Ca	10		10		10	
NH4	50		140		160	
SO4	600		1100		1900	
NO3	310		600		560	
pH	4.60		4.45		4.30	

Element	900807RN7	+/-	900807RN7P	+/-	900810CN1	+/-
Na	19	4	30	4	180	14
Mg			6	5	22	9
Al	3.4	1.9	3.2	1.8	43	4
Cl	45	7	120	15	650	66
K	37	13			310	48
Sc	0.12	0.01	0.066	0.009	0.11	0.01
Ti						
V	0.08	0.03	0.13	0.03	2.2	0.1
Cr	0.35	0.06	0.25	0.07	1.9	0.1
Mn	0.11	0.02	0.24	0.01	3.4	0.1
Fe	20	9			84	12
Co	0.032	0.022	0.028	0.024	0.063	0.025
Zn	2.6	0.3	4.3	0.7	30	4
As	0.05	0.02	0.011	0.004	3.7	0.4
Se					0.5	0.15
Br	0.64	0.23	1.5	0.5	5.4	1.6
Rb	0.12	0.09			0.58	0.28
Sr						
Mo						
Cd					0.06	0.03
In					0.007	0.011
Sb	0.032	0.003	0.023	0.003	0.35	0.03
Cs						
Ba	1.2	0.8	0.8	0.55	2.5	1.6
La	0.005	0.002			0.064	0.006
Ce					0.051	0.037
Nd					0.09	0.08
Sm	0.0006	0.0001	0.0006	0.0001	0.011	0.001
Au	0.27	0.03	0.17	0.02	0.069	0.021
Th						
U						
Ca	10		10			
NH4	70		120			
SO4	800		1300			
NO3	370		560			
pH	4.50		4.45		3.30	

Element	900810RN1	+/-	900810RN1P	+/-
Na	88	8	55	15
Mg	8.6	5.9		
Al	25	3	53	10
Cl	640	68	440	50
K	210	36		
Sc	0.05	0.01	0.55	0.04
Ti			30	15
V	0.84	0.06	0.62	0.14
Cr	0.072	0.063	1.3	0.3
Mn	0.97	0.03	1.5	0.1
Fe	26	14	140	39
Co	0.064	0.027	2.1	0.2
Zn	5.2	0.8	22	3
As	0.13	0.01	0.29	0.12
Se				
Br	3.7	1.1	4.2	1.4
Rb	0.72	0.36		
Sr				
Mo				
Cd				
In				
Sb	0.065	0.005	0.18	0.02
Cs			0.099	0.077
Ba				
La	0.034	0.003		
Ce	0.045	0.033	0.21	0.12
Nd	0.45	0.1	0.56	0.22
Sm	0.005	0.001	0.004	0.002
Au	0.12	0.02	1.2	0.1
Th	0.011	0.007	0.039	0.026
U			0.041	0.025
Ca				
NH4				
SO4				
NO3				
pH	3.75		3.70	

Appendix B1:

Trace Elemental Concentrations (ng/mL), Major Anion Concentrations (μg/mL), and pH Values in Wet Deposition at the Moss Lake in the Adirondack Region, New York

* The concentration of Au is in pg/mL;
** Example sample: WML92032
W: Wet Deposition
ML: Moss Lake
92: Year
03: Month
2: Week

Element	WML91101	+/-	WML91102	+/-	WML91103	+/-
Na	110	9	54	5	71	6
Mg	90	21	25	12	34	13
Al	40	3	120	6	26	2.4
K	29	13	20	10	26	10
Sc			0.011	0.001		
Ti			8.5	2.4		
V	0.23	0.04	0.3	0.04	0.26	0.03
Cr	0.39	0.05	0.25	0.04	0.69	0.06
Mn	3.6	0.1	1.8	0.03	1.6	0.03
Fe	21	7	26	6	36	9
Co	0.22	0.02	0.077	0.013	0.25	0.02
Zn	13	2	11	1	12	1
As	0.092	0.01	0.077	0.009	0.039	0.005
Se	0.16	0.07	0.12	0.06		
Br	2.1	0.6	1.3	0.4	0.8	0.25
Rb	0.58	0.01	0.11	0.07		
Sr	1.4	0.2				
Mo						
Cd						
In						
Sb	0.11	0.01	0.071	0.006	0.048	0.004
Cs						
Ba	2	1	0.68	0.46		
La	0.02	0.002	0.04	0.003	0.009	0.002
Ce			0.049	0.018		
Nd	0.075	0.044			0.14	0.04
Sm	0.003	0.0001	0.006	0.001	0.002	0.0001
Au	0.091	0.013	0.048	0.009	0.065	0.011
Th			0.011	0.004		
U			0.008	0.003		
SO4	3.9	0.4	3.1	0.3	2	0.2
NO3	2.6	0.3	2.3	0.2	2.6	0.3
pH	4.05	0.01	4.21	0.01	4.35	0.01

Element	WML91104	+/-	WML91112	+/-	WML91113	+/-
Na	55	5	38	4	41	4
Mg	15	7	10	7	5.7	4.8
Al	14	3	24	5	28	6
K	15	7	12	5	21	7
Sc	0.003	0.0004	0.003	0.0004	62	5
Ti			3.7	0.4	6.8	1.7
V	0.23	0.05	0.29	0.06	0.27	0.05
Cr	0.6	0.04	0.29	0.03	0.23	0.03
Mn	0.78	0.02	0.48	0.01	0.76	0.01
Fe	25	5	46	5	40	5
Co	0.11	0.01			0.047	0.012
Zn	6.4	0.7	5.7	0.6	8.3	0.9
As	0.03	0.01			0.066	0.009
Se					0.23	0.07
Br	1.1	0.4	0.32	0.13	2.3	0.8
Rb	0.18	0.01			0.078	0.047
Sr	0.22	0.16				
Mo			0.052	0.027	0.03	0.02
Cd					0.02	0.01
In	0.002	0.001				
Sb			0.012	0.001	0.081	0.007
Cs						
Ba					0.67	0.34
La	0.01	0.002	0.008	0.002	0.014	0.002
Ce						
Nd			0.038	0.027		
Sm	0.002	0.0001	0.002	0.0001	0.003	0.0001
Au	0.034	0.006			0.008	0.004
Th						
U	0.006	0.003			0.023	0.003
SO4	1.7	0.2	0.16	0.02	2.3	0.2
NO3	0.75	0.08	0.33	0.03	2	0.2
pH	4.42	0.00	5.18	0.03	4.18	0.02

Element	WML91114	+/-	WML91115	+/-	WML91121	+/-
Na	37	4	67	6	77	6
Mg			7.8	3.7	15	7
Al	18	4	24	4	17	4
K	13	5	19	4	31	8
Sc			0.002	0.0005	0.0006	0.0005
Ti	2.1	1.4			4.2	2
V	0.2	0.04	0.19	0.031	0.32	0.04
Cr	0.2	0.04	0.2	0.03	0.099	0.034
Mn	0.29	0.01	0.35	0.01	1.7	0.03
Fe	16	5	20	5	13	5
Co			0.036	0.012	0.1	0.01
Zn	6.7	0.8	7.1	0.8	7.7	0.8
As	0.017	0.005	0.036	0.008	0.087	0.011
Se					0.14	0.06
Br	0.59	0.2	1	0.3	2.1	0.6
Rb			0.08	0.04	0.091	0.064
Sr						
Mo						
Cd						
In						
Sb	0.021	0.002	0.028	0.002	0.072	0.006
Cs						
Ba					0.36	0.26
La	0.006	0.001	0.009	0.002	0.005	0.001
Ce					0.048	0.022
Nd						
Sm	0.002	0.0001	0.002	0.0001	0.0006	0.0001
Au			0.05	0.01	0.34	0.03
Th						
U	0.004	0.003	0.005	0.003		
SO4	1.3	0.1	0.92	0.09	2.3	0.2
NO3	1.4	0.1	1.1	0.1	2	0.2
pH	4.35	0.01	4.48	0.10	4.29	0.10

Element	WML91122	+/-	WML91123	+/-	WML91124	+/-
Na	64	5	34	3	43	4
Mg	26	7	6.9	4	9	6
Al	24	4	16	4	26	6
K	36	7	5	2	14	6
Sc	0.002	0.0005	0.002	0.0005	0.004	0.001
Ti	1.8	1	4.4	1.8	4.9	2.6
V	0.27	0.04	0.13	0.04	0.17	0.05
Cr	0.22	0.03	0.67	0.03	0.38	0.03
Mn	1.8	0.03	0.51	0.01	0.29	0.01
Fe	23	5	14	5	21	5
Co	0.037	0.013			0.063	0.013
Zn	7	1	8.2	0.9	12	1
As	0.04	0.01	0.05	0.01	0.024	0.012
Se						
Br	1.1	0.3	0.79	0.3	0.82	0.31
Rb			0.071	0.052	0.12	0.05
Sr						
Mo					0.03	0.02
Cd						
In						
Sb	0.032	0.003	0.034	0.003	0.02	0.002
Cs						
Ba	0.96	0.34	0.5	0.28		
La	0.006	0.001	0.008	0.001	0.013	0.002
Ce	0.037	0.022				
Nd						
Sm	0.002	0.0001	0.002	0.0001	0.003	0.0001
Au	0.095	0.013			0.008	0.004
Th					0.006	0.003
U	0.004	0.003	0.008	0.004	0.009	0.003
SO4	1.9	0.2	0.82	0.08	0.12	0.01
NO3	1.9	0.2	1.8	0.2	0.18	0.02
pH	4.58	0.02	4.44	0.02	5.45	0.10

Element	WML92011	+/-	WML92012	+/-	WML92013	+/-
Na	210	15	58	5	83	7
Mg	28	12			7.8	4.5
Al	49	9	23	5	27	5
K	26	1	15	5	37	9
Sc	0.003	0.0005	0.004	0.001	0.002	0.001
Ti					2.8	1.8
V	0.22	0.07	0.24	0.05	0.27	0.05
Cr	0.29	0.03	0.42	0.04	0.3	0.04
Mn	0.9	0.02	0.42	0.01	1.2	0.02
Fe	24	5	25	5	43	6
Co	0.045	0.012	0.08	0.01	0.18	0.02
Zn	9.6	1.1	15	2	8.6	0.9
As	0.03	0.01			0.023	0.006
Se						
Br	1.6	0.6	0.74	0.28	0.53	0.19
Rb	0.1	0.05	0.078	0.068		
Sr						
Mo						
Cd					0.42	0.17
In						
Sb	0.028	0.003	0.029	0.003	0.019	0.002
Cs						
Ba	0.86	0.49				
La	0.011	0.002	0.009	0.002	0.008	0.001
Ce						
Nd						
Sm	0.002	0.0004	0.003	0.0001	0.003	0.0001
Au	0.1	0.01	0.026	0.005		
Th						
U	0.005	0.003	0.01	0.003	0.006	0.003
SO4	0.67	0.07	1	0.1	0.62	0.06
NO3	0.25	0.03	0.71	0.07	0.69	0.07
pH	5.36	0.04	4.56	0.03	4.70	0.05

Element	WML91122	+/-	WML91123	+/-	WML91124	+/-
Na	64	5	34	3	43	4
Mg	26	7	6.9	4	9	6
Al	24	4	16	4	26	6
K	36	7	5	2	14	6
Sc	0.002	0.0005	0.002	0.0005	0.004	0.001
Ti	1.8	1	4.4	1.8	4.9	2.6
V	0.27	0.04	0.13	0.04	0.17	0.05
Cr	0.22	0.03	0.67	0.03	0.38	0.03
Mn	1.8	0.03	0.51	0.01	0.29	0.01
Fe	23	5	14	5	21	5
Co	0.037	0.013			0.063	0.013
Zn	7	1	8.2	0.9	12	1
As	0.04	0.01	0.05	0.01	0.024	0.012
Se						
Br	1.1	0.3	0.79	0.3	0.82	0.31
Rb			0.071	0.052	0.12	0.05
Sr						
Mo					0.03	0.02
Cd						
In						
Sb	0.032	0.003	0.034	0.003	0.02	0.002
Cs						
Ba	0.96	0.34	0.5	0.28		
La	0.006	0.001	0.008	0.001	0.013	0.002
Ce	0.037	0.022				
Nd						
Sm	0.002	0.0001	0.002	0.0001	0.003	0.0001
Au	0.095	0.013			0.008	0.004
Th					0.006	0.003
U	0.004	0.003	0.008	0.004	0.009	0.003
SO4	1.9	0.2	0.82	0.08	0.12	0.01
NO3	1.9	0.2	1.8	0.2	0.18	0.02
pH	4.58	0.02	4.44	0.02	5.45	0.10

Element	WML92011	+/-	WML92012	+/-	WML92013	+/-
Na	210	15	58	5	83	7
Mg	28	12			7.8	4.5
Al	49	9	23	5	27	5
K	26	1	15	5	37	9
Sc	0.003	0.0005	0.004	0.001	0.002	0.001
Ti					2.8	1.8
V	0.22	0.07	0.24	0.05	0.27	0.05
Cr	0.29	0.03	0.42	0.04	0.3	0.04
Mn	0.9	0.02	0.42	0.01	1.2	0.02
Fe	24	5	25	5	43	6
Co	0.045	0.012	0.08	0.01	0.18	0.02
Zn	9.6	1.1	15	2	8.6	0.9
As	0.03	0.01			0.023	0.006
Se						
Br	1.6	0.6	0.74	0.28	0.53	0.19
Rb	0.1	0.05	0.078	0.068		
Sr						
Mo						
Cd					0.42	0.17
In						
Sb	0.028	0.003	0.029	0.003	0.019	0.002
Cs						
Ba	0.86	0.49				
La	0.011	0.002	0.009	0.002	0.008	0.001
Ce						
Nd						
Sm	0.002	0.0004	0.003	0.0001	0.003	0.0001
Au	0.1	0.01	0.026	0.005		
Th						
U	0.005	0.003	0.01	0.003	0.006	0.003
SO4	0.67	0.07	1	0.1	0.62	0.06
NO3	0.25	0.03	0.71	0.07	0.69	0.07
pH	5.36	0.04	4.56	0.03	4.70	0.05

Element	WML92014	+/-	WML92022	+/-	WML92023	+/-
Na	72	6	43	4	45	4
Mg	2.8	2.5	4.9	2.6	4.9	4.2
Al	40	5	22	4	19	5
K	18	5	21	5	16	6
Sc	0.003	0.0004	0.003	0.0004	0.002	0.0004
Ti			3.2	1.3	1.8	1.3
V	0.26	0.04	0.54	0.06	0.23	0.05
Cr	0.36	0.03	0.3	0.03	0.2	0.03
Mn	1.4	0.02	0.64	0.01	0.55	0.01
Fe	21	5	28	5	12	5
Co	0.18	0.01	0.03	0.01	0.039	0.012
Zn	8.6	0.9	7.9	0.9	7.2	0.8
As	0.028	0.006	0.034	0.006	0.064	0.015
Se					0.081	0.057
Br	0.68	0.23	0.74	0.25	1.1	0.4
Rb					0.093	0.038
Sr						
Mo					0.022	0.02
Cd					0.013	0.01
In						
Sb	0.022	0.002	0.043	0.004	0.043	0.004
Cs						
Ba	0.51	0.33			0.45	0.32
La	0.012	0.002	0.23	0.02		
Ce						
Nd	0.042	0.027				
Sm	0.003	0.0001	0.003	0.0001	0.002	0.0001
Au	0.066	0.011			0.16	0.01
Th						
U	0.012	0.003	0.004	0.003		
SO4	0.62	0.06	1.4	0.1	1.9	0.2
NO3	1.1	0.1	1.4	0.1	2	0.2
pH	4.65	0.05	4.42	0.02	4.30	0.02

Element	WML92024	+/-	WML92031	+/-	WML92032	+/-
Na	110	8	170	12	63	5
Mg	13	5	7.6	2.9		
Al	32	6	22	4	10	3
K	27	7	25	7	25	7
Sc	0.004	0.001	0.003	0.0004	0.002	0.0004
Ti	5.1	2.8	3.2	1.3		
V	0.27	0.05	0.38	0.05	0.31	0.06
Cr	0.37	0.04	0.26	0.03	0.21	0.03
Mn	1.2	0.02	0.71	0.01	0.84	0.02
Fe	20	6	22	5	14	5
Co	0.071	0.014	0.02	0.01	0.04	0.01
Zn	8.9	1	9.8	1.1	5.5	0.6
As	0.092	0.012	0.027	0.007	0.015	0.01
Se						
Br	1.8	0.6	1.8	0.6	0.62	0.22
Rb	0.11	0.08			0.11	0.04
Sr						
Mo						
Cd					0.051	0.028
In					0.003	0.002
Sb	0.055	0.005	0.036	0.003	0.023	0.002
Cs						
Ba						
La	0.075	0.006	0.008	0.002	0.007	0.001
Ce						
Nd	0.12	0.03				
Sm	0.003	0.0001	0.002	0.0001	0.0006	0.0001
Au	0.009	0.005			0.22	0.01
Th						
U	0.008	0.003	0.006	0.003		
SO4	1.2	0.1	2.3	0.2	0.84	0.08
NO3	1.8	0.2	1.2	0.1	1	0.1
pH	4.35	0.00	4.22	0.02	4.61	0.02

Element	WML92034	+/-	WML92041	+/-	WML92042	+/-
Na	130	10	93	7	41	4
Mg	7.3	3.1	12	4	7.1	3.7
Al	20	3	31	5	21	4
K	40	7	39	8	22	5
Sc	0.003	0.001	0.002	0.0004	0.0006	0.0004
Ti			2.3	1.2		
V	0.4	0.05	0.38	0.05	0.3	0.04
Cr	0.48	0.04	0.84	0.04	0.25	0.03
Mn	0.69	0.01	2.5	0.04	0.74	0.01
Fe	19	5	46	5	12	5
Co	0.032	0.012	0.12	0.01	0.061	0.012
Zn	7.6	0.9	12	1	6.2	0.7
As	0.035	0.013	0.11	0.02	0.086	0.015
Se			0.2	0.06	0.069	0.053
Br	1.4	0.4	2.8	0.8	1.4	0.4
Rb					0.083	0.031
Sr					0.36	0.26
Mo	0.035	0.022	0.034	0.022		
Cd						
In	0.002	0.001			0.06	0.03
Sb	0.033	0.003	0.099	0.008	0.12	0.01
Cs						
Ba	0.36	0.33	0.55	0.27	1.1	0.3
La	0.012	0.002	0.46	0.03	0.014	0.002
Ce			0.034	0.017	0.038	0.016
Nd						
Sm	0.002	0.0001	0.005	0.001	0.004	0.0001
Au	0.022	0.005	0.017	0.005	4.6	0.4
Th						
U			0.007	0.003	0.004	0.003
SO4	0.95	0.1	2.3	0.2	2.8	0.3
NO3	0.59	0.06	1.6	0.2	2.2	0.2
pH	4.65	0.02	4.28	0.02	4.11	0.01

Element	WML92043	+/-	WML92044	+/-	WML92051	+/-
Na	41	4	63	5	50	5
Mg	3.5	2.5	25	7	21	8
Al	27	4	27	5	34	5
K	20	6	42	9	17	11
Sc	0.0006	0.0004	0.003	0.0004	0.0006	0.0004
Ti			3.3	1.5	2.9	1.3
V	0.25	0.03	0.39	0.07	0.14	0.03
Cr	0.23	0.03	0.43	0.03	0.15	0.03
Mn	0.49	0.01	1.7	0.03	10	0.1
Fe	17	5	24	5	20	5
Co	0.018	0.011	0.12	0.01	0.1	0.01
Zn	6.3	0.7	12	1	5.3	0.6
As	0.024	0.009	0.062	0.013	0.018	0.004
Se			0.15	0.06		
Br	0.32	0.12	1.2	0.4	1.3	0.4
Rb			0.13	0.04		
Sr						
Mo	0.054	0.024	0.031	0.022		
Cd						
In					0.003	0.002
Sb	0.025	0.002	0.065	0.005	0.023	0.002
Cs						
Ba			1.3	0.4	0.97	0.31
La	0.011	0.002	0.15	0.01	0.009	0.001
Ce			0.039	0.016		
Nd						
Sm	0.002	0.0001	0.003	0.0001	0.002	0.0001
Au	0.046	0.009	0.021	0.005	0.34	0.03
Th						
U	0.004	0.003			0.003	0.002
SO4	1.1	0.1	2.5	0.3	0.86	0.09
NO3	0.92	0.1	1.7	0.2	0.72	0.07
pH	4.40	0.02	4.13	0.01	5.16	0.09

Element	**WML92053**	**+/-**	**WML92054**	**+/-**	**WML92064**	**+/-**
Na	79	6	150	11	42	4
Mg	36	10	10	4	22	8
Al	27	5	16	3	45	8
K	63	12	17	7	49	21
Sc	0.004	0.001	0.001	0.0004		
Ti						
V	0.43	0.07	0.3	0.04	0.11	0.04
Cr	0.29	0.03	0.53	0.04	0.098	0.043
Mn	3.2	0.05	1	0.02	2.5	0.04
Fe	26	5	12	5	16	8
Co	0.29	0.02	0.1	0.01	0.23	0.02
Zn	11	1.2	8.1	0.9	8.3	1
As	0.089	0.015	0.036	0.014	0.11	0.01
Se	0.11	0.06			0.16	0.06
Br	1.7	0.5	0.94	0.31	1.6	0.5
Rb					0.13	0.2
Sr						
Mo						
Cd	0.042	0.026			0.066	0.024
In						
Sb	0.094	0.007	0.075	0.006	0.1	0.01
Cs						
Ba	1	0.45	4	0.5	0.71	0.55
La	0.018	0.002	0.077	0.006	0.056	0.004
Ce					0.023	0.021
Nd					0.11	0.05
Sm	0.004	0.0001	0.002	0.0001	0.004	0.0001
Au	0.085	0.008	0.11	0.01	0.72	0.06
Th						
U	0.0004	0.003				
SO4	3.9	0.4	0.81	0.08	2.2	0.02
NO3	2.4	0.2	0.87	0.09	3.5	0.04
pH	4.08	0.01	4.82	0.02	3.73	0.02

Element	WML92071	+/-	WML92072	+/-	WML92073	+/-
Na	57	5	89	7	23	3
Mg	68	28	6	4.2		
Al	34	9	38	3	10	2
K	48	11	96	11	39	10
Sc			0.03	0.01		
Ti			1.8	1.7	6.9	3.3
V	0.26	0.06	0.065	0.025		
Cr			0.056	0.043		
Mn	2.1	0.1	1.8	0.03	0.8	0.02
Fe			57	9		
Co	0.086	0.015	0.15	0.03	0.072	0.018
Zn	2.5	0.3	2.5	0.4	3.6	0.4
As	0.063	0.007	0.099	0.011	0.039	0.005
Se						
Br	0.83	0.25	1.2	0.4	1	0.3
Rb						
Sr						
Mo						
Cd	0.016	0.014	0.027	0.019	0.075	0.023
In						
Sb	0.079	0.006	0.051	0.004	0.042	0.003
Cs						
Ba	0.72	0.44	0.98	0.4	0.59	0.43
La	0.02	0.002	0.012	0.002	0.015	0.002
Ce						
Nd	0.13	0.04				
Sm	0.003	0.0001	0.003	0.0001	0.0005	0.0001
Au	11	1	1.1	0.1	3.3	0.3
Th						
U						
SO4	2.9	0.3	3.5	0.4	3.9	0.4
NO3	3.3	0.3	1.7	0.2	1.8	0.2
pH	4.00	0.01	4.17	0.02	4.05	0.01

Element	WML92074	+/-	WML92075	+/-	WML92081	+/-
Na	46	4	17	2	29	3
Mg			17	9	9.1	4.3
Al	21	2	5	2	12	2
K	42	7	120	13	59	6
Sc					0.024	0.004
Ti					2.4	1.8
V	0.019	0.018	0.14	0.02	0.13	0.02
Cr	0.078	0.039	0.14	0.04		
Mn	0.49	0.01	0.99	0.02	1.1	0.02
Fe	13	7	14	6		
Co	0.07	0.02	0.071	0.013	0.097	0.017
Zn	1.9	0.36	3.3	0.4	2.6	0.3
As	0.043	0.005	0.058	0.007	0.066	0.007
Se			0.12	0.06		
Br	0.79	0.24	1	0.3	1.1	0.3
Rb			0.15	0.08		
Sr						
Mo						
Cd	0.017	0.015	0.026	0.015		
In						
Sb	0.027	0.002	0.064	0.005	0.057	0.005
Cs						
Ba	0.96	0.3			0.92	0.38
La	0.007	0.001	0.009	0.001	0.012	0.002
Ce						
Nd						
Sm	0.002	0.0001	0.0005	0.0001	0.002	0.0001
Au	0.69	0.06	0.3	0.02	2.5	0.2
Th						
U						
SO4	1.8	0.2	5.3	0.5	3.2	0.3
NO3	0.79	0.08	2.3	0.2	1.9	0.2
pH	4.29	0.02	3.93	0.01	4.00	0.01

Element	WML92082	+/-	WML92084	+/-	WML92091	+/-
Na	46	4	35	4	13	2
Mg	9.5	6.3	8.5	5.9	7.9	5
Al					1.7	1.3
K	120	19	11	6	33	7
Sc						
Ti						
V	0.019	0.017	0.071	0.018	0.14	0.02
Cr	0.14	0.04				
Mn	2.9	0.1	1.1	0.1	0.33	0.01
Fe	34	6				
Co	0.13	0.02	0.11	0.02	0.12	0.01
Zn	9.2	0.9	2.3	0.5	2.1	0.3
As	0.24	0.03	0.037	0.005	0.05	0.01
Se	0.18	0.07			0.068	0.063
Br	2	0.6	1.1	0.3	0.9	0.27
Rb					0.1	0.09
Sr			0.23	0.17		
Mo						
Cd	0.045	0.018				
In	0.002	0.003				
Sb	0.11	0.01	0.03	0.003	0.046	0.004
Cs						
Ba	1.5	0.6	0.38	0.29		
La	0.055	0.004			0.002	0.001
Ce	0.029	0.021				
Nd	0.049	0.042				
Sm	0.007	0.001	0.0005	0.0001		
Au	1.3	0.1	0.68	0.06	0.59	0.04
Th	0.005	0.004				
U						
SO4	2.1	0.2	1.8	0.2	2.6	0.3
NO3	3.1	0.3	0.93	0.1	1.1	0.1
pH	3.96	0.01	3.97	0.03	4.19	0.02

Element	WML92092	+/-	WML92093	+/-	WML92094	+/-
Na	13	2	28	3	160	12
Mg	4.1	4.7	8.8	5.8	130	25
Al			2.2	1.3	28	2
K	46	11	13	7	150	20
Sc	0.036	0.004				
Ti						
V	0.051	0.018	0.12	0.02	0.19	0.02
Cr	0.099	0.037			0.12	0.07
Mn	0.59	0.01	0.82	0.02	9.5	0.1
Fe						
Co	0.061	0.015	0.2	0.02	0.22	0.03
Zn	1.1	0.2	3.5	0.6	9.4	1.5
As	0.045	0.005	0.057	0.006	0.13	0.01
Se			0.11	0.09	0.17	0.13
Br	0.72	0.22	1.4	0.4	1.3	0.4
Rb						
Sr					0.6	0.5
Mo						
Cd			0.03	0.01	0.18	0.05
In						
Sb	0.033	0.003	0.048	0.004	0.07	0.01
Cs	0.007	0.011				
Ba	0.34	0.33			0.82	0.47
La	0.0001	0.001	0.015	0.002	0.092	0.007
Ce			0.037	0.02		
Nd	0.12	0.03			0.14	0.05
Sm	0.001	0.0001	0.0005	0.0001	0.0005	0.0001
Au	1.3	0.1	3.1	0.2	0.34	0.04
Th					0.024	0.008
U						
SO4	2.5	0.3	3	0.3	1.7	0.2
NO3	1.1	0.1	1.2	0.1	0.83	0.08
pH	4.29	0.03	4.19	0.01	4.33	0.01

Element	WML92102	+/-	WML92103	+/-	WML92104	+/-
Na	27	3	24	3	51	5
Mg	20	13	9.6	6.7	13	7
Al			3.9	1.3	11	2
K	65	18	53	10	380	35
Sc			0.025	0.006		
Ti						
V	0.046	0.018	0.12	0.02	0.17	0.03
Cr	0.053	0.039			0.06	0.05
Mn	6.2	0.1	1.4	0.02	4.3	0.1
Fe					18	9
Co	0.091	0.015	0.18	0.02	0.31	0.02
Zn	2.9	0.4	2	0.3	5.3	0.8
As	0.017	0.003	0.1	0.01	0.25	0.03
Se					0.31	0.1
Br	0.6	0.2	1.4	0.4	2.5	0.7
Rb						
Sr						
Mo						
Cd			0.024	0.017	0.061	0.021
In						
Sb	0.012	0.001	0.055	0.004	0.12	0.01
Cs						
Ba					2.7	1
La	0.002	0.001	0.011	0.002	0.01	0.002
Ce						
Nd			0.12	0.05	0.23	0.06
Sm	0.0005	0.0001	0.0005	0.0001	0.002	0.0001
Au	0.67	0.04	0.66	0.04	0.67	0.06
Th					0.028	0.006
U	0.004	0.002				
SO4	0.34	0.03	3.1	0.3	3	0.3
NO3	0.74	0.07	2	0.2	2.6	0.3
pH	4.71	0.05	4.14	0.02	4.13	0.01

Element	WML92105	+/-	WML92111	+/-	WML92112	+/-
Na	22	3	33	4	59	5
Mg	3.8	3.6	7.2	5.4	14	6
Al			1.2	1.1	4.5	1.3
K	28	5	38	10	65	12
Sc					0.032	0.004
Ti	1.4	0.8				
V	0.019	0.013	0.097	0.017	0.081	0.02
Cr	0.058	0.042	0.094	0.041	0.058	0.037
Mn	0.55	0.01	0.44	0.01	1.2	0.02
Fe						
Co	0.089	0.016	0.091	0.015	0.036	0.015
Zn	2.4	0.5	8.4	0.9	2.5	0.3
As	0.019	0.003	0.089	0.009	0.017	0.004
Se	0.11	0.06				
Br	0.51	0.16	0.54	0.17	0.84	0.25
Rb			0.19	0.18		
Sr						
Mo						
Cd	0.026	0.017	0.044	0.017	0.036	0.023
In						
Sb	0.011	0.001	0.023	0.002	0.029	0.003
Cs						
Ba						
La	0.24	0.02	0.63	0.04	0.11	0.01
Ce						
Nd						
Sm	0.0005	0.0001	0.0005	0.0001	0.0005	0.0001
Au	0.076	0.014	1.6	0.1	0.22	0.02
Th						
U						
SO4	0.29	0.03	1.7	0.2	0.26	0.03
NO3	1.3	0.1	2	0.2	1.1	0.1
pH	4.47	0.02	4.32	0.01	4.65	0.04

Element	WML92113	+/-	WML92114	+/-	WML92121	+/-
Na	44	4	54	5	100	8
Mg	6.8	5.6	10	5	61	15
Al	3.4	1.4	4.3	1.2	20	2
K	21	12	65	12	130	17
Sc						
Ti					1.7	1.3
V	0.057	0.021	0.12	0.02	0.21	0.02
Cr			0.49	0.05	0.28	0.05
Mn	1.5	0.03	2.6	0.1	3.7	0.1
Fe	13	5	23	7	21	9
Co	0.3	0.02	0.13	0.02	0.19	0.02
Zn	4.7	0.8	53	6	12	1
As	0.053	0.006	0.079	0.008	0.13	0.01
Se					0.27	0.09
Br	1.7	0.5	1.1	0.3	1.3	0.4
Rb						
Sr						
Mo						
Cd	0.076	0.024	0.12	0.03	0.16	0.04
In						
Sb	0.025	0.002	0.053	0.004	0.072	0.006
Cs						
Ba			0.39	0.34		
La	0.36	0.02	0.18	0.01	0.59	0.04
Ce						
Nd					0.13	0.05
Sm	0.0005	0.0001	0.0005	0.0001	0.002	0.0001
Au	0.31	0.03	1.5	0.1	0.23	0.02
Th						
U			0.006	0.003		
SO4	1.2	0.1	1.5	0.2	1.2	0.1
NO3	0.92	0.1	1.9	0.2	3.5	0.4
pH	4.48	0.01	4.29	0.02	4.22	0.02

Element	WML92123	+/-	WML92124	+/-	WML93011	+/-
Na	27	3	140	11	60	5
Mg	7.1	6.1	80	23	6.6	4.4
Al	5.9	1.6	20	3	2.6	1.3
K	70	12	58	19	33	6
Sc	0.002	0.001				
Ti					3.3	1.4
V	0.12	0.02	0.16	0.04	0.062	0.018
Cr	0.37	0.04	0.22	0.04	0.083	0.035
Mn	0.74	0.02	7.3	0.1	0.38	0.01
Fe	33	6	30	6	6.1	5.3
Co	0.11	0.01	0.11	0.01	0.015	0.013
Zn	4.5	0.6	6.7	0.7	2.1	0.3
As	0.23	0.02	0.26	0.03	0.05	0.006
Se	0.093	0.063	0.26	0.07		
Br	2.3	0.6	2	0.6	1	0.3
Rb	0.11	0.09	0.15	0.09		
Sr			1.4	1		
Mo	0.032	0.022				
Cd	0.15	0.06	0.095	0.028	0.13	0.05
In						
Sb	0.08	0.01	0.11	0.01	0.024	0.002
Cs						
Ba			4	1		
La	0.14	0.01	0.24	0.02	0.02	0.002
Ce	0.036	0.017				
Nd						
Sm	0.002	0.0001	0.002	0.0001	0.0005	0.0001
Au	0.55	0.06	0.99	0.1	0.63	0.05
Th						
U						
SO4	1.4	0.1	4	0.4	1.1	0.1
NO3	1.6	0.2	4.8	0.5	0.81	0.08
pH	4.32	0.00	4.17	0.00	4.48	0.01

Element	WML93013	+/-	WML93014	+/-	WML93015	+/-
Na	15	3	120	10	39	4
Mg					31	9
Al	2.1	1.5	16	2	12	2
K	8.5	5.3	37	21	15	8
Sc	0.04	0.006	0.053	0.01	0.036	0.006
Ti						
V	0.18	0.03	0.26	0.04	0.068	0.025
Cr	0.14	0.05	0.76	0.08	0.42	0.05
Mn	0.41	0.01	1.5	0.03	1.4	0.03
Fe						
Co						
Zn			4.1	0.6	2.3	0.5
As	0.012	0.003	0.028	0.005	0.029	0.004
Se						
Br	0.092	0.069	0.74	0.24	0.65	0.22
Rb						
Sr						
Mo						
Cd			3.5	1.7		
In						
Sb	0.027	0.003	0.047	0.004	0.11	0.01
Cs						
Ba						
La	0.002	0.001	0.12	0.01	0.01	0.002
Ce						
Nd						
Sm			0.001	0.0001	0.001	0.0001
Au	0.26	0.05	0.44	0.08	0.3	0.04
Th						
U						
SO4	2.62	0.26	3.12	0.31	0.5	0.1
NO3	3.35	0.34	4.33	0.43	1.64	0.16
pH						

Element	WML93021	+/-	WML93022	+/-	WML93023	+/-
Na	960	64	110	9	20	3
Mg	100	20				
Al	15	2	7.9	1.8	7.6	1.8
K					19	5
Sc	0.077	0.025	0.04	0.006	0.049	0.012
Ti			2	0.5		
V	0.11	0.04	0.04	0.023	0.14	0.03
Cr	0.44	0.09	0.2	0.1	0.54	0.09
Mn	3.4	0.1	2	0.03	0.66	0.02
Fe	49	22	8.9	8.3	29	15
Co	6.6	0.3				
Zn	8.1	1.4	3.4	0.6	5	1
As	0.064	0.01	0.008	0.004	0.019	0.003
Se						
Br	1.3	0.4	0.26	0.11	0.19	0.1
Rb						
Sr						
Mo	0.044	0.041			0.031	0.03
Cd	0.085	0.038				
In						
Sb	0.037	0.004	0.006	0.001	0.022	0.003
Cs						
Ba						
La	0.079	0.007	0.01	0.002	0.023	0.003
Ce						
Nd						
Sm	0.002	0.0001	0.001	0.0001	0.001	0.0001
Au	0.37	0.05	0.92	0.14	0.63	0.11
Th						
U						
SO4	0.81	0.08	0.12	0.01	0.87	0.09
NO3	4.66	0.47	0.65	0.07	2.04	0.2
pH						

Element	WML93031	+/-	WML93032	+/-	WML93033	+/-
Na	33	4	16	3	470	32
Mg			8.8	5.7	16	14
Al	34	3	5.7	1.7	160	8
K	20	12	32	7	63	16
Sc	0.07	0.018	0.043	0.006	0.1	0.02
Ti			4.3	2.5	6.4	0.5
V	0.16	0.03	0.064	0.022	0.24	0.04
Cr	0.82	0.09	0.44	0.05	3.2	0.1
Mn	4.6	0.1	1.2	0.02	6.1	0.1
Fe	22	15	2.4	8.5	23	13
Co	0.12	0.03			0.035	0.027
Zn	5.3	1.4	2.4	0.4	13	2
As	0.1	0.01	0.007	0.003	0.058	0.008
Se	0.21	0.13				
Br	1.7	0.5	0.27	0.11	1.3	0.4
Rb						
Sr						
Mo	1.6	0.4	0.55	0.13	0.42	0.1
Cd	3.9	1			5.5	1.7
In						
Sb	0.041	0.004	0.005	0.001	0.037	0.004
Cs					0.019	0.013
Ba			0.64	0.23		
La	0.099	0.007			0.19	0.01
Ce						
Nd	0.34	0.09				
Sm	0.002	0.0001			0.007	0.001
Au	0.22	0.03	0.24	0.03	0.6	0.1
Th	0.018	0.009				
U						
SO4	2.25	0.23	0.12	0.01	1.12	0.01
NO3	2.86	0.29	0.41	0.04	2.21	0.02
pH						

Element	WML93034	+/-	WML93041	+/-	WML93042	+/-
Na	91	8	36	4	58	6
Mg			15	9	16	7
Al	2.5	1.8	2.7	1.8	1.8	1.7
K	38	16	43	15	13	8
Sc	0.051	0.016	0.07	0.02	0.07	0.02
Ti					5.6	2.8
V	0.061	0.026			0.053	0.023
Cr	0.87	0.11	0.71	0.08	0.26	0.08
Mn	0.63	0.02	4.3	0.1	0.2	0.01
Fe	46	18	16	15		
Co			0.039	0.027		
Zn	4.1	1	6.5	1.2	2.8	1
As	0.024	0.005	0.005	0.003		
Se						
Br	0.4	0.15	1.2	0.4	0.78	0.25
Rb						
Sr						
Mo	0.99	0.23	0.056	0.032		
Cd	0.99	0.48	4.6	1.1	0.049	0.028
In						
Sb	0.013	0.003	0.018	0.002	0.003	0.001
Cs						
Ba						
La	0.011	0.002	0.019	0.002		
Ce						
Nd			0.12	0.07		
Sm			0.002	0.0001		
Au	0.37	0.08	0.24	0.04	1.4	0.1
Th			0.012	0.008		
U					0.004	0.003
SO4	0.62	0.06	0.5	0.1	0.12	0.01
NO3	0.9	0.1	0.74	0.07	0.33	0.03
pH						

Element	WML93043	+/-	WML93044	+/-	WML93051	+/-
Na	74	7	18	3	23	3
Mg	12	8	5.5	3.7	9.8	6.3
Al	5.7	1.6	4.7	1.7	9.2	1.8
K	12	11	28	11	27	18
Sc	0.048	0.005	0.061	0.013	0.07	0.01
Ti						
V	0.038	0.021	0.039	0.022	0.066	0.025
Cr	0.45	0.05	0.64	0.08	0.35	0.06
Mn	1.1	0.02	0.6	0.02	4.3	0.1
Fe	15	8				
Co						
Zn	4.3	0.6	2.7	0.5	2.1	0.5
As	0.02	0.004	0.017	0.003	0.046	0.006
Se			0.28	0.19		
Br	1	0.3	0.46	0.16	0.65	0.22
Rb						
Sr						
Mo						
Cd	0.78	0.25	3.5	1.9	0.58	0.15
In						
Sb	0.022	0.002	0.022	0.003	0.024	0.002
Cs						
Ba	1	0.7				
La	0.13	0.01	0.007	0.002	0.015	0.002
Ce						
Nd	0.12	0.04				
Sm	0.001	0.0001	0.001	0.0001	0.001	0.0001
Au	0.91	0.14	1.2	0.2	0.19	0.03
Th						
U	0.008	0.003				
SO4	0.81	0.08	1.93	0.2	3.43	0.34
NO3	0.74	0.07	1.8	0.2	2.53	0.25
pH						

Element	WML93052	+/-	WML93053	+/-	WML93054	+/-
Na	78	7	16	3		
Mg	450	80	12	8		
Al	26	3				
K	160	38	17	11	9.9	7.9
Sc	0.067	0.009	0.04	0.01	0.068	0.007
Ti			5	2		
V	0.2	0.04	0.044	0.021		
Cr	0.53	0.07	0.23	0.06	0.3	0.1
Mn	18	0.3	0.97	0.02	0.15	0.01
Fe	12	9				
Co	0.15	0.03	0.056	0.026		
Zn	11	1	2.3	0.7	0.26	0.16
As	0.095	0.01	0.035	0.004	0.011	0.003
Se	0.18	0.1				
Br	4.5	1.2	0.61	0.2	0.13	0.08
Rb						
Sr	2.1	1.1			0.88	0.63
Mo	0.18	0.05				
Cd	0.64	0.19	0.18	0.06	0.16	0.1
In			0.004	0.003		
Sb	0.098	0.008	0.032	0.003	0.028	0.003
Cs						
Ba	4.1	1.4				
La	0.05	0.004	0.002	0.001	0.003	0.001
Ce						
Nd	0.64	0.11			0.059	0.042
Sm	0.005	0.001	0.001	0.0001	0.001	0.0001
Au	0.65	0.06	0.4	0.1	0.87	0.14
Th	0.007	0.006				
U						
SO4	9.92	0.99	7.67	0.77	3.43	0.34
NO3	7.23	0.72	3.84	0.38	3.19	0.32
pH						

Element	WML93061	+/-	WML93062	+/-	WML93063	+/-
Na	11	3	28	4	33	4
Mg			13	11	36	12
Al	3.3	1.6	12	2	2.8	1.5
K	53	18	19	12	67	17
Sc	0.046	0.005	0.053	0.006	0.032	0.008
Ti			5.7	2.7		
V	0.074	0.026	0.16	0.03	0.089	0.023
Cr	0.36	0.05	0.59	0.06	0.32	0.07
Mn	2.6	0.04	1.7	0.03	2	0.03
Fe	14	8	14	8		
Co			0.023	0.019		
Zn	4.2	0.6	2.6	0.3	3	0.7
As	0.02	0.003	0.03	0.004	0.039	0.005
Se						
Br	0.64	0.21	1	0.3	0.94	0.29
Rb						
Sr						
Mo						
Cd	10	3	5.9	1.7	0.91	0.28
In						
Sb	0.033	0.003	0.098	0.008	0.045	0.004
Cs						
Ba			0.62	0.51	0.66	0.61
La	0.008	0.002	0.022	0.003	0.004	0.001
Ce						
Nd						
Sm	0.001	0.0001	0.002	0.0001	0.001	0.0001
Au	0.31	0.04	0.25	0.03	2.2	0.3
Th						
U						
SO4	5.18	0.52	6.24	0.62	9.36	0.94
NO3	3.19	0.32	8.99	0.9	7.03	0.7
pH						

Element	WML93064	+/-	WML93071	+/-	WML93072	+/-
Na	16	3	58	6	110	9
Mg	9.2	5.6	22	10	69	18
Al	28	3	84	5	29	3
K	30	15	98	20	270	32
Sc	0.053	0.007	0.086	0.009	0.074	0.018
Ti						
V	0.099	0.025			0.2	0.03
Cr	0.28	0.06	0.81	0.07	0.4	0.09
Mn	2.4	0.04	1.7	0.03	11	0.2
Fe	17	10	30	11		
Co	0.21	0.03	0.04	0.02	0.2	0.04
Zn	2.5	0.4	11	2	5.6	1.3
As	0.053	0.006	0.046	0.006	0.13	0.01
Se					0.14	0.12
Br	1.2	0.4	1.4	0.4	3.2	0.9
Rb						
Sr						
Mo						
Cd	13	7	30	7	0.17	0.06
In						
Sb	0.072	0.006	0.043	0.004	0.083	0.007
Cs			0.027	0.019		
Ba					1.8	1
La	0.063	0.005	0.032	0.003	0.018	0.003
Ce			0.24	0.04		
Nd	0.14	0.07	0.13	0.06	0.53	0.11
Sm	0.007	0.001	0.004	0.001	0.005	0.001
Au	0.92	0.15	0.48	0.06	0.38	0.04
Th					0.059	0.009
U						
SO4	8.11	0.81	3.99	0.4	9.05	0.91
NO3	5.56	0.56	5.89	0.59	4.58	0.46
pH						

Element	WML93073	+/-	WML93074	+/-	WML93075	+/-
Na	39	4	20	3	23	3
Mg	9.7	6.7			21	12
Al	28	3	9	2	10	2
K	39	16			46	17
Sc	0.042	0.008	0.048	0.008	0.042	0.008
Ti	3.6	2.1				
V	0.1	0.03	0.083	0.025	0.11	0.03
Cr	1.2	0.1	0.59	0.08	0.8	0.07
Mn	1.4	0.03	1	0.02	1.8	0.03
Fe	20	10				
Co			0.032	0.022	0.006	0.025
Zn	5	1	2.5	0.6	4.3	0.9
As	0.028	0.004	0.017	0.003	0.032	0.004
Se						
Br	0.22	0.1	0.58	0.2	0.41	0.15
Rb						
Sr						
Mo						
Cd	0.15	0.05			0.42	0.11
In						
Sb	0.053	0.004	0.03	0.003	0.033	0.003
Cs						
Ba					0.58	0.52
La	0.031	0.003	0.009	0.001	0.002	0.001
Ce						
Nd						
Sm	0.003	0.0001	0.001	0.0001	0.001	0.0001
Au	1.8	0.3	0.69	0.12	0.15	0.03
Th						
U						
SO4	7.98	0.8	1.56	0.16	5.68	0.57
NO3	2.62	0.26	1.23	0.12	3.43	0.34
pH						

Element	WML93081	+/-	WML93082	+/-	WML93083	+/-
Na	15	3	11	3	51	5
Mg	21	10	17	8	9.8	5.2
Al	7	2	6.8	1.8	67	4.4
K	25	13			25	16
Sc	0.048	0.009	0.043	0.005	0.077	0.011
Ti						
V	0.071	0.018	0.11	0.02	0.16	0.03
Cr			0.81	0.06	0.25	0.09
Mn	1.1	0.02	0.97	0.02	8.9	0.1
Fe					90	13
Co	0.023	0.022	0.033	0.019	0.085	0.037
Zn	3.6	0.6	3.6	0.5	6.4	0.8
As	0.021	0.003	0.035	0.004	0.1	0.01
Se					0.29	0.16
Br	0.54	0.19	0.35	0.14	1.6	0.5
Rb						
Sr						
Mo						
Cd	0.98	0.29	0.57	0.18	3.9	2.1
In						
Sb	0.041	0.003	0.058	0.005	0.12	0.01
Cs						
Ba			0.69	0.5		
La	0.023	0.003	0.093	0.007	6.2	0.4
Ce					0.22	0.04
Nd						
Sm	0.001	0.0001	0.001	0.0001	0.022	0.002
Au	0.26	0.03	0.17	0.04	0.53	0.1
Th						
U						
SO4	2.5	0.3	6.11	0.61	9.73	0.97
NO3	1.88	0.19	2.94	0.29	4.58	0.46
pH						

Element	WML93084	+/-	WML93091	+/-	WML93092	+/-
Na	54	5	15	3	26	4
Mg	23	12	12	7	41	18
Al	16	2	5.5	1.8	6.5	2.6
K	37	12	25	13	36	16
Sc	0.055	0.007	0.058	0.013	0.039	0.005
Ti			3.2	2.3		
V			0.16	0.03	0.096	0.034
Cr	0.22	0.06	1.2	0.1	1.2	0.1
Mn	1.8	0.03	1.1	0.02	2.9	0.05
Fe	8.9	8.7				
Co			0.04	0.02		
Zn	3	1	1.9	0.5	4.1	0.5
As	0.042	0.005	0.027	0.004	0.05	0.01
Se					0.087	0.081
Br	0.94	0.29	0.49	0.17	0.75	0.24
Rb						
Sr						
Mo						
Cd	0.86	0.22	2	0.59	0.4	0.1
In						
Sb	0.057	0.005	0.032	0.003	0.056	0.005
Cs						
Ba	.54	0.48			1.6	0.8
La	.12	.01	0.1	0.01	0.077	0.006
Ce						
Nd	0.19	0.05				
Sm	0.004	0.001			0.001	0.0001
Au	0.33	0.04	0.46	0.05	0.43	0.04
Th						
U						
SO4	5.86	0.59	4.68	0.47	4.87	0.49
NO3	2.45	0.25	2.45	0.25	5.15	0.52
pH						

Element	WML93093	+/-	WML93094	+/-	WML93101	+/-
Na	71	7	10	3	19	3
Mg	8.2	6.6			40	16
Al	29	4	9.2	2.4	9.4	2.7
K	51	16	17	9	53	14
Sc	0.043	0.004	0.067	0.008	0.04	0.004
Ti						
V	0.22	0.05	0.085	0.029	0.13	0.04
Cr	0.31	0.05	0.56	0.06	0.39	0.05
Mn	1.8	0.03	0.4	0.01	1.8	0.03
Fe	6.7	6.6				
Co	0.36	0.02				
Zn	5.5	0.6	3	0.5	2.7	0.4
As	0.084	0.049	0.027	0.004	0.017	0.013
Se						
Br	0.92	0.29	0.26	0.11	0.51	0.18
Rb	0.15	0.06				
Sr	1.4	0.8				
Mo						
Cd	0.54	0.11	1.3	0.2	0.75	0.11
In						
Sb	0.048	0.004	0.026	0.002	0.032	0.003
Cs						
Ba	1.6	0.8				
La	0.1	0.01	0.022	0.002		
Ce			0.027	0.024		
Nd						
Sm	0.001	0.0001	0.001	0.0001		
Au	0.7	0.06	0.63	0.06	0.16	0.01
Th						
U						
SO4	6.99	0.7	1.87	0.19	3.31	0.33
NO3	2.78	0.28	1.31	0.13	6.46	0.65
pH						

Element	WML93102	+/-	WML93103	+/-	WML93104	+/-
Na	39	4	9.8	2.6	32	4
Mg	31	15			200	72
Al	7.6	3.7	5.4	3.5	32	14
K	42	14			320	61
Sc	0.047	0.007	0.049	0.004	0.062	0.006
Ti			10	3		
V	0.21	0.05	0.12	0.04	0.14	0.11
Cr	0.53	0.06	0.46	0.05	0.41	0.05
Mn	1.8	0.03	0.6	0.01	70	1
Fe	7.9	7.7				
Co						
Zn	6	1	4.3	0.5	2.3	0.37
As	0.11	0.01			0.05	0.01
Se	0.23	0.09				
Br	2	1	2.1	0.6	0.45	0.16
Rb			0.98	0.1		
Sr					3.5	2.8
Mo						
Cd	0.29	0.06	0.69	0.13	0.36	0.07
In						
Sb	0.1	0.01	0.039	0.004	0.036	0.003
Cs						
Ba	2.1	0.9				
La	0.049	0.004	0.009	0.003	0.003	0.001
Ce						
Nd	0.078	0.057				
Sm	0.001	0.0001			0.001	0.0001
Au	0.35	0.03	0.56	0.05	0.77	0.07
Th						
U						
SO4	6.49	0.65	3.06	0.31	2.06	0.21
NO3	4.25	0.43	1.88	0.19	1.31	0.13
pH						

Element	WML93105	+/-
Na	12	3
Mg	14	9
Al	4.6	3
K	30	10
Sc	0.048	0.006
Ti		
V	0.13	0.04
Cr	0.24	0.05
Mn	0.57	0.01
Fe		
Co	0.034	0.019
Zn	3.1	0.5
As	0.044	0.005
Se		
Br	0.33	0.13
Rb		
Sr		
Mo	0.032	0.028
Cd	1.3	0.2
In		
Sb	0.033	0.003
Cs		
Ba	1.1	0.7
La		
Ce		
Nd		
Sm	0.002	0.0002
Au	0.12	0.01
Th		
U		
SO4	1.31	0.13
NO3	1.39	0.14
pH		

Appendix B2:

Trace Elemental Concentrations (ng/mL), Major Anion Concentrations (µg/mL), and pH Values in Wet Deposition at the Willsboro in the Adirondack Region, New York

* The concentration of Au is in pg/mL;

** Example sample: WWI92105

W: Wet Deposition

WI: Willsboro

92: Year

10: Month

5: Week

Element	**WWI92032**	**+/-**	**WWI92034**	**+/-**	**WWI92042**	**+/-**
Na	130	10	82	7	57	5
Mg	65	15	31	10	33	10
Al	75	4	38	3	25	2
K	110	18	36	10	36	10
Sc			0.002	0.001		
Ti						
V	0.39	0.04	0.24	0.03	0.37	0.03
Cr	0.2	0.04	0.29	0.04	3.3	0.1
Mn	1.9	0.1	0.88	0.02	1.1	0.1
Fe	25	7	24	6	22	6
Co	0.2	0.02	0.11	0.01	0.18	0.02
Zn	80	9	26	3	8.8	1
As	0.12	0.01	0.051	0.007	0.057	0.006
Se						
Br	1.3	0.4	1.4	0.4	0.84	0.26
Rb	0.22	0.16				
Sr	1.3	0.6	0.66	0.17	0.44	0.17
Mo						
Cd					0.014	0.011
In			0.002	0.001		
Sb	0.036	0.003	0.024	0.002	0.049	0.004
Cs	0.023	0.012				
Ba	2.6	0.6	1.1	0.5	0.42	0.38
La	0.031	0.003	0.013	0.002	0.009	0.001
Ce						
Nd						
Sm	0.004	0.001	0.003	0.001	0.002	0.001
Au	0.14	0.01	0.1	0.01	0.14	0.01
Th						
U			0.004	0.003		
SO4	1.9	0.2	1	0.1	1.1	0.1
NO3	0.63	0.06	0.63	0.06	0.69	0.07
pH	5	0.01	4.6	0.02	4.5	0.01

Element	WWI92043	+/-	WWI92075	+/-	WWI92081	+/-
Na	77	6	23	3	15	2
Mg	31	10	8.3	3.8	8.7	7.7
Al	37	2	12	2	15	2
K	120	17	45	9	15	9
Sc			0.025	0.006		
Ti						
V	0.31	0.03	0.17	0.03	0.2	0.03
Cr	0.26	0.04	0.02	0.04	0.23	0.05
Mn	1	0.1	0.61	0.01	1	0.02
Fe	28	6			9.8	6.4
Co	0.099	0.014	0.029	0.018	0.16	0.02
Zn	21	2	5	0.4	15	2
As	0.038	0.006	0.035	0.004	0.05	0.01
Se						
Br	0.53	0.18	0.93	0.28	1.3	0.4
Rb						
Sr						
Mo						
Cd	0.02	0.01			0.027	0.017
In						
Sb	0.035	0.003	0.038	0.003	0.08	0.01
Cs						
Ba	0.94	0.45			0.44	0.41
La	0.008	0.001	0.004	0.001	0.036	0.003
Ce	0.049	0.018				
Nd	0.061	0.03	0.082	0.044		
Sm			0.0005	0.0001	0.003	0.001
Au	0.081	0.011	1.8	0.1	1.3	0.1
Th	0.006	0.004				
U						
SO4	0.77	0.08	11	1	3.7	0.4
NO3	2.1	0.2	6.5	0.7	1.6	0.2
pH	4.4	0.01	4.1	0.01	4.1	0.01

Element	WWI92084	+/-	WWI92091	+/-	WWI92092	+/-
Na	89	7	23	3	27	3
Mg	44	12	22	8	13	7
Al	27	2	2.6	1.4	5.2	1.7
K	410	31	130	14	65	10
Sc			0.003	0.001	0.033	0.007
Ti						
V	0.23	0.03	0.12	0.02	0.13	0.03
Cr	0.39	0.04	0.42	0.06	0.053	0.041
Mn	3.3	0.1	0.5	0.01	0.67	0.01
Fe	30	7	14	9		
Co	0.21	0.02	0.21	0.02		
Zn	150	18	10	1	6.6	0.7
As	0.22	0.02	0.04	0.004	0.044	0.005
Se	0.15	0.07				
Br	2.3	0.6	0.93	0.28	1.2	0.3
Rb			0.37	0.35		
Sr						
Mo						
Cd	0.12	0.04	0.058	0.021		
In						
Sb	0.11	0.01	0.06	0.01	0.033	0.003
Cs						
Ba	2	0.4			0.6	0.34
La	0.17	0.01	0.032	0.003	0.003	0.001
Ce						
Nd			0.13	0.05		
Sm	0.004	0.0001	0.001	0.0001	0.001	0.0001
Au	2.2	0.2	2.8	0.2	0.41	0.03
Th			0.025	0.006		
U	0.009	0.003	0.005	0.003		
SO4	17	2	4.3	0.4	2.9	0.3
NO3	5	0.1	6.9	0.7	1.6	0.2
pH	4	0.02	4.1	0.01	4.3	0.01

Element	WWI92093	+/-	WWI92094	+/-	WWI92102	+/-
Na	61	5	26	3	200	14
Mg	17	10	4.1	3.3	39	10
Al	12	2	4.4	1.5	5.5	2
K	88	14	54	5	130	17
Sc						
Ti						
V	0.19	0.03	0.055	0.013	0.16	0.03
Cr	0.1	0.04	0.11	0.05		
Mn	1.6	0.02	0.33	0.01	0.26	0.01
Fe			17	5		
Co			0.2	0.02	0.2	0.03
Zn	19	1.9	6.8	1	5.8	1.2
As	0.08	0.01	0.025	0.003	0.02	0.004
Se						
Br	1.5	0.4	0.68	0.21	1.4	0.4
Rb			0.49	0.36		
Sr	0.96	0.87				
Mo						
Cd	0.26	0.06			0.052	0.024
In						
Sb	0.07	0.01	0.043	0.004	0.02	0.002
Cs						
Ba	1.8	0.6			0.9	0.47
La	0.003	0.001	0.01	0.002		
Ce						
Nd					0.14	0.06
Sm	0.001	0.0001				
Au	5.2	0.4	1.2	0.1	1.8	0.1
Th			0.017	0.006	0.009	0.007
U						
SO4	5.7	0.6	1.8	0.2	1.3	0.1
NO3	3.4	0.3	3.2	0.3	4.9	0.5
pH	4.1	0.02	4.2	0.03	4.4	0

Element	WWI92104	+/-	WWI92105	+/-	WWI92111	+/-
Na	26	3	19	3	12	4
Mg	17	9				
Al	13	10	1.6	0.4	7.1	2.6
K	4500	280	1900	130	40	14
Sc	0.061	0.026				
Ti						
V	0.26	0.08			0.085	0.034
Cr					2	0.1
Mn	0.75	0.02	0.41	0.01	0.22	0.01
Fe						
Co	0.042	0.032	0.22	0.03		
Zn	9.7	1.2	8.1	1.3	16	2
As	0.09	0.01	0.045	0.005	0.025	0.007
Se						
Br	1.9	0.5	1.2	0.4	0.45	0.19
Rb						
Sr						
Mo					0.6	0.15
Cd	0.074	0.033	0.041	0.023		
In						
Sb	0.037	0.004	0.023	0.002	0.034	0.003
Cs						
Ba						
La			0.003	0.001	0.005	0.002
Ce						
Nd	0.24	0.07	0.11	0.06		
Sm	0.0005	0.0001			0.0003	0.0001
Au	0.5	0.04	1.1	0.1	1.6	0.1
Th	1.3	0.1	0.62	0.04		
U						
SO4	2.6	0.3	0.26	0.03	0.86	0.09
NO3	1.7	0.2	0.42	0.04	0.38	0.04
pH	4.3	0.01	4.8	0.02	4.34	0.01

Element	WWI92112	+/-	WWI92113	+/-	WWI92114	+/-
Na	38	5	78	8	56	6
Mg	9.4	7.1	25	16		
Al	3	2.5				
K	46	16	120	33	27	22
Sc						
Ti						
V	0.28	0.05	0.4	0.05	0.33	0.04
Cr						
Mn	0.52	0.02	1.5	0.04	1.2	0.03
Fe						
Co			0.11	0.03		
Zn	8.2	0.9	5	0.7	4.1	0.4
As	0.039	0.007	0.04	0.01	0.018	0.004
Se						
Br	2.1	0.7	1.8	0.5	0.41	0.17
Rb						
Sr						
Mo	0.075	0.043			0.071	0.041
Cd			0.054	0.028		
In	0.006	0.005	0.005	0.004		
Sb	0.035	0.003	0.018	0.002	0.004	0.001
Cs						
Ba						
La	0.006	0.002			0.003	0.002
Ce			0.082	0.034		
Nd	0.23	0.06				
Sm	0.0003	0.0002	0.0003	0.0002	0.0003	0.0002
Au	0.49	0.05	0.33	0.03	0.045	0.009
Th						
U						
SO4	1.9	0.2	1.4	0.1	1	0.1
NO3	1.7	0.2	1.2	0.1	1.5	0.2
pH	4.04	0.02	4.59	0.01	4.23	0.004

Element	WWI92123	+/-	WWI93011	+/-	WWI93013	+/-
Na	48	6	430	31	31	5
Mg	47	24	160	36	13	12
Al	280	15	230	17	200	12
K	85	20			160	25
Sc						
Ti	5.9	5.4				
V	1	0.1	6.7	0.4	0.74	0.09
Cr	0.066	0.062			0.16	0.07
Mn	0.8	0.03	9.1	0.2	0.23	0.02
Fe	14	9	27	22		
Co			0.31	0.04		
Zn	39	4	52	6	30	3
As	0.055	0.009	0.046	0.008	0.021	0.005
Se						
Br	0.33	0.16	2.6	0.8	0.81	0.28
Rb	0.19	0.06				
Sr						
Mo	1.3	0.3	0.19	0.07	0.094	0.045
Cd			0.076	0.042		
In	0.012	0.01	0.021	0.015		
Sb	0.03	0.003	0.036	0.004	0.003	0.001
Cs						
Ba	2.2	1.8				
La	0.006	0.002			0.008	0.002
Ce	0.43	0.04				
Nd						
Sm	0.001	0.0002	0.0003	0.0002	0.0003	0.0002
Au	0.053	0.012	0.3	0.04	0.57	0.05
Th			0.025	0.011		
U						
SO4	2.2	0.2	3.8	0.4	0.69	0.07
NO3	3.1	0.3	3.3	0.3	2.1	0.2
pH	3.64	0.02	5.58	0.01	4.63	0.01

Element	WWI93014	+/-	WWI93015	+/-	WWI93022	+/-
Na	260	20	190	15	21	4
Mg	130	33	110	32		
Al	250	15	26	7	30	5
K	570	90	390	65		
Sc						
Ti						
V	1.3	0.2	0.61	0.1	0.17	0.06
Cr	0.14	0.06				
Mn	1	0.03	1.2	0.03	0.45	0.02
Fe						
Co	0.03	0.02				
Zn	46	5	9.1	1	3.3	0.37
As	0.06	0.011	0.021	0.007	0.005	0.003
Se						
Br	2.1	0.6	1.9	0.6	0.39	0.17
Rb	0.5	0.14	0.14	0.08	0.093	0.064
Sr			2.6	1.3		
Mo	0.051	0.04			0.1	0.05
Cd	0.099	0.034	0.038	0.034		
In						
Sb	0.028	0.003	0.033	0.003	0.011	0.001
Cs						
Ba	3.9	2.3			1.6	1.1
La	0.007	0.003				
Ce	0.11	0.04				
Nd						
Sm	0.001	0.0002			0.0003	0.0002
Au	0.11	0.02	0.017	0.012	0.36	0.04
Th						
U						
SO4	1.6	0.2	0.93	0.09	0.25	0.03
NO3	2	0.2	3.4	0.3	2.2	0.2
pH	4.8	0.01	4.69	0.004	4.63	0.01

Element	WWI93023	+/-	WWI93031	+/-	WWI93032	+/-
Na	22	4	170	14	68	7
Mg	21	18	64	25	36	20
Al	22	4	58	7	6.4	2.4
K	24	19	130	53	210	31
Sc						
Ti						
V	0.15	0.05	0.43	0.05		
Cr			0.14	0.08	0.076	0.065
Mn	0.61	0.02	1.3	0.03	0.62	0.03
Fe	22	9	16	13		
Co			0.25	0.03		
Zn	7.8	0.8	100	11	57	6
As	0.017	0.005	0.064	0.009	0.041	0.007
Se						
Br	0.26	0.13	6.8	1.9	0.41	0.18
Rb						
Sr						
Mo	0.086	0.045	0.81	0.19		
Cd			0.066	0.028		
In						
Sb	0.004	0.001	0.026	0.003	0.019	0.002
Cs						
Ba						
La			0.007	0.002	0.006	0.002
Ce			0.068	0.038		
Nd			0.57	0.12		
Sm	0.001	0.0002	0.001	0.0002	0.0003	0.0002
Au	0.23	0.03	0.16	0.01	0.12	0.02
Th						
U						
SO4	0.15	0.02	2.1	0.2	0.58	0.06
NO3	0.55	0.06	1.7	0.2	8.5	0.9
pH	4.91	0.02	4.74	0.004	4.09	0.02

Element	WWI93033	+/-	WWI93034	+/-	WWI93041	+/-
Na	150	12	180	14	20	4
Mg	11	9	41	15		
Al	17	3	36	3	4.9	2.3
K	73	26	470	68	17	11
Sc						
Ti						
V	0.87	0.07	0.11	0.05	0.11	0.03
Cr	0.092	0.062				
Mn	1.2	0.03	0.58	0.02	0.32	0.02
Fe	11	9	16	11		
Co						
Zn	5.4	0.6	52	6	1.8	0.2
As	0.13	0.02	0.016	0.005	0.007	0.005
Se						
Br	1.3	0.4	1.3	0.4	0.49	0.2
Rb	0.061	0.043			0.096	0.053
Sr						
Mo	0.038	0.037				
Cd			0.031	0.025	0.08	0.03
In						
Sb	0.13	0.01	0.014	0.002	0.028	0.003
Cs						
Ba						
La	0.011	0.002			0.005	0.002
Ce						
Nd						
Sm	0.001	0.0002	0.0003	0.0002	0.0003	0.0002
Au	0.75	0.07	0.26	0.03	0.063	0.009
Th						
U						
SO4	0.15	0.02	1.2	0.1	0.4	0.04
NO3	3.6	0.4	1.4	0.1	0.67	0.07
pH	4.01	0.01	6.16	0.02	4.23	0.01

Element	WWI93042	+/-	WWI93043	+/-	WWI93044	+/-
Na	72	7	240	18	16	4
Mg	32	15	35	12	13	12
Al	33	3	6.1	4.4		
K	57	20	86	1	49	16
Sc						
Ti						
V	0.1	0.04	0.12	0.06		
Cr						
Mn	0.28	0.02	0.51	0.03	0.4	0.02
Fe						
Co						
Zn	18	2	2.1	0.2	85	9
As	0.012	0.004	0.035	0.009	0.016	0.004
Se						
Br	2	1	4.4	1.3	0.24	0.13
Rb			0.21	0.09	0.17	0.08
Sr						
Mo						
Cd			0.12	0.05		
In						
Sb	0.014	0.002	0.035	0.003	0.005	0.001
Cs						
Ba						
La						
Ce					0.088	0.032
Nd			0.16	0.06		
Sm	0.0003	0.0002	0.0003	0.0002	0.0003	0.0002
Au	0.32	0.03	0.51	0.05	0.21	0.02
Th						
U						
SO4	0.6	0.06	0.9	0.09	1.8	0.2
NO3	0.6	0.06	0.94	0.09	1.1	0.1
pH	4.31	0.01	5.07	0.02	4.74	0.004

Element	WWI93051	+/-	WWI93052	+/-	WWI93054	+/-
Na	67	7	13	4	22	4
Mg	150	51				
Al	27	4			7.2	2.5
K	260	55	22	14	36	13
Sc			0.007	0.001		
Ti						
V	0.39	0.07	0.2	0.04	0.28	0.04
Cr	0.11	0.06			0.15	0.06
Mn	9.2	0.1	0.83	0.02	0.72	0.03
Fe	13	9	18	10	25	10
Co	0.037	0.024				
Zn	35	4	2.4	0.4	5.8	0.6
As	0.12	0.02	0.044	0.006	0.025	0.005
Se						
Br	5.2	1.5	0.11	0.1	1	0.4
Rb	0.39	0.11			0.29	0.08
Sr						
Mo					0.23	0.06
Cd						
In						
Sb	0.096	0.008	0.027	0.003	0.026	0.003
Cs						
Ba	5.2	2.2	1.1	0.8		
La	0.032	0.003				
Ce	0.076	0.034				
Nd						
Sm	0.004	0.001	0.0003	0.0002	0.0003	0.0002
Au	0.074	0.011	0.074	0.013	0.34	0.04
Th						
U					0.012	0.004
SO4	5.1	0.5	2.9	0.3	1.9	0.2
NO3	4.6	0.5	2.1	0.2	1.3	0.1
pH	4.53	0.004	3.94	0.01	3.83	0.02

Element	WWI93061	+/-	WWI93062	+/-	WWI93063	+/-
Na	17	4	37	5	32	5
Mg			38	13	31	13
Al	2.7	2.2	5.6	2.3	5.4	2.6
K	69	23	110	27	120	23
Sc						
Ti						
V	0.17	0.04	0.22	0.04	0.28	0.04
Cr	0.13	0.06	0.098	0.063	0.15	0.07
Mn	1.4	0.03	1.4	0.03	1.6	0.04
Fe	15	10				
Co	0.038	0.025			0.055	0.025
Zn	4.9	0.6	6.2	0.7	8.5	1
As	0.012	0.004	0.04	0.01	0.052	0.006
Se						
Br	0.17	0.11	1.1	0.4	0.49	0.2
Rb	0.2	0.11	0.47	0.1	0.21	0.16
Sr						
Mo						
Cd						
In						
Sb	0.009	0.001	0.022	0.002	0.061	0.005
Cs						
Ba	1.5	1.4			1.6	1.2
La	0.015	0.002	0.007	0.002		
Ce						
Nd	0.073	0.054				
Sm	0.0003	0.0002	0.001	0.0002	0.002	0.0002
Au	0.18	0.02	0.074	0.01	0.75	0.05
Th						
U	0.018	0.004				
SO4	0.8	0.08	2.2	0.2	2.2	0.2
NO3	1.9	0.2	1.8	0.2	1.2	0.1
pH	3.84	0.01	4.17	0.01	3.82	0.01

Element	WWI93064	+/-	WWI93072	+/-	WWI93074	+/-
Na	61	7	120	11	85	8
Mg	18	12	43	20	39	13
Al	10	3	14	3	2.8	2.7
K	260	38			270	46
Sc						
Ti			5	4	5.1	3.9
V	0.32	0.05	0.42	0.05	0.097	0.043
Cr	0.08	0.07	0.22	0.06		
Mn	2	0.04	2.3	0.05	0.36	0.02
Fe			19	10		
Co	0.073	0.027			0.047	0.024
Zn	11	1	3.1	0.4	3.1	0.4
As	0.036	0.006	0.039	0.006	0.059	0.008
Se						
Br	1.8	0.6	1.9	0.6	1	0.3
Rb	0.23	0.17	0.07	0.06		
Sr	2.3	1.6				
Mo						
Cd						
In	0.008	0.006				
Sb	0.032	0.003	0.048	0.004	0.023	0.002
Cs						
Ba					2.1	1.4
La						
Ce					0.093	0.037
Nd						
Sm	0.001	0.0001	0.002	0.0001	0.0003	0.0002
Au	0.51	0.05	0.23	0.03	0.37	0.02
Th						
U						
SO4	2.7	0.3	3.8	0.4	0.85	0.09
NO3	2.1	0.2	2.5	0.3	0.48	0.05
pH	4.24	0.01	3.29	0.01	4.92	0.01

Element	WWI93075	+/-	WWI93081	+/-	WWI93082	+/-
Na	44	6	46	6	66	7
Mg	42	15	16	7	18	9
Al	22	3	17	3	12	3
K	34	22	110	21	130	28
Sc					0.007	0.001
Ti						
V	0.23	0.04	0.53	0.05	0.38	0.03
Cr	0.11	0.06	0.13	0.06	0.11	0.06
Mn	1.8	0.04	1.6	0.04	1.4	0.04
Fe	19	10	13	9	18	10
Co					0.06	0.02
Zn	4	0.5	9.9	1	8.7	0.9
As	0.048	0.008	0.054	0.009	0.039	0.007
Se	0.02	0.1				
Br	1.5	0.5	2.5	0.8	0.7	0.25
Rb	0.085	0.069	0.26	0.08		
Sr	0.83	0.76				
Mo			0.13	0.05		
Cd	0.093	0.053	0.045	0.032		
In						
Sb	0.054	0.005	0.06	0.005	0.066	0.005
Cs						
Ba						
La	0.005	0.002			0.008	0.002
Ce	0.033	0.032			0.092	0.034
Nd						
Sm	0.003	0.001	0.001	0.0002	0.001	0.0002
Au	0.17	0.02	0.51	0.05	1	0.1
Th						
U						
SO4	2.7	0.3	4.6	0.5	4.1	0.4
NO3	2.1	0.2	2.9	0.3	3.1	0.3
pH	3.64	0.01	3.15	0.01	3.21	0.01

Element	WWI93083	+/-	WWI93084	+/-	WWI93091	+/-
Na	19	4	27	5	14	4
Mg					8.5	7
Al	5.4	2.2	14	3	15	3
K	24	15	48	23		
Sc						
Ti	3.3	2.1				
V	0.39	0.05	0.21	0.05	0.26	0.05
Cr					0.076	0.065
Mn	0.55	0.02	2.7	0.1	0.68	0.03
Fe						
Co						
Zn	2.1	0.3	5.6	0.7	2.2	0.3
As	0.026	0.005	0.043	0.007	0.035	0.005
Se						
Br	0.42	0.18	0.45	0.19	0.71	0.26
Rb	0.11	0.1				
Sr						
Mo						
Cd						
In						
Sb	0.031	0.003	0.057	0.005	0.034	0.003
Cs						
Ba						
La			0.003	0.002		
Ce			0.048	0.034		
Nd						
Sm	0.0003	0.0002	0.002	0.0002	0.0003	0.0002
Au	0.46	0.02	0.42	0.03	0.17	0.02
Th						
U					0.009	0.004
SO4	1.7	0.2	4.5	0.5	2.6	0.3
NO3	0.87	0.09	1.7	0.2	1.1	0.1
pH	3.55	0.01	3.25	0.01	3.16	0.02

Element	WWI93092	+/-	WWI93094	+/-	WWI93101	+/-
Na	37	5	25	5	23	4
Mg	25	18			28	15
Al	20	4	11	4	15	3
K	95	34				
Sc						
Ti						
V	0.32	0.06	0.2	0.05	0.25	0.04
Cr	0.069	0.062				
Mn	2.7	0.1	0.92	0.03	0.84	0.02
Fe	19	9				
Co			0.061	0.026		
Zn	7	0.8	3.1	0.5	3.2	0.6
As	0.07	0.01	0.074	0.009	0.036	0.005
Se			1.1	0.1		
Br	0.7	0.25	0.44	0.18	0.39	0.18
Rb	0.086	0.045	0.21	0.18		
Sr						
Mo	0.044	0.039			0.092	0.045
Cd	2.6	0.6	0.065	0.028		
In						
Sb	0.043	0.004	0.06	0.01	0.045	0.004
Cs						
Ba						
La	0.009	0.002				
Ce	0.057	0.032	40	2	0.038	0.035
Nd						
Sm	0.003	0.001	0.0003	0.0002	0.001	0.0001
Au	1.3	0.1	2.1	0.1	0.21	0.02
Th						
U						
SO4	5.5	0.6	2.4	0.2	3.1	0.3
NO3	2.6	0.3	1.4	0.1	1.7	0.2
pH	3.27	0.01	3.55	0.01	3.13	0.01

Element	WWI93102	+/-	WWI93103	+/-	WWI93104	+/-
Na			98	9	90	9
Mg	8.7	6.2	35	15	35	14
Al	5.2	2.7	5.1	2.9	5	2.7
K			67	22	190	29
Sc						
Ti						
V	0.041	0.034	0.38	0.05	0.13	0.04
Cr	0.087	0.062				
Mn	0.097	0.015	0.78	0.02	0.54	0.02
Fe						
Co			0.059	0.025		
Zn			8	0.9	7.5	1
As	0.014	0.005	0.15	0.02	0.033	0.005
Se						
Br	0.19	0.12	9.5	2.7	0.96	0.33
Rb	0.12	0.07				
Sr						
Mo						
Cd			0.14	0.04		
In						
Sb	0.012	0.002	0.037	0.003	0.038	0.004
Cs						
Ba						
La			0.019	0.003	0.005	0.002
Ce			0.045	0.034		
Nd			0.23	0.08		
Sm	0.0003	0.0002	0.0003	0.0002	0.0003	0.0002
Au	0.25	0.03	0.5	0.05	0.14	0.01
Th						
U						
SO4	4.3	0.4	1.2	0.1	1.7	0.2
NO3	1.8	0.2	1.7	0.2	1	0.1
pH	3.25	0.02	3.81	0.01	3.49	0.02