ABSTRACT

Title of Dissertation: Spatial and Temporal Variations in ^{36}Cl Deposition in the Northern United States

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Chlorine-36,a cosmogenic radioisotope, has been developed for use as a tracer in hydrological systems. The deposition of atmospheric ^{36}Cl, although of primary importance to hydrological applications, has not been well studied. To begin to address this problem, ^{36}Cl has been measured in monthly, wet-only, precipitation samples collected from February, 1991, to January, 1993, at the Elms Environmental Education Center in St. Mary's County, Maryland. In addition, bulk deposition samples were collected over a 1 y period at seven sites across the Northern United States and analyzed for ^{36}Cl.

The mean, wet-only ^{36}Cl/Cl ratio for the 2 y sampling period is 68±19 ($\times 10^{-15}$), and the mean ^{36}Cl concentration is 1.2±0.1 ($\times 10^{6}$) atoms/L. The ^{36}Cl wet deposition flux data reveal a distinct seasonal deposition pattern, with peaks occurring in March and April. This pattern is attributed to stratospheric/tropospheric exchange. The mean ^{36}Cl wet deposition flux is 38.2±5 atoms/m^{2}s. Comparison between wet-only and bulk deposition samples indicates that the difference accounts for approximately 25% of the total ^{36}Cl deposition flux at the Elms site.

A new model, using ^{90}Sr to predict the ^{36}Cl deposition pattern, is developed to predict $^{36}Cl/Cl$ ratios across the United States. Chlorine-36/Cl ratios in bulk deposition samples collected across the northern United States agree well with the model predictions. A mean global ^{36}Cl production rate of approximately 28 to 38 atoms/m^2s is indicated by these samples.

A comparison between ^{36}Cl concentrations in the Aquia and Magothy aquifers is southern Maryland and bulk deposition samples collected at the Elms, MD, site indicated that modern precipitation can account for the ^{36}Cl content in the youngest water in these aquifers. Surface water samples from the Susquehanna River basin reveal ^{36}Cl and stable chloride concentrations an order of magnitude higher than in bulk deposition samples collected at State College, PA. The source of excess ^{36}Cl in the Susquehanna is not known. Possible explanations include 'bomb-pulse' ^{36}Cl and in-situ ^{36}Cl production in surface rocks.

SPATIAL AND TEMPORAL VARIATIONS IN CHLORINE-36 DEPOSITION IN THE NORTHERN UNITED STATES

by

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Chapter 1

INTRODUCTION

The ability of Accelerator Mass Spectrometry (AMS) to measure natural levels of long-lived cosmogenic radionuclides has resulted in the rapid development of applications ranging from archeology to molecular biology. Many of the isotopes now measured by AMS were previously unsuitable for most applications, due to the experimental difficulty involved in measuring rare isotopes with extremely low specific activities. With AMS, the combined advantages of isotope separation by mass spectrometry and elemental identification using high energy nuclear detection techniques enables the measurement of long-lived isotopes at very low abundance ratios.

As quickly as AMS facilities developed the capability to measure these elusive isotopes, scientists found useful applications. Archeological studies were revolutionized by the quick and relatively non-destructive ^{14}C measurements made possible by AMS. Material scientists now use AMS to detect impurities and dopants in semiconductors, and the biomedical field is rapidly developing ultra-sensitive tracer techniques using AMS. However, the most widespread use of AMS radionuclides has been in the Earth and planetary sciences. Geology, cosmochemistry, oceanography, hydrology and, more recently, meteorology have all begun to benefit from AMS measurements.

Chlorine-36 is among the cosmogenic radioisotopes recently developed as a result of AMS. Early efforts to measure natural ^{36}Cl by radioactive decay were moderately successful [SCHAEFFER (1960)], yet required long counting times and very large samples. These difficulties were overcome as a result of AMS, and now sufficient facilities exist to provide ^{36}Cl measurements for any interested researcher. This isotope has already been proven to be useful as a hydrological tracer, yet the surface of its full potential has hardly been scratched. While numerous studies exist using ^{36}Cl as a groundwater tracer, experimental data concerning ^{36}Cl production rates and transport mechanisms is rare. In the rush to develop useful hydrological applications, a crucial element has been overlooked, and that is the ^{36}Cl supply. Chlorine-36 production rates have been estimated, and atmospheric transport mechanisms have been assumed. Since any radioactive decay dating depends critically on the initial concentration of the radionuclide, the sources of ^{36}Cl must be thoroughly investigated before substantial weight can be placed on hydrological results.

1.1 COSMOGENIC RADIOISOTOPES

Cosmic radiation constantly bombards the Earth's atmosphere. The discovery of this phenomenon occurred shortly after the development of radiation detectors. In an attempt to reduce the effect of background radiation, which was attributed exclusively to terrestrial uranium-thorium decay chain products, radiation detectors were carried by balloon to altitudes up to 9000 m. The surprising result was an increase, rather than a decrease, in measured background radiation. The subsequent conclusion led to the discovery of what is now known as "cosmic radiation".

Primary cosmic radiation consists mainly of high energy protons and alpha particles. Most originate within the Earth's galaxy as a result of distant supernova (galactic cosmic rays) or from the Sun (solar cosmic rays). When these particles collide with nitrogen, oxygen, argon and other species in the upper atmosphere, a variety of radioactive products are formed. Secondary particles, including neutrons, protons and alpha particles, can in turn react with atmospheric constituents to produce radioisotopes. Table 1.1 lists the most common of these cosmogenic radioisotopes. The production of these isotopes depends on many factors, including the flux and type of cosmic ray particles, their energy spectra and the relevant reaction cross sections.

Table 1.1

Cosmogenic Radionuclides (from LAL and PETERS (1958))

Isotope	Half life	Estimated Global Inventory
^{3}He	stable	3.2 x 10^{3} tons
^{10}Be	2.5 x 10^{6} y	430 tons
^{26}Al	7.4 x 10^{5} y	1.1 tons
^{36}Cl	3.1 x 10^{5} y	15 tons
^{14}C	5730 y	75 tons
^{32}Si	500 y	1.4 kg
^{3}H	12.5 y	3.5 kg

1.2 INTRODUCTION TO ^{36}Cl

Chlorine-36 is a long-lived cosmogenic radionuclide. It is produced in the atmosphere and on the Earth's surface as a result of cosmic ray interactions. Approximately 70% all atmospheric (usually referred to as 'meteoric') ^{36}Cl is produced in the stratosphere, and 30% is produced in the troposphere. Production of ^{36}Cl also takes place in the lithosphere by neutron activation of stable ^{35}Cl. Chlorine-36 undergoes beta decay to ^{36}Ar with a half-life of 3.01 x 10^5y [BENTLEY et al. (1986)].

1.3 PRODUCTION MECHANISMS

1.3.1 METEORIC ^{36}Cl

The primary natural source of ^{36}Cl is cosmic ray interactions in the upper atmosphere. Most ^{36}Cl is produced as a result of either nuclear spallation (Eq. 1) or neutron activation (Eq. 2).

$$^{40}\mathrm{Ar}\,(x,x'\alpha)^{36}\mathrm{Cl} \qquad \text{(Eq. 1.1)}$$

$$^{36}\mathrm{Ar}\,(n,p)^{36}\mathrm{Cl} \qquad \text{(Eq. 1.2)}$$

($\sigma_{\mathrm{thermal}}$= 1.5 mb [JIANG et al. (1990)])

$$^{35}\mathrm{Cl}(n,\gamma)^{36}\mathrm{Cl} \qquad \text{(Eq. 1.3)}$$

($\sigma_{\mathrm{thermal}}$ = 43 b [FRIEDLANDER et al. (1981)])

While the reaction described in Eq. 3 occurs in the atmosphere, its contribution is negligible due to the relatively low abundance of the target nuclide ^{35}Cl.

Several attempts have been made to calculate the cosmogenic ^{36}Cl production rate. The original estimate by LAL and PETERS (1958) of 1.1 atoms/m^{2}s was revised by ONUFREIV (1968) to give a total of 1.6 atoms/m^{2}s. However, a recent determination of the cross section for Eq. 2 suggests that this reaction is insignificant, thus reducing the estimated production rate again to 1.1 atoms/m^2s [JIANG et al. (1990), ANDREWS and FONTES (1992)]. As mentioned previously, approximately 70% of the ^{36}Cl produced in the atmosphere is stratospheric in origin, the remaining 30% is produced in the upper troposphere.

1.3.2 LITHOSPHERIC ^{36}Cl

While the vast majority of cosmic radiation is attenuated in the atmosphere, a small amount reaches the Earth's surface. Secondary cosmic neutrons, produced by spallation of K and Ca, can activate abundant ^{35}Cl to produce ^{36}Cl in the surface ocean and crustal rocks (Eq. 1.3). The production rate varies greatly with depth and with stable Cl^- content. This source of ^{36}Cl is limited to the upper few meters of the earth's crust (or surface ocean), but can be important in areas with high Cl^- concentrations due to the relatively high thermal neutron reaction cross section (sigma) [ANDREWS and FONTES (1992)]. The ^{36}Cl production rate due to in-situ thermal neutron activation can be calculated using Equation 1.4.

$$N_{(^{36}Cl)} = \sigma\ N_{(^{35}Cl)}\ \phi\ (1-e^{-\lambda t})/\lambda \qquad \text{(Eq. 1.4)}$$

where: N = number of atoms

σ = the ^{35}Cl neutron activation cross-section

ϕ = the neutron flux

λ = the ^{36}Cl decay constant

t = exposure time

The estimated secular equilibrium ^{36}Cl/Cl ratio for most rocks at sea level is on the order of 1 x 10^{-11} [BENTLEY et al. (1986)]. ANDREWS and FONTES (1992) calculate that, without mixing, the equilibrium ^{36}Cl/Cl ratio in the upper few meters of the ocean would be 1.3 x 10^{-12}. However, oceanic circulation causes a dilution with ^{36}Cl depleted deep water and the resulting ratio is approximately 4 x 10^{-15}.

Production of ^{36}Cl can occur deeper within the Earth in areas with significant uranium-thorium concentrations. Neutrons produced by reactions between decay chain alpha particles and various light elements, or during spontaneous fission of ^{238,235}U, can activate ^{35}Cl and produce ^{36}Cl. As a result, groundwater ^{36}Cl concentrations in certain areas can increase predictably with depth. A study in Stripa, Sweden, takes advantage of ^{36}Cl ingrowth with depth to estimate groundwater residence time [ANDREWS, FONTES, MICHELOT and ELMORE (1986)].

1.3.3 ANTHROPOGENIC ^{36}Cl

Nuclear weapons tests during the 1950's and early 1960's injected enough ^{36}Cl into the stratosphere to raise the global background level by nearly 3 orders of magnitude [BENTLEY et al., (1982)]. The detonations responsible for this "bomb-pulse" took place in the Pacific atolls, where the neutrons released during the blasts could activate the abundant marine chloride. The bomb-pulse has been clearly identified in Greenland ice core samples [SUTER (1987), SYNAL (1990), ELMORE (1982)], in a series of shallow ground water samples taken in Ontario, Canada [BENTLEY (1982)], and in arid soil samples from the southwestern United States [PHILLIPS (1990)].

Due to the specific circumstances involved in the production of "bomb-pulse" ^{36}Cl (it was primarily produced during early tests in the Pacific atolls) and its behavior in the atmosphere, background concentrations have now returned to natural pre-bomb levels. This is not the case with many other weapons-produced radionuclides. For instance, ^{129}I concentrations have remained elevated since the bomb-pulse because ^{129}I is a fission product continually released in small amounts from nuclear power plants and reprocessing facilities. Carbon-14 concentrations remain elevated due to its relatively long atmospheric residence time (10-20 y) . Chlorine-36 is neither a fission product, nor does it have an unusually long atmospheric residence time (2 y). As a result, atmospheric ^{36}Cl background concentrations are generally believed to have returned to pre-bomb levels.

1.3.4 OTHER SOURCES

It should be noted here that the literature contains mounting evidence that the current calculated production rates significantly underestimate actual ^{36}Cl production (ice core data by SUTER (1987), SYNAL et al.(1990); groundwater data by MICHELOT and FONTES (1989), MARGARITZ (1990), PURDY (1991), ANDREWS AND FONTES (1992); precipitation data by KNEIS et al. (1994)). ANDREWS and FONTES (1992) address this discrepancy with respect to groundwater studies and conclude that *in-situ* ^{36}Cl production in the soil zone (0-5 m) and subsequent dissolution may be more important than previously considered. It is also concluded by Andrews and Fontes that, in view of the ice core data, cosmogenic production is probably higher than expected, however, no further explanation is given.

1.4 ^{36}Cl APPLICATIONS

Several characteristics of ^{36}Cl make it an attractive tracer for geological and hydrological applications. The 3.01 x 10^5 year half-life makes ^{36}Cl a suitable tracer for geological time scales. In addition, chlorine has a very high electron affinity and exists as Cl^- in nearly all natural hydrological systems. This hydrophilic anion is extremely soluble, and acts conservatively in most groundwater systems, undergoing little or no chemical interaction.

An important fact that must be noted here is the relatively low abundance of ^{36}Cl in the oceans. The mean residence time of a chloride atom a marine environment is sufficiently long for nearly all of the ^{36}Cl to decay. As a result, marine chloride is considered "dead", with a ^{36}Cl/Cl ratio of less than 5 (x 10^{-15}).

1.4.1 HYDROSPHERIC/GROUNDWATER APPLICATIONS

(a) INITIAL STUDIES

One of the first and most extensive studies of ^{36}Cl in groundwater systems was performed in the Great Artesian Basin, Australia [BENTLEY et al. (1986b), TORGERSEN et al. (1991)]. The Great Artesian Basin is a multilayered formation, with a primary freshwater aquifer of Jurassic sandstone. Chlorine-36/Cl^- ratios indicated two distinct groundwater groups. One group contained low ^{36}Cl/Cl ratios. These were located in the distal end of the aquifer, and were interpreted as having undergone ^{36}Cl decay [BENTLEY et al. (1986b)]. Groundwater ages calculated using ^{36}Cl radioactive decay agreed with hydrodynamically determined ages for samples from the primary aquifer. The second group contained high ^{36}Cl/Cl ratios, and were located at or near the recharge area. ANDREWS and FONTES (1992) attributed the high ^{36}Cl content of these waters to evaporative concentration. Whether or not these two groundwater reservoirs "communicate" is still under debate [MAZOR (1992), PHILLIPS (1993), ANDREWS and FONTES (1992)].

Another extensive study of ^{36}Cl in groundwater was performed in the Milk River Aquifer, Alberta, Canada [BENTLEY (1986c), NOLTE (1990, 1991)]. Again, high ^{36}Cl concentrations were observed in the recharge area, and were attributed to in-situ ^{36}Cl production [FONTES and ANDREWS (1992)]. However the source of high concentrations of ^{36}Cl in the recharge area of this aquifer has been questioned by MAZOR (1992), who argued that the bomb-pulse was responsible.

While most of the existing data on ^{36}Cl in groundwater systems was collected with the intention of dating old ground water by radioactive decay, questions concerning the sources of ^{36}Cl to these ground waters have complicated matters. As a result, serious doubts have arisen as to the applicability of ^{36}Cl as a tracer for radioactive decay dating purposes. In their review of this matter ANDREWS and FONTES (1992) suggest that at the present time ^{36}Cl is most useful in situations where *in-situ* ingrowth can be used as a dating technique, and where the bomb-pulse peak can be used as a tracer for short term (~100 y) processes. These limitations can be overcome with a better understanding of ^{36}Cl systematics, particularly with respect to sources.

(a) AQUIA AND MAGOTHY AQUIFERS, SOUTHERN MARYLAND

PURDY (1991) completed an extensive study of isotopic and chemical tracers in the Aquia Aquifer in Southern Maryland. A primary focus of this study was the investigation of ^{36}Cl as a tracer in the Atlantic Coastal Plain Aquifers. The Aquia was chosen because it is a hydrodynamically well-characterized, confined aquifer, with an estimated linear flow velocity of 4.0 m/y. Low Cl^- concentrations throughout the aquifer indicated that the system was well flushed of formation water.

Chlorine-36 concentrations in the Aquia were found to range from approximately 2 to 6 $\times 10^6$ atoms/L. Aside from an outcrop sample which showed clear evidence of the bomb-pulse, the highest concentrations were found in samples furthest from the aquifer outcrop. Possible explanations for this increase included ion filtration processes, in-situ ^{36}Cl production within the aquifer, climate variations and variations in the ^{36}Cl production rate due to cosmic ray flux modulations. Geochemical analyses ruled out neutron-induced *in-situ* production; however, none of the remaining possibilities could be completely discounted. The measured $^{36}Cl/Cl$ ratios in the Aquia ranged from approximately 100 to 300 ($\times 10^{-15}$). It was noted that both the ^{36}Cl concentrations and the $^{36}Cl/Cl$ ratios were 2 to 5 times higher in the Aquia than expected from LAL and PETERS (1967) production rate calculation and from the BENTLEY et al. (1986) ratio model.

A second Atlantic Coastal Plain Aquifer, the Magothy, is under investigation in a project related to the Aquia. Chlorine-36 measurements have been made for several samples taken from the Magothy. The results show $^{36}Cl/Cl$ ratios ranging from 150 to 350 ($\times 10^{-15}$), again 2 to 5 times higher than expected.

1.4.2 ATMOSPHERIC ^{36}Cl

The first measurements of ^{36}Cl in rainwater were made by SCHAEFFER, THOMPSON and LARK (1960). Beta emission was used to measure the ^{36}Cl in chloride extracted from 4000-8000 L of rainwater. ELMORE et al. (1979) published the first results of ^{36}Cl analyses of rainwater using AMS, opening the door to practical applications of the isotope. Since that time, atmospheric scientists have become interested in the possibility of using ^{36}Cl as a tracer for atmospheric processes. Stratospheric ^{36}Cl is a potentially useful tracer for stratospheric/tropospheric mixing processes which control the distribution of atmospheric contaminants. Recent attention has been given to the use of ^{36}Cl for the study of stratospheric chlorine chemistry in relation to ozone destruction. However, despite the attractive possibilities, relatively few studies have been published to date concerning the behavior of ^{36}Cl in the atmosphere.

(a) ICE CORE STUDIES

The earliest and most complete studies of atmospheric ^{36}Cl deposition were made using ice cores from the Greenland Dye-3 [ELMORE et al. (1982), SYNAL et al. (1990)] and Camp Century [ELMORE et al. (1987)] sites. These ice cores offered not only a record of cosmogenic isotope deposition, but of atmospheric chemical composition. In addition, the measurement of annual ^{18}O variations offered an independent dating scheme and allowed ^{36}Cl to be used in a manner analogous to the use of ^{14}C in tree rings.

The studies by ELMORE et al.(1982), SUTER et al.(1987) and SYNAL et al.(1990) provided a clear representation of the ^{36}Cl bomb pulse. Combined data from these two studies are shown in Figure 1.1. SYNAL et al. (1990) used these data to develop a model of the atmospheric transport of bomb-produced ^{36}Cl. Using this model, they were able to calculate a mean ^{36}Cl residence time in the stratosphere of 2.0 ± 0.3 years. An important implication of this calculation is that bomb-pulse ^{36}Cl is no longer a significant fraction of the present ^{36}Cl deposition flux. Another important finding reported by both SUTER et al. (1989) and SYNAL et al. (1990) was that the mean ^{36}Cl concentration in pre-bomb ice was 3 to 5 times higher than that expected from production rate calculations.

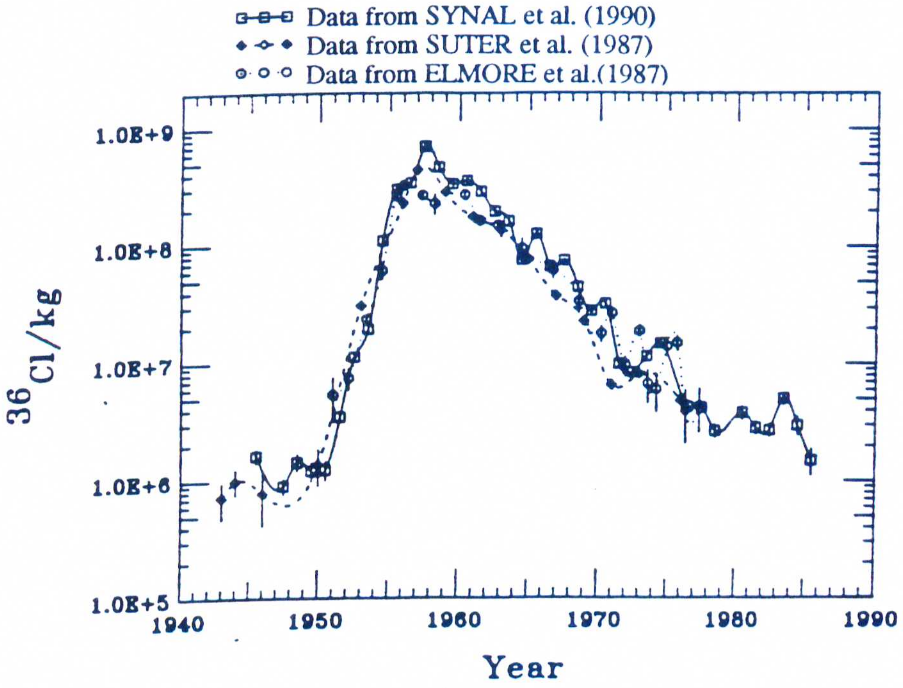
The study published by ELMORE et al. (1987) contained a 400 y record of ^{36}Cl deposition. The purpose of this study was to investigate the feasibility of using ^{10}Be/^{36}Cl ratios as a means of dating old ice. The initial assumptions were that the cosmic ray production rate dependence of these isotopes would be similar, as well as their atmospheric transport rates. Thus the ^{10}Be/^{36}Cl ratio should decrease simply as a function of radioactive decay. The results showed significant unexplained variations in the ^{10}Be/^{36}Cl ratios. In addition, the average ^{10}Be/^{36}Cl ratio of 8.3 was found to be considerably smaller than the predictions of 30 to 42 [LAL and PETERS (1967)]. It was concluded that variations in the ^{10}Be/^{36}Cl ratio were poorly understood, but could be caused by climatic effects or by an unknown, cosmic ray-independent source of ^{36}Cl.

(b) PRECIPITATION STUDIES

Data pertaining to ^{36}Cl in modern precipitation are scarce, and are limited to individual rain events. SCHAEFFER, THOMPSON and LARK (1960), ELMORE et al. (1979) and FINKLE (1980) published results of rainwater ^{36}Cl analyses either

Figure 1.1

Bomb pulse ^{36}Cl in ice cores taken from the Dye-3 site in Greenland. The graph shows data from three separate studies; SYNAL et al. (1990), SUTER et al. (1987) and ELMORE et al. (1987). [adapted from SYNAL et al. (1990)]


Data from SYNAL et al. (1990)
Data from SUTER et al. (1987)
Data from ELMORE et al.(1987)
^{36}Cl/kg
1.0E+9
1.0E+8
1.0E+7
1.0E+6
1.0E+5
1940
1950
1960
1970
1980
1990
Year

to demonstrate feasibility, or as a minor supplement to a related study. To date, the only published study specifically dealing with ^{36}Cl in precipitation is that by HERUT et al. (1992).

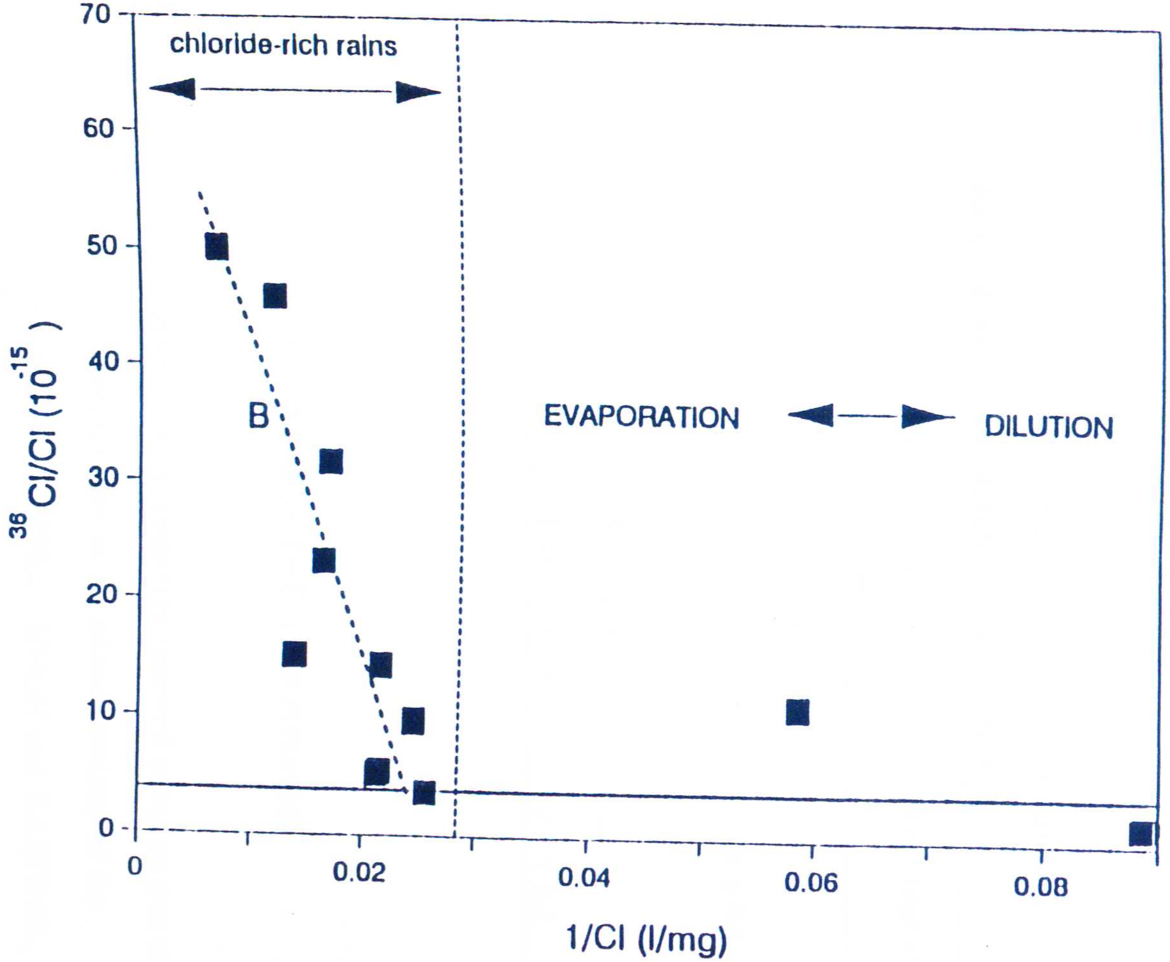
HERUT et al. (1992) studied ^{36}Cl concentrations in rainwater samples collected during individual rain events in Israel in 1988 and 1989. Their publication deals entirely with "chloride-rich" samples, arbitrarily defined as having at least 1 meq Cl^-/L (35.45 ppm Cl^-). The relationship between the $^{36}Cl/Cl$ ratio and the stable Cl^- concentration is given in Figure 1.2. It was concluded that line B represented a mixing process between marine chloride, with a $^{36}Cl/Cl$ ratio of approximately 4×10^{-15}, and a second, less obvious source, with a $^{36}Cl/Cl$ ratio of $50 - 70 \times 10^{-15}$. Possibilities for the second source included (a) stratospheric ^{36}Cl and (b) suspended dust from arid regions where the residence time of Cl^- on the surface had been sufficiently long for in-situ ^{36}Cl production to result in the elevated ratios. The authors discounted the stratospheric source, stating that stratospheric chloride could not account for the marine ionic ratios (Na^+/Cl^-, Mg^{2+}/Cl^-) observed in all of the samples. The mineral source was the favored explanation, with the possibility of an intense storm system admixing sea-spray with mineral dust given as an example.

(c) ATMOSPHERIC STUDIES

WHALEN et al. (1990) measured ^{36}Cl in air samples collected in the lower stratosphere in an investigation of the use of ^{36}Cl as a tracer for stratospheric Cl chemistry. Aerosols and gaseous HCl samples were collected and it was determined that approximately 90% of ^{36}Cl atoms occur as HCl. Table 1.2 gives a summary of their results. WHALEN et al. (1990) are the first

Figure 1.2

^{36}Cl vs. 1/Cl$^-$ in "chloride-rich" rains from Israel. Line B represents a mixing line between a high ^{36}Cl/Cl ratio reservoir and a low ^{36}Cl/Cl ratio source [taken from HERUT et al. (1992)].


chloride-rich rains
B
EVAPORATION
DILUTION
^{36}Cl/Cl (10^{-15})
70
60
50
40
30
20
10
0
0
0.02
0.04
0.06
0.08
1/Cl (l/mg)

to address the question of partitioning of ^{36}Cl between particulate and gaseous phases. Their discovery of the importance of gas-phase ^{36}Cl has already had an important impact on the understanding of atmospheric ^{36}Cl behavior.

Table 1.2

^{36}Cl Analyses of Stratospheric Air Samples (taken from WHALEN et al. (1990)).

Sample	^{36}Cl/Cl (x 10^{-15})	^{36}Cl (atoms/m^3 STP)	HCl (ppbv)
#1 Particulate	63±7	1.45±0.16 x 10^3	—
HCl	655±52	19.9±1.8 x 10^3	0.26 ± 0.5
#2 Particulate	350±20	30±2 x 10^3	—
HCl	3260±130	290±20 x 10^3	2.0 ± 0.2

1.5 THE CHEMISTRY OF CHLORINE IN THE ATMOSPHERE

The atmospheric chemistry of Cl is receiving renewed attention due to the apparently major role the Cl species play in the photochemistry of the stratosphere [ROWLAND and MOLINA (1975)]. SINGH and KASTING (1988) have estimated that 40 to 90% of non methane hydrocarbon oxidation in the stratosphere is caused by reactions with Cl.

1.5.1 CHLORINE IN THE TROPOSPHERE

Nearly all of the chlorine in the lower atmosphere originates in the oceans. Marine aerosols are injected into the atmosphere as a result of breaking waves on the ocean surface [CICERONE (1981)]. The bulk of atmospheric Cl^- is found in large aerosol particles with diameters of 1 to 10 microns at concentrations of 1 to 10 micrograms/m^3 [CICERONE (1981) and references therein]. Most of this chloride remains in the aerosol and returns to the ocean via wet or dry deposition. However, an estimated 3 to 20% of the chloride in marine aerosols is released as gaseous inorganic chlorine [KEENE et al.(1990)]. The mechanisms responsible for this volatilization are not well understood. Acidification of marine aerosols by the dissolution of HNO_3 and H_2SO_4 results in the release of HCl [CICERONE (1981) and references therein, BRIMBLECOMBE and CLEGG (1988)]. KEENE et al. (1990) assert that this mechanism cannot completely account for observed Cl^- deficits in marine aerosols. They propose an ozone-initiated sequence of reactions which occurs at the aerosol surface and eventually leads to the formation of HCl.

Although debates continue regarding the mechanisms of Cl release from marine aerosols, it is generally accepted that HCl is the predominant gaseous inorganic chloride species in the troposphere. FARMER et al.(1976) made the first IR spectroscopic measurements of HCl and found tropospheric concentrations of 1-2 ppbv which were in general agreement with previous determinations [CICERONE (1981)]. More recently, HARRIS et al.(1992) report HCl concentrations of less than 0.25 ppbv in the marine boundary layer. The tropospheric residence time of HCl has been estimated to be 2-7 days [WOFSY(1974), CICERONE (1981), KRITZ and RANCHER(1980)], the primary removal mechanisms being wet or dry deposition.

1.5.2 CHLORINE IN THE STRATOSPHERE

Gaseous inorganic chlorine is formed in the stratosphere as a product of the decomposition of organic chlorine compounds [CICERONE (1981)]. The mole fraction of gaseous inorganic Cl increases from less than 10^{-10} at the tropopause to 1-2 x 10^{-9} between 30 and 40 km, due to photochemical production mechanisms [WOFSY (1978), CICERONE (1981), SINGH and KASTING (1988)]. FARMER et al. (1976) detected HCl, the predominant Cl species in the stratosphere. Anderson et al. (1980) reported profiles of Cl· and ClO which play important roles in stratospheric photochemistry.

Reactions involving stratospheric Cl are of recent interest because of their role in stratospheric ozone depletion. The World Meteorological Organization (WMO) published a detailed review of chlorine species in the stratosphere [WMO (1992)]. SOLOMON (1990) and others have asserted that as much as 80% of the chlorine in the stratosphere is anthropogenic, derived from the breakdown of chlorofluorocarbons. Methyl chloride, produced mainly in the oceans, is the only significant source of natural chloride to the stratosphere. Volcanic eruptions have been thought to introduce inorganic chloride into the stratosphere. MANKIN and COFFEY (1984) demonstrated a 40% increase in stratospheric HCl following the eruption of El Chichon in March and April, 1982. However, TABAZADEH and TURCO (1993) have recently shown that, in most cases, HCl is strongly scavenged during the early phases of a volcanic eruption and is not substantially injected into the stratosphere.

1.6 OBJECTIVES OF THIS PROJECT

As emphasized throughout this chapter, the full potential of ^{36}Cl as a tracer in both atmospheric and hydrospheric applications has yet to be realized. While ^{36}Cl has been developed as a hydrological tracer , relatively little attention has been paid to its atmospheric supply. Mounting evidence suggests that current cosmogenic production rate calculations underestimate (by a factor of 2 or more) the actual supply. This gap in knowledge seriously undermines the use of ^{36}Cl as a dating tool in groundwater systems. Knowledge of the input function is crucial to the application of such techniques. In addition, the use of ^{36}Cl as a tracer for atmospheric processes has been proposed, yet not tested. The full potential of this isotope simply cannot be realized until basic aspects of its behavior are understood. This project was developed with these concerns in mind, and the objectives are three-fold: (1) to determine the amount of ^{36}Cl currently being deposited in Southern Maryland and across the northern United States, (2) to learn about the atmospheric behavior of ^{36}Cl and (3) to investigate the relationship between ^{36}Cl deposition and surface and groundwater concentrations.

1.6.1 DETERMINATION OF MODERN ^{36}Cl BACKGROUND

Rainwater samples were collected at several sampling sites across the northern U.S. and analyzed for ^{36}Cl in an effort to better understand modern ^{36}Cl deposition. Intensive sampling was performed at the Elms Environmental Education Center, a sampling site in southern Maryland, for comparison with ^{36}Cl concentrations as determined in the Aquia and Magothy aquifers. A specific goal of this project was to determine the modern flux of meteoric ^{36}Cl in the region of the Aquia and the Magothy. This information is then used to determine whether modern ^{36}Cl deposition could account for the relatively high concentrations measured in those aquifers.

1.6.2 ATMOSPHERIC BEHAVIOR OF ^{36}Cl

The second goal of this project was to develop a basic understanding of the atmospheric behavior of ^{36}Cl, and to test the feasibility of using ^{36}Cl as a stratospheric tracer. Monthly precipitation samples were collected from the Elms site in southern Maryland and analyzed for ^{36}Cl. These are a significant contribution to the extremely limited existing database. Temporal variations in ^{36}Cl deposition are compared with better understood stratospheric tracers such as ^{7}Be, ^{90}Sr, $^{238,240}Pu$ and ozone. In addition, the importance of dry deposition of ^{36}Cl is assessed by comparing results from wet-only samples with those from bulk deposition samplers.

1.6.3 RELATIONSHIP BETWEEN ^{36}Cl DEPOSITION AND GROUND WATER AND SURFACE WATER ^{36}Cl CONCENTRATIONS

The final goal was to investigate the relationship between ^{36}Cl deposition and the ^{36}Cl content of ground water and surface water. Samples from the Aquia Aquifer in southern Maryland and the Susquehanna River in Pennsylvania have ^{36}Cl concentrations 2 to 3 times higher than expected (according to LAL and PETERS (1967) and BENTLEY et al. (1986)). Comparisons are made between ^{36}Cl concentrations in bulk precipitation and in samples from the Aquia and Magothy aquifers and the Susquehanna River, in an effort to assess the contribution of meteoric ^{36}Cl in these systems.

Chapter 2

SAMPLING AND EXPERIMENTAL METHODS

2.1 INTRODUCTION

A main objective of this study was to determine both the spatial and temporal variations in modern ^{36}Cl deposition. To achieve this goal, two precipitation sampling methods were employed. Temporal variations were studied by the sequential, monthly analysis of samples from a wet-only precipitation collector in St. Mary's county in southern Maryland. Details of the sampler and its location are given in Section 2.2.1. Spatial variations were studied by the analysis of bulk deposition samples taken from seven locations across the northern United States. These locations and details of the sample collectors are described in detail in Section 2.2.2.

In addition to precipitation samples, surface water samples were collected from five locations in the Susquehanna River basin and the Eastern Shore of Maryland. Details of the surface water sampling procedure, and locations of sampling sites, are given in Section 2.2.3.

Experimental methods, including ^{36}Cl analyses, sample preparation and common ion analyses are given in Section 2.3. The first half of Section 2.3 deals with ^{36}Cl analyses and includes a section on special issues in ^{36}Cl sample preparation. The second half of Section 2.3 pertains to anion and cation analyses, pH and conductivity. A final section pertains to the analysis of chloride in algae grown in the open sample collectors.

2.2 SAMPLING METHODS

2.2.1 ELMS WET-ONLY RAINWATER SAMPLES

(a) Elms Site Description

A major portion of this study involved the collection of rainwater samples on a monthly basis from a single site. The Elms Environmental Education Center located in St. Mary's county in Southern Maryland was chosen as the location for this part of the study. Several considerations were taken into account in the selection of this site. Since the site was to be serviced often, a location near the University of Maryland was desirable. However, close proximity to the Baltimore - Washington metropolitan area increased the risk of sample contamination by urban and industrial influences. The Elms site is located 60 miles southeast of Washington D.C. It has been used as a study site for several atmospheric research projects carried out by groups at the University of Maryland Chesapeake Biological Laboratory, the University of Delaware Center for Marine Studies, and the State of Maryland Department of Air Quality (MDAQ). Studies at the site have involved trace metal monitoring, volatile organic carbon and pesticide studies , and atmospheric aerosol studies , as well as pH, major anion and major cation monitoring [LEISTER et al. (1993), BAKER (1992), WU (1993) MDAQ (1993)]. The Patuxent Naval Air Base is located 10 mi. northwest of the Elms site. The base closely monitors the meteorological conditions in the area, providing valuable information about temperature, wind speed and direction, and precipitation type.

The Elms site is located on St. Johns Cemetery Road east of Rt. 235 near St. Mary's City, Maryland, 60 miles south of Washington D.C. (Figure 2.1). The sampling site is located on a flat, grassy field at the eastern edge of the Elms property. The field is bordered by trees to the north and west, and by a tidal salt marsh to the south. The sampler apparatus is located approximately 50 yards from the edge of the salt marsh. Access to the site is provided by a dirt road passing approximately 30 yards from the sampler platform. There is very little automobile traffic in the vicinity of the site.

(b) Elms Sampler Description

The sampler used for the collection of monthly samples was designed and maintained by Dr. Joel Baker at the University of Maryland Chesapeake Biological Laboratory and his research group. It was designed to collect large amounts of rainwater for subsequent organic carbon and pesticide analysis, and was used for this purpose concurrently throughout the ^{36}Cl study period. Baker and his research group were responsible for general maintenance and periodic repairs. A detailed description of the sampler is given in Dickhut et al. (in preparation).

Figure 2.2 shows two photographs of the sampler apparatus. A basic diagram of the sampler is given in Figure 2.3. The sampler consists of a 1-m^2 round stainless steel funnel, with an aluminum lid. A resistance-based rain sensor triggers a pneumatic device responsible for opening and closing the lid. The rain sensor is heated slightly, allowing the sampler to open during periods of snow, and enhancing evaporation from the sensor, thereby ensuring that the sampler closes soon after a rain event. A calibrated tipping gauge mounted beside the sampler is used to measure the total amount of rainfall. Data from the sampler is collected and

Figure 2.1

Location of the Elms sampling site in southern Maryland.

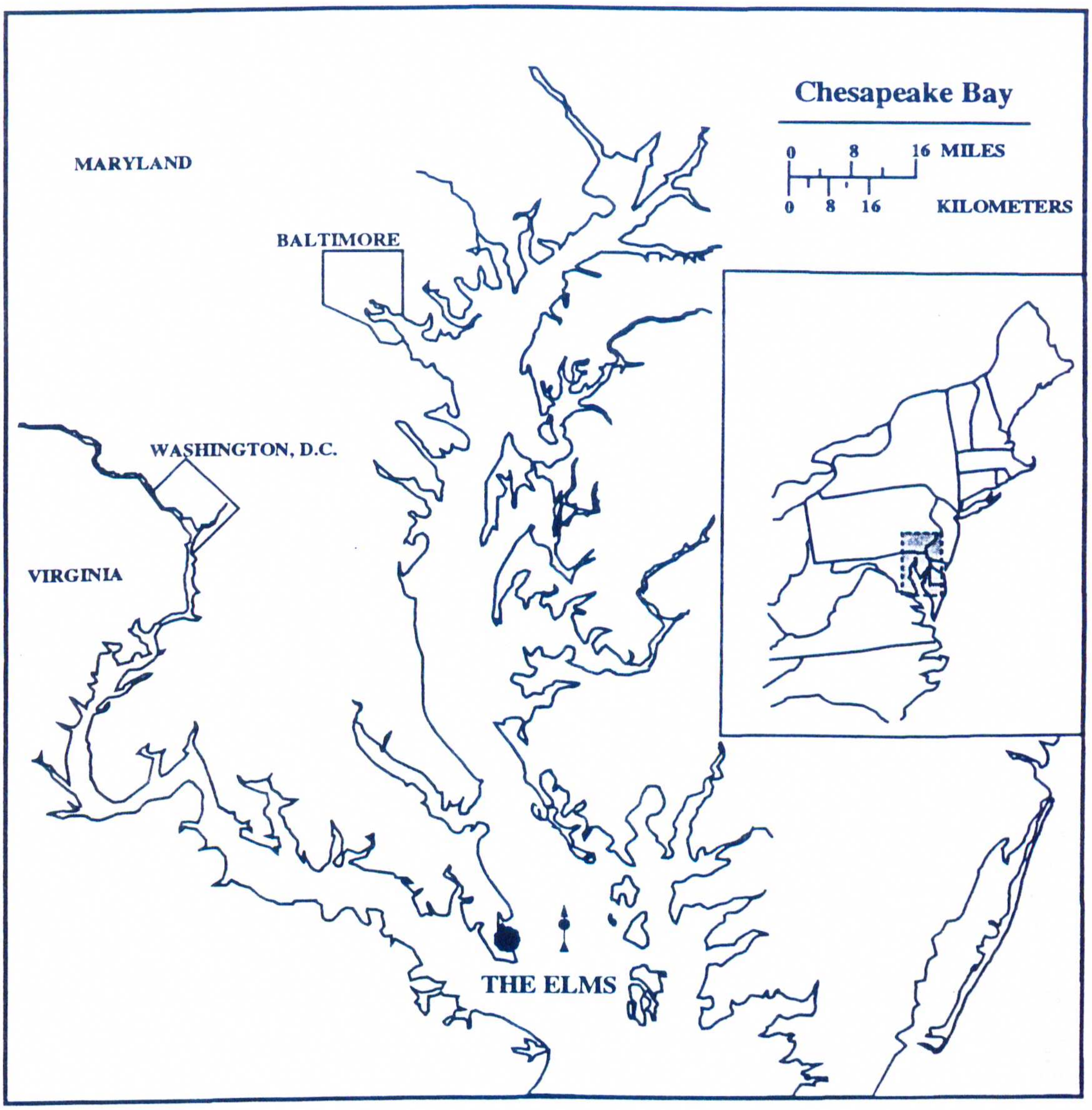
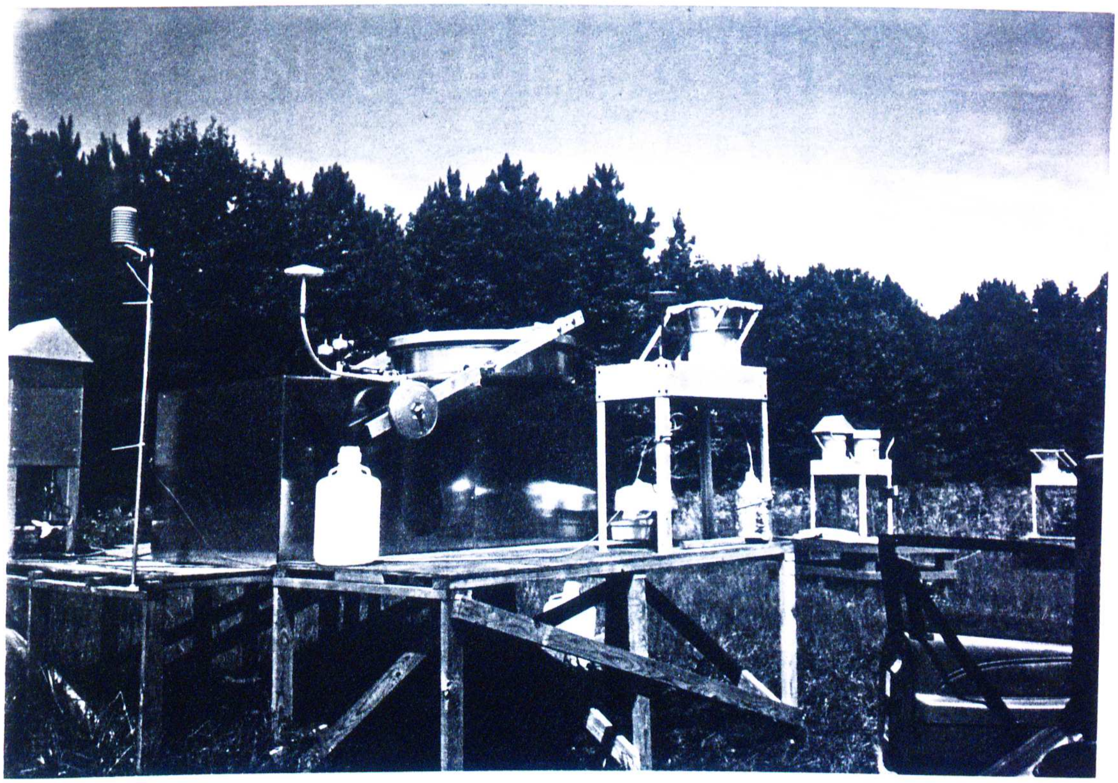

Chesapeake Bay
0 8 16 MILES
0 8 16 KILOMETERS
MARYLAND
BALTIMORE
WASHINGTON, D.C.
VIRGINIA
THE ELMS

Figure 2.2

(a) Photograph of the Elms sampling site. The wet-only sampler used for this study is located in the foreground

(b) Photograph of the wet-only sample collection apparatus located at the Elms sampling site



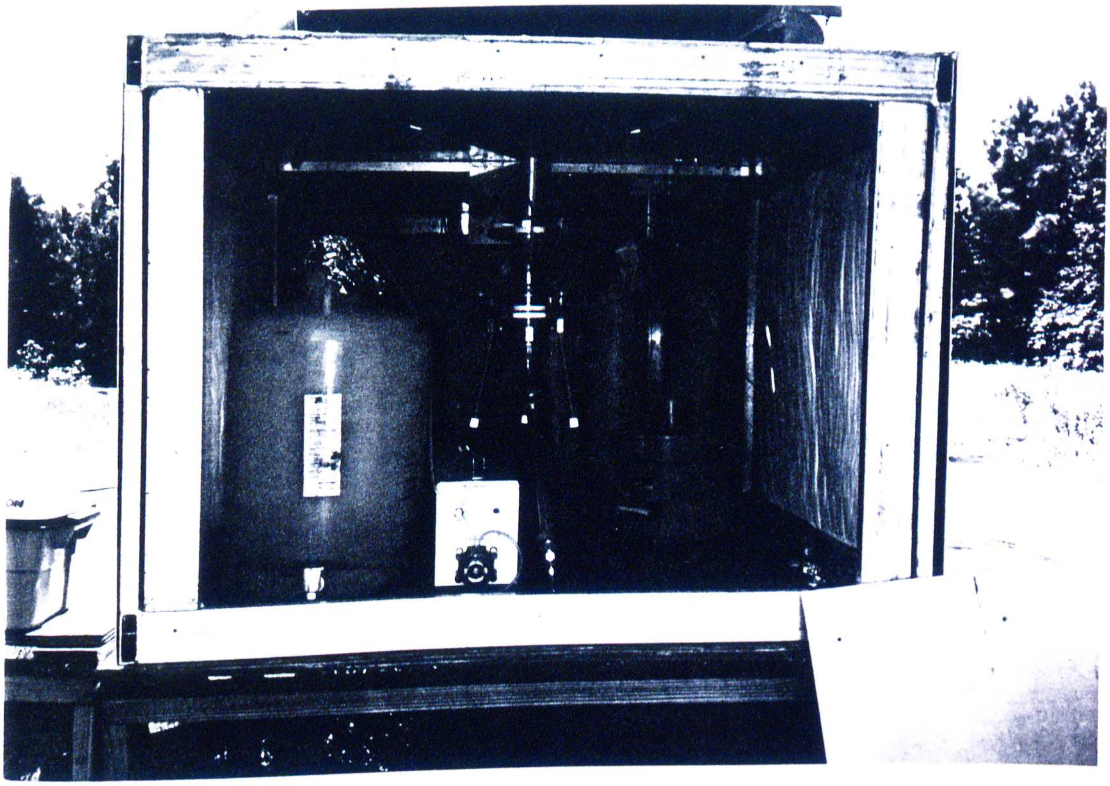
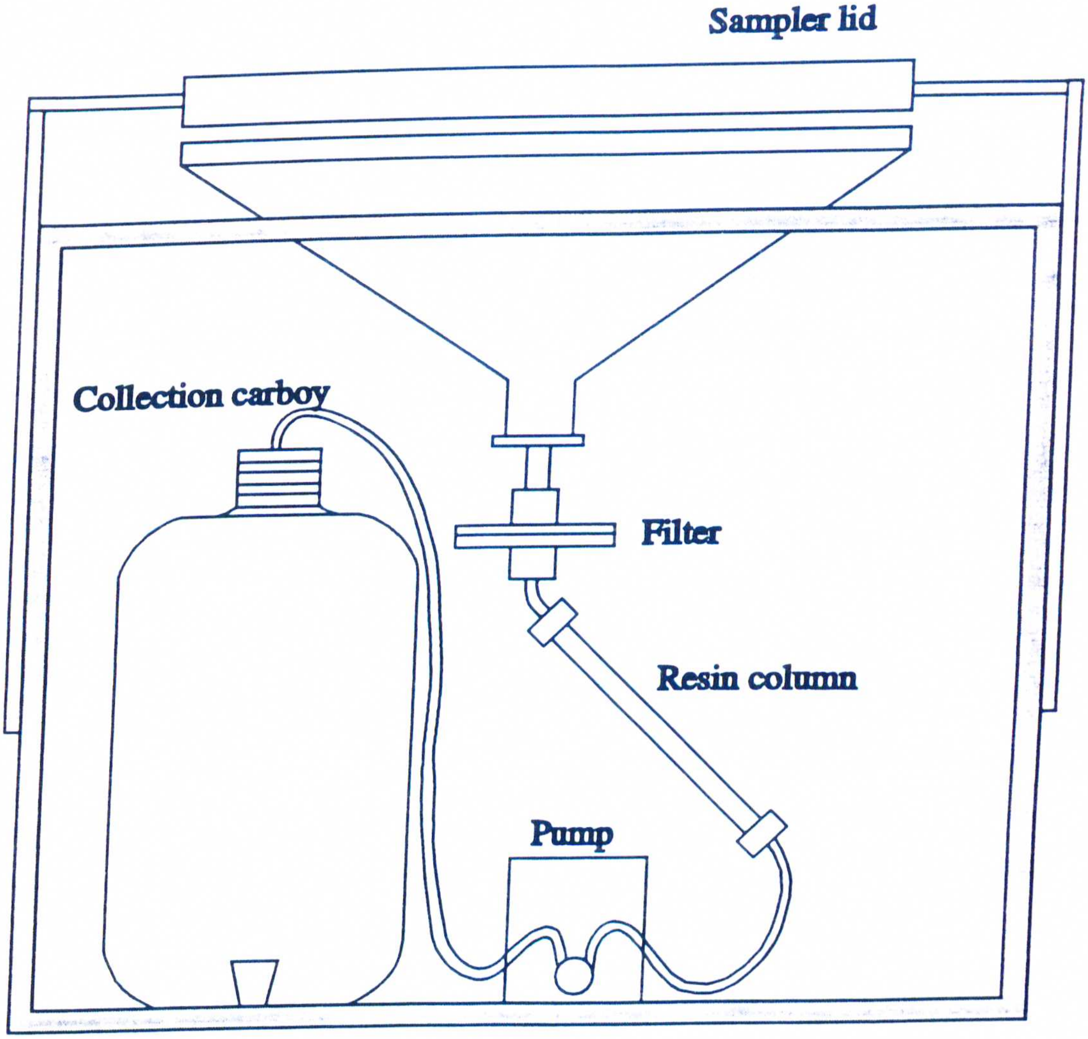


Figure 2.3

Diagram showing the basic components of the wet-only sample collection apparatus. The sampler lid is controlled by a conductance-based rain sensor (not shown).


Sampler lid
Collection carboy
Filter
Resin column
Pump

recorded by a computerized *in -situ* data collector. Time and date are continuously recorded, as well as sampler status (open or closed) and several meteorological parameters including: rainfall, air temperature, and wind speed and direction.

Wet precipitation is collected in the open funnel and passes through a 142-mm glass fiber filter (Gelman type A/E) to remove atmospheric dust and other particles. The sample then moves through a resin column containing Amberlite XAD-2 resin (Rohm and Haas, Co.). A length of silicone tubing connects the outlet of the column with two 55-L collection carboys. A liquid level sensor situated above the resin column controls a Masterflex peristaltic pump on the silicone outlet tube. Rainwater entering the column raises the water level above the sensor, which turns the pump on. When the event is over the water level drops again, which turns the pump off and prevents the column from draining.

(c) Elms Sample Collection Procedure

Samples from the Elms rainwater sampler were collected on a biweekly basis throughout the study period. This sampling schedule was set to coincide with the biweekly service and cleaning routine carried out by Baker and his group, and thereby ease the exchange of information pertaining to the sampler.

The biweekly service protocol involved cleaning the sampler and changing the resin column. From the beginning of this study (February 1991) to the summer of 1992 the servicing protocol was performed by Diane Leister, a graduate student directly responsible for the sampler. A technician, Cheryl A. Clark , serviced the sampler during the remainder of the study.

The servicing and cleaning procedure began with the removal of the resin column and the filter. The funnel was then rinsed with deionized water, wiped with glass wool to remove remaining particles and washed with Alconox soap and water. Acetone was then used as a rinse to remove any remaining organic material. The filter was replaced and a new resin column was attached. A final deionized water rinse ensured that the system was free from contamination.

Retrieval of the samples took place while the sampler was apart for cleaning. The collection carboy was first "swirled" several times to ensure that the sample was completely homogeneous. The total volume of the collected sample was then measured and recorded. A small amount of the sample was used to rinse a 23-L storage carboy. The remaining sample was then transferred to the storage carboy. Chloride concentration and pH were measured upon return to the lab. Samples were then stored at 4 °C.

2.2.2 OPEN SAMPLES

Seven sites across the northern United States were selected for the collection of bulk precipitation samples for ^{36}Cl analysis. Sites were selected at varying distances from the coast in an effort to establish the spatial variation pattern of ^{36}Cl deposition. Other site selection criteria included: availability of supporting meteorological data, ease of sampler deployment and monitoring, and isolation from possible sources of contamination and/or tampering. Site locations are shown in Figure 2.4, and locations and site descriptions are given in Table 2.1. Detailed directions to each site are given in Appendix A.

Figure 2.4

Map of the United States showing open sampling site locations. Details pertaining to the exact locations of these sites are given in Appendix A.

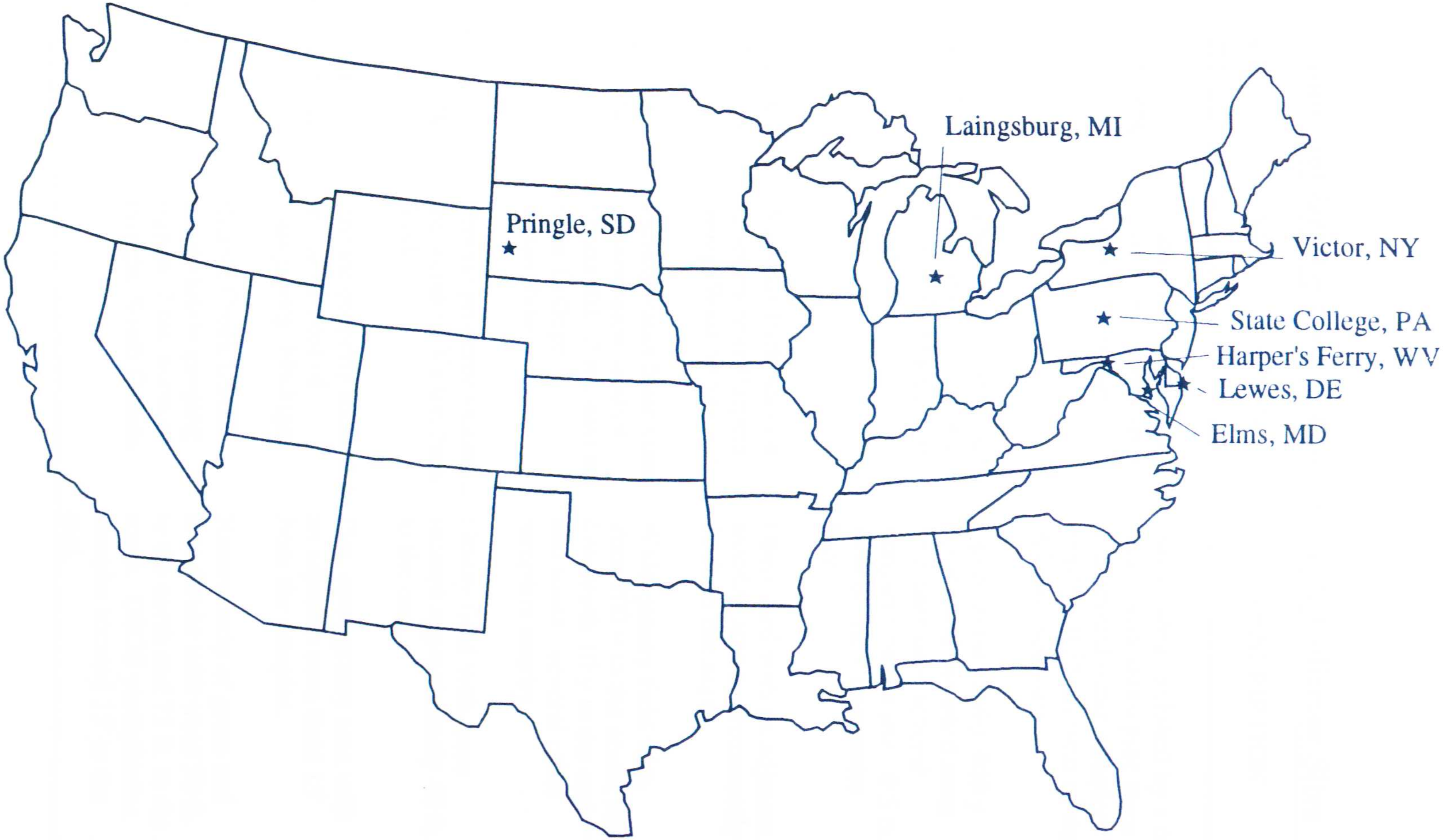

Laingsburg, MI
Pringle, SD
Victor, NY
State College, PA
Harper's Ferry, WV
Lewes, DE
Elms, MD

Table 2.1

Locations and Descriptions of Open Sample Collector Sites

SITE NAME LAT./LONG.	SITE LOCATION	SITE DESCRIPTION
Lewes, DE 38° 45'N 75° 08'W	Cape Henlopen State Park, 2 mi southeast of Lewes, Delaware	Sandy area enclosed by a 6' fence with small pine trees and several other samplers nearby. 0.25 mi west of the Atlantic seacoast.
Elms, MD 38° 25'N 76° 22'W	The Elms Environmental Education Center, 4 mi. east of St. Mary's City, Maryland	Open, grassy field, 400 y across with wooded areas on either side, several samplers on the site. 0.5 mi west of the Chesapeake Bay.
Harpers Ferry, WV 39° 20'N 77° 55'W	National Park Service property near Harpers Ferry, West Virginia.	Open yard with an adjacent wooded area approximately 20 ft. to the north.
State College, PA 40° 41'N 77° 55'W	Pennsylvania State Game Commission land on Scotia Rd., 2 mi. east of State College, Pennsylvania	Wide, grassy field with trees 200 y to the north, and low brush 10 y to the east and south. several other samplers nearby.
Victor, NY 42° 58'N 77° 28'W	Private property located 2 mi. south of Victor, New York	Grassy field with trees located approximately 40 ft. to the east.
Laingsburg, MI 42° 55'N 84° 15'W	Private property located 4 mi. northwest of Laingsburg, Michigan	Flat, open grassy area with an adjacent corn field 15' from the sampler.
Black Hills, SD 43° 40'N 103° 25'W	Beaver Creek USGS precipitation gauging station, 2 mi. north of Pringle, South Dakota	Narrow strip of grass and low shrubs with trees 50 ft. to the north and 75 ft. to the south. USGS precipitation sampler located 15' to the east.

(a) Open Sample Collectors

The study of spatial variations in ^{36}Cl deposition required the development of bulk precipitation collectors which could be easily and inexpensively deployed in a variety of locations, and would require little or no attention during the collection period. In addition, a sufficient volume of sample had to be collected for ^{36}Cl analysis.

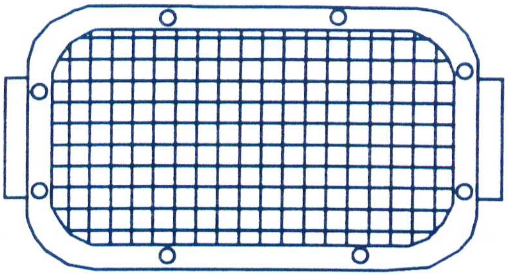
The open samplers developed for this study were simple and inexpensive. A Tucker brand 30 gallon trash container made from low-density polyethylene was modified for use as a bulk precipitation collector. The top of the sampler measured 24.5 ± 0.2 cm x 70 ± 0.2 cm, giving a total collection area of 1715 ± 15 cm^2. The total height was 120 ± 1 cm. Galvanized steel 1/2 inch mesh hardware cloth screening was used to cover the opening of the sampler to exclude potential contaminants (such as birds, tree branches etc.) and to prevent tampering by any person or animal wandering through the site . The inner section of the container lid was removed, leaving only the rim which was used to hold the screen in place. Several 1/2 inch nuts and bolts held the lid and screen securely. Samplers were set 3 to 4 inches into the ground and secured by two painted iron fenceposts. Figure 2.5 shows a diagram of an open sampler.

(b) Open Sample Collection Procedure

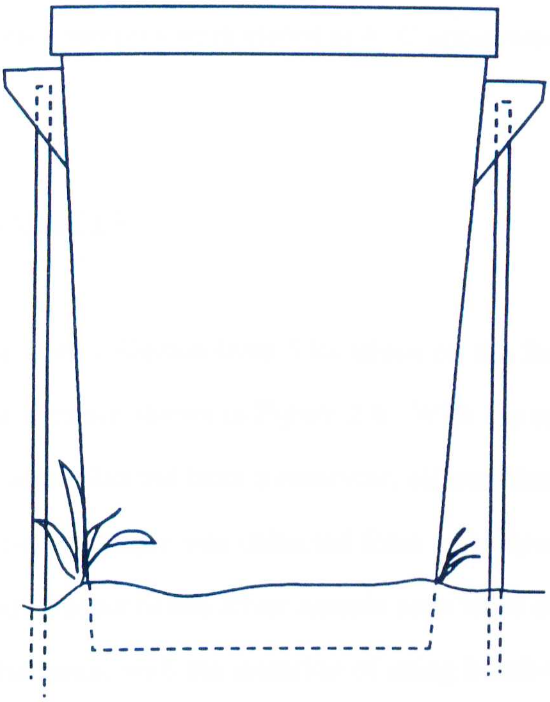
Open sample collectors were serviced on differing time schedules depending on location. The Elms site was serviced every four months, and each sample was analyzed for ^{36}Cl. All other samplers were serviced once or twice during the sampling period, and the collected fractions were integrated into one annual ^{36}Cl sample for each site.

Figure 2.5

Diagram of the open sample collector showing the top view (24.5 cm x 70 cm) and side view (70 cm x 120 cm).



Top View



Side View

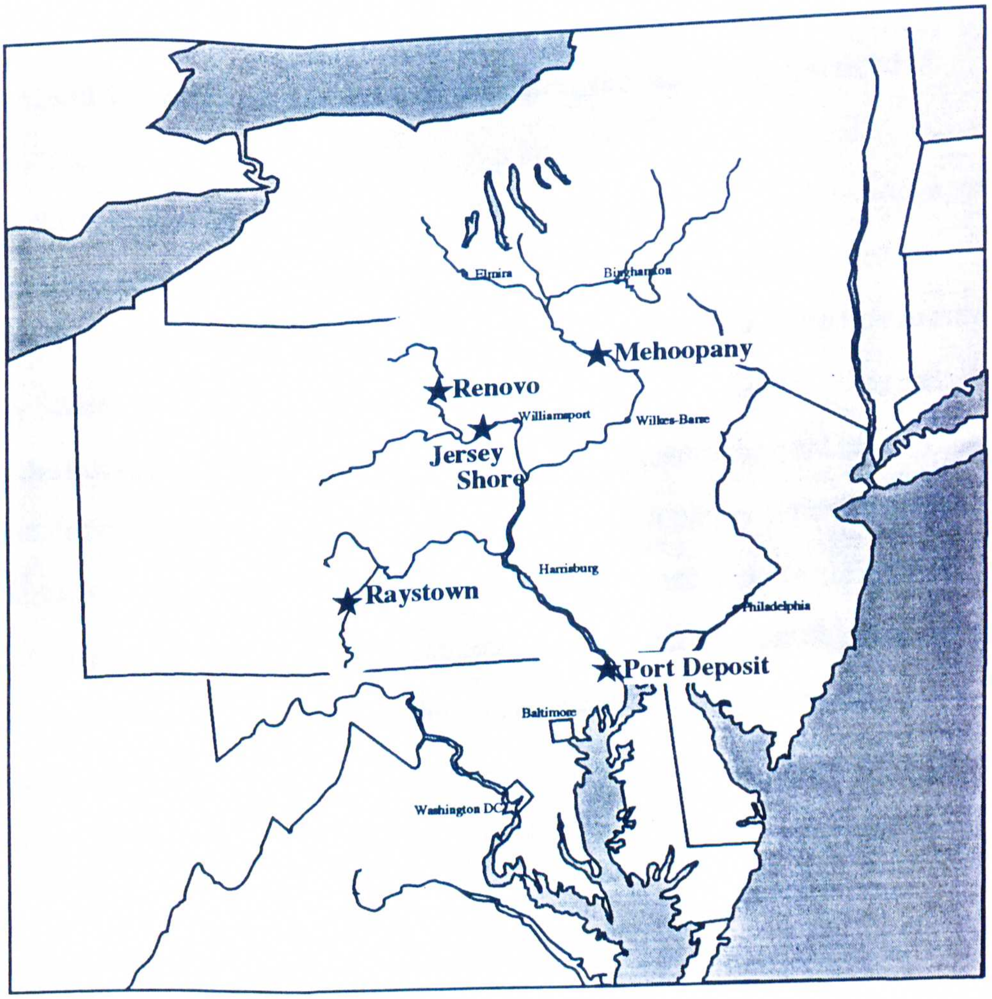
The open sample collection procedure was very straightforward. Gloves were worn throughout the entire procedure to prevent contamination of the sample. First the lid of the sampler was removed by removing all nuts and bolts. A 2-L graduated cylinder was used to measure the volume of the collected sample and to transfer the sample to a clean carboy. If the sample contained a visually significant amount of algae, the entire sample, including algae, was collected and returned to the lab. If very little algae was present, only two carboys were collected and the remainder of the sample was discarded (after careful measurement of the total sample volume). The sampler and lid were then rinsed well with MilliQ water. If algae was present on the side walls of the sampler, it was removed by rinsing and wiping the sides gently by hand (wearing a clean glove). Rinse fractions containing algae were added to the last carboy. Final rinse fractions were discarded, and the lid of the sampler was replaced. Samples were stored at 4 °C upon return to the lab.

2.2.3 SURFACE WATER SAMPLES

Surface water samples were collected from 5 locations on the Susquehanna River in Pennsylvania. These sites are shown in Figure 2.6. With the exception of the Raystown sample, which was collected from a reservoir, all samples were taken from flowing water. An additional sample was collected from a shallow pond on the Eastern Shore of Maryland. Susquehanna River sample sites were chosen to represent various regions of the basin, with the intention of using bomb-pulse ^{36}Cl to derive river basin retention times. Locations and details pertaining to the surface water sample sites are given in this Section. Additional information pertaining to the locations of these sites is given in Appendix A.

Figure 2.6

Map of the Susquehanna River basin showing surface water sampling sites. Details of the locations of these sites are given in Appendix A.


Elmira
Binghamton
Mehoopany
Renovo
Williamsport
Wilkes-Barre
Jersey Shore
Harrisburg
Raystown
Philadelphia
Port Deposit
Baltimore
Washington DC

(a) Sampling Procedure

The collection of surface water samples for ^{36}Cl analysis was simple and straightforward. The primary concern throughout the sample collection process was avoiding chloride and ^{36}Cl contamination. Gloves were worn throughout the process, and all equipment was acid-washed using the procedure described in Section 2.3.

Sample sites on the Susquehanna River were chosen with a low bridge, pier or protruding rocks for easy access to flowing water. A 2-gallon, low-density polyethylene bucket was used for retrieving the samples. For the two bridge sites (Jersey Shore, PA, and Renovo, PA), a clean nylon cord was used to raise and lower the bucket from the bridge. Care was taken to prevent the cord from getting wet and dripping into the sample. Samples taken from a pier or protruding rock were simply scooped. All samples were transferred immediately to clean 23-L storage carboys. Two carboys were collected at each site. On-site chloride and pH analysis was performed immediately after collection. Upon return to the laboratory, all samples were stored at 4°C.

(b) Surface Water Sites

Figure 2.6 shows the locations of sample collection sites on the Susquehanna River and the Eastern Shore of Maryland. Detailed information about these sampling locations is given in Appendix A. The objective of measuring Susquehanna River samples was to determine the amount of bomb-pulse ^{36}Cl retained in the basin. If indeed the basin retained ^{36}Cl deposited during the 1950's and 1960's, it would be present in the baseflow, or ground water, fraction It was therefore advantageous to collect samples from the river when the discharge was mainly baseflow, and the contribution from runoff was minimum. This was accomplished by consulting with the United States Geological Survey (USGS) office in Harrisburg, PA, for stream gauge data, and sampling when the river was well below normal. Details are given in Appendix A.

2.3 EXPERIMENTAL METHODS

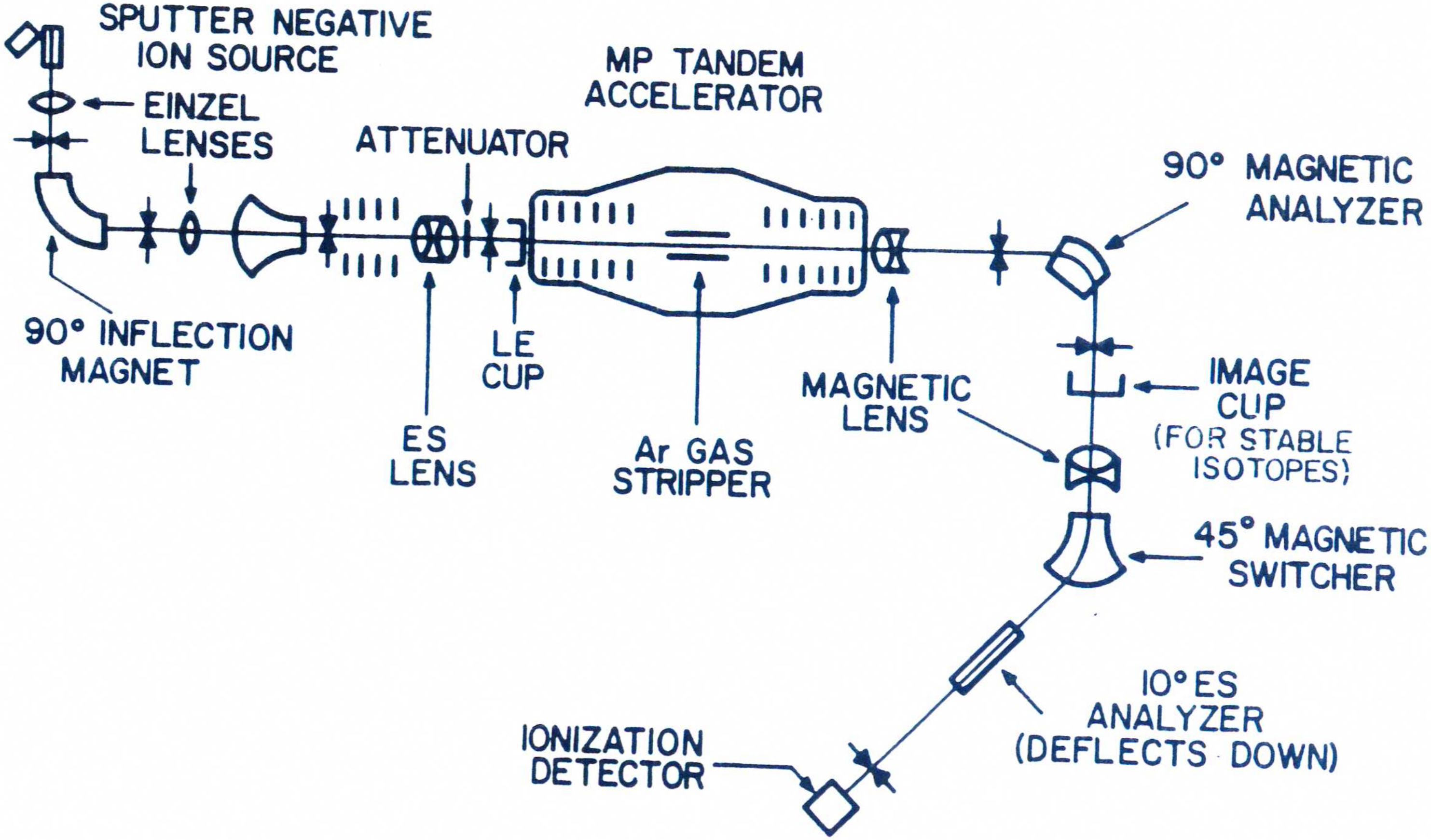
2.3.1 ACCELERATOR MASS SPECTROMETRY

Samples were analyzed for ^{36}Cl using Tandem Accelerator Mass Spectrometry (TAMS). The TAMS instrument at the University of Rochester is shown in Figure 2.7. It is a mass spectrometer based on a tandem Van de Graaff accelerator. A cesium gun ion source is used to sputter negative ions from the sample. These are focused and passed through a 90° inflection magnet, then accelerated toward a fixed positive potential. When the negative ions reach the positive terminal they pass through a carbon foil, which strips off the valence electrons, and destroys any molecular species. The result is a beam of positively charged ions accelerating away from the positive terminal, toward ground potential. After passing through a series of mass/charge analyzers, the individual ions are counted in a gas ionization detector.

Figure 2.7

The TAMS instrument at the University of Rochester Nuclear Structure Research Laboratory [taken from KUBIK et al. (1990)].

ROCHESTER TAMS APPARATUS



The complete destruction of molecules in the foil stripper is a clear advantage of the TAMS method. Another advantage is the separation of interfering isobars, for instance ^{36}S in ^{36}Cl measurements, by measuring the rate of energy loss in the ionization chamber. The resulting detection limits are on the order of 10^{-15} atoms ^{36}Cl/atom of stable isotope.

Throughout most of this study, samples were analyzed at the TAMS facility at the University of Rochester Nuclear Structures Research Laboratory (NSRL) in collaboration with Dr. Pankaj Sharma. Further details of the instrument and data analysis methods are given in ELMORE (1984). The remaining samples were analyzed at the Purdue Rare Isotope Measurement Laboratory (PRIME Lab). Table 3.1 in Section 3.3 shows a list of samples and the location of analysis.

To ensure that no systematic error was introduced between the laboratories, one sample was measured at both NSRL and PRIME Lab. The results were well within the margin of error, and are given in Table 2.2. Other cross measurements have been made and the results are given in BEASLEY et al. (1993).

Table 2.2

Sample Cross Analysis between NSRL and PRIME Lab

Sample: Elms March 1991

Laboratory (Date of analysis)	Cl-36/stable Cl^- ratio *
NSRL (5/91))	170 ±14 x 10^{-15}
PRIME Lab (3/93)	172 ±9 x 10^{-15}

* corrected for background

2.3.2 SAMPLE PREPARATION FOR TAMS ANALYSIS

Samples for TAMS ^{36}Cl analysis are introduced into the ion source as AgCl. Sample preparation for ^{36}Cl analysis involves preconcentration of the Cl^- in the sample, precipitation as AgCl and subsequent purification. Sulfur-36 is a stable, abundant, interfering isobar of ^{36}Cl. Extreme care must be taken to eliminate as much sulfur as possible from the sample.

Solutions of $AgNO_3$ and $BaNO_3$ used in sample preparation were prepared using reagent grade stock chemicals. Ultrapure concentrated HNO_3 was used in reprecipitation steps. Concentrated, reagent grade NH_4OH and HNO_3 were used to make rinsing solutions for the filtration steps, and for cleaning glassware. A 4-cartridge MilliQ water purification system provided deionized water with greater than 10 Mohm resistivity for solution preparation. This system was designed to remove suspended organic material, dissolved organic material, and dissolved inorganic ions. Water for glassware cleaning was first distilled, then passed through a deionizing resin column.

All glassware and utensils were cleaned first with Alconox soap solution to remove any conspicuous debris, then rinsed with dilute NH_4OH to dissolve any remaining AgCl. Items were then rinsed with deionized water, placed in a bath of 0.1M HNO_3, and given a final rinse with MilliQ water. All sample collection and storage containers were also cleaned using this standard procedure.

(A) Preconcentration

The first step in sample preparation was the preconcentration step. This step was necessary only for the rainwater samples, due to the very low Cl^-

concentration in rainwater (0.2 to 2.0 mg/L) . There were two main advantages to preconcentration. First, the volume of sample to be filtered was decreased from approximately 15 L to approximately 2 L, vastly reducing the amount of time necessary for the filtration step. Second, by increasing the Cl^- concentration in the sample, solubility losses were minimized. PURDY (1991) used an ion exchange resin as a simple means of preconcentrating the Cl^- in groundwater. However, the resin was found to be a small yet significant source of ^{36}Cl contamination.

In this study, evaporative preconcentration was used. The preconcentration apparatus consisted of a 12 L round-bottom flask, a two-part, 600-W adjustable temperature heating mantle and a condensation tube.

A known volume of sample (10 to 11 L) was transferred to the flask and boiled for 8 to 10 hours. After cooling to room temperature, the final volume was measured, and a 10 mL aliquot was taken for Cl^- analysis for comparison with the original [Cl^-]. The yield for the preconcentration step could then be calculated. Actual preconcentration yields ranged from 64 to 92 percent. A series of blanks and standard solutions were put through the preconcentration step to ensure that there would be no ^{36}Cl contamination of the samples. For the remaining sample preparation steps, preconcentrated samples were treated as any other sample.

(b) AgCl precipitation and purification

Chloride was precipitated from the samples as AgCl by the addition of 15 mL of 0.1 M $AgNO_3$ The precipitate was filtered using a Millipore 250-mL filtering system consisting of a glass base, a stainless steel filter support screen and a glass funnel cup. The system was mounted on a 1-L Erlenmeyer vacuum flask connected to a standard aspirator. Millipore 0.45-µm type HA filters were used in all filtration steps.

After filtration the AgCl precipitate was washed several times with dilute HNO_3. A few drops of $AgNO_3$ were added to an aliquot of the filtrate to test for any remaining, unprecipitated Cl^-. The AgCl was dissolved by the addition of 10 to 20 mL of 4 M NH_4OH to the filter cup. A 35-mL test tube caught the solution as it dripped through the filter system. Several rinses with 4 M NH_4OH ensured that all of the Cl^- was transferred to the test tube.

To remove sulfate from the AgCl precipitate, a $Ba(NO_3)_2$ solution was prepared by adding 100 mL of 1 M HNO_3 to an excess of $BaCO_3$ (approximately 25 g). A few drops of $Ba(NO_3)_2$ solution were added to the sample solution at this point to remove sulfate via the following reaction:

$$Ba(NO_3)_2(aq) + SO_4^{=}(aq) \dashrightarrow BaSO_4\,(s) + 2\,NO_3^-(aq)$$

The sample was allowed to stand overnight to ensure complete precipitation of the $BaSO_4$. The sample was then gravity filtered, and the precipitate was washed and discarded. Finally the sample was acidified to pH 1 by the addition of concentrated ultrapure HNO_3. This resulted in the reprecipitation of AgCl. In the early stages of the project the AgCl precipitate was filtered, then dried on the filter paper in an oven at 70°C. Later, the AgCl precipitate was isolated by centrifugation. After three washing and recentrifugation steps, the final product was dried in an oven at 80°C overnight. Samples were then stored in plastic vials and covered with Al foil to prevent photodecomposition of the AgCl.

Yields for the sample preparation procedure were calculated for all of the samples and blanks by comparing the final weight of AgCl with the original Cl^-

content. The range was 65% to 93%. Lower yields were associated with samples which were filtered and dried on the filter paper. Substantial losses occasionally occurred during removal of the dried sample from the filter. Centrifugation of the final product resulted in higher, more consistent yields.

2.3.3 (c) SPECIAL ISSUES IN SAMPLE PREPARATION

In general, the preparation of samples for ^{36}Cl analysis described in Section 2.3.2 is simple and straightforward. However, a few special considerations are needed to ensure that the final AgCl sample is uncontaminated and suitable for TAMS measurement.

(a) Chlorine-36 contamination

The problem of ^{36}Cl contamination is described in great detail in PURDY (1991). Her contamination study was prompted by the sudden appearance of significant levels of ^{36}Cl in routine sample blanks. In an effort to pinpoint the contamination source, many sample blanks were prepared under various laboratory conditions and analyzed for ^{36}Cl. Glassware, reagents, ion exchange resins and laboratory dust are all identified as possible sources of ^{36}Cl.

Several measures were taken to ensure that the risk of ^{36}Cl contamination during sample preparation was minimized. New glassware was purchased and used exclusively for low-level ^{36}Cl sample processing in an effort to curtail contamination due to "glassware memory". Fritted glass filter funnel bases, which were difficult to clean thoroughly, were replaced by stainless steel screens (Section 2.3.2). Old lot reagents, as described by PURDY, were discarded and replaced. The need for ion-exchange resins was eliminated by using evaporation to preconcentrate the Cl^- in the samples (Section 2.3.2 (a)). Finally, sample preparation was confined to laboratories with no known history of post-irradiation chemistry, or other high-level radiochemistry. The laboratory in Room 1510 in the University of Maryland Chemistry building was used until July 1990. Rooms 3117 and 3113 in the Chemistry building were used for the remainder of the project. Sample blanks analyzed as part of this study indicate clearly that the measures above have succeeded in minimizing ^{36}Cl contamination.

(b) Sample Blanks

Weeks Island halite was used consistently as blank material. This salt was originally obtained from the Weeks Island salt dome located on the Gulf Coast of Louisiana. The TAMS group at the University of Rochester routinely analyzed the salt, and found it to contain no measurable ^{36}Cl.

To prepare the lab/chemistry blanks, approximately 60 mg of Weeks Island halite was dissolved in 1 to 2 L of MilliQ water. This solution was then processed along with the samples according to the procedure described in Section 2.3.2. Every set of samples sent to the University of Rochester, or to PRIME lab, for ^{36}Cl analysis included a lab/chemistry blank.

Sample collector blanks were analyzed to test for ^{36}Cl contamination from the sample collection system. Approximately 5 L of a 10-mg/L Weeks Island halite solution was poured through the sample collector immediately after it was cleaned (Section 2.2.1 (b)). This solution was recovered from the sample collection carboy, processed as usual, and analyzed for ^{36}Cl. A complete list of blanks and the results of ^{36}Cl analysis are given in Table 2.3.

Table 2.3

Summary of ^{36}Cl Sample Blanks

Date processed	Associated sample set	Type of blank	^{36}Cl/Cl ($\times 10^{15}$)
7/31/89	Susquehanna R., Aberdeen "O-field"	lab/chemistry	22 ± 16*
12/10/89	U of MD rainwater	lab/chemistry	10 ± 9*
3/27/91	Elms rainwater	sample collector	0 ± 2.4
5/13/91	Elms rainwater	lab/chemistry	0 ± 3.7
6/17/91	Elms rainwater	lab/chemistry	0 ± 2.3
1/18/93	Elms rainwater	lab/chemistry	0 ± 2.2
2/9/93	Elms rainwater	sample collector	0 ± 2.4

* These blanks were processed in Room 1510 using fritted glass filter holders.

(c) Sulfur-36 removal

Recent improvements in the University of Rochester TAMS system, in particular the addition of a gas-filled magnet isobar separator, have significantly enhanced ^{36}Cl-^{36}S peak separation (KUBIK et al. (1987)). However, chemical removal of sulfur is still extremely important. The addition of Ba^{2+} and subsequent removal of $BaSO_4$ is usually sufficient to achieve a ^{36}S/^{36}Cl ratio of 10^6. Peak separation is good at this level, and the analysis is not affected. At higher sulfur concentrations the ^{36}Cl peak cannot be distinguished from the ^{36}S peak shoulder, and analysis is questionable if not impossible. With very high sulfur levels, contamination of the TAMS ion source is an additional concern.

Samples suspected of containing high concentrations of sulfur were redissolved so that the Ba^{2+} step could be repeated. This procedure was also used if the final AgCl product looked contaminated in any way (i.e., yellowish or brownish). As a result of these measures, only one sample from this study, March 1992, was rejected due to high S. The sample was measurable after additional processing at PRIME Lab.

(d) Carrier addition

In routine TAMS ^{36}Cl analysis, approximately 10 to 15 mg of AgCl is used. It is possible to analyze samples as small as 5 to 6 mg with special sample holders and with some sacrifice in precision. Rainwater sample collection methods for this project were designed to provide, on average, enough Cl^- for at least two ^{36}Cl analyses. However, in instances where there was insufficient sample for ^{36}Cl analysis, the addition of ^{36}Cl-free carrier was required.

The sample carrier used for this study was Weeks Island halite (Section 2.3.3 (b)), as it was known to contain no measurable ^{36}Cl. Two rainwater samples (1/29 to 2/12/91 and 2/12 to 2/26/91) required the addition of carrier. In order to avoid excessive dilution of the sample ^{36}Cl, the amount of carrier added was limited to 5.00 mg. A stock solution of 1.00 mg per mL Weeks Island Cl^- was prepared with MilliQ water, and 5.00 mL of this solution was added to a known volume of sample. After analysis, the ^{36}Cl/stable Cl ratio could be calculated as follows in Eq. 2.1:

$$^{36}\mathrm{Cl/Cl}_{(\mathrm{sample})} = \frac{^{36}\mathrm{Cl/Cl}_{(\mathrm{sample+carrier})}\,\mathrm{m}_{(\mathrm{sample+carrier})} - {}^{36}\mathrm{Cl/Cl}_{(\mathrm{carrier})}\,\mathrm{m}_{(\mathrm{carrier})}}{\mathrm{m}_{(\mathrm{sample})}}$$

(Eq. 2.1)

where: ^{36}Cl/Cl(sample+carrier) = the measured ratio

^{36}Cl/Cl(carrier) = the measured ratio in the carrier/blank material.

m = mass (g)

2.3.4 ANION ANALYSIS

Ion chromatography was used to determine the concentrations of major anions. Chloride determination was particularly important as it provided the information necessary for the calculation of ^{36}Cl concentration and deposition flux. In addition, samples were analyzed for F^-, NO_3^- and $SO_4^=$.

The ion chromatograph used for anion analyses was a Dionex QIC IonChrom Analyzer with chemically suppressed conductivity detection. Two Dionex HPIC-AG1 guard columns were used for separation. Guard columns were used rather than analytical columns because they provided rapid, efficient separation and they were inexpensive and easy to replace. An AFS-1 anion fiber suppresser was used to enhance the signal to noise ratio.

The eluent solution for the analyses was a buffer solution of 0.003 M $NaHCO_3$ and 0.0024 M Na_2CO_3. The eluent flow rate was 2.0 mL/min. A 0.001 M H_2SO_4 solution was used as the regenerant for the fiber suppresser. Standard solutions were prepared according to the expected analyte concentration range. Calibration curves for each analyte were defined by at least 5 standards. Table 2.4 lists the standards used for each analyte and the concentration ranges.

Table 2.4

Standards Used for Anion Analysis by Ion Chromatography

Analyte	Stock solution	Concentration range
Cl^-	NaCl	0.1 mg/L to 10 mg Cl^-/L
F^-	NaF	0.1 mg/L to 5 mg F^-/L
NO_3^-	$NaNO_3$	0.5 mg/L to 10mg NO_3^-/L
$SO_4^=$	Na_2SO_4	1 mg/L to 20 mg $SO_4^=$/L

Field Cl^- measurements were made at surface water sampling sites using a Hach Model CD-DT chloride test kit with a digital titrator. The procedure involved titration of the sample with mercuric nitrate using a diphenylcarbazone indicator. An absolute error of approximately 0.5 mg/L was associated with these measurements. Rainwater samples were also field tested for Cl^- early in the project. However after repeated analyses and comparison with I.C. measurements, the field measurements were deemed unnecessary. In all cases, surface water and rainwater, agreement between Hach Kit Cl^- measurements and I.C. $[Cl^-]$ measurements was well within experimental error.

2.3.5 CATION ANALYSIS

The concentrations of the major cations (Na^+, K^+, Ca^{++} and Mg^{++}) in the samples were determined by flame atomic absorption analysis (FAA). A Perkin-Elmer model 360 Atomic Absorption Analyzer was used for the analyses. All of the samples were well within the linear range of the instrument, therefore no sample dilution was necessary. Cesium nitrate (0.001 $g_{(salt)}/g_{(sample)}$) was used for ionization suppression in determining the alkali metals. For the alkaline earth metals, KNO_3 (0.001 $g_{(salt)}/g_{(sample)}$) was used for ionization suppression. Standard solutions were prepared by diluting 1000-mg/L stock solutions to the appropriate concentration range, and adding $Cs(NO_3)_2$ or KNO_3 as described above. Table 2.5 describes the standard solutions used for the analysis of each element. Instrumental settings, such as wavelength, slit width and fuel/oxidant ratio, were set according to recommended values given in the Perkin Elmer reference manual.

Table 2.5

Standard Solutions used in FAA Analyses

Analyte	Stock Solution	Concentration Range
Na^+	NaCl	0.010 to 1.50 mg Na^+/L
K^+	KCl	0.0010 to 0.050 mg K^+/L
Ca^{++}	$CaCl_2$	0.010 to 0.300 mg Ca^{++}/L
Mg^{++}	$MgCl_2$	0.010 to 0.150 mgMg^{++}/L

2.3.6 CONDUCTIVITY AND pH

Samples were analyzed for conductivity using a VWR Scientific Model 604 digital conductivity meter with a Model 515 conductivity dip cell. Samples were analyzed either immediately after collection (upon return to the laboratory), or after storage at 4°C. Stored samples were allowed to return to room temperature before analysis. Measurements were made according to the recommended procedure given in the instruction manual.

Field pH analyses were performed immediately following the collection of surface water samples using a Hach Pocket Pal pH tester. Field pH measurements were also made for rainwater samples in the early part of the study. All samples were analyzed in the laboratory using a Beckman Phi-11 pH meter. The uncertainty associated with these measurements was 0.05 pH units.

2.2.7 DETERMINATION OF Cl^- IN ALGAE

Samples collected from the bulk (open) samplers often contained visible amounts of algae, which had grown on the walls of the sampler. This algae probably contained chloride from the rainwater. If the algae incorporated a significant fraction of the available Cl^- within cell walls, then the measured Cl^- concentrations would be artificially low. To ensure that this was not the case, algae was collected as described in Section 2.2.2 (b), and analyzed for Cl^-. Results revealed that the algae did not contain a significant amount of Cl^-.

The procedure used to process the algae was taken from KRISHNAMURTHY (1990). The algae was filtered from two samples, Elms 2 and Lewes DE, using a 50-µm mesh nylon screen. The screen and algae were dried in a 70 °C oven overnight. The algae could then be removed from the screen and weighed. The algae was then transferred to a centrifuge tube and extracted with two 10-mL portions of MilliQ water. One 10-mL portion of 25% ultrapure nitric acid solution was then added to the residue and the solution was brought to a boil in a hot water bath. The sample was then centrifuged and washed twice. The nitric acid solution and all of the washings were combined and brought to a total of 100 mL with MilliQ water. The chloride concentration was then measured using a Hach model CD-DT chloride test kit with a digital titrator (described in Section 2.3.4). The results are shown in Table 2.6.

Table 2.6

Analyses of Chloride in Algae Samples

Sample	Dry weight of algae (g)	[Cl-] * (mg/L)	Estimated Chloride content of the algae
Lewes, DE	0.065	0.5	7.6 mg Cl^-/g dry algae
Elms, MD	0.044	not detected	$\leq$ 2 mg Cl-/g dry algae

* as measured in 100 mL of supernatant after digestion.

The estimated amount of chloride bound by algae in the Lewes, DE sample was 0.05 mg. Admittedly, the filtering procedure may not have completely removed all of the algae from the sample. However, the total chloride content of that sample was approximately 300 mg, nearly 4 orders of magnitude higher than the estimated amount of chloride in the algae. Thus, it was concluded that the amount of chloride incorporated into algae was negligible.

Chapter 3

TEMPORAL VARIATIONS IN ^{36}Cl DEPOSITION

The ability of accelerator mass spectrometry (AMS) to measure natural levels of ^{36}Cl has provided a unique tracer with a broad range of hydro/geological applications [BENTLEY et al. (1986), ELMORE (1984), many references in *Nucl. Instru. Meth. Phys. Res., B5* ,(1987)]. Numerous studies have been published using ^{36}Cl as a tracer in the Milk River Aquifer (Alberta, Canada), the Great Artesian Basin (Australia), and the Aquia Aquifer (southern Maryland), among others. While the development of hydrological applications has led to a fair understanding of the behavior of ^{36}Cl in ground water systems, very little is known about the atmospheric transport and deposition of this cosmogenic isotope.

This chapter discusses variations in ^{36}Cl deposition, as measured in wet-only and bulk precipitation samples collected at the Elms Environmental Education Center in Southern Maryland (see Section 2.2.1(a)). Chlorine-36 analyses of monthly wet-deposition samples collected at the Elms site are presented in Section 3.2. Variations in the ^{36}Cl/Cl ratio, the ^{36}Cl concentration and the ^{36}Cl deposition flux as a function of time are also presented. In Section 3.2.4 (a), a mathematical function is developed to describe these results in terms of seasonal variation and precipitation rate. In Section 3.3 results of analyses of bulk deposition samples are given and compared with the wet-only samples to derive information on ^{36}Cl dry deposition.

3.1 PREVIOUS ^{36}Cl DEPOSITION STUDIES

The historical record of ^{36}Cl deposition, as preserved in ice cores, has proven extremely useful in the study of deposition with relation to the "bomb-pulse" (see Chapter 1). Chlorine-36 measurements were made, with annual resolution, in an ice core drilled near the Dye-3 site [SUTER et al. (1987), SYNAL et al. (1990)], and in the top portion of the Camp Century ice core [ELMORE et al. (1987]. As shown in Figure 3.1, the results of these studies clearly demonstrate an increase in ^{36}Cl deposition beginning in 1950, a maximum in 1959, and a subsequent decrease in deposition as atmospheric weapons tests were phased out. Concentrations approach pre-bomb levels around 1985. SYNAL (1990) developed a box model to better explain the slope of the fallout pattern, using data from all known nuclear weapons tests as the input function. A stratospheric residence time of 2 ± 0.3 years was derived from the exponential decrease in the ^{36}Cl concentration. Anthropogenic ^{36}Cl fallout rates calculated using this model compare well with measured concentrations. It should be noted here, however, that the main source of bomb-pulse ^{36}Cl is neutron-activated marine Cl^-. Therefore, differences in atmospheric chemical behavior may exist between "bomb-pulse" and natural ^{36}Cl.

Data pertaining to modern ^{36}Cl in precipitation are scarce and, for the most part, are limited to individual rain events. [SCHAEFFER et al. (1960), ELMORE et al. (1987), FINKEL et al. (1980), HERUT et al. (1992)] As a result, little is known about the atmospheric transport and mechanisms that control ^{36}Cl deposition. Studies published pertaining to the atmospheric behavior of other cosmogenic (or weapons produced) radio-isotopes are useful only in a limited way, due to differences in production mechanisms, chemical behavior and physical transport.

Figure 3.1

Bomb pulse ^{36}Cl as measured in ice cores from the Dye-3 sampling site in Greenland. [taken from SYNAL et al. (1990)]. A comparison is shown between experimental ^{36}Cl flux data and atmospheric deposition model calculations. A ^{36}Cl stratospheric residence time of 2 y was used in the model to achieve the best fit. Arrows on the ordinate represent nuclear test detonations considered in the model. The height of each arrow is approximately proportional to the amount of ^{36}Cl presumed to have been released into the atmosphere (as calculated based on the yield and location of each test explosion).

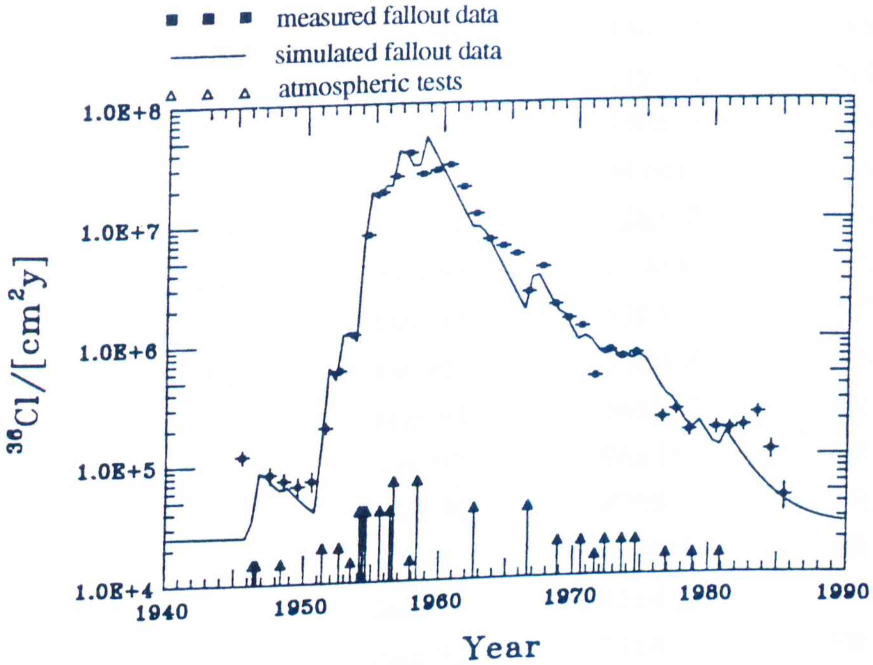

■ ■ ■ measured fallout data
simulated fallout data
△ △ △ atmospheric tests
1.0E+8
1.0E+7
1.0E+6
1.0E+5
1.0E+4
^{36}Cl/[cm^{2}y]
1940
1950
1960
1970
1980
1990
Year

Table 3.1

^{36}Cl/Cl ratios for Elms wet-only precipitation samples.

Collection Date		Sample I.D.	^{36}Cl/Cl$^-$ (x 10^{-15})	Laboratory
Beginning	End			
1/29/91	2/26/91	Feb-91	552±103	NSRL*
2/26/91	3/26/91	Mar-91	170±14	NSRL
3/26/91	4/23/91	Apr-91	123±12	NSRL
4/23/91	5/21/91	May-91	243±19	NSRL
6/18/91	7/2/91	Jun-91	156±15	NSRL
7/2/91	7/30/91	Jul-91	119±14	NSRL
7/30/91	8/27/91	Aug-91	150±15	NSRL
8/27/91	10/8/91	Sep-91	44.6±6.8	NSRL
10/8/91	11/5//91	Oct-91	128±12	NSRL
11/5/91	12/3/91	Nov-91	29.4±8.3	NSRL
12/3/91	12/31/91	Dec-91	53±5	NSRL
12/31/91	1/14/92	Jan-92	3.8±4.8	NSRL
3/11/92	3/24/92	Mar-92	568±37	PRIME Lab**
3/24/92	4/21/92	Apr-92	96±13	PRIME Lab
5/19/92	6/2/92	May-92	47±5	PRIME Lab
6/2/92	7/1/92	Jun-92	122±16	PRIME Lab
7/1/92	8/5/92	Jul-92	45±4	PRIME Lab
8/5/92	8/21/92	Aug-92	71±4	PRIME Lab
8/21/92	9/22/92	Sep-92	16±3	PRIME Lab
9/22/92	10/20/92	Oct-92	24±4	PRIME Lab
10/20/92	12/1/92	Nov-92	44±3	PRIME Lab
12/1/92	12/29/92	Dec-92	37±4	PRIME Lab
12/29/92	1/26/92	Jan-93	209±10	PRIME Lab
1/26/92	2/23/92	Feb-93	68±5	PRIME Lab

The given uncertainties stem from accelerator counting error and background correction.

*The University of Rochester Nuclear Structure Research Laboratory (NSRL).

**Purdue Rare Isotope Measurement Laboratory (PRIME Lab).

In general, the deposition of cosmogenic and bomb-produced isotopes is expected to be largely dependent on air mass exchange between the stratosphere and the troposphere.

3.2 CHLORINE-36 IN WET-ONLY PRECIPITATION SAMPLES

3.2.1 RESULTS

Wet-only precipitation samples were collected at the Elms Environmental Education Center in St. Mary's County, Maryland. The term "wet-only" refers to samples collected only during rain events using the sampler described in Section 2.2.1 (b). Samples were collected biweekly using the procedure given in Section 2.2.1 (b). For ^{36}Cl analysis, biweekly samples were combined by volume ratio to form integrated monthly samples. Table 3.1 gives the results of ^{36}Cl analysis of the wet-only samples. Ratios of ^{36}Cl/Cl are reported as measured by the University of Rochester Nuclear Structure Research Lab or PRIME Lab. Accelerator background corrections were made at NSRL or PRIME Lab, using the method described by ELMORE (1984b). Cross-calibration between the two laboratories was performed to ensure against systematic error. Details concerning cross-calibration are presented in Section 2.3.1 and Table 2.3. Additional corrections were made for samples prepared during periods when laboratory blanks contained measurable ^{36}Cl.

The ^{36}Cl/Cl ratio values lie over a wide range, from a high of 568±37 (x10^{-15}) in Mar-92 to a low of 3.8±4.8 (x10^{-15}) in Jan-92. High ratios are observed in the early spring (February-March), decreasing throughout the remainder of the year. The mean (chloride-weighted) ^{36}Cl/Cl ratio calculated for the entire 2 y sampling period is 68±19 ($x10^{-15}$). The annual mean ratios for the first and second sampling years differed by a factor of 1.27. During the first sampling year (Feb-91 to Jan-92) the mean ratio is 73.9±37 ($x10^{-15}$), and for the second sampling year (Mar-92 to Feb-93) the mean ratio is 58.2±5 ($x10^{-15}$).

Table 3.2 lists the values derived for ^{36}Cl concentrations and wet deposition fluxes. Concentrations of ^{36}Cl (in atoms/L) are calculated using the measured ^{36}Cl/Cl ratios and stable chloride concentrations (see Section 2.3.4) Deposition fluxes are calculated as follows in Eq. 1:

$$F_{^{36}Cl} = \frac{^{36}Cl/Cl \times [Cl^-] \times V \times 1.699 \times 10^{15}}{t} \qquad \text{(Eq. 3.1)}$$

where : $F_{^{36}Cl}$ = the ^{36}Cl deposition flux in atoms/m^2s

$[Cl^-]$ = the chloride concentration in mg/L

V = the volume (in liters) collected in a 1 m^2 area during the sampling period

t = the length (in seconds) of the sampling period

1.699×10^{15} = a constant representing the necessary unit conversions

The calculated ^{36}Cl concentrations (in atoms/L) range over an order of magnitude, from 4.16×10^5 in November 1991 to 9.94×10^6 in March 1992. The precipitation weighted mean concentration for the first sampling year is 1.28 ± 0.2 (x 10^6), and for the second year is 1.10 ± 0.1 (x 10^6). These values lie within experimental error of each other. The precipitation weighted mean concentration for the entire sampling period is 1.19 ± 0.13 (x 10^6).

Table 3.2.

^{36}Cl concentrations and deposition fluxes for Elms precipitation samples.

Sample I.D.	Volume (Liters)	$[Cl^-]$ (mg/L)	^{36}Cl/Cl ($x10^{-15}$)	$[^{36}Cl]$ ($x10^{6}$) (atoms/L)	Flux ($x10^{-3}$) (atoms/m^{2}s)
Feb-91	29.1±0.1	0.217±0.02	552±103	2.04±0.4.	2.44±4
Mar-91	77.2±0.1	0.736±0.02	170±14	2.13±0.2	67.8±6
Apr-91	121.1±0.1	0.845±0.02	123±12	1.77±0.2	88.4±9
May-91	39.0±0.1	0.468±0.02	243±19	1.93±0.2	31.1±3
Jun-91	61.5±0.1	0.335±0.02	156±15	0.88±0.09	45.1±4
Jul-91	132.5±0.1	0.539±0.02	119±14	1.09±0.1	59.7±7
Aug-91	69.7±0.1	0.299±0.02	150±15	0.76±0.07	22.0±2
Sep-91	132.2±0.1	0.930±0.02	44.6±6.8	0.70±0.1	26.3±4
Oct-91	68.6±0.1	1.38±0.02	128±12	3.00±0.3	85.1±8
Nov-91	61.8±0.1	0.831±0.02	29.4±8.3	0.41±0.1	10.6±3
Dec-91	61.4±0.1	0.550±0.02	53±5	0.49±0.04	12.6±1
Jan-92	24.8±0.1	5.57±0.02	3.8±4.8	3.60±0.4	7.3±9
Mar-92	12.6±0.1	1.03±0.02	568±37	9.94±0.6	51.8±4
Apr-92	(41.7±0.1)*	0.778±0.02	96±13	1.27±0.2	(43.7±5)*
May-92	100.4±0.1	1.16±0.02	47±5	0.92±0.1	76.9±8
Jun-92	34.0±0.1	1.04±0.02	122±16	2.16±0.3	30.3±4
Jul-92	72.2±0.1	1.44±0.02	45±4	1.10±0.1	32.9±3
Aug-92	199.5±0.1	0.507±0.02	71±4	0.61±0.04	40.3±2
Sep-92	139.8±0.1	2.24±0.02	16±3	6.09±0.1	35.2±6
Oct-92	40.3±0.1	2.26±0.02	24±4	0.92±0.1	15.3±3
Nov-92	50.4±0.1	1.36±0.02	44±3	1.02±0.07	21.2±2
Dec-92	117.9±0.1	1.61±0.02	37±4	1.01±0.1	39.5±4
Jan-93	72.16±0.1	0.481±0.02	209±10	1.71±0.08	50.9±3
Feb-93	58.6±0.1	1.10±0.02	68±5	1.27±0.1	30.8±2

The reported uncertainties are calculated by propagation of relevant measurement uncertainties. See Section 3.3.2 below.

* These values were corrected for sampling error (missing precipitation)

Calculated ^{36}Cl wet deposition fluxes (in atoms/m^{2}sec) vary considerably as well, with values ranging from 74 ± 9 in April 1992 to 8.8 ± 0.8 in January 1993. Higher fluxes occur during the spring. The precipitation weighted mean flux for the first sampling year is 40.7± 7 atoms/m^{2}sec, and for the second year is 35.8± 4 atoms/m^{2}sec. The precipitation weighted mean flux for the entire sampling period was 38.2± 5 atoms/m^{2}sec.

Figures 3.2, 3.3 and 3.4 are graphic representations of the measured $^{36}Cl/Cl$ ratios, ^{36}Cl concentrations, and ^{36}Cl deposition fluxes, respectively. Values are plotted versus the mean date for each sampling period. A clear seasonal ^{36}Cl deposition pattern is the most evident feature in the wet precipitation data. Figure 3.5 shows stable chloride concentrations in mg/L.

3.2.2 REPORTED UNCERTAINTIES

The uncertainties given in Tables 3.1 and 3.2 were calculated by the propagation of relevant measurement uncertainties. In all cases, the reported uncertainty is dominated by the error associated with the $^{36}Cl/Cl$ ratio measurement. This ratio error was calculated at the accelerator facility. The method by which it was calculated was described in detail by ELMORE et al. (1984). Normally, it was derived from the experimental count rate by the assumption of a Poisson distribution. The ratio errors associated with this study were approximately 10% of the measured value. Ratio errors for individual samples are given both in Table 3.1 and 3.2.

Other measurement errors, although minor compared with the ratio error, were included in the ^{36}Cl concentration and deposition flux uncertainty calculations. The measurement of [Cl^-] by ion chromatography involved an

Figure 3.2

^{36}Cl/Cl ratios in Elms wet-only precipitation samples versus time. Data are shown for the 2 y sampling period, beginning with January 1, 1991. Highest ratios are observed in February, 1991 and March, 1992.

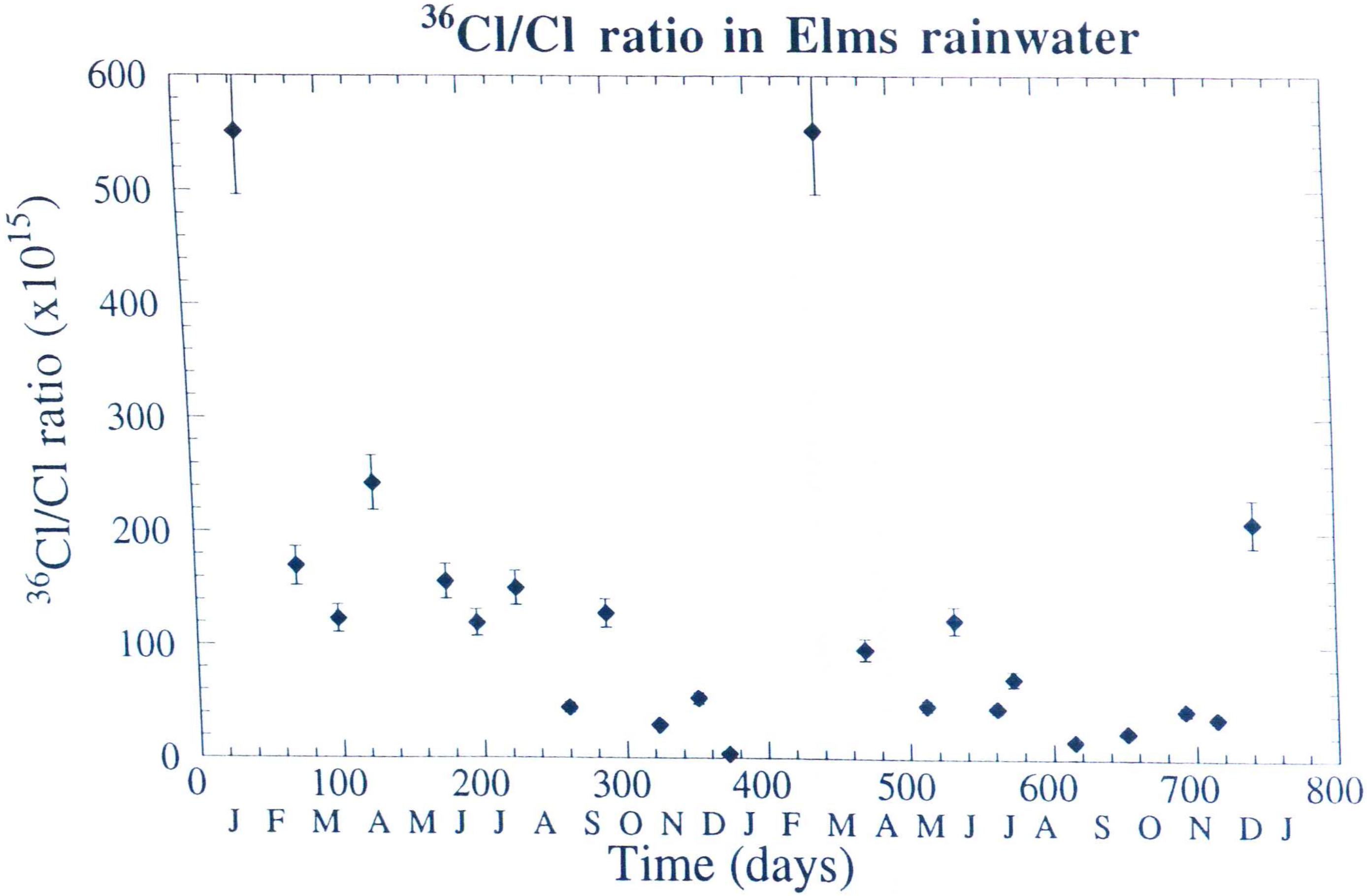

^{36}Cl/Cl ratio in Elms rainwater
^{36}Cl/Cl ratio (x10^{15})
0
100
200
300
400
500
600
0
100
200
300
400
500
600
700
800
J F M A M J J A S O N D J F M A M J J A S O N D J
Time (days)

Figure 3.3

^{36}Cl concentration (in atoms/L) in Elms wet-only precipitation samples. Data are shown for the 2 y sampling period, beginning with January 1, 1991.

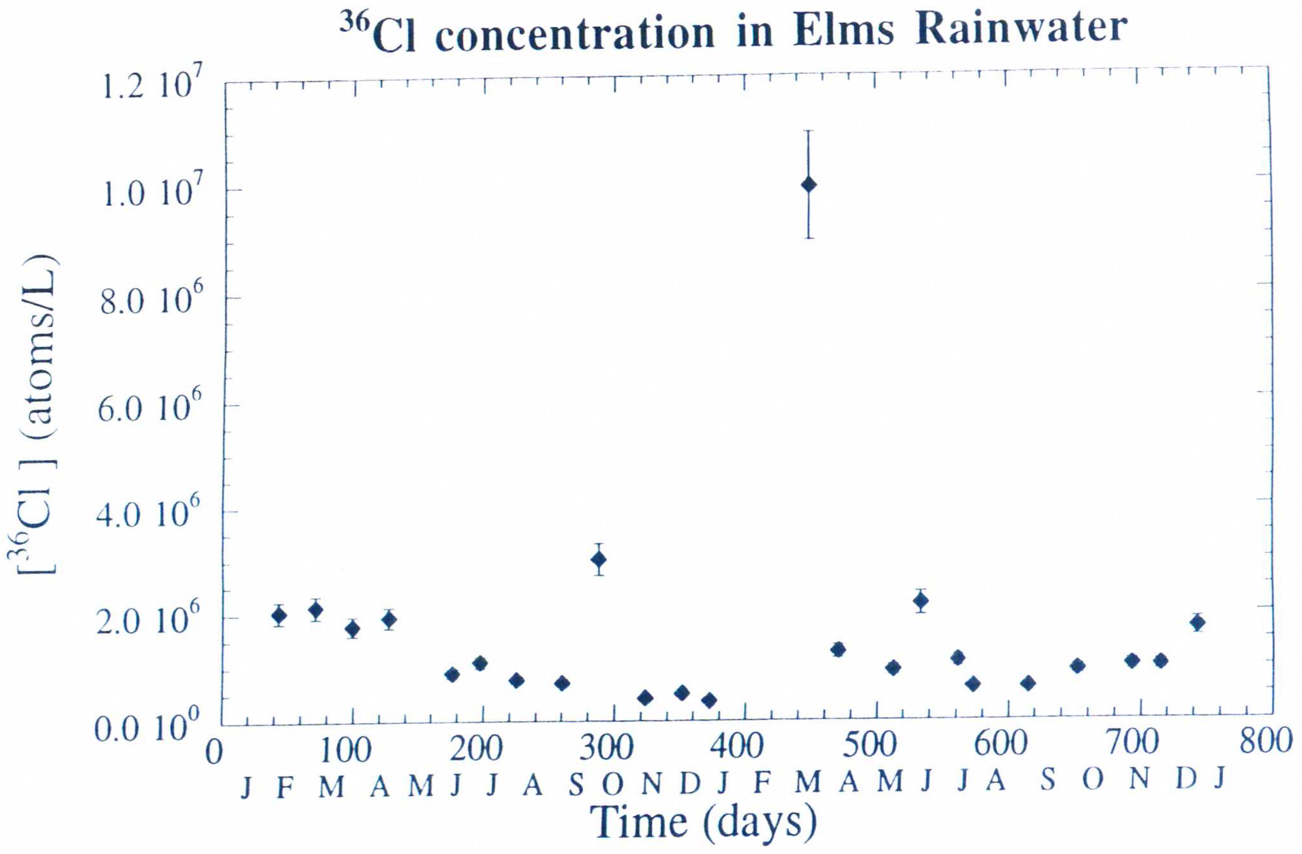
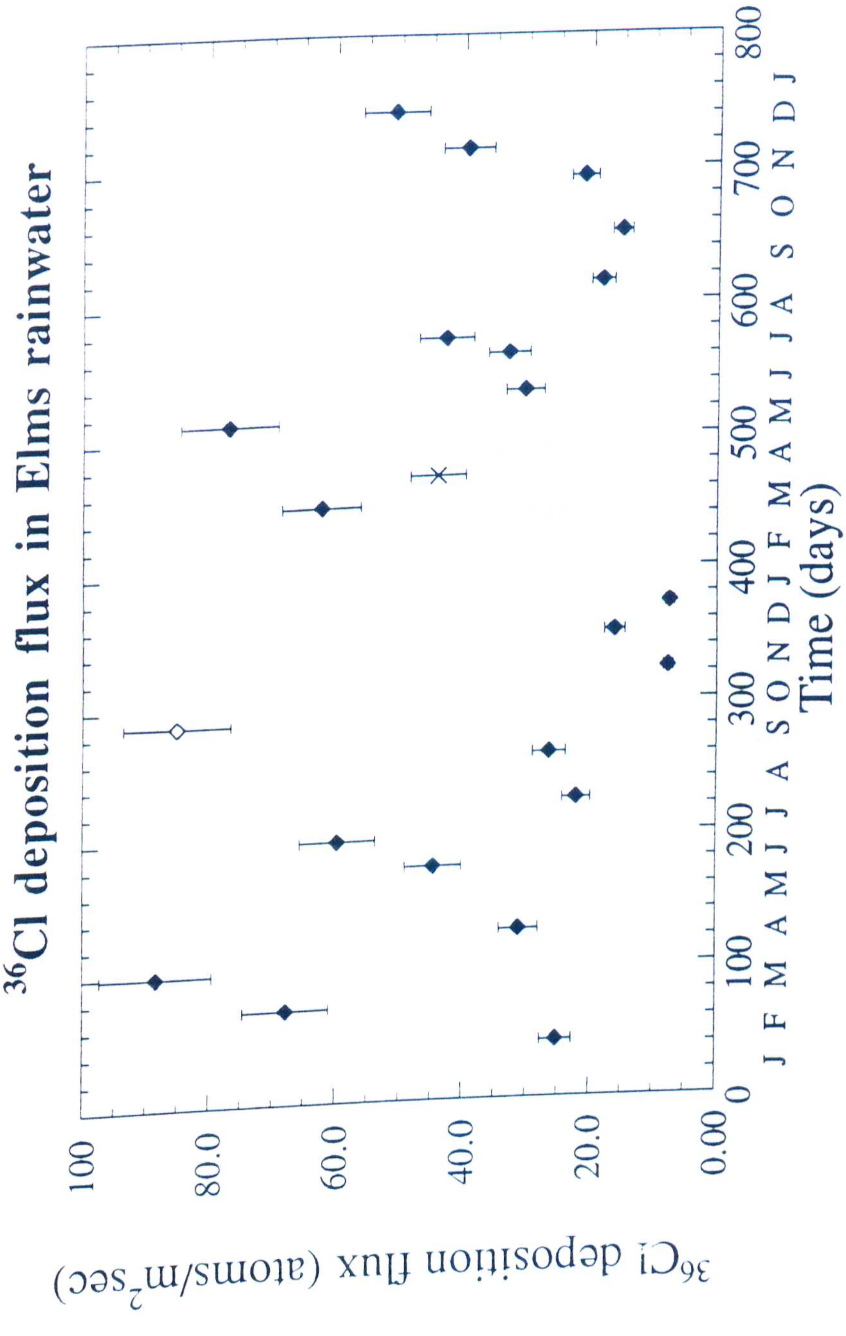

^{36}Cl concentration in Elms Rainwater
[^{36}Cl] (atoms/L)
1.2 10^7
1.0 10^7
8.0 10^6
6.0 10^6
4.0 10^6
2.0 10^6
0.0 10^0
0
100
200
300
400
500
600
700
800
J F M A M J J A S O N D J F M A M J J A S O N D J
Time (days)

Figure 3.4

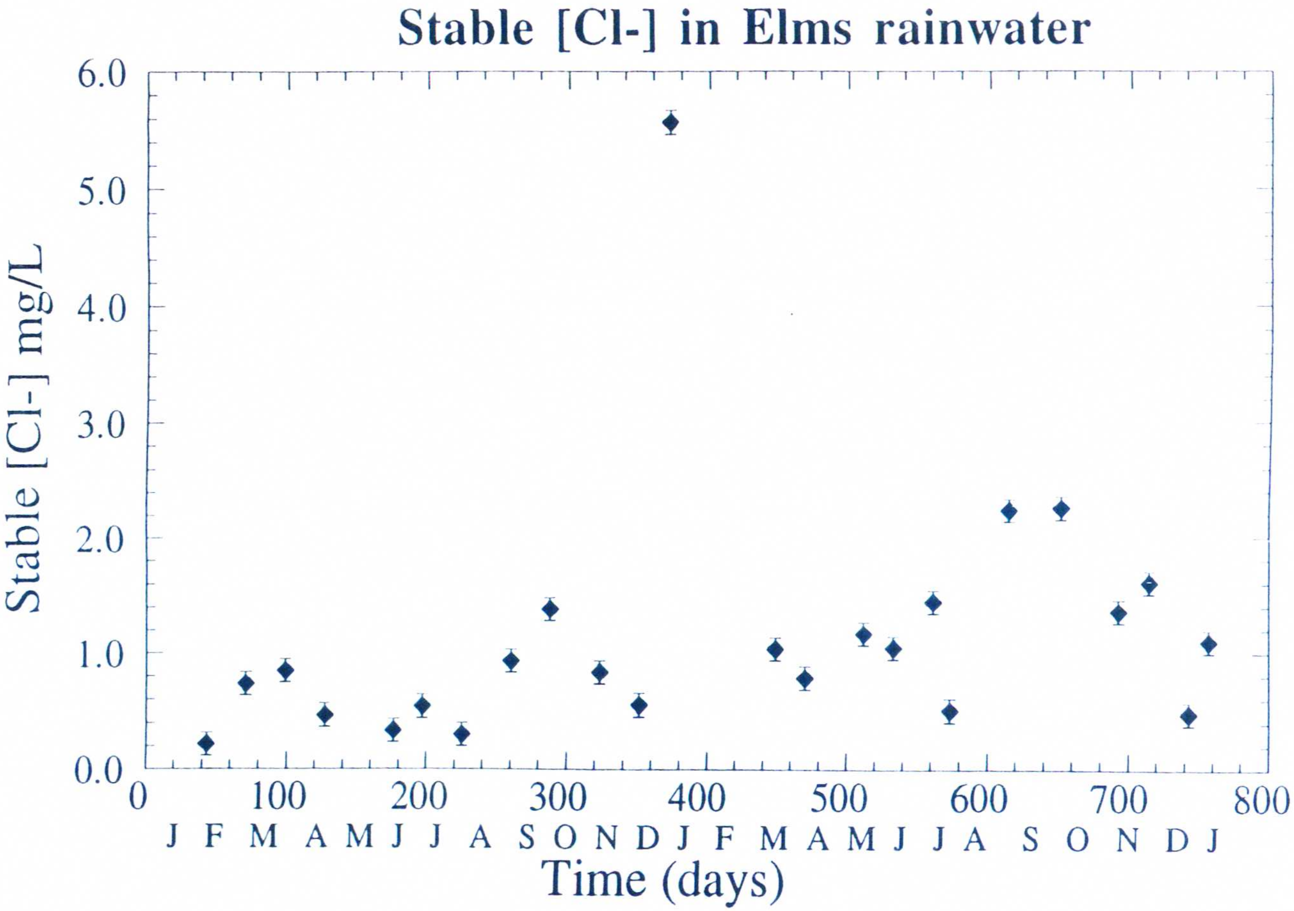
^{36}Cl deposition flux as measured in Elms wet-only precipitation samples. Data are shown for the 2 y sampling period, beginning with January 1, 1991. With the exception of October, 1991 (shown as an open diamond), highest ratios are observed in the spring, with peaks in April, 1991 and March 1992. The X represents April 1992, which was estimated as described in the Section 3.2.3.



^{36}Cl deposition flux in Elms rainwater
^{36}Cl deposition flux (atoms/m^{2}sec)
100
80.0
60.0
40.0
20.0
0.00
0
100
200
300
400
500
600
700
800
J F M A M J J A S O N D J F M A M J J A S O N D J
Time (days)

Figure 3.5

Stable chloride (mg/L) as measured in Elms wet-only precipitation samples. Data are plotted versus time for the 2 y sampling period, beginning with January 1, 1991.


Stable [Cl-] in Elms rainwater
Stable [Cl-] mg/L
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0
100
200
300
400
500
600
700
800
J F M A M J J A S O N D J F M A M J J A S O N D J
Time (days)

estimated 1-2% error. Sample volume measurements involved an absolute error of 0.1 L, approximately 0.1% of the measured values. Errors associated with the length of the sampling period, the area of the sample collector and evaporation from the collection carboy were even smaller and were considered negligible.

3.2.3 ANOMALOUS POINTS

Two apparently anomalous points appear in the ^{36}Cl deposition flux plot (Figure 3.4). These occur in October 1991 and April 1992. The April 1992 anomaly can be attributed to sampling error. Several sampler breakdowns occurred during the late winter and early spring of that year (D. LEISTER, Chesapeake Biological Laboratory, personal communication). As a result, precipitation was missed and an anomalously low deposition flux was obtained for that period. If a correction is made for the missing precipitation, assuming a constant ^{36}Cl concentration, the calculated flux changes from 11.4 atoms/m^{2}s to 43.7 atoms/m^{2}s. The corrected value is shown as an X in Figure 3.4, and no longer appears anomalous.

The deposition flux value obtained for October 1991, shown in Figure 3.4 as an open diamond, is anomalously high. The measured ^{36}Cl/Cl ratio for October 1991 ($128 \pm 12 \times 10^{-15}$) was approximately 5 times higher than in October 1992. The stable chloride concentration was elevated in that sample as well, however it was not the highest in the data set. As a result, the calculated ^{36}Cl concentration is anomolously high, as is the calculated deposition flux. The cause of the anomaly is not clear. When considering the deposition flux, the sample does not appear to follow the trend of the data. However, it does not lie outside the range of the rest of the data set. Thus it is possible that the calculated flux is real. In that case, possible explanations include unusual or unseasonal meteorological patterns.

Tropopause folding events can mix stratospheric air into the troposphere causing sharp increases in surface concentrations of stratospheric tracers (see Section 3.2.4). A second stratospheric tracer, such as ^{7}Be or ozone would be useful in determining the source of apparent excess ^{36}Cl in this sample. It is recommended that a stratospheric co-tracer be used in future studies of this type.

3.2.4 DISCUSSION

The mean ^{36}Cl/stable Cl ratio is expected to lie within a range of 40 to 80 (x10^{-15}) as predicted for the location of the sampling site by BENTLEY, PHILLIPS and DAVIS (1986). A correction applied to the ^{36}Ar(n,p)^{36}Cl production rate by ANDREWS and FONTES (1992) gives a revised range of 28 to 55 (x10^{-15}). The mean (total chloride weighted) ratio calculated for this data set is 68±19 (x10^{-15}), somewhat higher than predicted. Factors that influence the ^{36}Cl/Cl ratio are the ^{36}Cl production rate, the ^{36}Cl deposition pattern (for instance, higher deposition fluxes occur at the mid-latitudes) and the stable chloride concentrations. The deviation of the measured ^{36}Cl/Cl ratio above the expected range supports present indications that the ^{36}Cl fallout is significantly underestimated by ^{40}Ar spallation [SUTER et al.(1987), SYNAL et al. (1990), ANDREWS and FONTES (1992)]. Further discussion concerning this discrepancy is presented in Section 3.3.

(a) Seasonal Variation in ^{36}Cl Deposition

Seasonal fluctuations are apparent, particularly in the ^{36}Cl/Cl ratio (Figure 3.2) and deposition flux (Figure 3.3) data. Maximum ratios were measured in February/March, maximum wet deposition fluxes occurred in March/April. Figure 3.6 shows the displacement of these peaks. This discrepancy can be accounted for by the stable chloride behavior. Spring rains caused an increase in stable chloride deposition, as shown in Figure 3.7, diluting the $^{36}Cl/Cl$ ratio. The ^{36}Cl wet deposition flux is dependent on stratospheric/tropospheric mixing, as well as precipitation rate. Stratospheric/tropospheric mixing begins to increase in intensity in the early spring, resulting in an early increase in the ^{36}Cl ratio.

While this data set is the first to demonstrate seasonal dependence for ^{36}Cl deposition, similar seasonal variations are observed in a host of stratospheric tracers, including ^{90}Sr, $^{7,10}Be$, ^{239,240} Pu and ozone. REITER (1978) gives an overview of radionuclides monitored in surface air at Battelle Pacific Northwest Laboratories in Richland, Washington. Air concentrations of thirty radionuclides are given as a function of time from 1961 to 1976. The radionuclides presented by REITER were introduced into the stratosphere as fission products during the period of atmospheric nuclear weapons testing. Clear, 3- to 10-fold seasonal fluctuations are observed for nearly all of these isotopes, with maxima occurring in late spring. For example, Figure 3.8 shows ^{90}Sr concentrations in surface air at Richland, Washington from 1961 to 1976. Also shown are documented atmospheric test detonations. Despite an irregular input pattern, ^{90}Sr air concentrations fluctuate periodically, with a single annual peak. Numerous additional studies have been published, many of which are discussed in Reiter's review.

Cosmogenic isotopes have been shown to undergo seasonal deposition fluctuations as well. RAISBECK and YIOU (1979) measured ^{10}Be in monthly precipitation samples during the early development of AMS ^{10}Be measurements. Their preliminary results suggested a seasonal pattern, with a 2-fold depositional increase occurring in March. DUTKIEWICZ and HUSAIN (1985) used stratospheric $^{7}Be/^{90}Sr$ ratios to estimate the stratospheric contribution to surface air

Figure 3.6

^{36}Cl/Cl ratios (open circles with a solid line) and ^{36}Cl deposition flux (solid diamonds with a dashed line) plotted versus time for the 2 y sampling period. A smoothed curve was fitted to the data to aid the eye. Note that the ^{36}Cl/Cl ratio peak occurs slightly before the ^{36}Cl deposition flux peak.

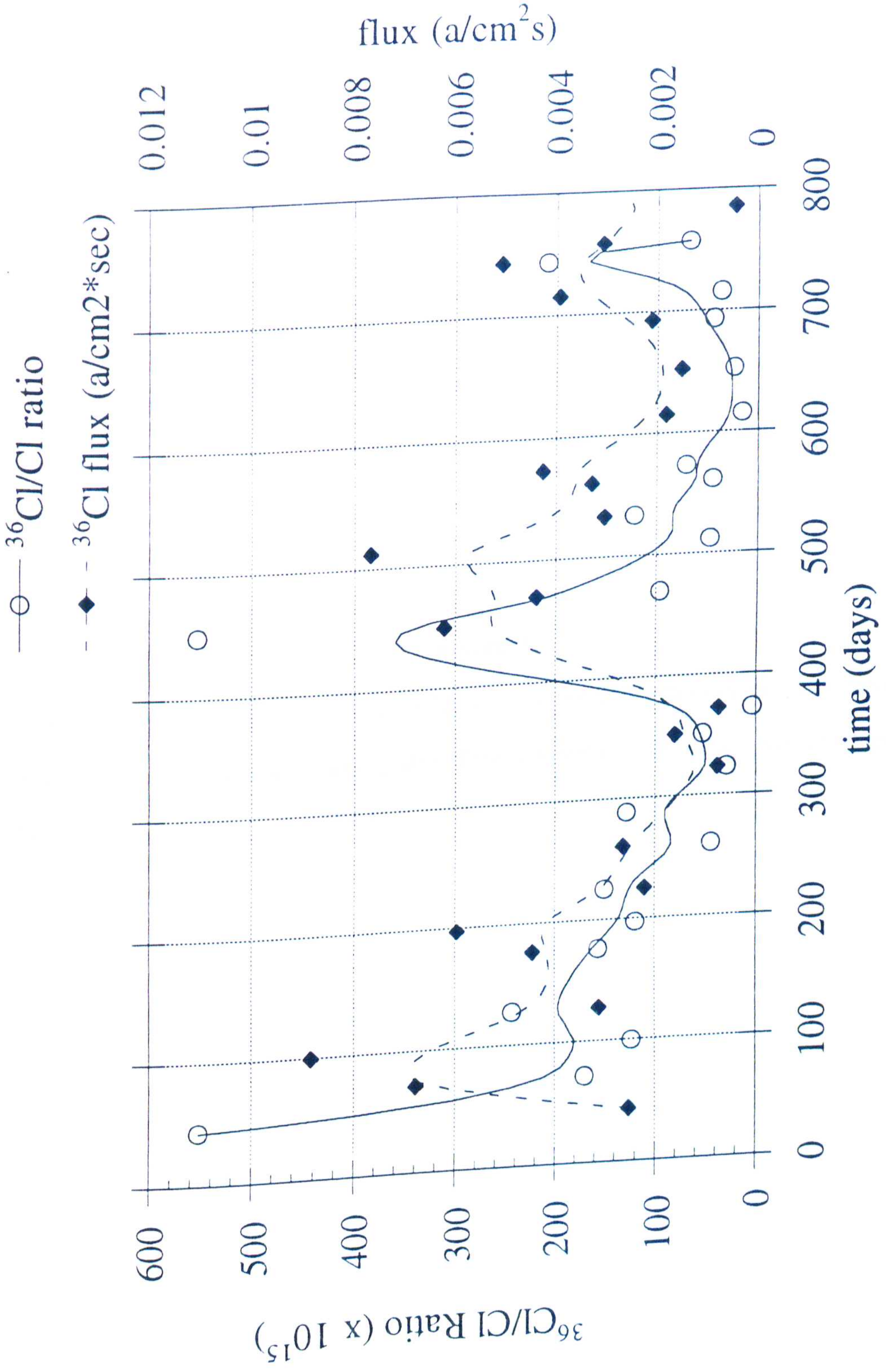

^{36}Cl/Cl ratio
^{36}Cl flux (a/cm2*sec)
flux (a/cm^{2}s)
0.012
0.01
0.008
0.006
0.004
0.002
0
time (days)
0
100
200
300
400
500
600
700
800
^{36}Cl/Cl Ratio (x 10^{15})
600
500
400
300
200
100
0

Figure 3.7

Stable chloride deposition (in mg/m^{2}d) as measured in wet-only precipitation samples from the Elms sampling site. Data are shown for the 2 y sampling period, beginning with January 1, 1991.

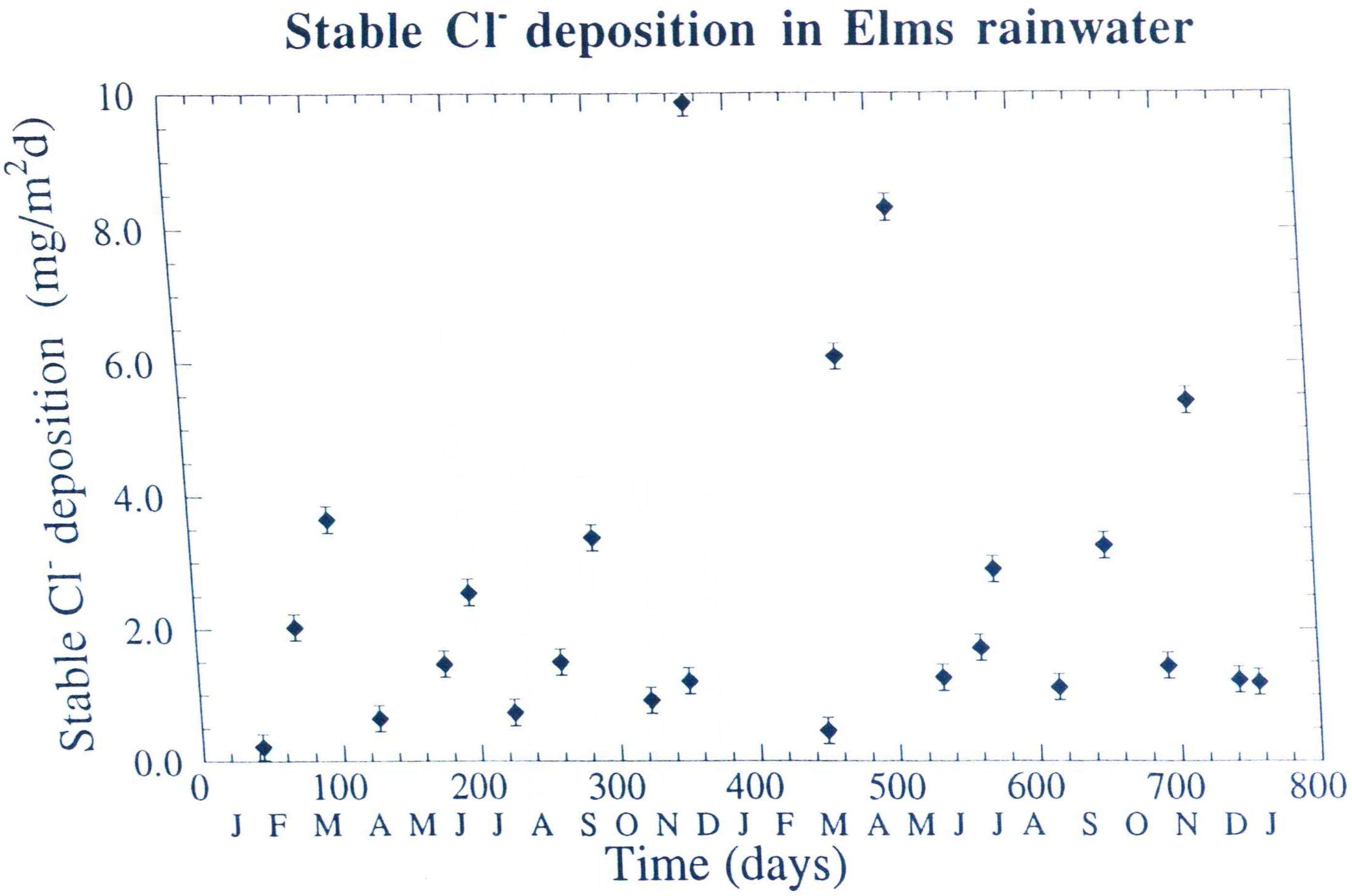
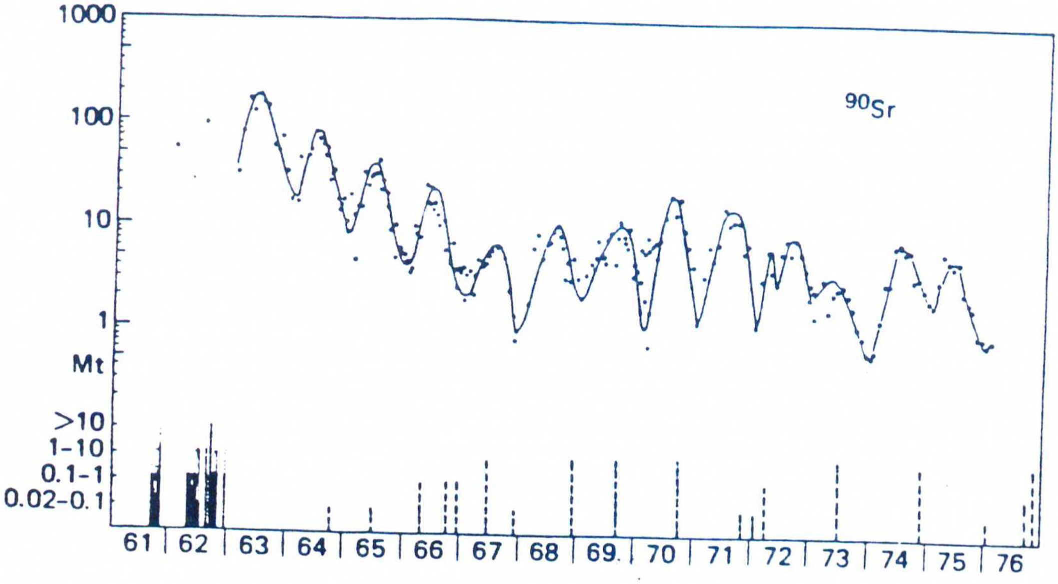

Stable Cl⁻ deposition in Elms rainwater
Stable Cl⁻ deposition (mg/m²d)
0.0
2.0
4.0
6.0
8.0
10
0
100
200
300
400
500
600
700
800
J F M A M J J A S O N D J F M A M J J A S O N D J
Time (days)

Figure 3.8

Strontium-90 concentrations (in dpm/10^3cm^3) in surface air at Richland, Washington, during 1961-1976. Vertical lines at the ordinate represent nuclear test detonations by the USSR, China and the United States. Note that the data show a seasonal pattern, with peaks occurring in the spring/early summer, regardless of the occurrence of test detonations (taken from REITER (1975)).


1000
100
10
1
Mt
>10
1-10
0.1-1
0.02-0.1
90Sr
61
62
63
64
65
66
67
68
69
70
71
72
73
74
75
76

^{7}Be concentrations. The calculated stratospheric component revealed a distinct seasonal pattern, reaching a maximum between April and May (Figure 3.9).

The transport processes responsible for the spring peak are discussed in a review article by REITER (1975). These processes are also addressed thoroughly, and in great detail, in WMO (1986). Stratospheric/tropospheric air mass exchange is the predominant mechanism which controls the deposition of these isotopes. Research on stratosphere-troposphere exchange began with concern about radioactive fallout in the 1960's. It remains an important area of research today, as the processes involved are responsible for the distribution of atmospheric contaminants, including species responsible for ozone destruction.

Four processes are primarily responsible for mass exchange across the tropopause. The most effective of these is Hadley cell circulation, which introduces tropospheric air into the stratosphere in the tropics, and returns stratospheric air into the troposphere in the middle and high latitudes. This mechanism is estimated to be responsible for a total annual flux of approximately 38% of the mass of the northern hemispheric stratosphere across the tropopause [REITER (1975)]

Seasonal shifts in tropopause height are responsible for an additional flux of approximately 10% of the mass of one hemisphere per year across the tropopause. This effect was first pointed out by STALEY (1962), who gave an average of the monthly variation in tropopause height for four different latitudes (Figure 3.10) The increase in the height of the tropopause in the warmer summer months results in the inclusion of stratospheric air into the troposphere were trace species in it can be scavenged. Additionally, in the case of cosmogenic isotopes including ^{36}Cl, a higher tropopause results in more cosmic rays penetrating the troposphere, and the fraction of these isotopes produced in the troposphere increases.

Figure 3.9

Seasonal profile of the stratospheric ^{7}Be component in surface air for the mid-latitudes (38°N to 51°N). [From DUTKIEWICZ and HUSSAR (1985)].

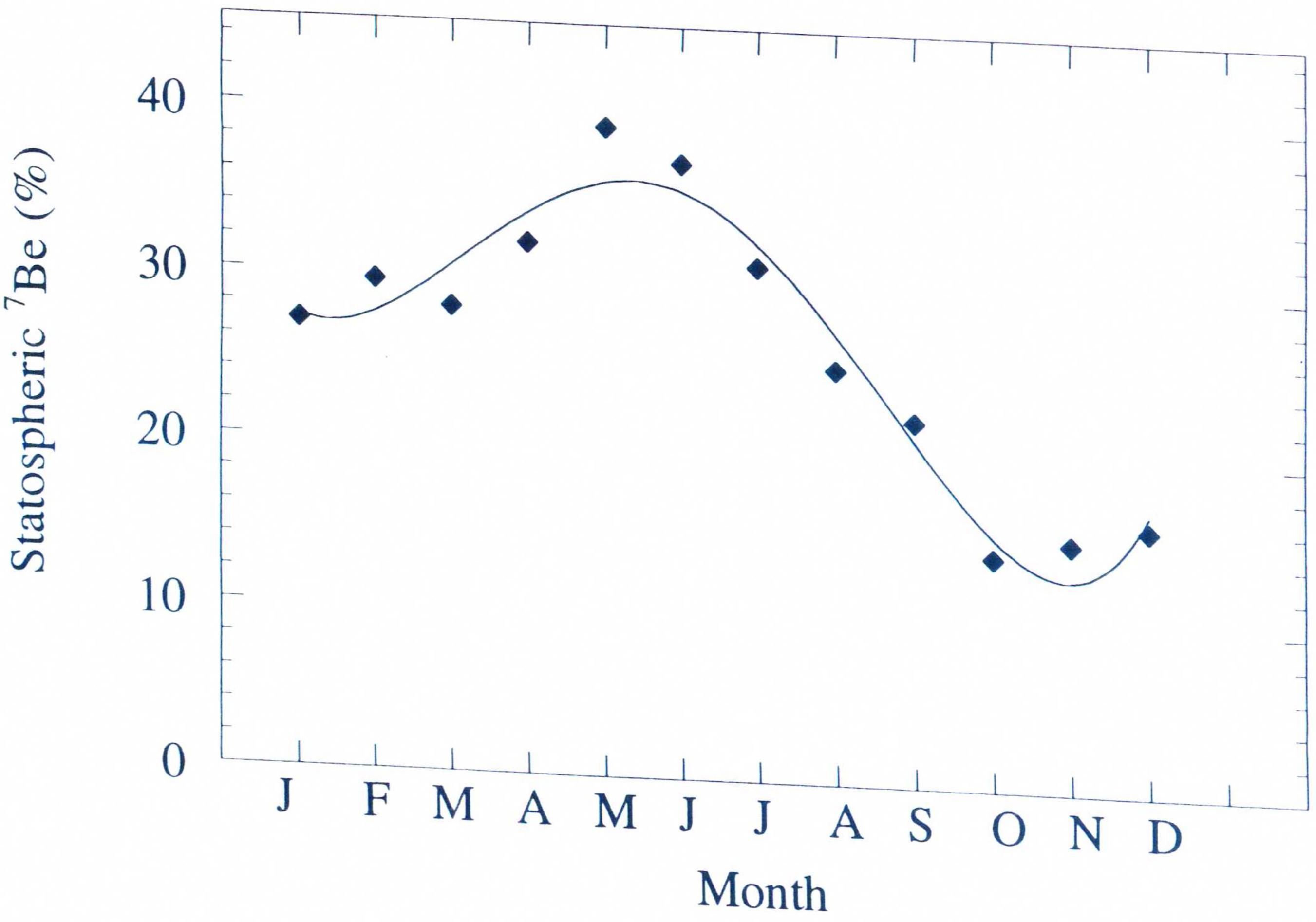
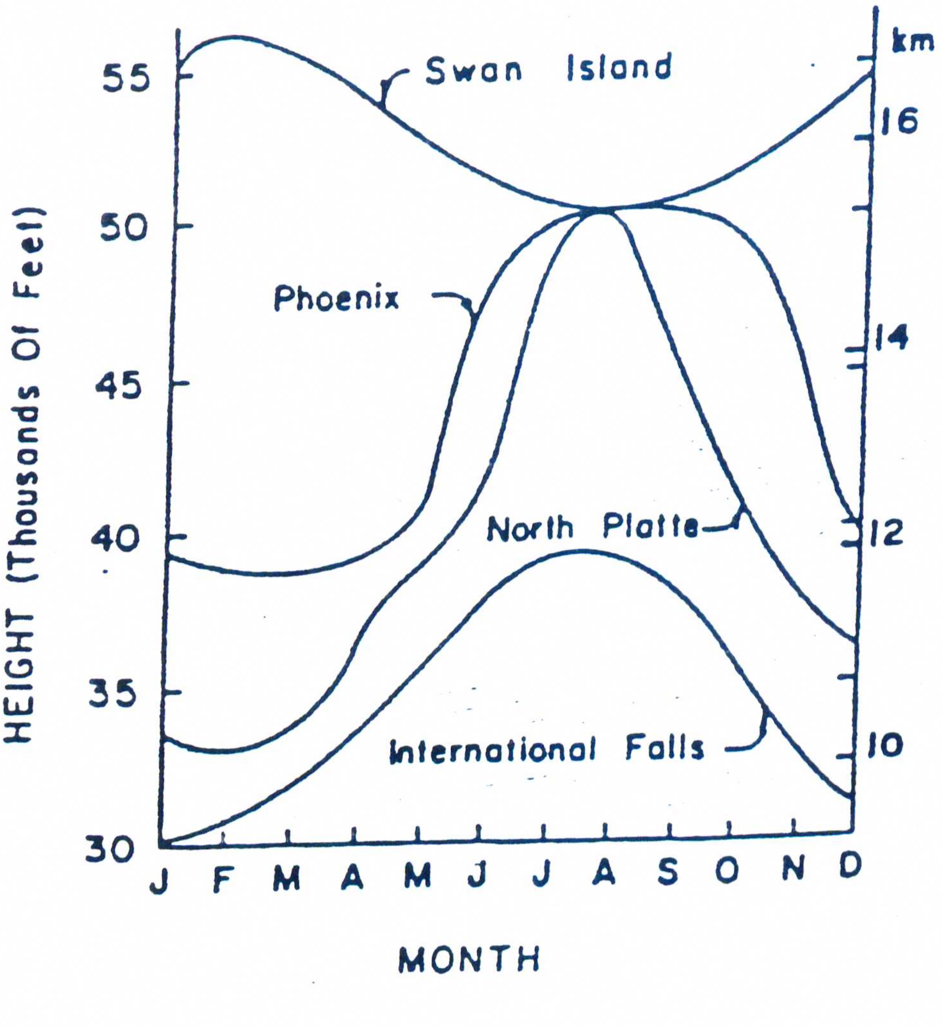

Statospheric ^{7}Be (%)
0
10
20
30
40
J
F
M
A
M
J
J
A
S
O
N
D
Month

Figure 3.10

Average tropopause heights for the period 1946 to 1952, as measured at Swan Island (17°N), Phoenix (33°N), North Platte (41°N) and International Falls (49°N). [From STALEY (1962)].


HEIGHT (Thousands Of Feel)
55
50
45
40
35
30
km
16
14
12
10
Swan Island
Phoenix
North Platte
International Falls
J F M A M J J A S O N D
MONTH

Tropopause folding events and clear air turbulence (CAT), both associated with jet stream air motion, also result in the injection of stratospheric air into the troposphere. The study of these events began in the early 1960's, due to occasional observations of high concentrations of radioactive fallout (REITER (1975)) . These events tend to occur in the mid-latitudes, where the boundary between the stratosphere and troposphere becomes ill-defined. The term 'tropopause folding' is used to describe the process in which the tropopause deforms, becomes vertical in the jet stream core and eventually folds beneath the core. A schematic diagram of this phenomenon is given in Figure 3.11. Tropopause folding events occur at isolated times and places, more frequently in the spring and summer (REITER (1975)).

Finally, there are several smaller scale processes which result in mass transport across the tropopause. These include small scale eddy turbulence, large thunderstorms with "overshooting tops" (which penetrate the stratosphere), and mesoscale convective systems, as demonstrated by POULIDA (1993).

DIBB (1989) published a study of atmospheric ^{7}Be deposition at the Chesapeake Bay Biological Laboratory in Solomon's Island, Maryland. The sampling site for DIBB's (1989) study was located approximately 10 mi. from the Elms Environmental Education Center, the sampling site for this ^{36}Cl study. Beryllium-7 is a cosmogenic isotope with a relatively short (53.3 d) half-life. Like ^{36}Cl, it is produced predominantly in the stratosphere. DIBB (1989) used his data to investigate the relationship between temporal variability in ^{7}Be deposition and atmospheric processes. His data reveal a seasonal pattern with deposition peaks occurring April and May.

Figure 3.11

Schematic view of mass flow from the stratosphere to the troposphere in the vicinity of the jet stream. [From REITER (1975)].

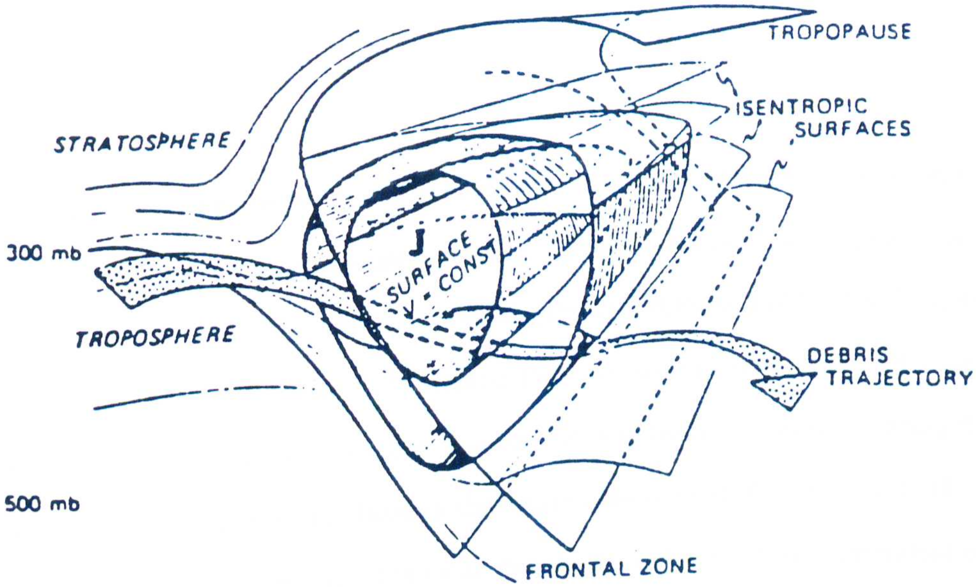

TROPOPAUSE
ISENTROPIC
SURFACES
STRATOSPHERE
300 mb
J
SURFACE
V = CONST
TROPOSPHERE
DEBRIS
TRAJECTORY
500 mb
FRONTAL ZONE

Figure 3.12 shows DIBB's monthly ^{7}Be deposition data, corrected for decay to the middle of each month. For comparison, ^{36}Cl deposition flux data from this study are plotted as well. Both isotopes undergo similar seasonal deposition variations, with peaks occurring between March and May. It must be noted that the ^{7}Be data were collected during 1986-1987 and the ^{36}Cl data were collected during 1991-1993. The observed scatter in the data probably reflects variations in the precipitation rate.

(b) Deposition Flux Function

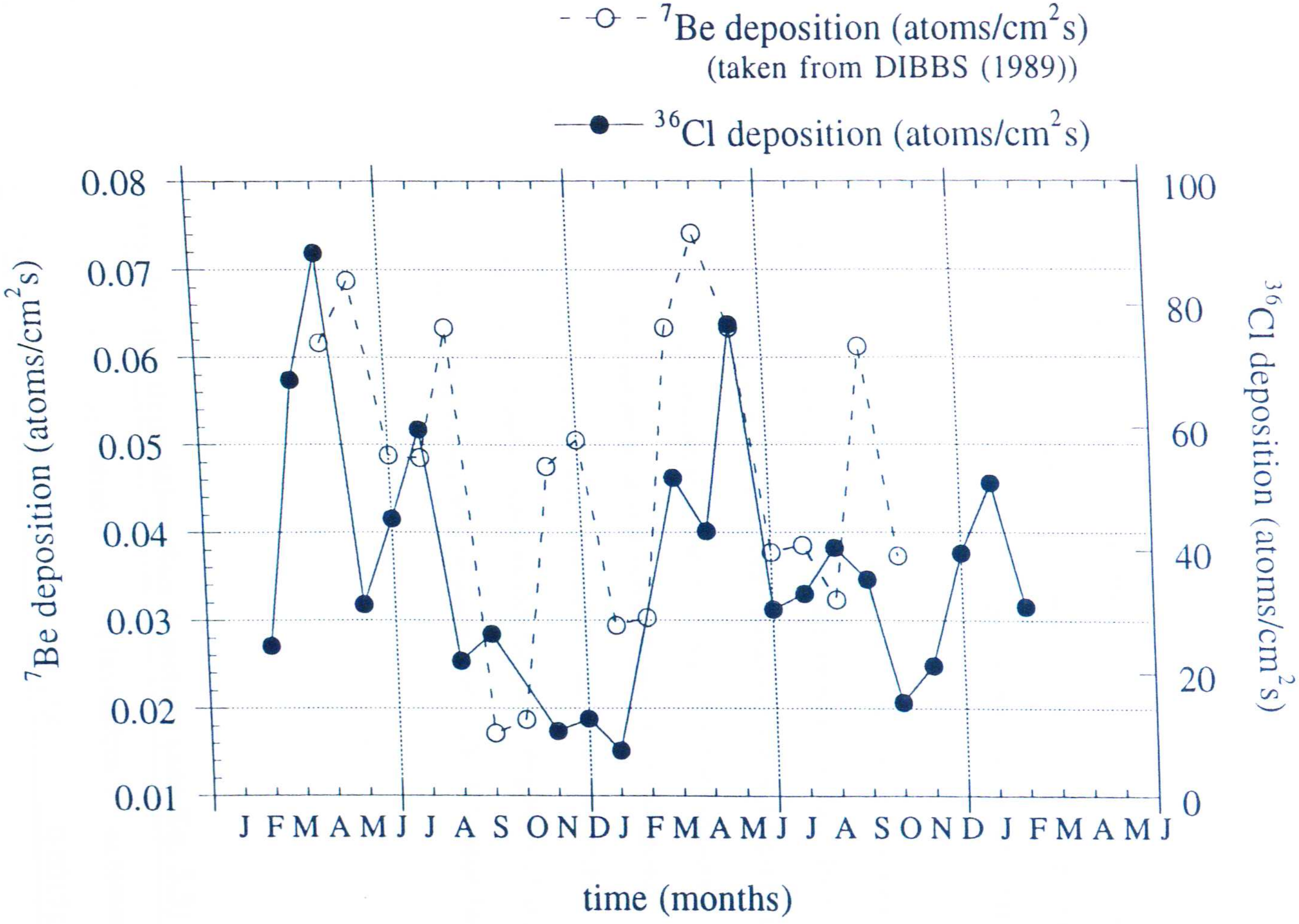
It has been postulated, and is commonly assumed, that the deposition flux of a cosmogenic isotope within a particular latitudinal belt would be proportional to the amount of precipitation (BROWN et al. (1989), MONAGHAN (1987), LAL and PETERS (1967)). Figure 3.13 depicts the correlation between the ^{36}Cl wet deposition flux and the precipitation rate for the data from this study. Fitting the data with a least-squares line through the origin results in an R^2 value of 0.38, indicating a weak correlation. It is clear that the flux is not simply dependent on the precipitation rate, but on other factors as well.

As discussed previously in this chapter, ^{36}Cl deposition undergoes seasonal variation, due to meteorological factors unrelated to precipitation rate. A simple mathematical function is proposed to describe the deposition flux in terms of time (season) and precipitation rate. This equation is as follows:

$$\text{Flux} = a_1 P \sin(\Theta + a_2) + a_3 P + a_4 \qquad \text{(Eq. 3.2)}$$

Figure 3.12

Comparison between ^{7}Be deposition at Solomon's Island, MD from 1986 to 1987, as measured by DIBB (1989), and ^{36}Cl deposition as measured at the Elms, MD from 1991 to 1992 in this study. Note the similarity in the seasonal deposition patterns.


- -○- - ^{7}Be deposition (atoms/cm^{2}s)
(taken from DIBBS (1989))
—●— ^{36}Cl deposition (atoms/cm^{2}s)
^{7}Be deposition (atoms/cm^{2}s)
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
^{36}Cl deposition (atoms/cm^{2}s)
100
80
60
40
20
0
J F M A M J J A S O N D J F M A M J J A S O N D J F M A M J
time (months)

where: Flux = ^{36}Cl deposition flux (atoms/cm^{2}s)

a_n = fitting parameter

P = precipitation rate (mm/d)

$\Theta = $ time (in units of $\frac{\text{Julian date}(360)}{365}$)

In this formulation, a sine function is used to describe the seasonal fluctuation, an approximation which fits the data quite well. The precipitation rate (P) is the total amount of precipitation that fell during the sampling period divided by the total number of days.

The model fitting program SCIENTIST (MicroMath Scientific Software, Salt Lake City, Utah) was used to solve the equation for parameters (a_n). This program uses a least squares algorithm to find model parameters which best fit the given data set. The results are as follows in Table 3.3. A plot of the measured fluxes with the simulated fluxes versus time is given in Figure 3.14. With the exception of two obvious outliers, which were not used in the fitting procedure (Oct-91 and April-92), the model closely approximates the data. Figure 3.15 is a correlation plot of the observed flux versus the simulated flux. The R^2 value for this plot is 0.83.

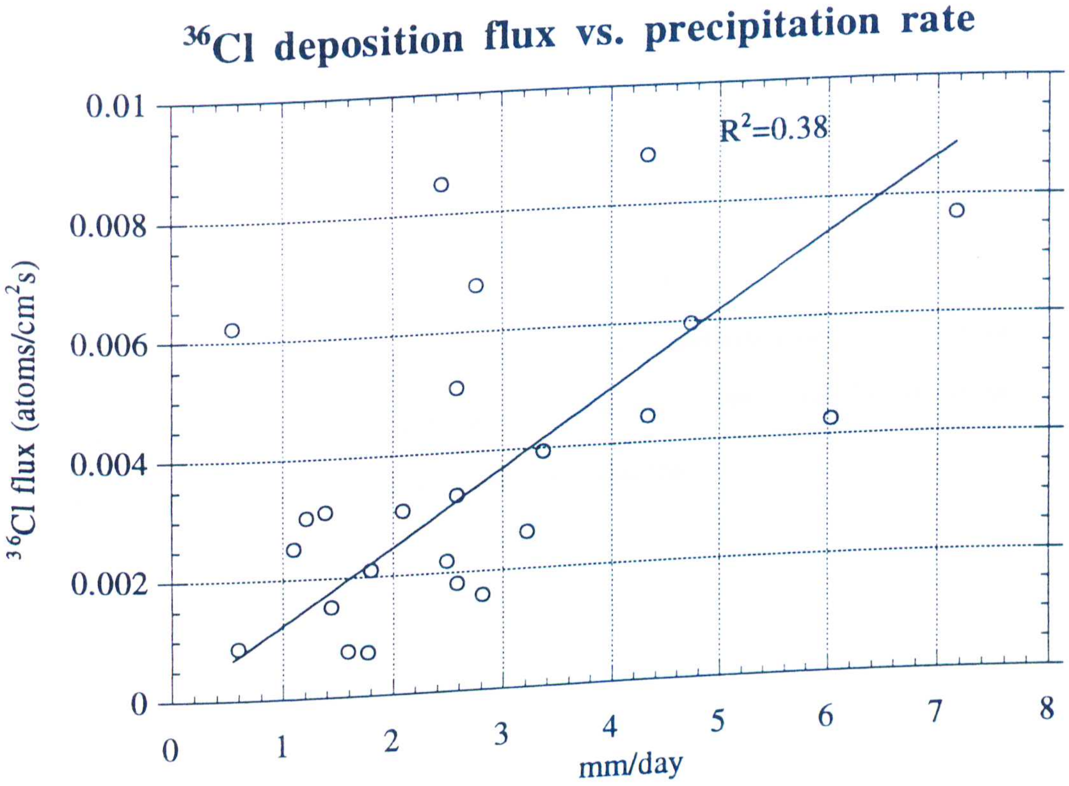
Table 3.3

Parameters (a_n) for the deposition flux function (see Eq. 3.3)

Parameter	a_1 (atoms/cm^3)	a_2 (radians)	a_3 (atoms/cm^3)	a_4 (atoms/cm^{2}s)
Value	0.005504	-0.13766	0.006158	0.0017152

Figure 3.13

^{36}Cl deposition flux (in atoms/m^{2}s) versus precipitation rate (in mm/d) for wet-only precipitation samples from the Elms site. A weak correlation ($R^2 = 0.38$) exists in the data.



^{36}Cl deposition flux vs. precipitation rate
^{36}Cl flux (atoms/cm^{2}s)
0.01
0.008
0.006
0.004
0.002
0
0
1
2
3
4
5
6
7
8
mm/day
R^2=0.38

Figure 3.14

Observed ^{36}Cl deposition fluxes (open circles) and simulated fluxes (solid diamonds) versus time, beginning with January 1, 1991. The results of the functional form agree well with the observations.

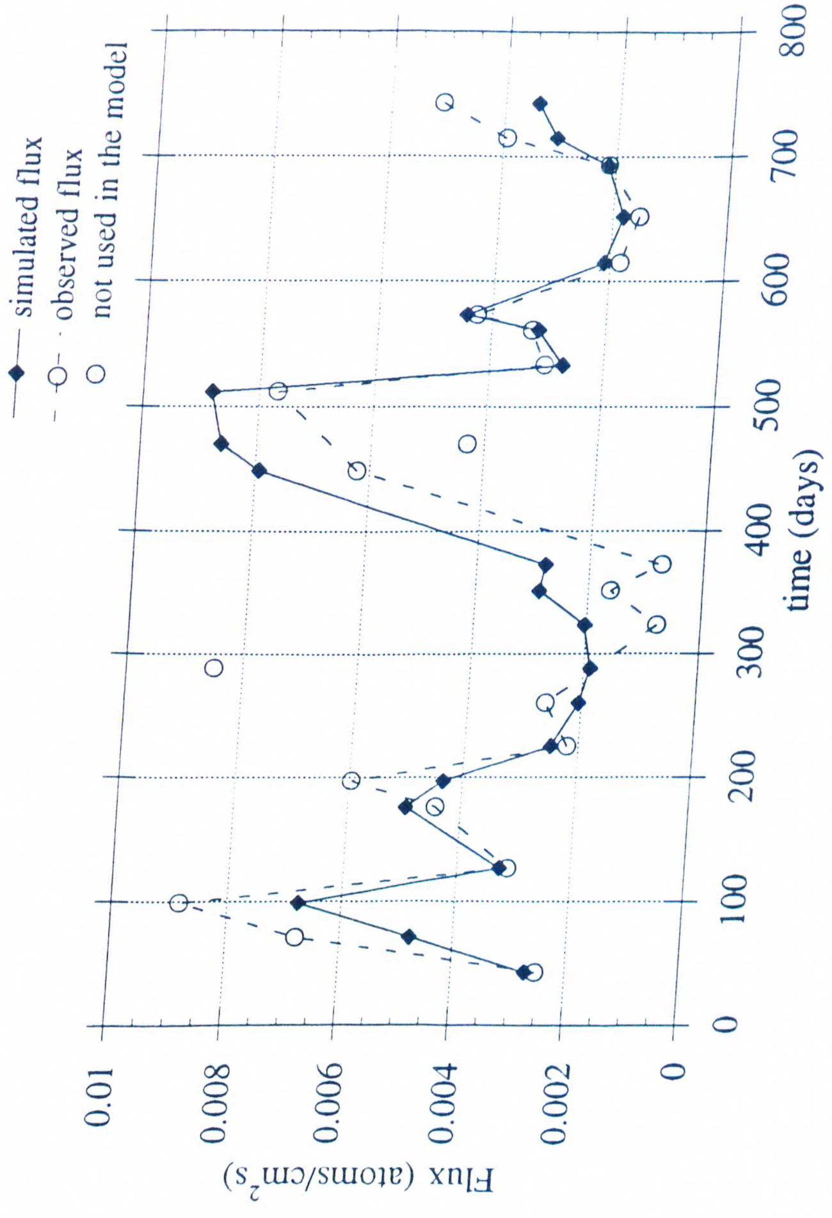
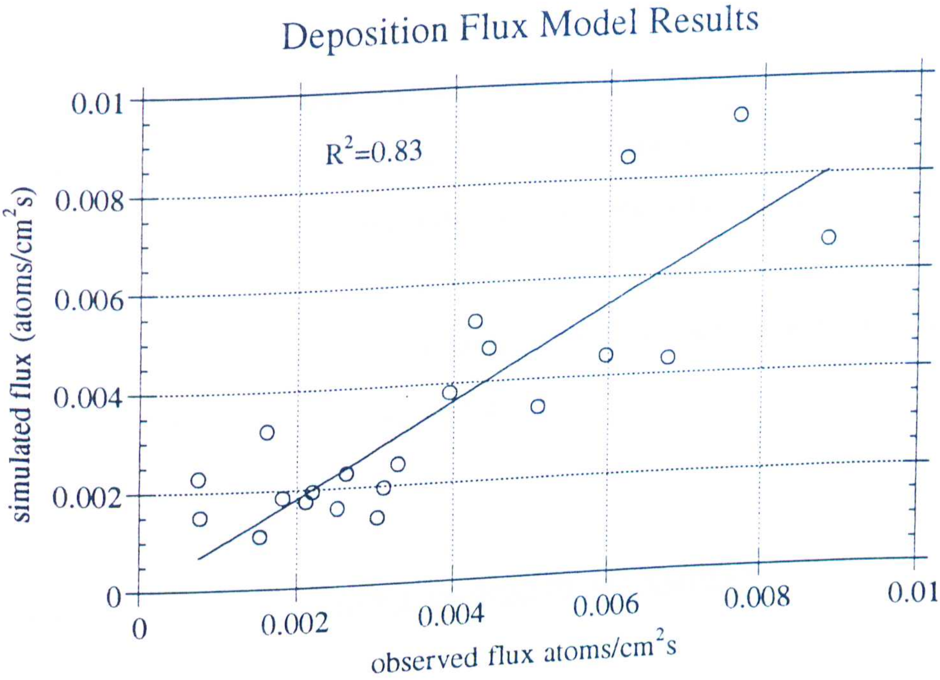

simulated flux
observed flux
not used in the model
Flux (atoms/cm^{2}s)
0.01
0.008
0.006
0.004
0.002
0
time (days)
0
100
200
300
400
500
600
700
800

Figure 3.15

Correlation plot between observed ^{36}Cl deposition fluxes and simulated fluxes. $R^2 = 0.83$.



Deposition Flux Model Results

Residual plots were also made to determine how well the function accounted for each variable (season and precipitation rate). Figure 3.16 (a) shows a plot of residuals (calculated as the difference between the observed flux and the model simulation) versus time. For easy comparison the two sampling years are superimposed, with day 1 as the first of February. No clear trend is evident in the scatter of the data above and below the x axis. This indicates that the model does not systematically deviate from the observed flux with respect to time (or season). A similar plot of residuals versus precipitation rate is given in Figure 3.16(b). Again, there is no clear trend in the scatter of the data, indicating that the calculated flux does not systematically deviate from the observed flux with respect to precipitation rate. These plots are good indications that the model reasonably accounts for these major components.

3.3 CHLORINE-36 IN BULK DEPOSITION SAMPLES

Bulk deposition samples (referred to as 'open samples') were collected at the Elms site in addition to the wet-only deposition samples. The sample collection apparatus and procedure for these samples is described in Section 2.2.1 (b). These samples were collected for comparison with the wet-only deposition samples. Two goals were considered. The first goal was to determine the total ^{36}Cl deposition flux for comparison with theoretical values. The second, yet equally important, goal was to investigate the significance of ^{36}Cl dry deposition.

Figure 3.16

(a) Plot of residuals (calculated as the difference between observed and simulated fluxes) versus time. Data from the 2 sampling years are superimposed.

(b) Plot of residuals versus precipitation rate.

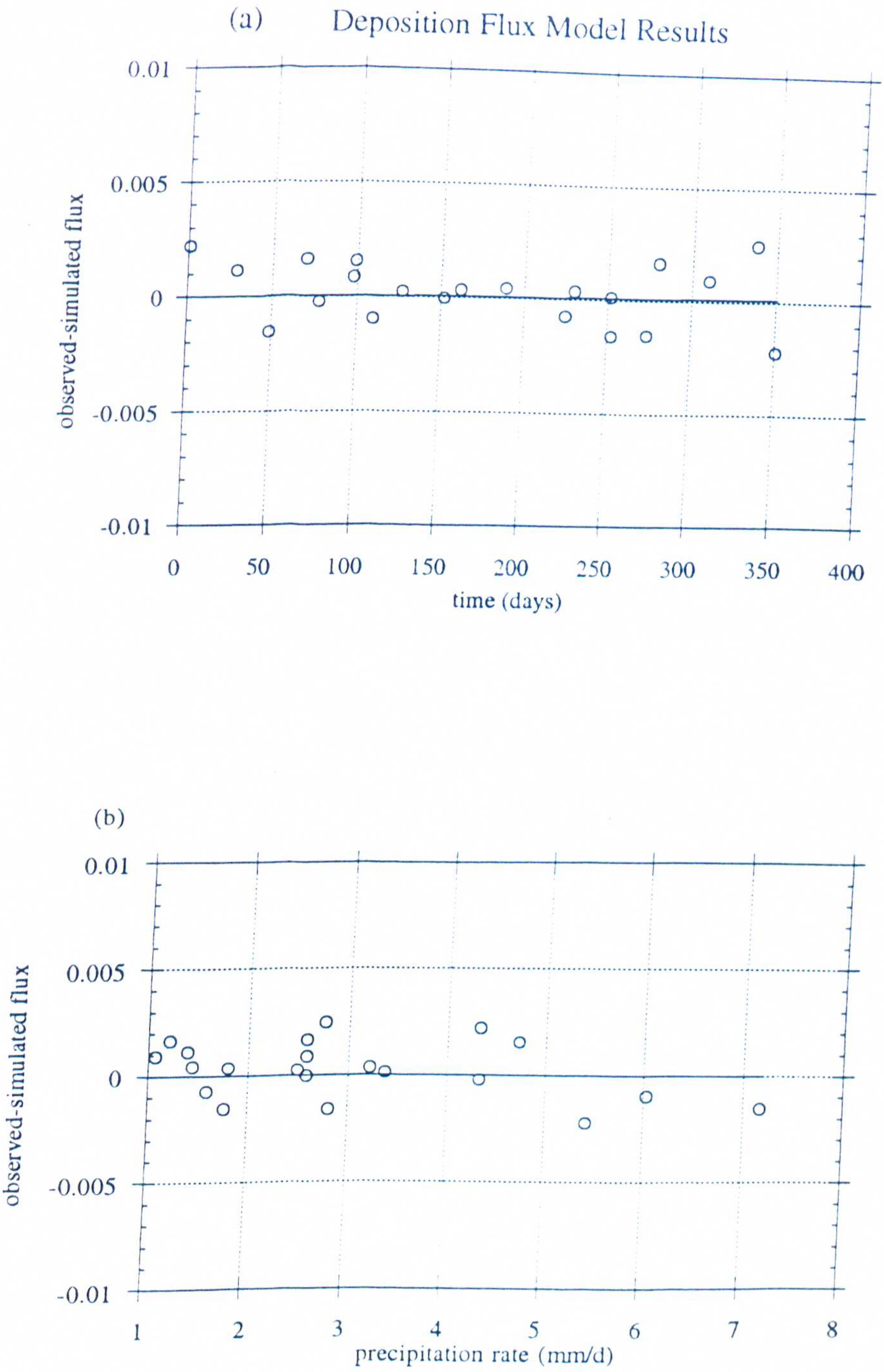

(a)
Deposition Flux Model Results
0.01
0.005
0
-0.005
-0.01
observed-simulated flux
0
50
100
150
200
250
300
350
400
time (days)
(b)
0.01
0.005
0
-0.005
-0.01
observed-simulated flux
1
2
3
4
5
6
7
8
precipitation rate (mm/d)

Table 3.4.

Comparison between Open Collector Data and Wet-only Collector (in italics) Data

Collection Dates	Sample	^{36}Cl/Cl (x 10^{15})	[^{36}Cl] * (x 10^{6}) [atoms/L]	^{36}Cl flux** [atoms/m^{2}s]
10/8/91 - 1/28/92	Open 1	58±11	[2.1±0.34]	49± 9
	wet-only	*34±28*	*1.3±0.3*	*[29±10]*
1/29/92 - 8/5/92	Open 2	89±9	[2.0±0.2]	67± 6
	wet-only	*86±8*	*1.8±0.2*	*[54± 9]*
8/6/92 - 10/6/92	Open 3	28±4	[0.84±1.2]	51± 7
	wet-only	*38±3*	*6.1±0.6*	*[38± 4]*
Mean	Open	61±8	[1.7±0.2]	59± 8
	wet-only	*49±21*	*1.2±0.2*	*[44± 9]*

* Values in brackets are derived based on rainfall data from the Elms tipping guage and from Maryland Department of Air Quality (MDAQ).

** Flux calculations for the open samples are similar to Eq. 3.1, except that a collection area of 1700 cm^{2} is taken into account.

Uncertainties are calculated based on measurement uncertainties in the ^{36}Cl/Cl ratio, the stable Cl^{-} concentration and (for flux calculations) the sampling period.

3.3.1 RESULTS

Table 3.4 gives the results of ^{36}Cl analysis for the open samples. For comparison, the corresponding data from the wet-only collector is also given in italics. The measured mean deposition flux (59± 8 atoms/m^{2}s) for these samples is approximately three times higher than the predicted fallout for 38° latitude (18 atoms/m^{2}s) [ANDREWS and FONTES (1992)]. This result is not particularly surprising, as there is mounting evidence in the literature suggesting that the ^{36}Cl fallout is significantly underestimated by present production mechanisms [ANDREWS and FONTES (1992), KNEIS (1993), SYNAL et al. (1990) and others]. Further discussion pertaining to the deviation of measured ^{36}Cl deposition fluxes from calculated production rates is presented in Chapter 4.

3.3.2 COMPARISON BETWEEN BULK AND WET-ONLY ^{36}Cl DEPOSITION

When comparing the wet-only and bulk deposition results from this study, sampling error was taken into special consideration. The wet-only sampler was a complicated, computer controlled piece of equipment, subject to occasional breakdown. As a result, precipitation was occasionally lost. The bulk collector did not suffer any breakdowns, thus any comparison between the two data sets must rely on an estimation of the ^{36}Cl content of the missing wet precipitation. Missed precipitation accounted for 3%, 51% and 5% of the total precipitation for Open 1, Open 2 and Open 3, respectively. Missing wet-only precipitation values were estimated by determining the ^{36}Cl deposition flux for the sampling periods immediately proceeding and following the missing period. The average of these values was used as the flux for the missing time period. An uncertainty range equal to the difference between the two adjacent flux values was attached to the estimated flux for the missing time period. The ^{36}Cl concentration was estimated for the missing time periods using the estimated flux and the total precipitation. After estimating the missing data, weighted mean ^{36}Cl deposition fluxes and concentrations were calculated to correspond with the open sampling periods. The given ^{36}Cl/Cl ratios are weighted mean values, with no corrections made for missing data.

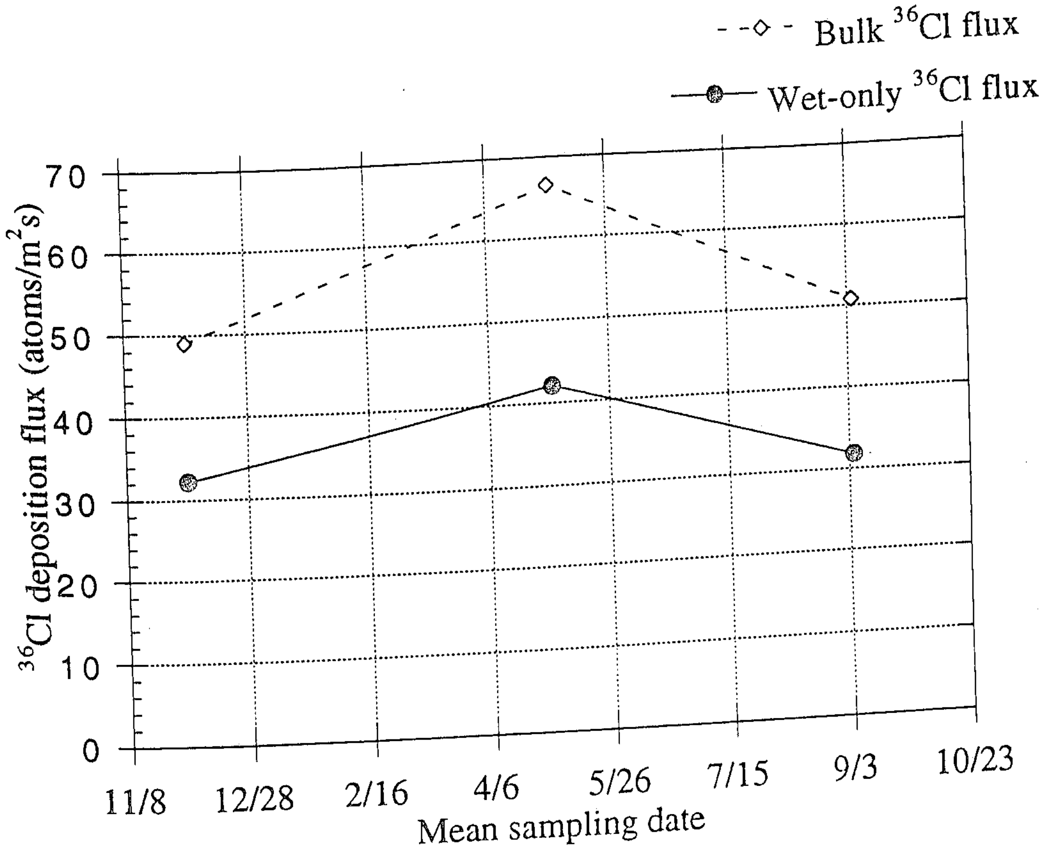
A first approximation of the dry deposition of ^{36}Cl was extracted by comparing ^{36}Cl flux values from the open samples with those from the wet-only samples as shown in Table 3.4. For the purposes here, the difference between the open and wet-only values as attributed to dry deposition. Admittedly, this is a crude approach to the measurement of dry deposition. It has been demonstrated that the dry deposition flux of sulfate particles can vary by a factor of 5 depending on the geometry and surface material of the sampler [DOLSKE and GATZ (1984)]. It is unlikely that the open collectors used in this study could collect chloride with the same efficiency as an equivalent area of the Earth's surface. The currently accepted method of collecting dry deposition involves the use of Teflon® plates. It was not feasible to measure ^{36}Cl dry deposition by this method due to the relatively large amount (approximately 2 mg) of chloride needed for ^{36}Cl analysis.

Averaged over the one year sampling period, the difference between wet-only and bulk deposition accounted for approximately 25% of the total ^{36}Cl flux. This percentage ranged from approximately 40% in the late fall/early winter (Open 1), to 19% in the spring/early summer (Open 3). Figure 3.17 shows a graphic comparison of the results, plotted versus the mean date of each sampling period.

Small variations in the ^{36}Cl/Cl ratio are apparent in the data. However, caution must be used in interpreting these variations due to the magnitude of the measurement uncertainty. It is interesting to note that in the late fall/early winter

Figure 3.17

^{36}Cl wet deposition fluxes, as measured in wet-only (solid circles) and open (open diamonds) samples.


Bulk ^{36}Cl flux
Wet-only ^{36}Cl flux
^{36}Cl deposition flux (atoms/m^{2}s)
70
60
50
40
30
20
10
0
11/8
12/28
2/16
4/6
5/26
7/15
9/3
10/23
Mean sampling date

(Open 1) the bulk deposition sample contained a higher $^{36}Cl/Cl$ ratio than the wet-only sampler. In the late summer/early fall (Open 3) the opposite occurred, and the wet-only sampler contained a higher ratio. One possible explanation for these variations is related to seasonal weather patterns. Winter rains in the east coast of the United States tend to come from low altitude cloud formations. These events might preferentially wash out marine chloride from the lower troposphere, resulting in a lower observed ratio in the wet-only sample during the Open 1 sampling period. During the summer, rain is more likely to come from large, high altitude thunderstorms. These events would be more likely to wash out ^{36}Cl from the upper troposphere, and possibly to incorporate some stratospheric air. Thus, the wet-only sample would have a higher ratio during the Open 3 sampling period. Note that these arguments are extremely speculative. Better quality data (i.e. no missing precipitation) are necessary to fully test this hypothesis.

A ^{36}Cl dry deposition velocity can be estimated by assuming that the difference between the wet-only and open fluxes is due to dry deposition. The equation for calculating dry deposition velocities is given in Eq. 3.3.

$$v_d = \frac{F}{\chi} \qquad \text{Eq. 3.3}$$

where: v_d = the dry deposition velocity (in cm/s)

F = the dry deposition flux

χ = the airborne concentration

The mean ^{36}Cl dry deposition flux (F) was calculated to be 17.8±17.8 atoms/m^2s. Gaseous HCl concentrations have been estimated to be 1 to 2 ppbv (approximately 2.7 - 4.4 x 10^{14} atoms Cl^-/m^3) in the marine troposphere. (SINGH and KASTING (1988) and references therein). Additionally, WU (1993) measured Cl on atmospheric aerosols at the Elms sampling site and found concentrations of approximately 27 ng/m^3 (0.17 x 10^{14} atoms Cl/m^3). If an airborne Cl$^-$ concentration of 3±1.5 x 10^{14} atoms/m^3 is assumed, along with a ^{36}Cl/Cl$^-$ ratio of 50 x 10^{-15}, the resulting dry deposition velocity (v_d) is 1.2 ±1 cm/s. This value lies within the range (0.2-6.3 cm/s) reported by SEHMEL (1980).

Chapter 4

SPATIAL VARIATIONS IN ^{36}Cl DEPOSITION

In 1986 a model was published by BENTLEY, PHILLIPS and DAVIS (1986) which predicted ^{36}Cl/Cl ratios in rainwater across the United States. Since then this model has been used to establish background ratios for several hydrological studies [PHILLIPS et al. (1988), FABRYKA-MARTIN et al. (1987), PURDY (1991]. Along with the model, the results of samples taken from the Southwest United States were also published, and these were in general agreement with the model. However, surface water samples from the Susquehanna R. in Pennsylvania, and groundwater samples from the Aquia Aquifer in Southern Maryland revealed ^{36}Cl/Cl ratios 3 to 5 times higher than the predicted values. In 1992, ANDREWS and FONTES (1992) published a correction to the ^{36}Cl production rates used in the original model, resulting in an even larger discrepancy between the predicted and measured values.

This chapter begins with a brief description of the original BENTLEY, PHILLIPS and DAVIS (1986) model and the results of sample measurements with ratios higher than expected. In Section 4.2 the development of a new model to predict fallout ratios is discussed. This new model is based on longitudinal, as well as latitudinal variations in ^{36}Cl deposition. Results of bulk deposition samples collected from seven sites across the northern United States are presented in Section 4.3 along with results of surface water samples collected in the Susquehanna River. Section 4.4 is a discussion of the comparison between the new model results and the sample measurements.

4.1 THE BENTLEY, PHILLIPS AND DAVIS MODEL

Figure 4.1 shows the BENTLEY, PHILLIPS AND DAVIS model as it was published in 1986. It gives expected $^{36}Cl/Cl$ ratios for the United States. In developing their model , Bentley et al. began with the estimated ^{36}Cl fallout rate. Figure 4.2 shows a curve that predicts the ^{36}Cl fallout as a function of geomagnetic latitude. This curve was generated based on a global average production rate of 11 atoms/m^{2}s, as calculated by LAL and PETERS (1967). The latitudinal distribution was empirically derived from the global pattern of fallout debris associated with nuclear weapons tests. The peak at approximately 40° is a function of stratospheric/tropospheric mixing in the mid latitudes.

After establishing the fallout rate, the $^{36}Cl/Cl$ ratio was calculated using the stable chloride concentrations in rainwater. BENTLEY et al. used stable chloride concentration data taken from JUNGE (1956). These data are shown in Figure 4.3. A major factor influencing the ratio model was the decreasing stable chloride concentrations with distance from the coast. The result is increasing $^{36}Cl/Cl$ ratios toward the center of the continent.

4.2 PREVIOUSLY MEASURED $^{36}Cl/Cl$ RATIOS

Chlorine-36/chloride ratios were measured in Susquehanna River water taken from Port Deposit, Maryland as part of an ongoing study of ^{36}Cl in the Atlantic

Figure 4.1

The BENTLEY et al. (1986) model for $^{36}Cl/Cl$ ratios (x 10^{15}) deposited over the United States.

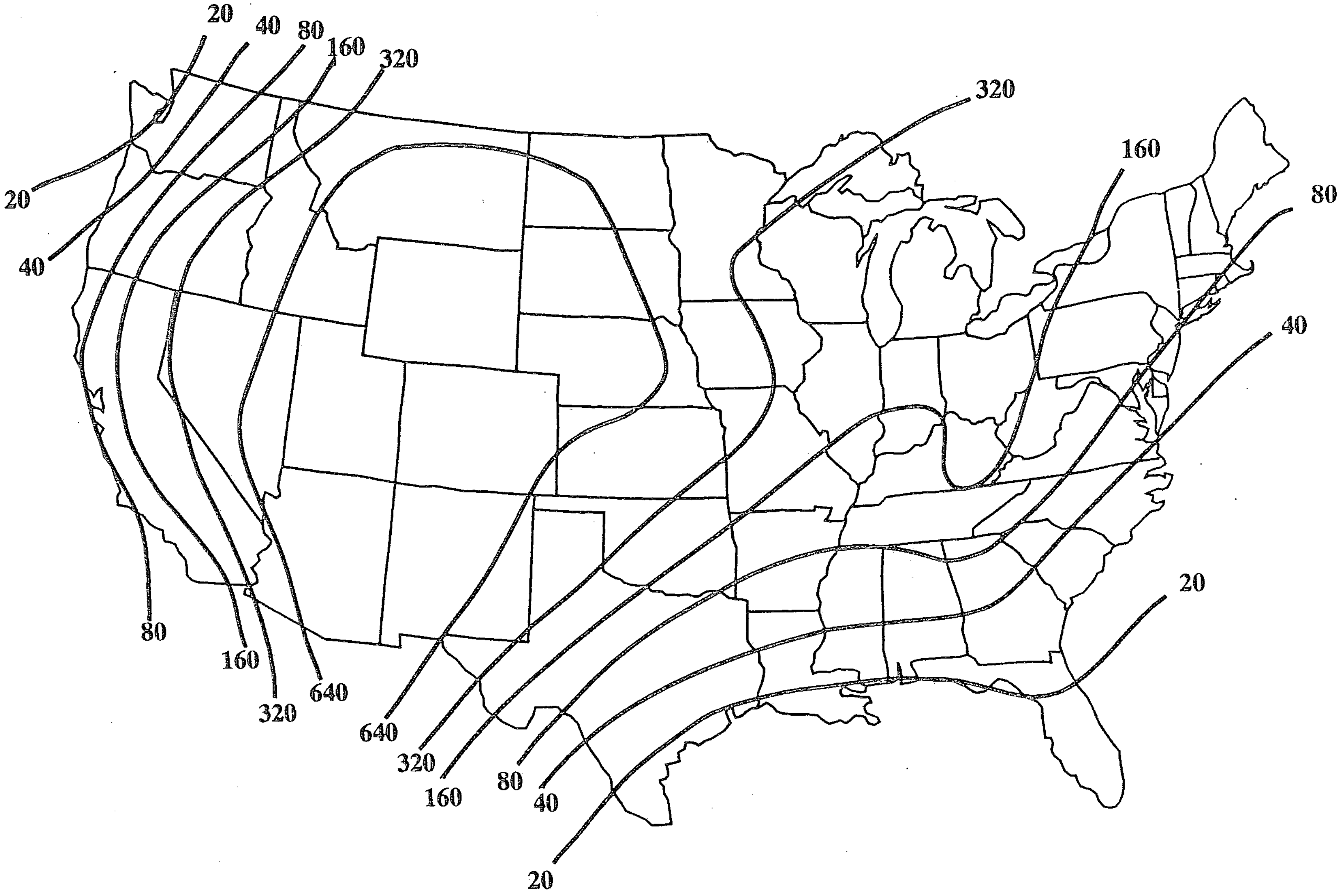

20
40
80
160
320
20
40
80
160
320
640
640
320
160
80
40
20
320
160
80
40
20

Figure 4.2

Meteoric ^{36}Cl deposition as a function of latitude [adapted from LAL and PETERS (1967) and ONUFREIV (1968)]. This deposition pattern was used in the development of the Bentley et al. model.

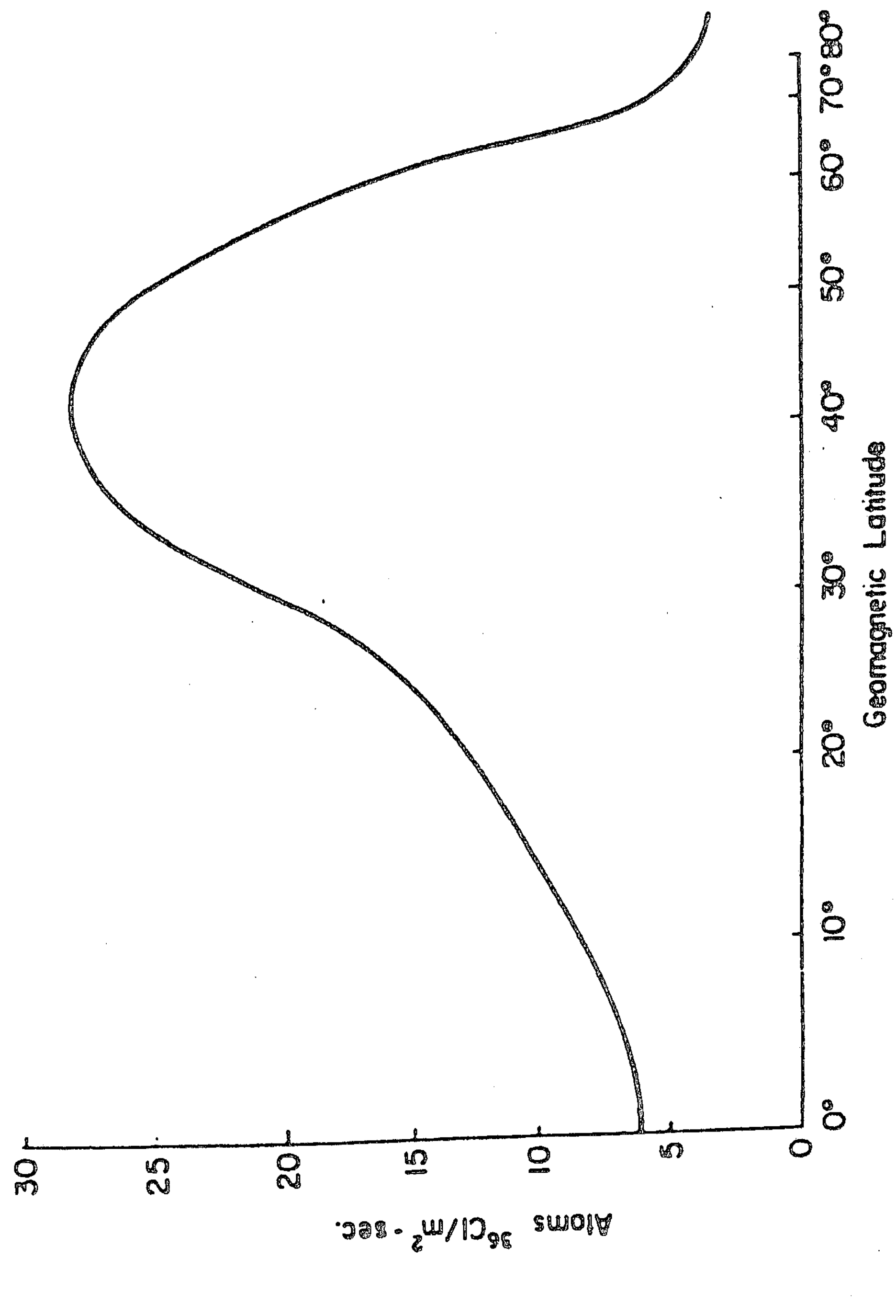
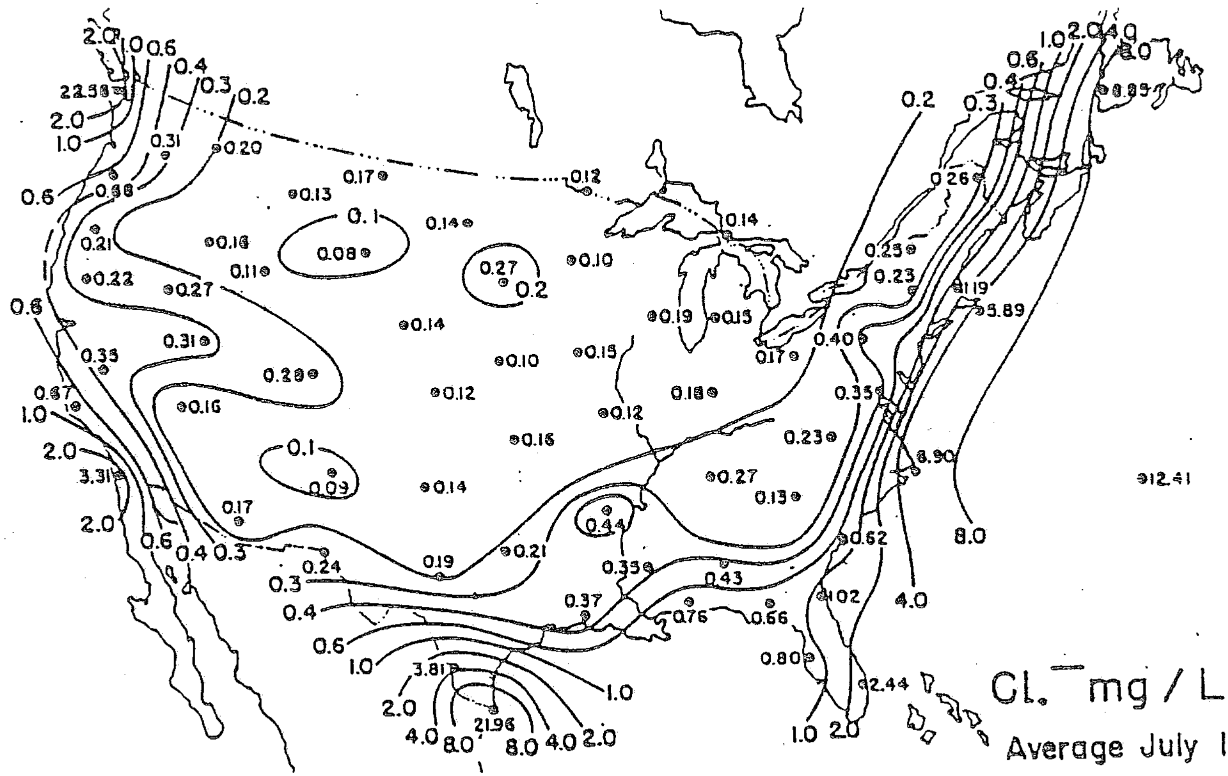

30
25
20
15
10
5
0
Atoms ^{36}Cl/m^2 - sec.
0°
10°
20°
30°
40°
50°
60°
70°
80°
Geomagnetic Latitude

Figure 4.3

Chloride concentrations in precipitation across the United States [taken from JUNGE and WERBY (1956)].



Cl.⁻ mg / Liter

Average July 1955

— June 1956

Coastal Plain Aquifers [PURDY (1992) personal communication]. The results are shown in Table 4.1

Table 4.1

^{36}Cl/Cl in the Susquehanna River

Sample	^{36}Cl/stable Cl ratio	Cl$^-$ conc. [mg/L]	^{36}Cl conc. (x 10^6) [atoms/liter]
Port Deposit, MD (lower Susq. R.)	286±23 (x10^{-15})	11.0±0.2	53±4

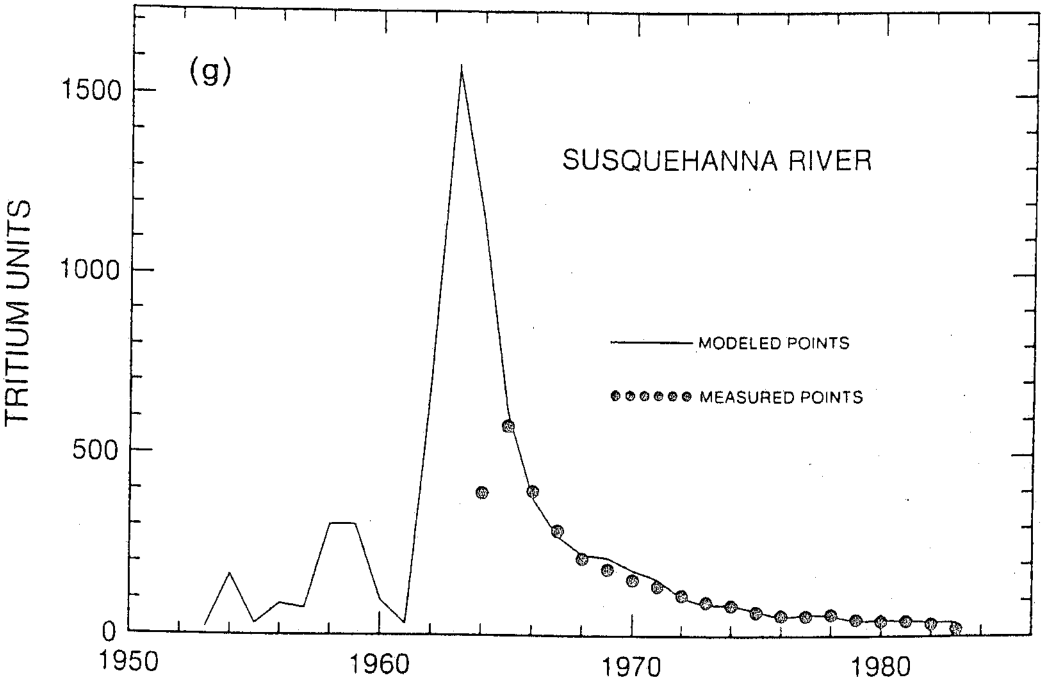
The reported uncertainty in the ^{36}Cl concentration value was calculated by propagation of the counting error in the ^{36}Cl/Cl$^-$ ratio measurement, and the estimated uncertainty in the stable Cl$^-$ measurement. Data from PURDY (1992) University of Maryland, personal communication.

The measured ^{36}Cl/Cl ratio for this sample, 286±23 x10^{-15}, was 2-3 times higher than BENTLEY's predicted range of 80-160 (x10^{-15}). One possible explanation for the high ratio measured in the Susquehanna River sample is the gradual release of residual "bomb-pulse" ^{36}Cl retained in the watershed. It is feasible that ^{36}Cl produced during the nuclear weapons tests in the 1950's and 1960's was introduced into the watershed, became entrained in long-term reservoirs and is slowly being released into the river.

MICHEL(1992) used tritium data to calculate the average residence time of water within the Susquehanna Basin. Tritium was produced during stratospheric thermonuclear weapons tests. Global tritium concentrations reached a peak approximately 10 y after the ^{36}Cl peak, which was associated with early, low altitude tests in the Pacific atolls [PHILLIPS (1988)]. Like ^{36}Cl, tritium is a conservative tracer in groundwater systems. Figure 4.4 shows the measured tritium concentrations with the model used for the residence time

Figure 4.4

Measured (solid circles) and modeled (solid line) tritium concentrations in the outflow of the Susquehanna River basin. [taken from MICHEL (1992)].

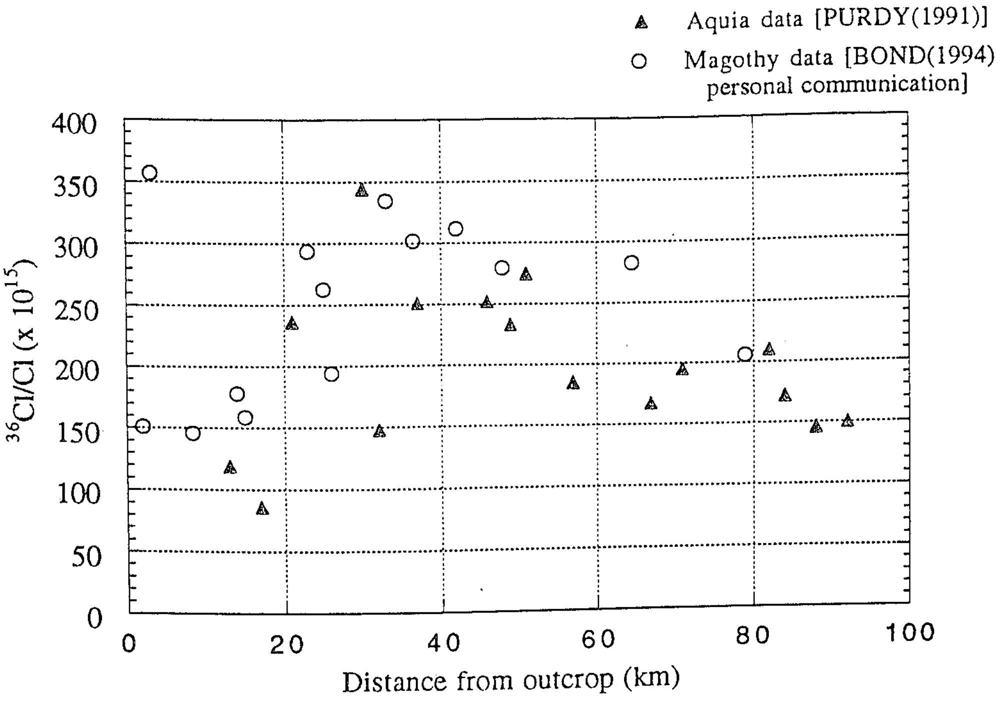

(g)
SUSQUEHANNA RIVER
TRITIUM UNITS
1500
1000
500
0
1950
1960
1970
1980
MODELED POINTS
MEASURED POINTS

calculation. An average residence time of approximately 10 y was calculated. It is clear that at the present time tritium concentrations in the Susquehanna have returned to very near pre-bomb levels. Since the ^{36}Cl peak preceded the tritium peak by 10 y, and it is unlikely that the river basin could exclusively retain chloride on this time scale, it is probable that ^{36}Cl concentrations have returned to near pre-bomb levels as well. Thus, it is concluded that the $^{36}Cl/Cl$ ratios measured in Susquehanna River samples collected in 1991 and 1992 are not significantly influenced by the "bomb pulse". To test this conclusion, rainwater samples were collected for comparison with the Susquehanna River samples, and will be discussed in Chapter 5.

Other evidence indicating that the Bentley, Phillips and Davis model does not adequately account for ^{36}Cl deposition in the Eastern U.S. comes from the Aquia and Magothy aquifers in southern Maryland. The Aquia formation is a confined aquifer belonging to the series of layered, unconsolidated sediments that make up the Atlantic Coastal Plain. It outcrops in a narrow band extending across Prince George's and Anne Arundel counties in Maryland, and extends beneath portions of Maryland, Delaware and Virginia, providing drinking water to eight counties. The Magothy aquifer also belongs to the Atlantic Coastal Plain group and underlies the Aquia. PURDY (1991) performed a detailed study of ^{36}Cl and other isotopic tracers in the Aquia. Figure 4.5 gives the results of ^{36}Cl analysis with increasing distance from the aquifer outcrop. According to the Bentley, Phillips and Davis model, the predicted $^{36}Cl/Cl$ ratios for these samples are between 50 and 100 ($\times 10^{-15}$). In most cases, the measured $^{36}Cl/Cl$ ratios are 2 to 5 times higher than expected. Tritium analyses confirmed that there was no 'bomb-pulse' ^{36}Cl present in these samples, the oldest of which is believed to be approximately 40,000 y. In addition, surface and subsurface

Figure 4.5

$^{36}Cl/Cl$ ratios in the Aquia aquifer and the Magothy aquifer in southern Maryland. [PURDY (1991), BOND (1994), personal communication]


Aquia data [PURDY(1991)]
Magothy data [BOND(1994) personal communication]
^{36}Cl/Cl (x 10^{15})
400
350
300
250
200
150
100
50
0
0
20
40
60
80
100
Distance from outcrop (km)

production of ^{36}Cl has been ruled out for several reasons discussed in detail by PURDY (1991). The conclusion was that the ^{36}Cl in the Aquia groundwater came primarily from recharging precipitation. The magnitude of the measured ^{36}Cl ratios lends evidence to the argument that the current model inadequately predicts ^{36}Cl deposition in this region, and has so for the past 40,000 y.

4.3 NEW MODEL FOR PREDICTING ^{36}Cl/Cl RATIOS

In light of the data presented in Section 4.2, a new model has been developed to predict ^{36}Cl/Cl ratios across the United States. It is clear that while the Bentley, Phillips and Davis model is able to correctly predict ^{36}Cl/Cl ratios in the southwestern United States, the model under-predicts ratios in the East by a factor of 2 to 5. Simply adjusting the model by increasing the ^{36}Cl production rate would result in an overprediction of ratios in the southwest. Changes need to be made concerning the ^{36}Cl deposition pattern and the stable Cl- distribution pattern. It has become clear that, in order to reconcile the difference between the model predictions and the measured ratios, the entire model should be reassessed.

4.3.1 CHLORINE-36 PRODUCTION RATE

As described in the Introduction (Chapter 1), ^{36}Cl is produced in the atmosphere as a result of cosmogenic interactions with various target isotopes. The production rate of ^{36}Cl, as well as several other cosmogenic isotopes, was originally estimated by LAL and PETERS (1967). Ideally, the production rate of a cosmogenic isotope would be calculated with accurate knowledge of the flux and type of cosmic ray particles entering the atmosphere, the energy spectrum associated with each type of particle, the amount of target material and the cross-sections of each relevant production reaction. Sufficient cosmic ray flux and target abundance data exist for these calculations, however, the nuclear reaction cross-sections have only been estimated based on measurements of similar reactions at lower energies. To overcome this problem, LAL and PETERS used data from ionization chambers at various latitudes and altitudes, along with reaction rates measured in cloud chambers, to empirically evaluate isotope production rates. It is generally accepted that, because of the estimations involved, the resulting production rate could easily be wrong by a factor of 2 [D. LAL (1992), personal communication].

Several other researchers have attempted to calculate ^{36}Cl production rates using various other estimations. In the most recent attempt, JIANG (1990) measured the cross section for the reaction $^{36}Ar(n_{(thermal)},p)^{36}Cl$ by irradiating ^{36}Ar enriched gas and measuring the ^{36}Cl product using AMS. These data resulted in a calculated production rate a factor of 0.68 lower than the LAL and PETERS value. This development was particularly intriguing since mounting evidence already existed to suspect that the ^{36}Cl production rate had been seriously underestimated. [SUTER (1987), PURDY (1991), and others.] Table 4.2 lists estimates of the ^{36}Cl production rate by several authors.

The fundamental difference between the estimates given by LAL and PETERS, O'BRIEN and BLINOV is the method by which the production rates are calculated. LAL and PETERS performed empirical calculations, using experimental data for the flux and energy spectra of cosmic ray particle. O'BRIEN and BLINOV used detailed physical models, which took into account parameters such as solar wind and solar and geomagnetic field modulation. The results of these theoretical models could be extended back to pre-experimental time periods (e.g., the ancient past).

Table 4.2

Calculated ^{36}Cl production rates by various authors

SOURCE	^{36}Cl PRODUCTION RATE (atoms/m^2/sec)
LAL AND PETERS (1967)	11
O'BRIEN (1990)	9.8
BLINOV (1988)	19
ANDREWS AND FONTES (1992) (revision of LAL and PETERS (1967))	7.6

For the purpose of the current model, the production rate calculated by BLINOV (1988) was used (19 atoms/m^{2}s). The reason for using this value was purely empirical. It is clear that the production rate necessary to fit the data should be approximately a factor of 2 higher than that derived by LAL and PETERS. The BLINOV value was used simply because it fit the data.

4.3.2 PREDICTING THE ^{36}Cl DEPOSITION PATTERN

(a) Stratospheric Contribution

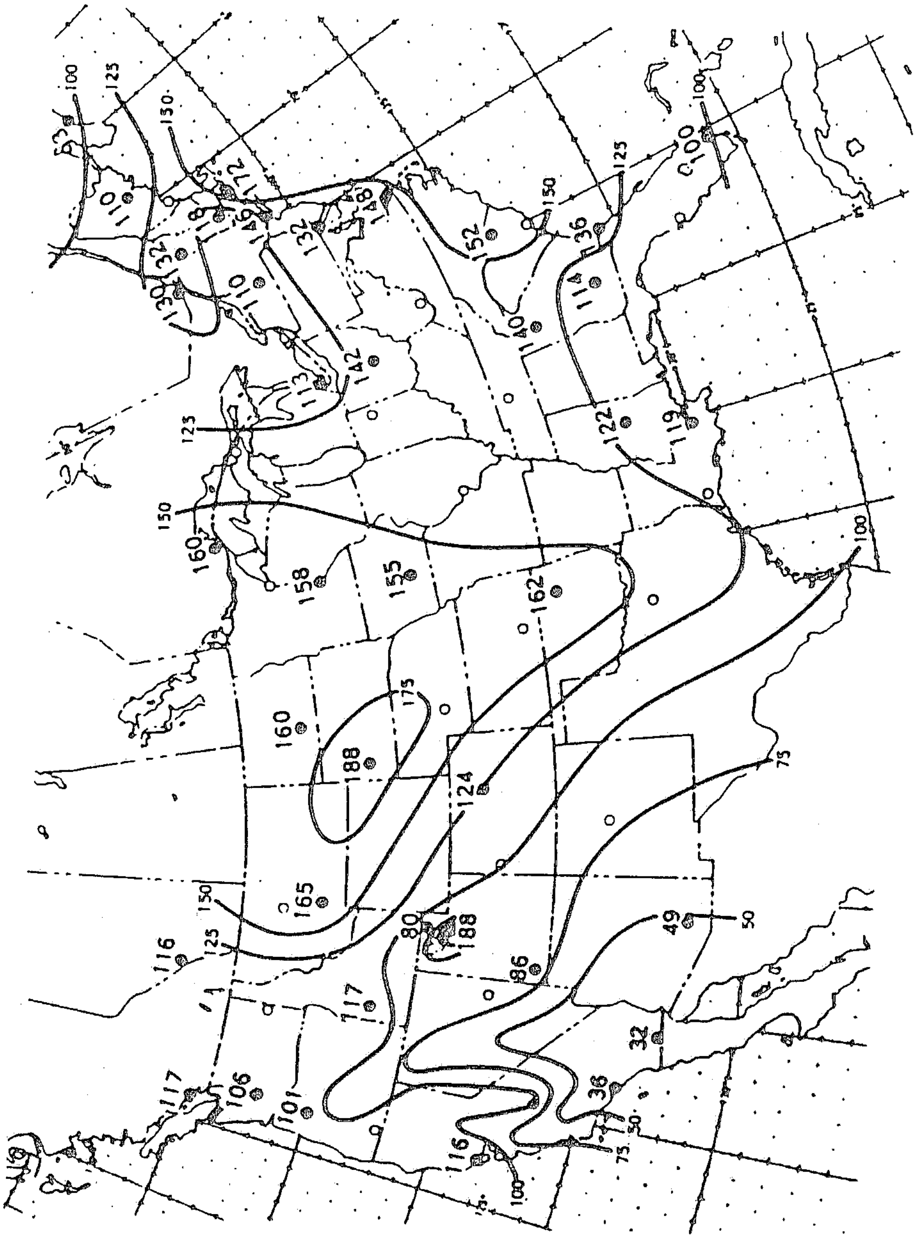
The first step toward developing the new model was to treat the ^{36}Cl produced in the stratosphere and in the troposphere separately. LAL and PETERS (1967) concluded that approximately 70% of all atmospheric ^{36}Cl is produced in the stratosphere. As discussed in Chapter 3, this stratospheric ^{36}Cl is mixed into the troposphere in the mid-latitudes, where it is available for scavenging. A first approximation of the results of this process was presented in Figure 4.2, with deposition shown simply as a function of latitude. However, it is well known that landforms, such as mountain ranges, have distinct and often predictable effects on meteorological processes, including those responsible for stratospheric/tropospheric mixing. Thus, it can be expected that the pattern of ^{36}Cl deposition in the U.S. is affected by its major landforms, with longitudinal as well as latitudinal variations.

Evidence for longitudinal variations can be seen in the deposition pattern of ^{90}Sr. Strontium-90 was produced by weapons tests in the 1950's and 1960's and injected into the stratosphere. Its subsequent deposition has been monitored carefully due to possible health effects. The decision to use ^{90}Sr was based on the availability of data from an extensive sampling network in North America. Figure 4.6, taken from LIST et al. (1965), shows ^{90}Sr concentrations in soils in millicuries/mi^2 in early 1964. Contour lines follow the Rocky Mountain range,providing evidence for the effect of this range on stratospheric/tropospheric mixing. The highest ^{90}Sr concentrations occur east of the Rockies, while the lowest concentrations occur in the southwestern states. MILLER et al. (1974) found this pattern to be characteristic for other weapons-related radionuclides as well.

The ^{90}Sr data set was used to predict the deposition of stratospheric ^{36}Cl. This was accomplished by dividing the ^{90}Sr concentration at each sampling site, or control point, by the mean northern hemispheric ^{90}Sr concentration of 80.6 mCi/mi^2 given in TOONKLE (1979). The resulting geographical focusing

Figure 4.6

^{90}Sr in soil (millicuries/mi^2) as measured in 1963 and 1964 [taken from LIST et al. (1965)].


100
125
130
150
172
149
132
148
152
150
125
136
114
140
142
113
123
110
132
130
100
122
119
150
160
158
155
162
160
188
175
124
165
150
125
116
80
188
86
117
49
50
75
32
36
117
106
101
116
100
75
50

factor was then used to weight the mean stratospheric ^{36}Cl production rate to give the stratospheric contribution (C_s) to the total deposition (Eq. 4.2)

$$C_s = R_p \times 0.7 \times \frac{(^{90}\text{Sr conc.})}{(\text{mean hemispheric } ^{90}\text{Sr conc.})} \qquad \text{(Eq. 4.2)}$$

where: R_p = the ^{36}Cl production rate

0.7 = the fraction of ^{36}Cl produced in the stratosphere

An important assumption was made here concerning the deposition mechanisms of ^{36}Cl and ^{90}Sr. In order to use ^{90}Sr to predict the ^{36}Cl deposition pattern, it must be assumed that the two isotopes have similar deposition mechanisms. This assumption may be somewhat weak due to differences in atmospheric behavior. WHALEN et al. (1991) published preliminary results of an investigation of stratospheric ^{36}Cl which showed that 90% of ^{36}Cl atoms in the stratosphere are associated with gaseous HCl. Strontium-90, however, is known to be associated with sulfate particles in the stratosphere. Thus, it is not certain that the deposition mechanisms of these isotopes are the same. Tritium was investigated as a possible tracer for this model; however, the International Atomic Energy Agency (IAEA) tritium network was not dense enough in the United States for good resolution. In addition, tritium systematics are somewhat complicated in the atmosphere due to chemical and isotopic fractionation effects and re-evaporation [REITER (1978), LIBBY (1963)].

A second assumption made in calculating the stratospheric contribution is that the stratosphere is well mixed during the residence times of ^{36}Cl and ^{90}Sr. The importance of this assumption is that ^{36}Cl deposition is independent of the latitudinal variations in its production rate. Similarly, ^{90}Sr deposition is independent of the latitude at which it was introduced into the stratosphere.

This assumption for ^{36}Cl was first made by LAL and PETERS (1967), and is supported by the global fallout pattern.

(b) Tropospheric Contribution

Chlorine-36 produced in the upper troposphere is immediately available to be scavenged and deposited by washout or rainout. As a result, it is possible to express tropospheric ^{36}Cl deposition in terms of relative precipitation rates. The results of ^{36}Cl analysis of rainwater samples and the ^{36}Cl deposition flux model described in Chapter 3 support this assertion. In the model, ^{36}Cl deposition is fit as a function of precipitation rate, as well as season. In addition, deposition studies of other cosmogenic isotopes indicate a positive correlation between deposition and rainfall (e.g. BROWN (1989), DIBB (1989), MONAGHAN (1987)). It therefore seems reasonable to model the tropospheric contribution (C_t) to total ^{36}Cl deposition as a function of relative precipitation rate. Equation 4.3 describes the calculation:

$$C_t = R_p \text{ x } 0.3 \text{ x } \frac{\text{(annual precip.)}}{\text{(mean zonal annual precip.)}}, \qquad \text{(Eq. 4.3)}$$

where R_p = the mean global ^{36}Cl production rate

0.3 = the fraction of ^{36}Cl produced in the stratosphere

Rainfall data were derived from the National Atmospheric Deposition Program/National Trends Network 1989 annual summaries [NADP (1990)]. The data were screened to meet the NADP/NTN Data Completeness Criteria using guidelines given in the report. A mean zonal rainfall value of 980 mm/y for 30° to 50° N was taken from BAUMGARTNER and REICHEL (1975).

The stratospheric and tropospheric contributions were then added together to give the total expected ^{36}Cl deposition flux. Table 4.3 gives the location and calculated values for each of the selected sites. The given sites correspond with those in Figure 4.6 for which ^{90}Sr concentrations were measured, and are used as control points for the model calculations.

After calculating the ^{36}Cl deposition flux, the expected ^{36}Cl concentrations (in atoms per liter) was calculated for each control point using Eq. 4.4.

$$[^{36}Cl] = \frac{F \times 3.156 \times 10^7}{P}, \qquad \text{(Eq. 4.4)}$$

where: $[^{36}Cl]$ = the ^{36}Cl concentrations in atoms/L

F = the deposition flux at the given site

P = the mean annual precipitation [NADP/NTN (1992)]

Table 4.3

Locations and calculated values for sites used to model ^{36}Cl deposition ratios.

City	State /Prov	Lat. North	Long. West	Total Calculated Flux (atoms/m^{2}s)	Calculated Ratio (x 10^{-15})
El Centro	Ca.	32.47	115.33	5.17	183
Los Angeles	Ca	34.00	118.15	8.07	40
Tucson	Az.	32.15	111.00	9.35	245
Logan	Ut.	41.46	111.51	14.06	596
Ceder City	Ut.	37.40	113.10	14.69	269
Halifax	N.Sc	44.39	63.36	23.92	6
Miami	Fl.	25.45	80.11	25.55	13
Salem	Or.	44.55	123.03	22.51	68
Seattle	Wa.	47.36	122.20	22.98	89
Bangor	Me.	44.47	68.47	23.92	70
Ithaca	NY.	42.25	76.30	22.65	344
Detroit	Mi.	42.22	83.10	22.60	350
Cordele	Ga.	31.55	83.50	25.27	116
SanFrancisco	Ca.	37.45	122.26	21.23	182
Banff	Alta.	51.10	115.34	20.40	298
Biose	Id.	43.38	116.12	19.70	1003
Vancouver	Br.C.	49.16	123.06	27.83	24
Brattleboro	Vt.	42.50	72.35	24.89	324
New Orleans	La.	30.00	90.05	28.48	73
Forest	Ms.	32.22	89.29	28.19	124
Denver	Co.	39.44	104.59	21.21	1069
Montreal	Qbc.	45.36	73.38	26.81	200
Burlington	Vt.	44.30	73.15	25.67	637
Wilmington	De.	39.45	75.33	27.61	103
Jacksonville	Fl.	30.20	81.40	29.24	27
Atlanta	Ga.	33.45	84.23	29.70	179
Columbus	Oh.	40.00	83.00	27.92	368
NewYork	NY.	40.40	73.58	29.74	124

City	State /Prov.	Lat. North	Long. West	Total Calculated Flux (atoms/m^{2}s)	Calculated Ratio (x 10^{-15})
Norfolk	Va.	36.55	76.15	30.29	49
Florence	SC.	34.10	79.45	30.63	142
DesMoines	Io.	41.35	93.37	28.90	610
Minneapolis	Mn.	44.58	93.15	28.41	791
Bismark	ND	46.48	100.46	26.74	1286
Thunder Bay	Ont.	48.28	89.12	24.02	356
Tulsa	Ok.	36.08	95.58	31.12	332
Bozeman	Mt.	45.41	111.00	27.37	1532
NewPort	RI.	41.29	71.16	33.19	29
Rapid City	SD.	44.06	103.14	31.37	1304

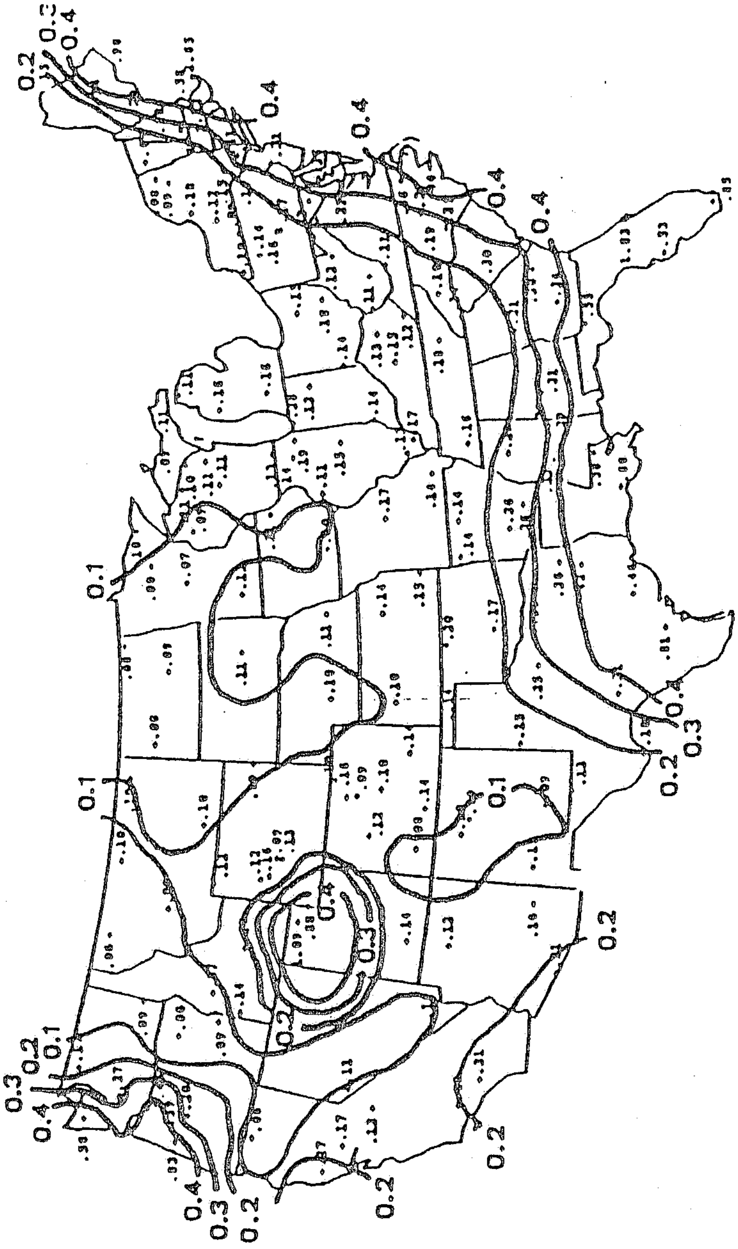
4.3.3 STABLE CHORIDE CONCENTRATIONS

In developing the original ^{36}Cl/Cl ratio model, BENTLEY, PHILLIPS and DAVIS (1986) used stable chloride concentrations taken from JUNGE (1956). A more complete and reliable data set is now available through the National Atmospheric Deposition Program/National Trends Network [NADP/NTN (1990)]. This network has been in operation since 1979. Stable chloride data for the present model was taken from the 1989 Annual Data Summary, which lists precipitation-weighted average chloride concentrations for each year of site operation. The NADP/NTN Data Completeness Criteria were applied for quality assurance as directed in the report. Figure 4.7 show the NADP/NTN average chloride concentrations as published in the Annual Data Summary. These data represent wet-only deposition collected on a per event basis. Concentrations used in the model were determined by finding the NADP/NTN sampling site nearest each model control point (as described in section 4.3.2 (a)). In most cases, an NADP site was located within a 100 mi. radius of the control point. Interpolation was used for instances where the distance between the control point and the nearest NADP/NTN site (or sites) was more than 200 miles. The uncertainty associated with these values was estimated to be 10%.

The NADP/NTN data set provides three distinct advantages over the JUNGE (1956) data set used in the Bentley, Phillips and Davis model. First, the NADP/NTN data set contains nearly three times as many sampling stations as the JUNGE data set. In addition, most NADP/NTN sampling sites have been in operation for 10 years or more, while the JUNGE data set was averaged over just one year. Finally, NADP/NTN chloride concentrations were measured

Figure 4.7

Chloride concentrations in precipitation from the NADP/NTN rainwater sampling network [taken from NADP/NTN (1991)].


0.1
0.1
0.1
0.2
0.2
0.2
0.2
0.2
0.2
0.2
0.3
0.3
0.3
0.3
0.3
0.4
0.4
0.4
0.4
0.4
0.4
0.4
0.4

by ion-chromatography, a method which replaced the complicated gravimetric technique used by JUNGE. It must be noted, however, that the NADP-NTN network samples wet-only deposition. Therefore, the stable chloride concentrations used in the model calculations are a lower limit, and do not include dry deposition.

4.3.4 THE ^{36}Cl/Cl RATIO MODEL RESULTS

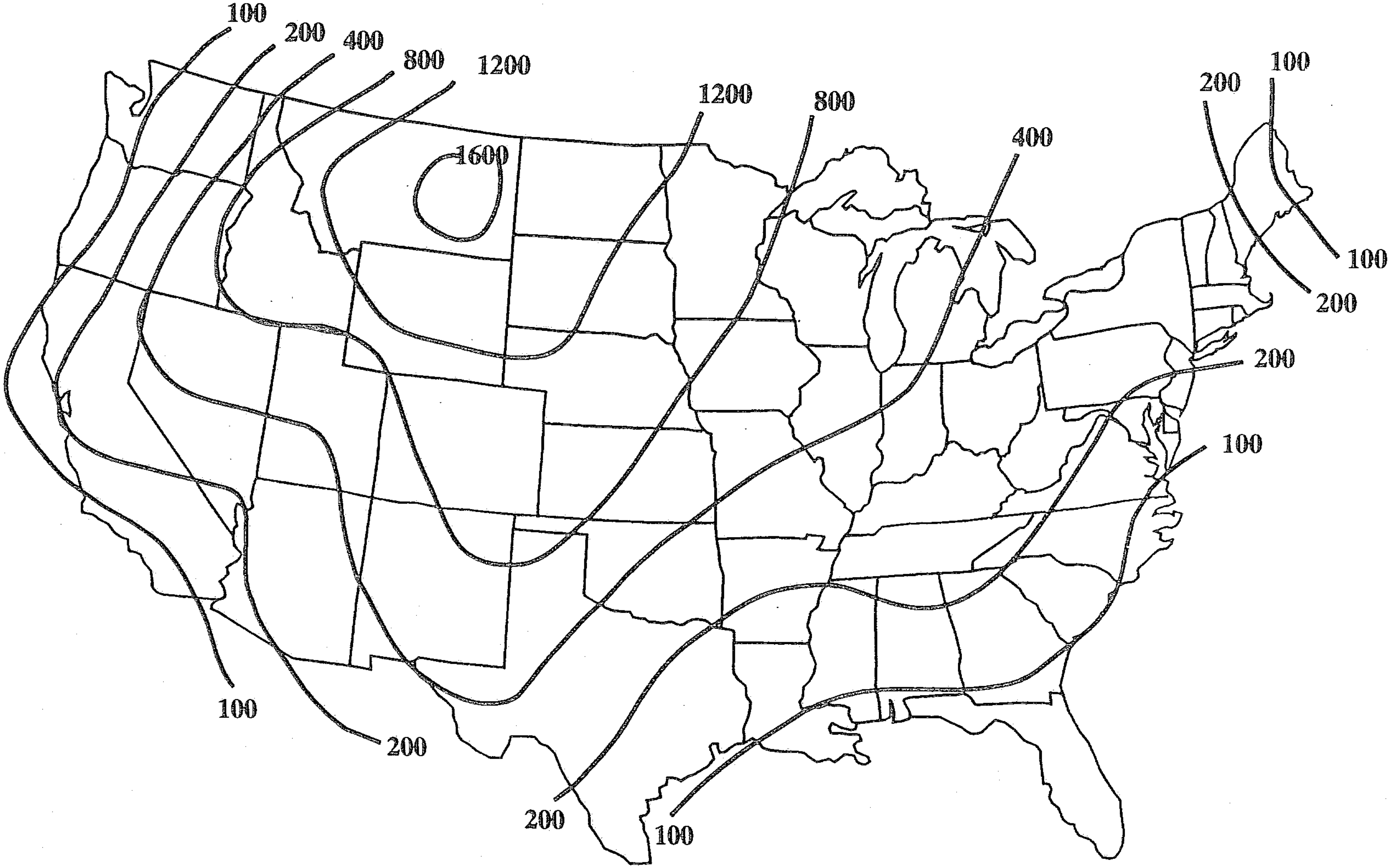
The calculated ^{36}Cl/Cl ratios are given in Table 4.3. Figure 4.8 shows the site locations and calculated ratios on a map of the United States. Contour lines were calculated using GRads, a program developed at the University of Maryland Department of Meteorology for the application of Cressman objective analyses (Dr. B. Doty (1992), University of Maryland Department of Meteorology, personal communication). The model predicts ratios of 100 to 200 along the coasts, with increasing ratios toward the center of the continent. The highest ratios are predicted in the northern plains states, due to the combined effects of high ^{36}Cl deposition and low stable chloride concentrations. The contour lines of this model are similar to those of the BENTLEY et al. model; however, the predicted ratios are approximately a factor of two higher.

4.4 EXPERIMENTAL RESULTS OF OPEN SAMPLE COLLECTION

To test this model, bulk precipitation samples were collected at seven sampling sites across the Northern United States. Detailed descriptions of

Figure 4.8

Calculated ^{36}Cl/Cl ratios across the United States (x 10^{15}).


100
200
400
800
1200
1600
1200
800
400
200
100
100
200
200
100
100
200
200
100

these sites were given in Chapter 2. The results of ^{36}Cl analyses of these samples are given in Table 4.4.

Table 4.4

Results of ^{36}Cl analyses of bulk precipitation samples

Open Sample	Start and end date	^{36}Cl/Cl (x 10^{-15})	[^{36}Cl]* (x 10^6) (atoms/L)	^{36}Cl flux (atoms/m^{2}s)
Elms Open 1	10/8/91- 1/28/91	57.9 ± 11	2.61±0.5	49.0±9
Elms Open 2	1/28/91- 8/5/92	89.4 ± 8.6	2.97 ±0.3	66.5 ±6
Elms Open 3	8/5/92- 10/6/92	28.2 ± 3.7	0.91±0.01	50.8±6
Lewes	11/7/91- 11/11/92	23.5 ±2.0	2.91±0.3	46.9±4
Harpers Ferry	11/21/91- 5/11/92	184 ± 21	1.43 ±0.2	41.7 ±5
Penn State 1	11/8/91- 2/19/92	274 ± 30	3.48 ±0.4	82.5 ±8
Penn State 2**	5/29/92- 11/2/92	731 ± 63	8.25±0.7	148 ±1
Victor	10/24/91- 10/25/92	337 ± 17	2.2 ±0.1	63.7±3
MSU	11/30/91- 8/17/92	453 ± 29	4.4 ±0.3	70.5 ±5
MSU 2	8/17/92 - 8/19/93	310 ± 110	2.1±0.7	56.4 ±19
Black Hills	8/15/92- 8/28/93	4220 ± 510	11.0±0.1	75.5 ±7

* Concentration values were corrected for evaporation using total rainfall data from the Maryland Department of Air Quality and from the National Climatic Data Center.

** The sampler was tampered with during this sampling period.

Due to evidence of seasonal variation in ^{36}Cl deposition, an effort was made to collect the samples over a period of one year. In two cases it was not possible to collect precipitation over an entire year. The collector at the Penn State site was tampered with during May 1992, resulting in the loss of rainwater collected between February 19 and May 29, 1992. A second tampering incident was suspected at that same site during September 1992, rendering the results of the Penn State 2 sample somewhat unreliable. Access to the Harpers Ferry site was limited after May 11, 1992 when the owners moved to a new location. As a result, the sample represents precipitation collected from November 21, 1991 to May 11, 1992.

4.5 COMPARISON BETWEEN OPEN SAMPLE DATA AND NEW MODEL PREDICTIONS

The open sample ^{36}Cl/Cl ratios are compared with model predictions in Figure 4.9. With the exception of the Black Hills sample, the results agree very well with the model predictions. Ratios increase with distance from the coast as expected, due to decreasing stable marine chloride input and increasing stratospheric ^{36}Cl input. Chlorine-36 deposition flux values increase with distance from the coast as illustrated in Figure 4.10. This increase reflects variation in the distribution of stratospheric ^{36}Cl.

While the ^{36}Cl/Cl ratio for the Black Hills sample appears anomalously high, it should be noted that the calculated ^{36}Cl deposition flux is only slightly higher than for the other samples. A higher deposition flux at this site was expected due to meteorological patterns which cause increased stratospheric-tropospheric mixing east of the Rocky Mountains.

Figure 4.9

^{36}Cl/Cl ratios (x10^{15}) in open precipitation samples shown with the model predictions. The calculated uncertainties for these values are approximately 10%.

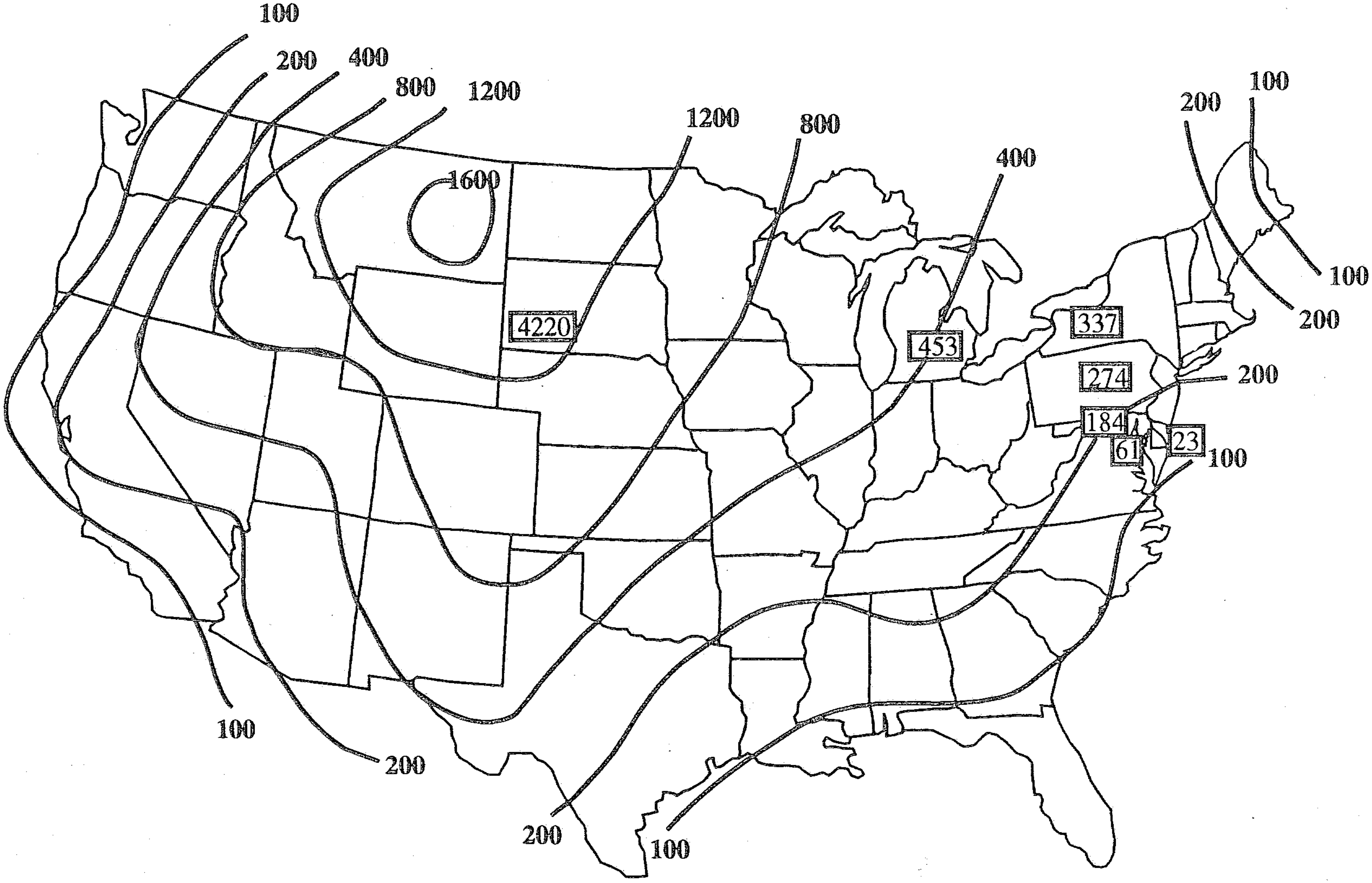
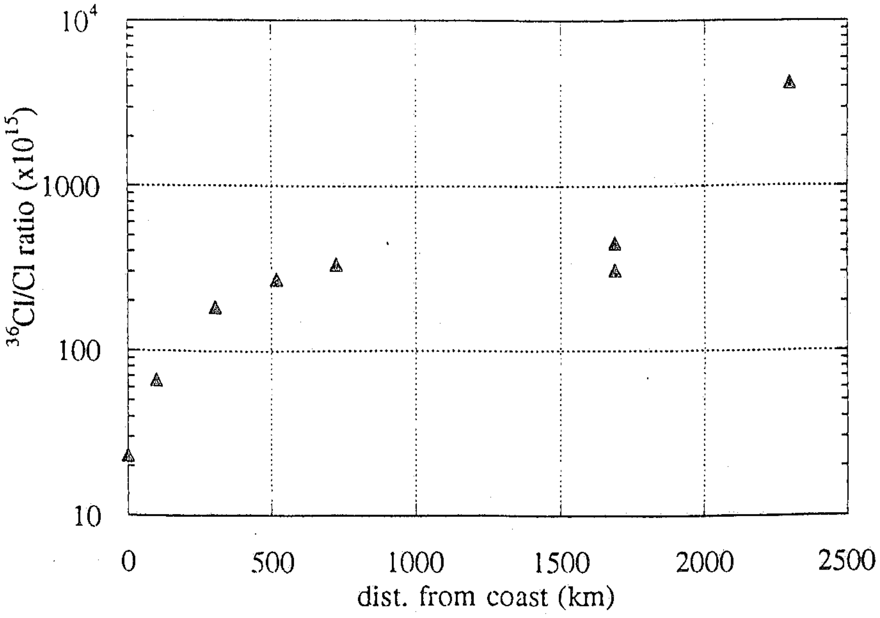

100
200
400
800
1200
1600
4220
1200
800
400
453
200
100
337
274
200
184
61
23
100
100
200
200
100
100
200
200
100

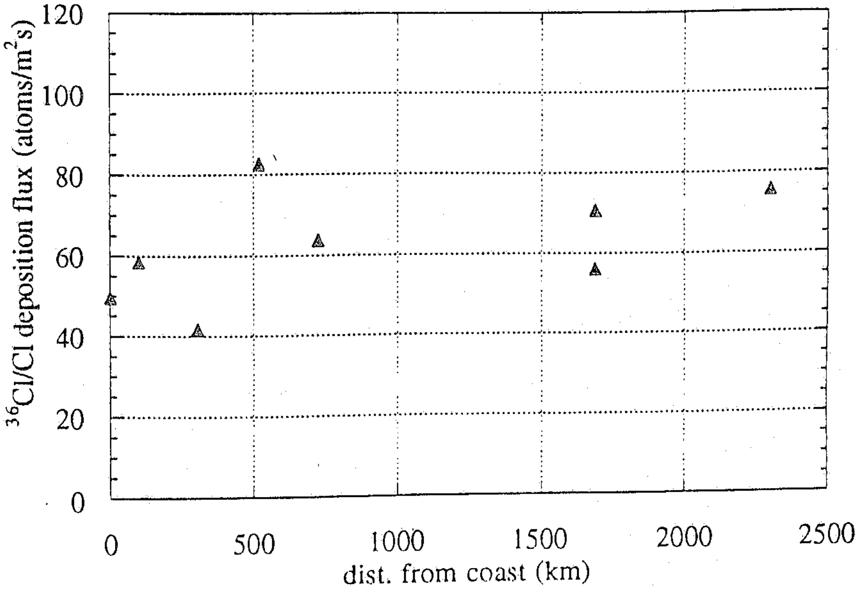
Figure 4.10

(a) ^{36}Cl/Cl ratios in open samples versus distance from the sea coast.

(b) ^{36}Cl deposition flux in open samples versus distance from the coast.



(a) ^{36}Cl/Cl vs. distance from the seacoast



(b) ^{36}Cl flux vs. distance from the seacoast

Although the model correctly predicts the $^{36}Cl/Cl$ ratios, the predicted deposition fluxes are approximately a factor of 2 lower than the measured fluxes. Correspondingly, the stable chloride concentrations (corrected for evaporation) are approximately a factor of two higher than expected according to the NADP/NTN data set. These two effects cancel each other to give $^{36}Cl/Cl$ ratios which are in agreement with the experimental data. Several possible explanations for this discrepancy have been investigated.

The possibility of contamination from the sample collection apparatus has been ruled out for two reasons. First, all of the sampler components underwent the extensive cleaning process described in Section 2.3.1 (b). Collector blanks, analyzed for stable chloride, revealed no evidence of contamination. Additionally, since the samplers were all identical, equipment related contamination would be a uniform effect. The amount of excess chloride, and ^{36}Cl, would be fairly constant. This is clearly not the case. In all of the samples, the measured fluxes are higher than the model predictions by a factor of 2, not by some constant amount.

Two possible scenarios remain which can explain this discrepancy. The first explanation is that the open sample collectors systematically "over-sampled" the deposited chloride. In other words, due to the geometry of the sampler and/or the collection surface (i.e. the wire screen cover), more chloride was collected in the sampler than would normally be deposited in an equivalent area of open ground.

Sampling bias is a plausible explanation for the discrepancy between the model-predicted deposition fluxes and the measured fluxes. In this case, the $^{36}Cl/Cl$ ratio would not be affected, since any extraneous chloride entering the sampler would be expected to carry the ambient $^{36}Cl/Cl$ signature. The model-predicted $^{36}Cl/Cl$ ratios agree well with the measured ratios.

It is well documented that samples taken from open, bucket-type collectors differ from those taken from other collector types [DOLSKE and GATZ (1984)]. Both wet and dry deposition can be affected. Aerodynamic turbulence is produced as a breeze passes over the opening of the sampler, causing more or less precipitation to enter the collector than would normally fall on the ground. An analogy can be made of a snow fence. Snow which is blown across an open field will pile up when it encounters a snow fence or other turbulence-causing obstruction. DOLSKE and GATZ compared sulfate dry deposition fluxes using several sampling geometries and surfaces. Included were Teflon® plates, polycarbonate petri dishes and dry buckets manufactured by Aerochemetrics, Inc. They found that petri dishes gave dry flux values twice as high as the flat plates, and that dry buckets gave values 5 times higher. Although it not currently known which of these methods most accurately represents natural dry deposition, the possibility that bucket-type collectors overestimate (or underestimate) dry deposition is clearly evident.

Another possible mechanism for oversampling involves the wire screen which was used to cover the opening of the sampler. While this screen was necessary to keep the sampler free from gross contamination (i.e., people using it as a trash can), the surface area of the screen may have provided a means by which extraneous chloride could enter the sampler. For instance, if the screen became wet with dew, a "sticky" surface would be available for the deposition of particulate or gaseous chloride. Any chloride thus collected, would subsequently get washed into the sampler during the next precipitation event.

The second scenario which could account for the observed discrepancy is somewhat more complicated, but carries an important implication. This second scenario requires additional sources of both stable chloride and ^{36}Cl. The implication is that the ^{36}Cl production rate used in the model is still a factor of 2 too low.

The stable chloride data used in the model was taken from the NADP/NTN rainwater sampling network. Measured stable chloride concentrations were consistently a factor of 2 to 3 higher than at nearby NADP/NTN sites. If the difference cannot be attributed to sampling bias, then remaining explanations include recycling of crustal chloride and dry deposition.

Recycling of crustal chloride is a process by which previously deposited chloride, residing in the upper soil layer, is reintroduced into the atmosphere as a constituent of continental dust. This chloride can then be re-deposited into the open samplers, causing artificially high deposition fluxes. This mechanism has been shown to affect ^{36}Cl measurements [HERUT (1992)] in extremely arid climates with caliche-type soils. However, in most areas the chloride concentration in surface soil is quite low, since it is an extremely mobile anion and is easily washed through the soil zone. As a result, the amount of chloride found in atmospheric aerosol particles that can be attributed to crustal dust is small [WARNECK (1988)]. The sampling sites used in this current study were chosen to minimize the introduction of crustal dust. The sites were located in vegetated areas and away from roads or other possible dust sources. Although recycled crustal chloride cannot be completely discounted, it considered to be a negligible source to these samples.

The most plausible explanation remaining in this second scenario is dry deposition. If the open samples accurately reflect the average amount of chloride deposited in the given area, then the chloride concentrations used in the model are systematically too low. Using the higher (measured) stable chloride concentrates in the model would have the effect of lowering the $^{36}Cl/Cl$ ratios by a factor of two. However, the predicted $^{36}Cl/Cl$ ratios agree well with the measured ratios. Thus for this scenario to fit the observations, the extra stable chloride must be "balanced" by a higher ^{36}Cl deposition flux.

If this second scenario is correct, and dry deposition accounts for the excess chloride, then a global ^{36}Cl production rate of approximately 40 atoms/m^{2}s would be necessary to account for the observed ratios. This value is nearly a factor of 4 higher than LAL and PETER's (1968) original estimate of 11 atoms/m^{2}s. Researchers involved in calculating cosmogenic isotope production rates admit that there is considerable uncertainty (a factor of 2 or so) associated with their estimates. To date, the highest published ^{36}Cl production rate estimate is 25 atoms/m^{2}s (HERUT (1992)).

It is not clear which of these two scenarios correctly explains the discrepancy between the observed deposition fluxes and the model predictions. Open collector sampling bias and dry deposion cannot be distinguished by comparison between the Elms open and wet-only results. Sampling bias is the simplest explanation. However, the effects of dry deposition can not be discounted. Perhaps a combination of the two effects is taking place. In that case, the global average ^{36}Cl production rate of approximately 40 atoms/m^{2}s, calculated using the dry deposition scenario, is an upper limit. Further research into the behavior of gaseous and particulate ^{36}Cl, and more data on ^{36}Cl in wet and dry deposition, may illuminate this problem.

Chapter 5

THE RELATIONSHIP BETWEEN ^{36}Cl DEPOSITION AND OBSERVED GROUND WATER AND SURFACE WATER CONCENTRATIONS.

Early interest in studying ^{36}Cl in groundwater developed from the need to monitor ground water flow near nuclear waste repositories [FABRYKA-MARTIN et al. (1987)]. Since then ^{36}Cl has become quite popular as a tracer and dating tool for hydrological systems, with applications including estimation of residence time of water in an aquifer system [PURDY (1991), NOLTE (1991)], water-rock interactions [MICHELOT et al. (1989)], liquid/vapor movement in arid soils [PHILLIPS (1988)], and determination of regional evapotranspiration [MARGARITZ (1990)). As the use of ^{36}Cl increases, so does our lack of understanding of ^{36}Cl groundwater systematics. Each new study seems to introduce new complexities in ^{36}Cl behavior

Recently there is mounting evidence that groundwater ^{36}Cl concentrations cannot be accounted for by the known production mechanisms as currently understood. The currently accepted ^{36}Cl production rates seem to systematically underestimate the amount of ^{36}Cl found in ice cores [SYNAL (1991) SUTER (1987)], ground water [PURDY (1991), ANDREWS and FONTES (1992)], and precipitation [MARGARITZ (1990), HAINSWORTH (1994)]. At the present time it is not clear whether this discrepancy is due to an additional, unknown source, or simply an underestimation of production rates.

This chapter deals with the relationship between measured^{36}Cl deposition and ^{36}Cl concentrations measured in the Susquehanna River Basin and the Aquia and Magothy aquifers in southern Maryland. Surface water and groundwater data are compared with precipitation data to determine whether modern atmospheric ^{36}Cl input can account for relatively high concentrations found in Maryland groundwater and the Susquehanna River. Possible focusing mechanisms, such as seasonal variations in groundwater recharge, and other possible sources are also discussed.

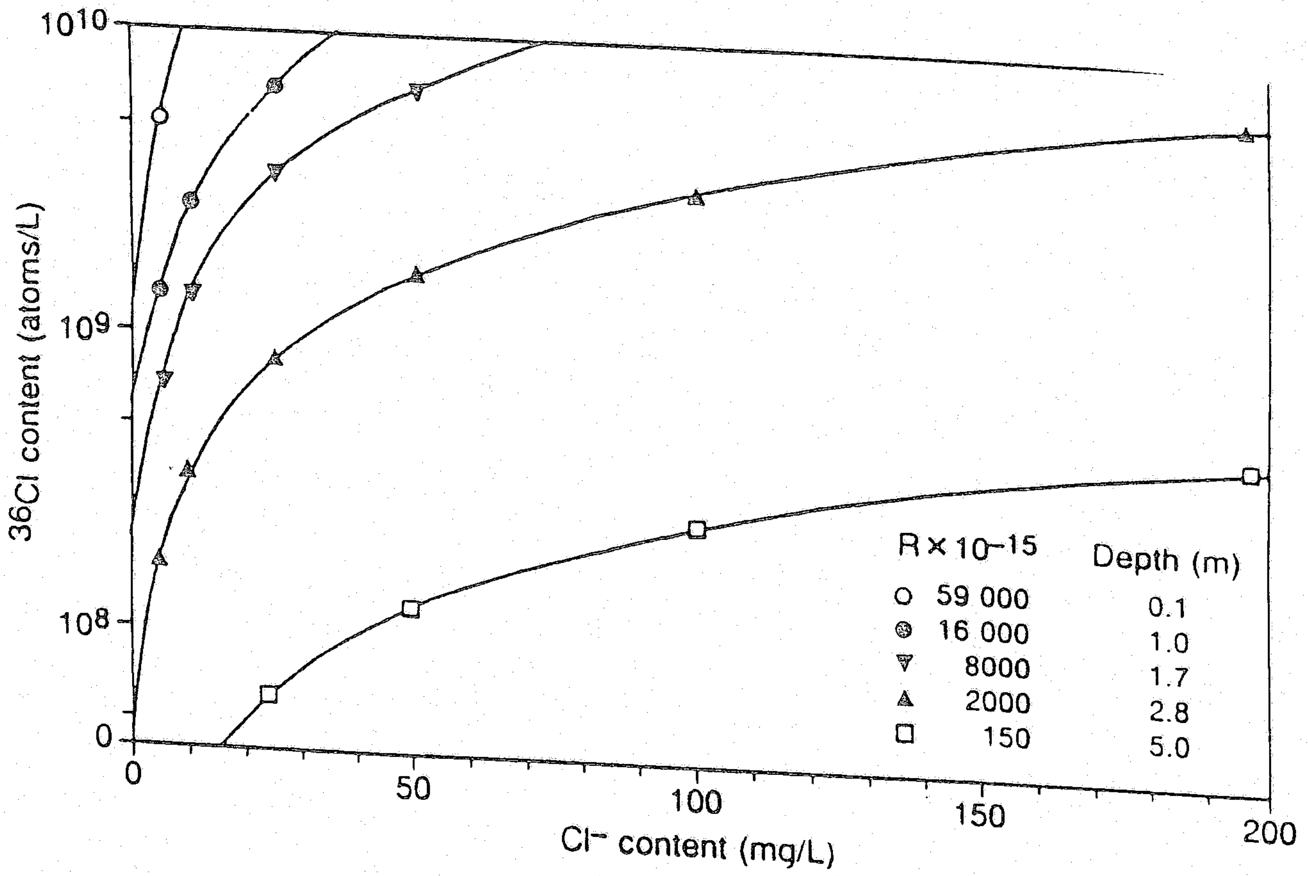
5.1 EVIDENCE OF EXCESS ^{36}Cl

5.1.1 EXCESS ^{36}Cl IN GROUNDWATER

There are indications that *in situ* soil production mechanisms could be responsible for high ^{36}Cl concentrations in aquifers such as the Milk River Aquifer in Alberta, Canada [ANDREWS and FONTES (1992)] In their review of the importance of *in-situ* ^{36}Cl production, Andrews and Fontes conclude that dissolution of ^{36}Cl produced in either the soil zone or the aquifer matrix can overwhelm the initial meteoric input. They argue that this effect is especially important in systems where the Cl^- content is high (10-100 ppm), due to the large neutron capture cross-section of ^{35}Cl. Fontes and Andrews calculated ^{36}Cl concentrations for groundwater in equilibrium with exposed chloride at various concentrations and depths. Their results are shown in Figure 5.1. It is clear that dissolution of a small amount of exposed Cl^- can have a marked effect on groundwater concentrations. It must be noted here, however, that the curves shown in Figure 5.1 assume that ^{36}Cl production has reached equilibrium. (after approximately 5 half lives, or 1.5 Ma). In order for this mechanism to be

Figure 5.1

The ^{36}Cl content of groundwater which dissolves cosmic ray exposed chloride from the epigene zone. The $^{36}Cl/Cl$ ratios, R, correspond to irradiation at the given depths as calculated for the Milk River Aquifer (57.2°N) [taken from FONTES and ANDREWS (1992].


10^{10}
10^9
10^8
0
^{36}Cl content (atoms/L)
0
50
100
150
200
Cl⁻ content (mg/L)
R × 10^{-15}
Depth (m)
○ 59 000 0.1
● 16 000 1.0
▼ 8000 1.7
▲ 2000 2.8
□ 150 5.0

important, large amounts of Cl^- must be irradiated at the surface for a long period of time (FONTES and ANDREWS (1992)).

Beneath the surface, *in-situ* production occurs when chloride rich minerals or fluid inclusions are activated by neutrons produced as by-products of uranium/thorium decay. Dissolution of this irradiated chloride into an aquifer can cause an increase in ^{36}Cl concentrations, as seen in the Stripa granite mine, Sweden [(Andrews et al. (1986)].

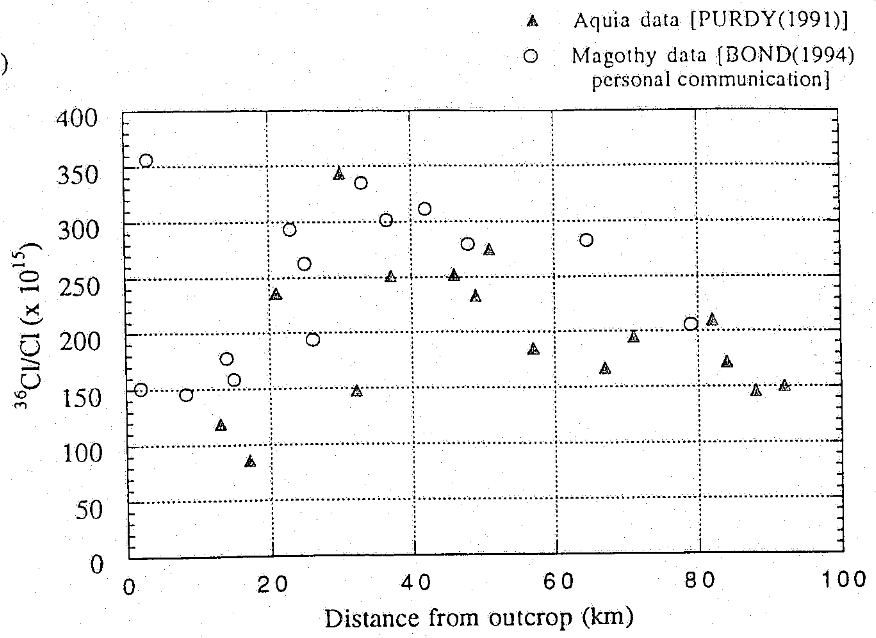
Additional evidence of the discrepancy between predicted ^{36}Cl production rates and ground water concentrations comes from PURDY (1991). She published an extensive study of ^{36}Cl in the Aquia Aquifer in southern Maryland. The Aquia is a confined aquifer with very low (1 to 2 ppm) chloride concentrations which indicate that it has been completely flushed of connate water. Figure 5.2 shows the $^{36}Cl/Cl$ ratios measured in Purdy's study versus distance of the sampling site from the aquifer outcrop. Also shown in Figure 5.2 are data from a current study of the Magothy Aquifer [BOND (1994)]. The Magothy lies underneath the Aquia aquifer, separated by a clay confining layer. It, too, has very low chloride concentrations and thus is assumed to have been completely flushed of connate water (and chloride). The measured $^{36}Cl/Cl$ ratios in these aquifers range from approximately 150 to 300 (x 10^{-15}), 3 to 5 times higher than predicted by deposition models and by modern precipitation ratios (see Chapter 4). Tritium was measured in samples from the Aquia Aquifer and, with the exception of a single sample taken from the recharge area, was found to be at or below the analytical detection limit. PURDY interpreted these results to mean that contamination of the Aquia samples (by leakage of modern water down the well head) was negligible. The relationship between data from Purdy and Bond, and ^{36}Cl deposition as measured in this study will be discussed in detail in Section 5.3.

Figure 5.2

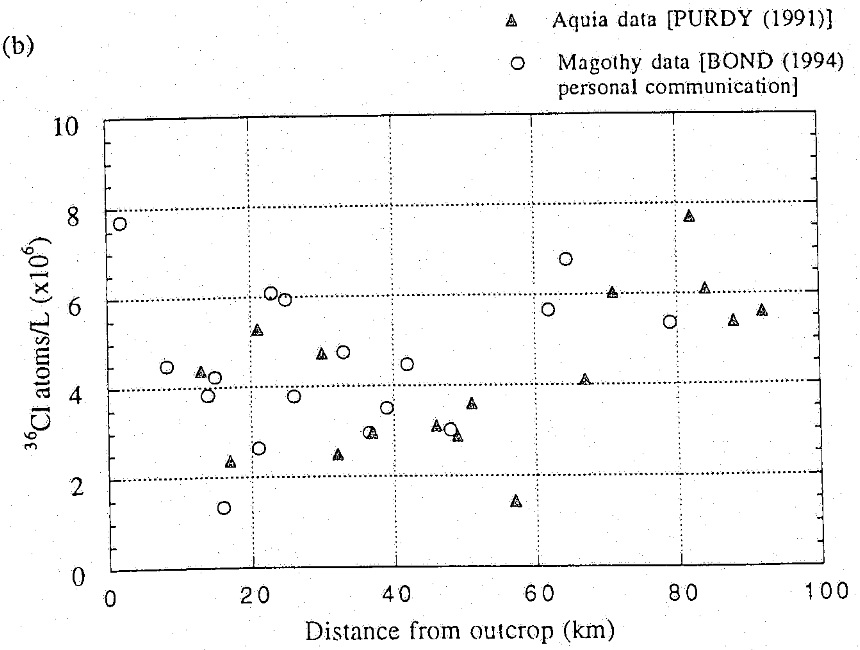
(a) $^{36}Cl/Cl$ ratios versus distance from the outcrop in the Aquia and Magothy aquifers in southern Maryland.

(b) ^{36}Cl concentrations versus distance from the outcrop in the Aquia and Magothy aquifers in southern Maryland.

(a)


Aquia data [PURDY(1991)]
Magothy data [BOND(1994) personal communication]
^{36}Cl/Cl (x 10^{15})
400
350
300
250
200
150
100
50
0
0
20
40
60
80
100
Distance from outcrop (km)

(b)


Aquia data [PURDY (1991)]
Magothy data [BOND (1994) personal communication]
^{36}Cl atoms/L (x10^{6})
10
8
6
4
2
0
0
20
40
60
80
100
Distance from outcrop (km)

5.1.2 EXCESS ^{36}Cl IN ICE CORES AND PRECIPITATION

Evidence of the discrepancy between predicted atmospheric ^{36}Cl production rates and measured values can be seen in ice cores and precipitation samples. Ice core studies are particularly useful in the determination of natural ^{36}Cl fallout because the bomb-pulse peak is clearly evident, and the isolation of material deposited before 1945 is possible. Variations in the ice accumulation rate from year to year create some complexity in the data interpretation, however, pre- 1950 average concentrations can be used to calculate ^{36}Cl deposition fluxes. Using this method a ^{36}Cl deposition flux of 48 atoms/m^2/s, one order of magnitude higher than predicted for the site [LAL and PETERS (1967], was calculated for a core taken at Camp Century (72.5° N) [ANDREWS AND FONTES (1992), ELMORE et al. (1987)]. Similar results were obtained for an ice core taken at Dye-3 [SUTER et al. (1987)].

Very few studies pertaining to ^{36}Cl in precipitation have been published to date. HERUT et al. (1992) published ^{36}Cl data from "chloride-rich" rainwaters collected in Israel. They reported ^{36}Cl concentrations of 0.9 to 6.3 x 10^6 atoms/L, with an expected value of 0.7 x 10^6 atoms/L. It must be noted, however, that Herut's study dealt specifically with rainwater samples which contained more than 35 ppm Cl^-, possible as a result of contamination with chloride rich crustal material.

KNEIS et al (1994) is conducting an intensive investigation of ^{36}Cl and ^{7,10}Be in precipitation collected in West Lafayette, IN. Preliminary results indicate ^{36}Cl deposition fluxes ranging from 10 to 200 atoms/m^{2}s, as compared to an expected flux of approximately 21 atoms/m^{2}s (according to ANDREWS and

FONTES (1992)). Furthermore, the mean ^{10}Be/^{36}Cl ratio measured in Kneis' study was 9.1, compared with a theoretical value of 40 (according to LAL and PETERS (1967). It was suggested by the authors that either the theoretical value is wrong, or there exists additional sources of ^{36}Cl to the atmosphere.

5.2 RESULTS

5.2.1 RESULTS OF SUSQUEHANNA RIVER SAMPLES

Surface water samples from the Susquehanna River were collected and analyzed for ^{36}Cl. Locations of the sampling sites and details pertaining to sample collection are given in Chapter 2 and Appendix A. The results are shown in Figure 5.1

5.2.2 BULK DEPOSITION SAMPLES FROM ELMS, MD AND STATE COLLEGE, PA.

Bulk deposition samples collected at the Elms Environmental Education Center in St. Mary's County, Maryland were analyzed for ^{36}Cl to determine the total ^{36}Cl deposition in the vicinity of the recharge zones of the Aquia and Magothy aquifers. In addition, bulk precipitation was collected at a sampling site near State College, PA and analyzed for ^{36}Cl for comparison with Susquehanna River data. These results are were presented in Section 4.4 (Table 4.4). A summary is given here in Table 5.2.

Table 5.1

Results of ^{36}Cl/Cl analysis of Susquehanna River and Eastern Shore, MD surface water samples

Sample	^{36}Cl/Cl$^-$ (x 10^{-15})	Cl$^-$ conc. [mg/L]	^{36}Cl conc. (x 10^6) [atoms/L]
Jersey Shore, PA (West Branch Susquehanna R.)	366±63	8.1± 0.05	50±9
Renovo, PA (West Branch Susquehanna R.)	361±53	7.5± 0.05	46±8
*Mehoopany, PA (East Branch Susquehanna R)	163±28	22.0± 0.05	61±8
Raystown, PA (Juniata R.)	338±25	9.0± 0.05	52±4
Port Deposit, MD ** (lower Susq. R.)	286±23	11.0± 0.05	53±4
Vienna, MD (pond water Eastern Shore,MD)	388±27	3.5± 0.05	23±2

* The high Cl$^-$ concentration in this sample may be caused by a manufacturing plant owned by Proctor and Gamble, located upstream from the sampling site.

** Collected and analyzed in 1988 by PURDY (1991) (personal communication)

Table 5.2

Bulk Deposition at Elms, MD and State College PA.

Sample	Collection Dates	$[Cl^-]$ (mg/L)	$^{36}Cl/Cl$ ($\times 10^{15}$)	$[^{36}Cl]$* ($\times 10^{6}$) atoms/L	^{36}Cl flux atoms/m^2s
Elms Open 1	10/8/91 - 1/28/92	2.15± 0.05	58±11	2.1±0.3	49 ± 9
Elms Open 2	1/29/92 - 8/5/92	1.31± 0.05	89±9	2.0±0.2	67 ± 6
Elms Open 3	8/6/92 - 10/6/92	1.78± 0.05	28±4	0.8±0.1	51 ± 7
Elms	annual mean	1.62± 0.05	61±8	1.7±0.2	59 ± 8
Penn State	11/8/91 - 2/19/92	0.50± 0.05	274±30	2.3±0.1	82 ± 11

* $[Cl^-]$ and $[^{36}Cl]$ values were corrected for evaporation during the sampling period using rainfall data from the Maryland Department of Air Quality (Elms) and the National Climatological Data Center (Penn State).

5.3 DISCUSSION

5.3.1 EVAPOTRANSPIRATION

In order to compare precipitation data with groundwater data one must first take into account the effect of evapotranspiration. Much of the precipitation that falls on a particular region returns to the atmosphere either by direct evaporation or by plant respiration. These processes results in an increase in concentration of dissolved species as they enter the groundwater. Evapotranspiration rates can vary tremendously from region to region, and must be estimated for each area of interest.

A typical, modern evapotranspiration rate for the recharge areas of the Aquia and Magothy aquifers is approximately 60% [Dr. Russell Brinsfield, Wye Research and Education Center, Maryland, personal communication (1994)]. For the Susquehanna River basin, the evapotranspiration rate can be estimated by comparing the average precipitation rate with the average river discharge. The river basin encompasses 7.13×10^{10} m^2 [SCHUBEL and PRITCHARD (1987)] and receives an average of 1.01 m of rainfall each year (NADP/NTN (1990)). Thus, a total of 7.20×10^{10} m^3 of precipitation enters the basin each year. The long term average discharge of the Susquehanna R. is 3.47×10^{10} m^3/y (SCHUBEL AND PRITCHARD (1987)). Assuming that the basin is in equilibrium (i.e. no net storage occurs), the calculated evapotranspiration rate is 52%.

5.3.2 COMPARISON BETWEEN THE AQUIA AND MAGOTHY AQUIFER DATA AND ELMS PRECIPITATION DATA

Table 5.3 shows a comparison between ^{36}Cl data for the Aquia and Magothy aquifers and bulk precipitation collected at the Elms. The aquifer data were corrected for evapotranspiration by assuming a 60% evapotranspiration rate.

Correspondingly, the precipitation data were corrected for evaporation to allow direct comparison.

Table 5.3 **Comparison between Aquia and Magothy aquifer data and Elms bulk deposition data.**

	$^{36}Cl/Cl^-$ ($x10^{-15}$)	Cl^- conc. (mg/L)	^{36}Cl conc. (x 10^6) (atoms/L)
Calculated Aquia/Magothy recharge	150 to 300	0.4 to 0.8 *	1.2 to 3.2 *
Elms bulk precipitation (annual mean)	61.2±7.9	1.5 ± 0.03	1.23

* These values are calculated from the aquifer data using a 60% evapotranspiration rate. (Dr. Russell Brinsfield, Wye Resource and Education Center, Maryland, personal communication)

The $^{36}Cl/Cl$ ratios in the Aquia and the Magothy are considerably higher than in the Elms precipitation. However, it should be noted that the stable chloride concentration in the Elms precipitation is considerably higher than those found in the aquifers. This effect is probably related to the proximity of the rainwater sampler to the Chesapeake Bay. The bay is a source of marine chloride, containing very little ^{36}Cl. If it is assumed that the difference in chloride concentrations between the calculated aquifer recharge and the Elms precipitation is due to marine chloride containing no ^{36}Cl, the $^{36}Cl/Cl^-$ratios are in better agreement, with the aquifer ratio remaining slightly higher.

A more appropriate comparison can be made using the ^{36}Cl concentrations, since this quantity is not affected by the addition of marine chloride. It can be seen in Table 5.3 that the ^{36}Cl concentration in Elms precipitation can account for the lowest end of the concentration range seen in the aquifers. These are the youngest of the groundwater samples. Thus, it can be concluded that the 36Cl in the most recent, pre-bomb aquifer samples can be attributed to modern atmospheric deposition. Samples taken from the distal ends of these aquifers contained at least twice as much ^{36}Cl as modern precipitation. Thus it appears that modern ^{36}Cl deposition cannot account for all of the ^{36}Cl found in the Aquia and Magothy aquifers, particularly in the oldest samples.

(a) Possible explanations for excess ^{36}Cl in older Aquia and Magothy aquifer samples

While detailed interpretations of ^{36}Cl systematics in these aquifers is beyond the scope of this study, the ^{36}Cl precipitation data presented in the previous chapters can be used to shed new light on some of the interpretations given by PURDY (1991). Particularly interesting is the application of modern ^{36}Cl deposition behavior to the question of how climate could have influenced the ^{36}Cl concentrations in these aquifers.

Tritium analyses were performed in the Aquia to rule out the possibility of contamination with bomb-pulse chloride [PURDY (1991)]. No measurable tritium was found, thus the bomb-pulse was ruled out as a possible source of excess ^{36}Cl. In addition, data from both the Aquia and the Magothy aquifer show rather gradual changes in ^{36}Cl concentration (Figure 5.2). It is unlikely the bomb-pulse contamination could produce these results.

Variations in Cosmic Ray flux.

Variations of the cosmic ray flux are expected to occur every 100 to 200 years due to solar modulation. The effect of this modulation on the ^{14}C production rate has been demonstrated in Douglas fir tree rings by STUVIER AND QUAY, (1980). In addition, modulations in the Earth's geomagnetic field causes variations in the cosmic ray flux in approximately 10,000 y cycles. Evidence of variation in cosmogenic radioisotope production due to geomagnetic modulation has been found in ice cores [SUTER et al, (1987), ELMORE et al. (1987)], coral rings [RADIOCARBON (1991)] and most recently, pack rat urine [SHARMA (1994) personal communication).

Although it has been demonstrated that variations in cosmogenic radioisotope production have occurred due to solar and geomagnetic modulation, the timing of these modulations is inconsistent with the variations seen in the Aquia. Ice core and preliminary pack rat urine data suggest that the ^{36}Cl production rate was approximately 40 to 50% higher (than today) during the last glacial maximum (18 ky before present). PURDY(1991) has demonstrated that during that period, ^{36}Cl concentrations in the Aquia were at their lowest values.

Climate Change over the past 40,000 y.

PURDY argues that the trends in both ^{36}Cl and Cl^- measured in the Aquia are best explained by climate change. She contends that the observed decrease in the ^{36}Cl concentrations in the Aquia during the last glacial maximum could be a result of increased precipitation in the recharge area during that period. She also suggests that this effect would mask the increase in the ^{36}Cl production rate due to geomagnetic modulation.

While it is possible that an increase in precipitation could have caused the decrease in ^{36}Cl concentrations seen in the Aquia, data from the present study suggest that it would be necessary for the precipitation rate to increase by at least a factor of 2. Figure 5.4 shows a plot of the ^{36}Cl deposition flux (with seasonal variation subtracted out using the mathematical function described in Section 3.5) versus precipitation rate. At low precipitation rates, ^{36}Cl flux is positively correlated with precipitation rate, and the resulting ^{36}Cl concentrations are fairly constant. At higher precipitation rates, the atmosphere becomes cleansed of ^{36}Cl, and the deposition flux levels off. The modern average precipitation rate in the recharge area of the Aquia is approximately 2.7 mm/d. An increase of a factor of 2 would be necessary before the ^{36}Cl concentration would begin to decrease. An even greater increase would be needed to mask the effect increased ^{36}Cl production due to geomagnetic modulation during that period.

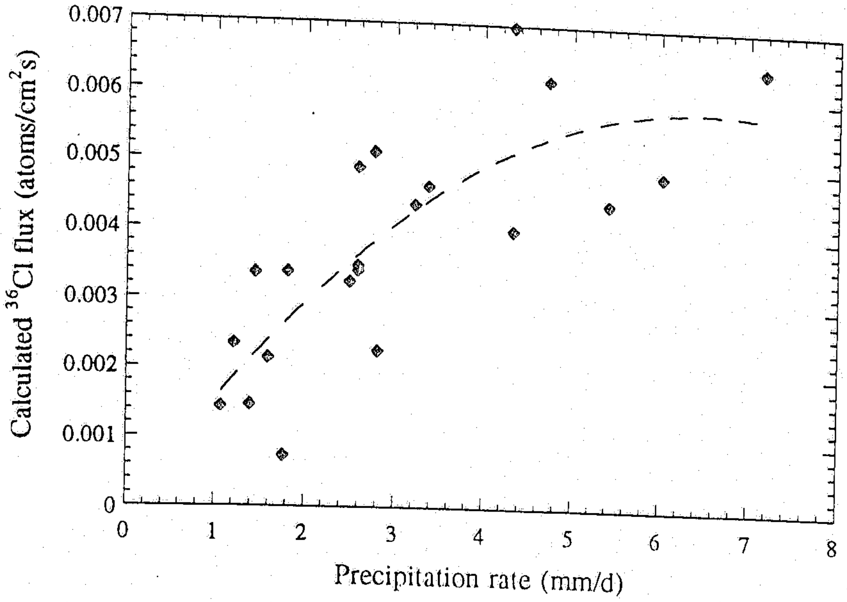
The excess ^{36}Cl found further down dip in the aquifer is more difficult to explain. As shown above, ^{36}Cl deposition is positively correlated with precipitation rate. Dry deposition of ^{36}Cl can be an important factor, especially in arid climates, and needs to be studied further.

Deep *In-situ* Production

Another possible explanation for the high ^{36}Cl concentrations in the oldest Aquia and Magothy aquifer samples is deep in situ production. PURDY (1991) discusses this possibility in detail. Preliminary gamma ray spectrometry analysis was performed on a sample from the Aquia Formation, and minimal amounts of uranium and thorium were found. Based on this result, it was concluded that deep *in-situ* production of ^{36}Cl could not account for the concentrations seen in the Aquia.

Figure 5.3

Derived relationship between ^{36}Cl deposition and precipitation rate calculated by subtracting the seasonal flux component as described in Section 3.2.4 (b). Note that the deposition flux increases with precipitation rate until the atmosphere is cleansed of ^{36}Cl and the flux approaches a constant value.


0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
Calculated ^{36}Cl flux (atoms/cm^{2}s)
0
1
2
3
4
5
6
7
8
Precipitation rate (mm/d)

Seasonal Variations in Aquifer Recharge.

The deposition of ^{36}Cl undergoes seasonal variations, as shown in Section 3.3, with maximum deposition occuring in the spring. If the Aquia and Magothy aquifers were recharged primarily during periods of maximum ^{36}Cl deposition, concentrations of ^{36}Cl in the groundwater could be higher than in the mean annual precipitation. THATCHER (1968) discusses this possibility with respect to tritium. He concluded that groundwater is recharged primarily during the wet season (February to June). However much of the water that enters the aquifers during the spring originally fell as precipitation during October to December, and was accumulated in the soil. Thus according to Thatcher, tritium concentrations in the groundwater would be lower than in annual average precipitation. More recent investigations by BRINSFIELD (1994, Wye Research and Education Center, personal communication) maintain that seasonal variation in groundwater recharge would not result in higher groundwater concentrations of deposited ions. BRINSFIELD's studies involve mass balances of solutes, particularly NO_3^-, in small watersheds. He shows that solutes are generally integrated in the soil zone over a year or two before entering the groundwater, in a process roughly analogous to a plugged flow reactor. Thus, by analogy, it appears that seasonal variation in groundwater recharge can not explain the observed groundwater ^{36}Cl concentrations.

5.3.3 COMPARISON BETWEEN ^{36}Cl IN THE SUSQUEHANNA RIVER BASIN AND IN STATE COLLEGE, PA BULK DEPOSITION SAMPLES

(a) Data Comparison

A comparison can be made between the Susquehanna River samples and bulk precipitation collected at Penn State, near State College, PA. This comparison is given in Table 5.4. The measured $^{36}Cl/Cl$ ratios in the Susquehanna River are only slightly higher than the precipitation ratio, while the ^{36}Cl concentrations are an order of magnitude higher. Also, the stable chloride concentrations are an order of magnitude higher. This was not the case with the Aquia and Magothy samples.

Table 5.4

Comparison between Susquehanna River data and State College bulk deposition data

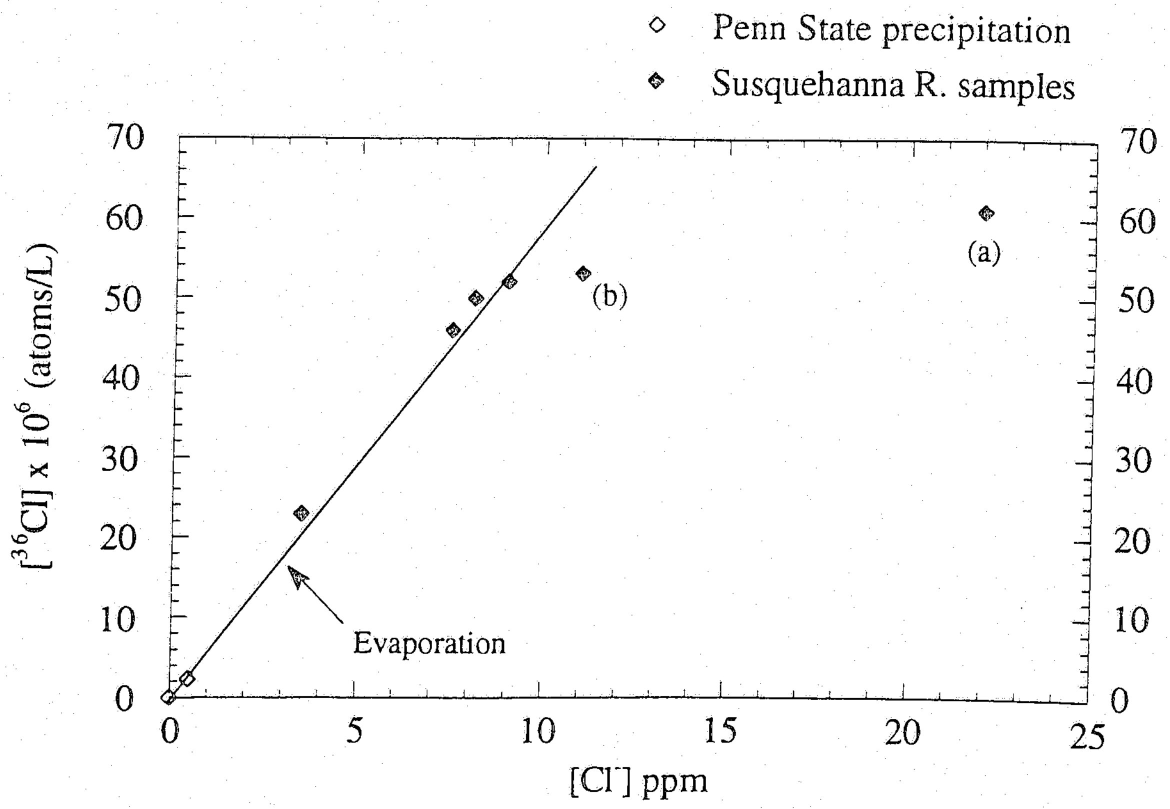
	$^{36}Cl/Cl$ ($\times 10^{-15}$)	[Cl-] (mg/L)	[^{36}Cl] ($\times 10^{6}$) (atoms/L)
Susquehanna River samples	300 - 400	7.5 - 11.0 ± 0.2	46 - 61
Calculated Susquehanna recharge	300 - 400	3.8 - 5.5 *	23 - 31 *
Penn State bulk precipitation	274±30	0.5 ± 0.1	2.3±0.1

* These values are calculated from the surface water data using a 50% evapotranspiration rate.

Figure 5.4 shows a plot of the ^{36}Cl concentration versus the stable chloride concentration for the Susquehanna River samples, with the Penn State precipitation sample. Most of the points in Figure 5.4 fall along an "evaporation line", and could be explained by evaporative concentration of the local precipitation. The two points showing stable chloride enrichment are probably due to anthropogenic influences. One of these points (a) represents a sample collected downstream from

Figure 5.4

Correlation plot of the ^{36}Cl concentrations versus stable chloride concentrations for surface waters from the Susquehanna River and bulk precipitation from State College, PA. Most points appear to lie along an "evaporation line". The two points (a) and (b) showing chloride enrichment can be explained by anthropogenic sources.


◇ Penn State precipitation
◆ Susquehanna R. samples
$[^{36}Cl] \times 10^6$ (atoms/L)
[Cl⁻] ppm
Evaporation
(a)
(b)
0
10
20
30
40
50
60
70
0
5
10
15
20
25

the Proctor and Gamble, Mehoopany, PA manufacturing plant. The other outlying point (b) represents a sample, taken near the mouth of the Susquehanna, which is an integration of discharge from the entire basin, including all anthropogenic influences.

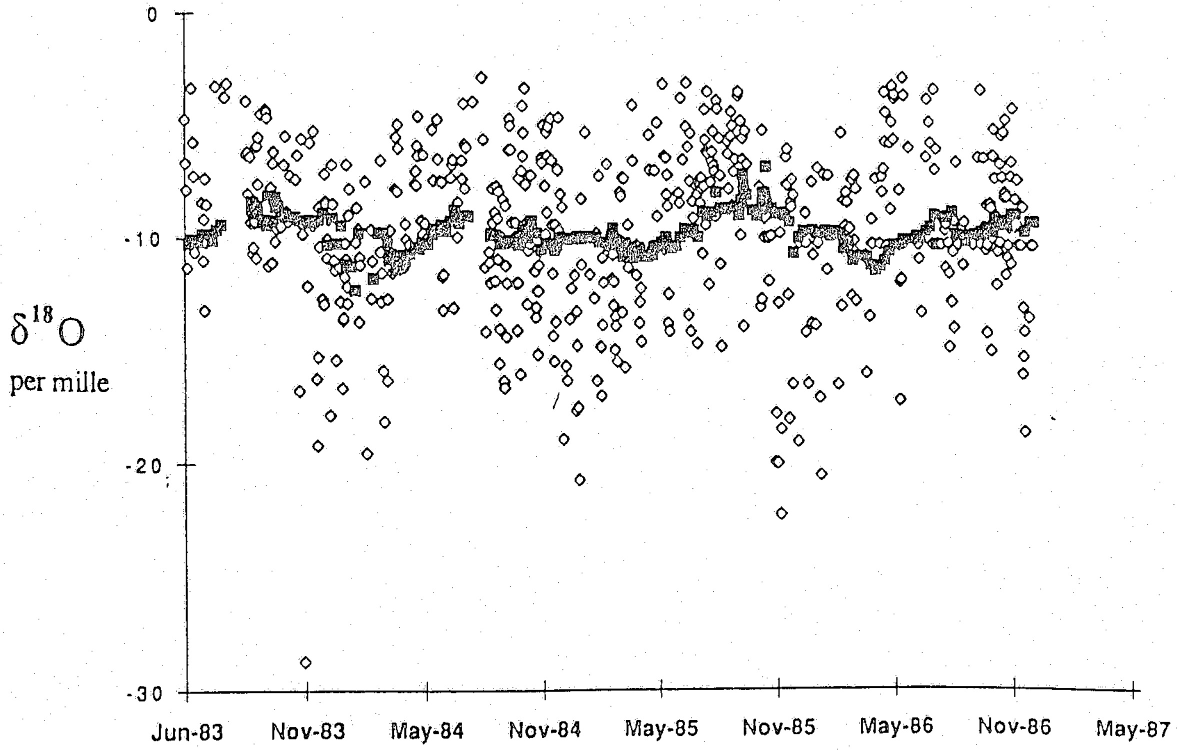
(b) Possible Explanations for the High ^{36}Cl Concentrations Observed in the Susquehanna River Samples

With the exception of the two outlying points discussed above, the remaining points in Figure 5.4 lie along an "evaporation" line, and could be explained evaporative concentration of the local precipitation. However, this explanation would require a relatively high (approximately 90%) evapotranspiration rate, as opposed to the previously derived evapotranspiration rate of approximately 50% for the Susquehanna River basin. The effective evapotranspiration rate for groundwater recharge may be somewhat higher than 50%, since the annual mean value includes spring runoff and snow melt (which could enter and leave the basin without experiencing much evaporation). Ths effect would be minor, however. CHRISTOPHERSEN and NEAL (1990) demonstrated that storm flow runoff from a catchment in Norway was mainly derived from water residing in the soil zone before the event. As a result, streamwater concentrations of conservative species were remarkably constant, despite large variations in precipitation concentrations. Figure 5.? shows this effect with respect to ^{18}O. The authors note that chloride would behave similarly.

Samples for this study were purposefully collected during low-flow, or base-flow, periods. According to BLACK (1991), base-flow is typically comprised of deep groundwater which has been stored in the basin, and the water that was sampled should therefore reflect "average" conditions. Thus it is unlikely that the

Figure 5.5

Measured daily ^{18}O concentrations (in per mil relative to Standard Mean Ocean Water) in precipitation (open diamonds) and weekly streamwater concentrations (solid squares) at Birkenes, southern Norway. Note that, despite large fluctuations in ^{18}O input, streamwater concentrations remain fairly constant, showing only weak seasonal fluctuations [taken from CHRISTOPHERSON and NEAL (1990)].


0
-10
-20
-30
$\delta^{18}O$
per mille
Jun-83
Nov-83
May-84
Nov-84
May-85
Nov-85
May-86
Nov-86
May-87

high concentrations of chloride and ^{36}Cl in the Susquehanna samples can be attributed to evaporative concentration.

An alternative explanation is that there is some additional source of both stable chloride and ^{36}Cl. FETH (1981) reviews the chloride mass balances of several large river basins and concludes that, in general, precipitation accounts for a small percentage of the chloride released from large drainage basins. Precipitation derived chloride is termed "cyclic" chloride since it originates in, and is returned to, the oceans. Anthropogenic chloride and chloride leached from underlying geological formations can have strong influences on river water chloride concentrations. A chloride mass balance for the Susquehanna River indicates that cyclic chloride accounts for approximately 10% of the total chord discharged. To derive this percentage, input was calculated by assuming a precipitation concentration of 0.5 mg Cl^-/L (Table 5.4), along with a deposition area of 7.13 x 10^{10} m^2 (SCHUBEL and PRITCHARD (1987) and annual precipitation rate of 1 m/y (NADP/NTN (1990)). Discharge was calculated by assuming a river water concentration of 11 mg Cl^-/L (for Port Deposit, MD, Table (5.1)) and a discharge of 3.47 x 10^{10} m^3/y (SCHUBEL and PRITCHARD (1987)).

Although it is possible that a single source could provide both stable chloride and ^{36}Cl in the necessary ratio, it is more likely that a number of sources are involved. Stable chloride could come from many sources including agricultural and industrial waste, acid mine drainage and road salt. Anthropogenic sources of chloride are assumed here to be stable, since most of the chloride used in industrial processes comes from ancient, ^{36}Cl free halite deposits. However, this assumption has not yet been tested.

The additional source of ^{36}Cl in the Susquehanna River samples is not as obvious. One possibility is that 'bomb-pulse' ^{36}Cl, retained in the river basin, is being gradually released. However data published by MICHEL (1992) indicate that by 1980 the concentration of tritium (which was also weapons-related) had returned to very near natural levels. The residence time calculated for the long-term reservoir of Susquehanna River basin was 10 y. Although there are possible mechanisms for retention of chloride, it is unlikely that this source would cause the large excess found in the Susquehanna samples.

Another possible source of the excess ^{36}Cl found in the Susquehanna River samples is *in situ* production. As discussed in Section 5.1, ^{36}Cl can be produced in the soil by cosmic irradiation. Dissolution of irradiated chloride from the soil layer could account for the observed ^{36}Cl concentrations, as well as the high Cl^- concentrations seen in the Susquehanna samples. Similar results have been obtained in the recharge area of the Milk River aquifer (NOLTE (1990)).

The *in-situ* ^{36}Cl production rate is difficult to accurately quantify in the Susquehanna basin without detailed knowledge of rock type and chemical composition, latitudinally and altitudinally dependent cosmic ray neutron and muon fluxes, exposure time and erosion rates [YOKOYAMA et al. (1977), LAL and PETERS (1967), ZREDA et al. (1991)]. In fact the most accurate means of quantifying in-situ ^{36}Cl production is by experimental determination. However, the secular equilibrium ^{36}Cl/Cl ratio can be roughly estimated by comparison with calculations made for the Milk River aquifer.

Equilibrium ^{36}Cl/Cl ratios of 60,000 x 10^{-15} for the top 10 cm of Milk River Sandstone, and 16,00 x 10^{-15} at a depth of 1 m were calculated by ANDREWS et al. (1991). At shallow depth, these high ratios are primarily due to secondary cosmic ray neutron interactions. An altitude scaling factor of approximately 0.3 [ZREDA et al. (1991)] can be applied to correct for the altitude difference between the Susquehanna basin (0.3 km, RAND MCNALLY (1992)), and the Milk River aquifer [1 km, NOLTE (1991)]. A latitudinal scaling factor of approximately 0.8 [YOKOYAMA et al. (1977)] can be used to correct for latitudinal variation. Assuming similar rock type (primarily sandstone and shale), equilibrium ratios of 15,000 x 10^{-15} to 3,000 x 10^{-15} might be expected in the surface rocks of the Susquehanna basin.

These calculations are based on many assumptions (primarily important is the assumption of similar rock type). However, it is apparent that a significant amount of ^{36}Cl can be produced in surface soils, and that the dissolution of a small amount of cosmic ray-exposed chloride can have a significant effect on groundwater ^{36}Cl concentrations.

One observation that is difficult to account for by either of the above explanations is the consistency of the ^{36}Cl/Cl ratios and the ^{36}Cl concentrations throughout the basin. With the exception of the Mehoopany sample, which was most likely contaminated with stable anthropogenic chloride, the measured ^{36}Cl/Cl ratios, from various parts of the basin, are within experimental error of each other. A similar consistency is seen in the ^{36}Cl concentrations, despite geological differences in the sample site locations. If the excess ^{36}Cl in the Susquehanna is due to the bomb-pulse, then groundwater retention times would have to be similar in all of the various sub-basins samples (the West Branch, the East Branch and the Juniata River), despite geological variations. The same argument applies to in-situ ^{36}Cl production. This observation alone does not, however, discount either the bomb-pulse theory or the *in-situ* production theory.

5.4 CONCLUSIONS

It is concluded from this study that modern ^{36}Cl deposition can not account for the relatively high ^{36}Cl concentrations in the Aquia and Magothy aquifers and the Susquehanna River basin. After taking into account reasonable evapotranspiration rates, ^{36}Cl concentrations in the Aquia and the Magothy remain up to twice as high as in local precipitation. In the Susquehanna River basin, ^{36}Cl and stable chloride concentrations were found to be an order of magnitude higher than in local precipitation.

The sources of excess ^{36}Cl in the aquifers and the river basin are almost certainly different. In the Aquia and the Magothy, the excess ^{36}Cl is found mainly in the oldest samples (farthest from the recharge). Possible explanations include climatic variations, fluctuations in the ^{36}Cl production rate and deep in-situ ^{36}Cl production.

The Susquehanna River contains excess stable chloride as well as ^{36}Cl. Possible sources of stable chloride to the river are numerous, including industry, agriculture and road salt. The source of excess ^{36}Cl in the basin is not as easily identified. Bomb-pulse ^{36}Cl could still be influencing the discharge of the Susquehanna, however it is not likely that such a large amount remains in the basin while tritium levels have returned to near background. Another possible source is leaching of ^{36}Cl produced in the soil

Chapter 6

SUMMARY, GENERAL CONCLUSIONS AND FUTURE WORK

The development of AMS has led to numerous applications of cosmogenic radioisotopes, particularly in the fields of biomedicine, archeology, cosmochemistry, geology and hydrology. Increasing number of samples are analyzed by AMS each year, as scientists develop new and exciting ways to use these previously unmeasurable isotopes. New AMS facilities are being developed world-wide, and existing facilities are continually improving their measurement capabilities, providing proof of the increasing value of AMS to the scientific community.

Chlorine-36 is a cosmogenic radioisotope which has been developed largely as a result of AMS. Originally of interest as a monitor for groundwater contamination at nuclear reprocessing facilities, ^{36}Cl is now widely used as a groundwater tracer in a variety of hydrological systems. However, a major aspect of ^{36}Cl in the hydrosphere has been overlooked. The deposition of atmospheric (or meteoric) ^{36}Cl, although of primary importance to hydrological applications, has not been well studied. This gap in knowledge critically undermines the use of ^{36}Cl as a dating tool in hydrological systems.

This project was developed to address these concerns. The primary objective was to carry out a detailed study of ^{36}Cl in precipitation, and thus make a significant contribution to the limited existing data base. Specifically, this project was aimed to determine the atmospheric ^{36}Cl currently being deposited in southern Maryland and across the northern United States.

6.1 TEMPORAL VARIATIONS IN ^{36}CL DEPOSITION

Wet-only precipitation samples were collected from a sampling site at the Elms Environmental Education center in southern Maryland. Samples were collected on a biweekly basis, then combined to form integrated monthly samples over a two year sampling period. These were then analyzed for ^{36}Cl to determine the ^{36}Cl/Cl deposition ratio, the ^{36}Cl concentration and the ^{36}Cl deposition flux.

The ^{36}Cl/Cl ratios ranged from a high of 586±37 ($\times 10^{-15}$) in March, 1992 to a low of 3.8±4.8 x 10^{-15} in January, 1992. Highest ^{36}Cl/Cl ratios were observed in the spring. The chloride-weighted mean annual ratio was 73.9±37 ($\times 10^{-15}$) for the first sampling year and 58±5 ($\times 10^{-15}$) for the second sampling year. The mean for the entire sampling period was 68±19 ($\times 10^{-15}$), a factor of 1.2 to 2.4 higher than predicted by using the currently accepted atmospheric ^{36}Cl production rate [FONTES and ANDREWS (1992)] and the ^{36}Cl/Cl deposition ratio model by BENTLEY et al. (1986).

The calculated ^{36}Cl wet deposition fluxes varied considerably as well, with values ranging from a high of 74±9 atoms/m^{2}s in April, 1992 to a low of 8.8±0.8 atoms/m^{2}s in January, 1993. Higher fluxes occurred during the spring. The precipitation weighted mean ^{36}Cl deposition flux for the entire sampling period was 38±5 atoms/m^{2}s.

The ^{36}Cl wet deposition flux data revealed a distinct seasonal deposition pattern, with peaks occuring in the March and April. While this data set is the first to demonstrate seasonal dependence for ^{36}Cl deposition, similar seasonal variations have been observed in a host of stratospheric tracers, including ^{90}Sr, ^{7,10}Be and ^{239,240}Pu. DIBB (1989) published a study of ^{7}Be deposition, with samples collected at Solomon's Island, MD, approximately 15 mi north of the Elms site. His results showed seasonal variations quite similar to those observed in the ^{36}Cl data. An important implication is that ^{36}Cl, which has been shown to exist as gaseous HCl in the stratosphere [WHALEN et al. (1991)], behaves similarly to particulate ^{7}Be.

Approximately 70% of all atmospheric ^{36}Cl is produced in the stratosphere [LAL and PETERS (1967)] and the stratospheric residence time is on the order of 2 years [SYNAL (1990)]. As a result, stratospheric ^{36}Cl concentrations are expected to be considerably higher than tropospheric concentrations, and seasonal ^{36}Cl deposition flux peaks can be attributed to mass exchange from the stratosphere to the troposphere. The mechanisms responsible for the spring peaks are discussed in detail in a review article by REITER (1975). These mechanisms include seasonal shifts in the height of the tropopause, tropopause folding events in the vicinity of the jet stream, eddy turbulence and large thunderstorms with "overshooting tops".

Bulk precipitation samples (referred to as 'open' samples) were collected at the Elms site in addition to the wet-only samples. Three open samples were collected: Open 1 (fall 1991/winter 1992), Open 2 (spring/summer 1992) and Open 3 (summer/fall 1993). The precipitation weighted mean ^{36}Cl deposition flux was 59±8 atoms/m^{2}s). If the latitudinally dependent ^{36}Cl deposition pattern of LAL and PETERS (1967) is assumed, the calculated global average production rate based on these results is 28 atoms/m^{2}s. This value is more than a factor of 2 higher than LAL and PETERS (1967) original production rate estimate (11 atoms/m^{2}s), and a factor of 3 higher than the current estimate of 9 atoms/m^{2}s [ANDREWS and FONTES (1992)]. These results support mounting evidence in literature that current atmospheric ^{36}Cl production rate estimates significantly underestimate actual production.

Dry deposition, roughly estimated to be the difference between wet-only and open ^{36}Cl deposition fluxes, accounts for approximately 25% of the total ^{36}Cl deposition flux. The difference between the wet-only and open ^{36}Cl deposition fluxes increased during the spring/summer sampling period, possibly indicating an increase in ^{36}Cl availability. A ^{36}Cl dry deposition velocity was estimated by using the calculated mean dry deposition flux of 17.8±17.8 atoms/m^{2}s, and assuming an atmospheric Cl$^-$ concentration of $3 \pm 1.5 \times 10^{14}$ atoms/m^3 [SINGH and KASTING(1988), WU (1993)]. The result is a dry deposition velocity of 1.2±1 cm/s, which falls within the range of 0.2 - 6.3 cm/s reported by SEHMEL (1980).

These results provide a basis by which to begin to interpret ^{36}Cl behavior in the atmosphere and in local hydrological systems. However, due to the large number of variables involved in any environmental study, a 2 y sampling period is not long enough to provide statistically sound results. It is important that this study be continued, to improve this existing data base, and to better understand outlying points. A stratospheric co-tracer, such as ozone or ^{7}Be, could be used to further study the question of stratospheric/tropospheric mixing. In addition, studies of gaseous and particulate ^{36}Cl in the atmosphere are necessary to better understand dry deposition. These studies would also yield important information on the nature and behavior of ^{36}Cl in tropospheric air.

6.2 SPATIAL VARIATIONS IN ^{36}Cl DEPOSITION

Chlorine-36 in groundwater samples from the Aquia and Magothy aquifers in southern Maryland revealed ^{36}Cl/Cl ratios 3-5 times higher than predicted by the model published by BENTLEY et al. (1986). In an effort to reconcile this difference, a new and more rigorous model was developed to predict ^{36}Cl/Cl ratios across the United States. Three major components of the model were reevaluated: the ^{36}Cl production rate, the ^{36}Cl distribution pattern and the stable chloride concentrations.

It was clear from the existing groundwater and surface water data that the ^{36}Cl production rate used in BENTLEY's model was too low. For this new model, the global production rate estimate of 19 atoms/m^{2}s by BLINOV (1988) was adopted. For prediction of the ^{36}Cl deposition pattern, the new model separated the ^{36}Cl produced in the stratosphere from that produced in the troposphere.

The stratospheric component was calculated by multiplying the stratospheric fraction of the global production rate by a geographic focusing factor, which was determined by the ^{90}Sr concentration in soils at various sites across the United States. Dividing the ^{90}Sr concentration at each site by the mean northern hemispheric ^{90}Sr concentration gave the geographic focusing factor. In this way, ^{90}Sr deposition is used to predict ^{36}Cl deposition, and longitudinal as well as latitudinal variation is accounted for. Stable chloride data for the model were taken from the NADP/NTN precipitation sampling network.

Bulk deposition samples were collected from seven sampling sites across the northern United States to test this new model. The ^{36}Cl/Cl ratio results agreed well with model predictions. These results are summarized in Table 6.1.

With the exception of the Black Hills, SD, sample, the measured ^{36}Cl/Cl ratios agree well with the model predictions. However, the measured ^{36}Cl deposition fluxes are a factor of two higher than those predicted by the model. Correspondingly, the measured stable chloride concentrations, after correcting for evaporation, are roughly a factor of 2 higher than the NADP/NTN concentrations used in the model.

Table 6.1

Results of bulk precipitation samples compared with model predictions

Sample site	Measured ^{36}Cl/Cl ratio (x 10^{-15})	Model prediction (x 10^{-15})
Lewes, DE	23±2	100-200
Elms, MD	61±9	100-200
Harpers Ferry, WV	184±21	200
State College, PA	274±30	200-400
Victor, NY	337±17	200-400
Laingsburg, MI	453±29	400
Black Hills, SD	4220±510	1200-1600

Dry deposition, which was not included in the NADP/NTN data, can explain part of the discrepancy between measured and predicted ^{36}Cl fluxes. In Chapter 3 it was determined that the difference bewteen wet-only and bulk deposition accounted for approximately 25% of the total ^{36}Cl deposition.

However, dry deposition did not cause a factor of 2 increase in the stable chloride concentration. Contamination due to the sampler apparatus was ruled out for several reasons, leaving two possible explanations. First, the geometry and surface of the collectors could have caused a positive sampling bias, thus resulting in an over-estimate of the ^{36}Cl deposition flux. This type of sampling error has been demonstrated in other bucket-type collectors. In this case, the ^{36}Cl/Cl ratio is unaffected, since the extraneous chloride would carry the ambient ^{36}Cl/Cl signature. In comparing ^{36}Cl results from the Elms wet-only sampler with those from the Elms open sampler, sampling bias could not be distinguished from dry deposition.

The dry deposition explanation carries an important implication. If the measured chloride concentrations and ^{36}Cl deposition fluxes are correct, then the mean global ^{36}Cl production rate must be approximately 38 atoms/m^{2}s, an additional factor of 2 higher than BLINOV's (1989) estimate.

6.3 THE RELATIONSHIP BETWEEN ^{36}CL DEPOSITION AND GROUND WATER AND SURFACE WATER CONCENTRATIONS.

Groundwater samples from the Aquia and Magothy aquifers in southern Maryland, and surface water samples from the Susquehanna River basin contained ^{36}Cl/Cl ratios 2 to 5 times higher than predicted in the BENTLEY et al. (1986) model. In order to better understand the nature of this discrepancy, bulk precipitation samples were collected at the Elms, MD site and the State College, PA, and the results were compared with the groundwater and surface water results.

In comparing the Aquia and Magothy groundwater with bulk precipitation from the Elms site, it was concluded that the ^{36}Cl content in the most recent pre-bomb samples can be attributed to local recharge. Ratios of ^{36}Cl/Cl in the aquifer samples were higher than those in Elms precipitation, however this difference was interpreted as being due to the proximity of the Elms sampler to the Chesapeake Bay, a large source of marine chloride. Samples from the distal ends of these aquifers contained at least twice as much ^{36}Cl as modern precipitation.

Surface water samples from the Susquehanna River basin were compared with bulk precipitation collected at State College, PA. The ^{36}Cl/Cl ratios were similar, however the ^{36}Cl concentrations were found to be an order of magnitude higher in the surface water than in local precipitation. Evaporative concentration was ruled out since the calculated evapotranspiration rate for the basin is 50%, not high enough to produce an order of magnitude concentration increase. In addition, a ^{36}Cl mass balance indicated that only 10% of the ^{36}Cl leaving the basin could be accounted for by local precipitation.

The ^{36}Cl bomb-pulse, and *in-situ* ^{36}Cl production were identified as possible sources of this additional ^{36}Cl. Tritium data indicate that the basin is almost completely flushed of water carrying the bomb-pulse signature. *In-situ* production of ^{36}Cl in the soil zone is believed to be an important source of ^{36}Cl in the Milk River aquifer in Alberta, Canada, and could possibly be an important source in the Susquehanna Basin as well. A detailed study of *in-situ* production in the Susquehanna River basin could help determine which of these sources, if any, is responsible for the ^{36}Cl concentrations in the Susquehanna.

Appendix A

1. SITE LOCATIONS AND DESCRIPTIONS FOR OPEN PRECIPITATION SAMPLE COLLECTION SITES

SITE: LEWES, DE

CONTACT: Cathy Conko
University of Delaware
College of Marine Studies
(302) 645-4300

SITE LOCATION: Cape Henlopen State Park, De

The sampler is located within the College of Marine Studies atmospheric sampling site, approximately 2 mi southeast of Lewes, DE. This site is located approximately 0.25 mi from the Atlantic seacoast. A six-foot fence surrounds the site. Several other samplers are located nearby. The ground is sandy, with small pine trees.

SITE: THE ELMS

CONTACT: Diane Leister
University of Maryland
Chesapeake Biological Laboratory
(410) 426-7307

SITE LOCATION: The Elms Environmental Education Center,
St. Mary's County, MD

The site is located on St. John's Cemetery Road, east of Rt. 235 near St. Mary's City, Maryland. This location is approximately 60 mi. south of Washington DC. The sampling site is located on a flat, grassy field at the eastern edge of the Elms property. The field is bordered by trees to the north and west, and by a tidal salt marsh to the south. The collector is located approximately 50 yards from the edge of the salt marsh.

SITE: HARPER'S FERRY, WV.

CONTACT: Sue Mackreth
(304) 535-2525

SITE LOCATION: National Park Service Property
Harper's Ferry, WV

The site is located on National Park Service property on Bakerstown Rd. in Harpers Ferry, WV, across from the Harper's Ferry water treatment plant. The sampler was set behind the house, in an open yard. A wire fence surrounded the sampler. A wooded area bordered the yard approximately 10 y away from the sampler to the north.

SITE: STATE COLLEGE, PA

CONTACT: Dr. Dennis Lamb
Department of Meteorology
Penn State University
(814) 865-0174

SITE LOCATION: Scotia Road Atmospheric Sampling Site

The sample collector is located in the Penn State atmospheric sampling site on Scotia Rd., 5 mi west of State College, PA. The property belongs to the Penn State Gamelands Commission. The collector is located on a wide, grassy field with trees approximately 200 y to the north and low brush 10 y to the east and south. Several other samplers are located on the site.

SITE: VICTOR, NY

CONTACT: Mr. George Hainsworth
(716) 925-3621

SITE LOCATION: Private Property, Victor, NY

The site is located on private property at 1544 Victor-Holcomb Rd, Victor, NY. The collector was deployed in a grassy field, with trees located approximately 40 ft to the east.

SITE: LAINGSBURG, MI

CONTACT Andrew (Skip) Vander Molen
(517) 353-1624
VDMOLEN@MSUSNCL

SITE LOCATION: Private Property, Laingsburg, MI

The site is located on private property at 7212 Parker Rd, Laingsburg, MI. The collector is deployed behind the house, on a flat, open grassy area. A cornfield borders the site approximately 15 ft. from the sampler.

SITE: BLACK HILLS, SD

CONTACT: Dan Driscoll
USGS
Rapid, City SD
(605) 394-1781

SITE LOCATION: Beaver Creek USGS precipitation gauging station at Pringle, SD

The site is located on National Forest Service property, 2 mi. north of Pringle, SD. The sampler is located on a strip of grass and low shrubs, with trees 50' to the north had 75 ft. to the south. A USGS precipitation gauge is located 15' to the east.

2. SITE LOCATIONS AND DIRECTIONS FOR SURFACE WATER SAMPLING SITES

SITE: MEHOOPANY, PA

East Branch, Susquehanna River

COLLECTION DATE: 7/24/89

SAMPLE SITE: Rte 87 bridge, Mehoopany, PA

The sample was collected from a rocky point 0.25 mi. south of the Rte. 87 bridge in Mehoopany, PA. From Wilkes Barre, take Rte 309 N. Go left on a small road (no name) just after Evens Falls. A path behind some houses leads to the river. The sample was collected from a small spit.

SITE: JERSEY SHORE, PA

West Branch, Susquehanna R.

COLLECTION DATE: 7/24/89

SAMPLE SITE: Rte. 44 Bridge, Jersey Shore, PA

The sample was collected from the Rte. 44 bridge in Jersey Shore, PA. From Williamsport, take Rte. 220 west to Rte. 44 south. The bridge is approximately 2 mi. south of Rte. 220.

SITE: RENOVO, PA

West Branch, Susquehanna R.

COLLECTION DATE: 7/24/89

SITE LOCATION: Rte. 144 bridge, Renovo, PA

The sample was collected from the Rte. 144 bridge in Renovo, PA. From Williamsport, take Rte. 220 west to Rte. 120 north. Follow Rte. 120 north to the town of Renovo. Go left on Rte. 144, the bridge is immediately ahead.

SITE: RAYSTOWN RESERVOIR

Juniata River

COLLECTION DATE: 2/20/92

SITE LOCATION: A marina pier at Raystown Lake National Recreational Area

The sample was collected from a marina pier at Raystown Lake National Recreation Area, 3 mi. north of Marklesburg, PA. From Hagerstown, MD, take Rte. 70 north to Breezewood, PA. Then take Rte. 30 west to Rte. 26 at Everett, PA. Follow Rte. 26 north past Marklesburg. The marina road is on the right.

Appendix B

EXPERIMENTAL DATA

1. Precipitation (in mm), pH, and Conductivity (in mmhos)

Start date	End date	precip. (mm)	pH (±0.05)	conduct.
1/29/91	2/12/91	19.2	4.65	11.0
2/12/91	2/26/91	9.8	4.31	29.8
2/26/91	3/12/91	23.9	5.03	6.5
3/19/91	3/26/91	2.41	4.62	10.6
3/27/91	4/2/91	54.1	4.50	23.2
4/3/91	4/16/91	22.8	4.75	8.9
4/16/91	4/23/91	44.6	5.12	16.5
4/23/91	5/7/91	22.45	4.25	27.9
5/7/91	5/21/91	16.5	4.31	28.8
5/21/91	6/11/91	*	*	*
6/11/91	6/18/91	15.1	4.50	23.5
6/18/91	6/25/91	58.7	5.32	30.6
6/25/91	7/2/91	2.8	4.25	n.a.
7/2/91	7/9/91	55.6	3.72	65.4
7/9/91	7/16/91	6.93	4.54	23.6
7/16/91	7/23/91	0		
7/23/91	7/30/91	70.1	4.65	24.5
7/30/91	8/6/91	0		
8/6/91	8/13/91	50.8	4.55	27.3
8/13/91	8/27/91	18.9	3.82	15.6
8/27/91	9/10/91	44.9	5.98	86.2
9/10/91	9/24/91	14.9	5.25	19.8
9/24/91	10/8/91	72.4	4.36	30.6
10/8/91	10/22/91	68.6	4.63	25.3
10/22/91	11/5/91	0		
11/5/91	11/18/91	6.9	6.11	36.9
11/18/91	12/3/91	37.6	5.89	21.1
12/3/91	12/4/91	17.35	4.20	53.2
12/4/91	12/17/91	18.7	4.40	40.2
12/17/91	12/31/91	42.7	4.94	15.7
12/31/91	1/14/92	24.8	5.06	23.8

Start date	End date	precip. (mm)	pH	cond. (mmho)
1/14/92	1/28/92	*	*	*
1/28/92	2/24/92	25.4	4.54	53.7
2/24/92	3/11/92	*	*	*
3/11/92	3/24/92	12.6	4.62	29.6
3/24/92	4/7/92	2.57	4.12	85.2
4/7/92	4/21/92	8.37	4.95	42.3
4/21/92	5/5/92	28	5.23	19.8
5/5/92	5/19/92	10.9	4.76	28.6
5/19/92	6/2/92	100	4.18	14.6
6/2/92	6/16/92	8.51	4.62	62.3
6/16/92	7/1/92	25.5	3.99	40.1
7/1/92	7/14/92	18.13	4.56	26.4
7/14/92	7/28/92	54.09	4.85	16.6
7/28/92	8/5/92	0		
8/5/92	8/12/92	24.5	5.62	32.3
8/12/92	8/21/92	175	5.03	19.9
8/21/92	9/8/92	66	4.29	28.6
9/8/92	9/22/92	6.25	4.85	42.6
9/22/92	9/26/92	19.53	4.68	30.1
9/26/92	10/6/92	13.5	4.30	52.6
10/6/92	10/20/92	7.24	4.60	27.6
10/20/92	11/3/92	50.4	5.32	21.9
11/3/92	11/16/92	0		
11/16/92	12/1/92	16.1	4.52	56.2
12/1/92	12/15/92	64.5	4.19	26.0
12/15/92	12/29/92	37.4	4.83	21.7
12/29/92	1/12/93	55	5.29	35.2
1/12/93	1/26/93	17.16	4.69	26.7
1/26/93	2/9/93	0		

Start date	End date	[Cl-] (mg/L)	$[NO_3^-]$ (mg/L)	$[SO_4^=]$ (mg/L)
1/29/91	2/12/91	0.14	na.	4.64
2/12/91	2/26/91	0.37	n.a.	8.01
2/26/91	3/12/91	0.71	n.a.	8.67
3/19/91	3/26/91	1.00	n.a.	2.56
3/27/91	4/2/91	0.20	n.a.	9.45
4/3/91	4/16/91	1.49	n.a	3.85
4/16/91	4/23/91	1.30	n.a	5.45
4/23/91	5/7/91	0.65	n.a	1.96
5/7/91	5/21/91	0.22	n.a	9.85
5/21/91	6/11/91	*	*	*
6/11/91	6/18/91	0.55	1.20	6.57
6/18/91	6/25/91	0.33	0.96	5.68
6/25/91	7/2/91	0.39	0.85	5.75
7/2/91	7/9/91	1.12	1.09	8.24
7/9/91	7/16/91	0.55	0.97	2.67
7/16/91	7/23/91	*	*	*
7/23/91	7/30/91	0.16	0.62	4.62
7/30/91	8/6/91	*	*	*
8/6/91	8/13/91	0.37	0.53	5.52
8/13/91	8/27/91	0.12	0.96	3.95
8/27/91	9/10/91	0.97	0.67	4.55
9/10/91	9/24/91	4.48	1.47	7.97
9/24/91	10/8/91	0.18	0.16	3.54
10/8/91	10/22/91	1.38	0.63	4.79
10/22/91	11/5/91	*	*	*
11/5/91	11/18/91	3.08	3.53	8.85
11/18/91	12/3/91	0.66	0.89	5.50
12/3/91	12/4/91	0.32	0.97	4.82
12/4/91	12/17/91	1.22	1.55	4.65
12/17/91	12/31/91	0.26	0.67	3.73
12/31/91	1/14/92	5.57	0.46	1.91

Start date	End date	[Cl-] (mg/L)	[NO$_3^-$] (mg/L)	[SO4=] (mg/L)
1/14/92	1/28/92	*	*	*
1/28/92	2/24/92	0.98	1.02	6.26
2/24/92	3/11/92	*	*	*
3/11/92	3/24/92	1.45	0.63	6.52
3/24/92	4/7/92	0.61	0.25	5.71
4/7/92	4/21/92	0.78	0.54	4.64
4/21/92	5/5/92	0.78	0.78	6.44
5/5/92	5/19/92	1.70	0.60	2.25
5/19/92	6/2/92	1.16	0.22	8.16
6/2/92	6/16/92	0.37	0.39	6.22
6/16/92	7/1/92	1.26	0.26	2.06
7/1/92	7/14/92	1.24	0.63	6.35
7/14/92	7/28/92	1.51	2.41	13.99
7/28/92	8/5/92	*	*	*
8/5/92	8/12/92	0.31	0.38	6.62
8/12/92	8/21/92	0.53	0.53	2.25
8/21/92	9/8/92	2.40	2.89	1.03
9/8/92	9/22/92	0.57	0.56	5.44
9/22/92	9/26/92	3.50	3.24	9.62
9/26/92	10/6/92	0.76	1.59	8.64
10/6/92	10/20/92	1.69	2.10	16.08
10/20/92	11/3/92	1.36	0.99	3.73
11/3/92	11/16/92	*	*	*
11/16/92	12/1/92	1.52	0.69	2.64
12/1/92	12/15/92	2.01	1.65	1.95
12/15/92	12/29/92	0.96	0.96	5.75
12/29/92	1/12/93	0.43	0.55	6.12
1/12/93	1/26/93	0.66	1.40	4.10
1/26/93	2/9/93	*	*	*

Start date	End date	[Ca++]	[Mg++]	[K+]
1/29/91	2/12/91	0.192	0.028	0.112
2/12/91	2/26/91	0.374	0.060	0.122
2/26/91	3/12/91	.0261	0.071	0.078
3/19/91	3/26/91	3.010	0.209	0.369
3/27/91	4/2/91	0.124	0.039	0.198
4/3/91	4/16/91	1.521	0.249	0.439
4/16/91	4/23/91	0.079	0.117	0.143
4/23/91	5/7/91	0.283	0.092	0.172
5/7/91	5/21/91	0.282	0.092	0.154
5/21/91	6/11/91	*	*	*
6/11/91	6/18/91	0.226	0.087	0.093
6/18/91	6/25/91	0.033	0.096	0.117
6/25/91	7/2/91	0.476	0.031	0.004
7/2/91	7/9/91	0.147	0.184	0.156
7/9/91	7/16/91	0.397	0.096	0.071
7/16/91	7/23/91	*	*	*
7/23/91	7/30/91	0.056	0.231	0.091
7/30/91	8/6/91	*	*	*
8/6/91	8/13/91	0.056	0.031	0.018
8/13/91	8/27/91	0.102	0.039	0.017
8/27/91	9/10/91	0.170	0.054	0.045
9/10/91	9/24/91	0.374	0.398	0.058
9/24/91	10/8/91	0.011	0.024	0.198
10/8/91	10/22/91	0.079	0.092	0.083
10/22/91	11/5/91	*	*	*
11/5/91	11/18/91	0.510	0.350	0.063
11/18/91	12/3/91	0.056	0.068	0.185
12/3/91	12/4/91	0.033	0.018	0.033
12/4/91	12/17/91	0.102	0.104	0.004
12/17/91	12/31/91	0.033	0.026	0.076
12/31/91	1/14/92	0.215	0.379	0.001

Start date	End date	[Ca++]	[Mg++]	[K+]
1/14/92	1/28/92	*	*	*
1/28/92	2/24/92	1.298	0.720	0.129
2/24/92	3/11/92	*	*	*
3/11/92	3/24/92	0.647	0.546	0.252
3/24/92	4/7/92	0.465	0.218	0.304
4/7/92	4/21/92	0.579	0.857	0.313
4/21/92	5/5/92	0.079	0.106	0.238
5/5/92	5/19/92	0.215	0.100	0.009
5/19/92	6/2/92	0.170	0.119	0.236
6/2/92	6/16/92	0.215	0.127	0.086
6/16/92	7/1/92	0.056	0.089	0.083
7/1/92	7/14/92	0.192	0.077	0.035
7/14/92	7/28/92	0.011	0.027	0.126
7/28/92	8/5/92	*	*	*
8/5/92	8/12/92	0.192	0.147	0.040
8/12/92	8/21/92	0.011	0.118	0.045
8/21/92	9/8/92	0.079	0.228	0.156
9/8/92	9/22/92	0.283	0.083	0.117
9/22/92	9/26/92	0.102	0.179	0.172
9/26/92	10/6/92	0.192	0.096	0.122
10/6/92	10/20/92	0.306	0.136	0.154
10/20/92	11/3/92	0.102	0.125	0.145
11/3/92	11/16/92	*0.170	*	*
11/16/92	12/1/92	0.045	0.064	0.095
12/1/92	12/15/92	0.033	0.028	0.038
12/15/92	12/29/92	0.0221	0.066	0.063
12/29/92	1/12/93	0.147	0.073	0.073
1/12/93	1/26/93	0.102	0.072	0.093
1/26/93	2/9/93	*	*	*

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