

The Relationship of Prevailing Land Uses to Precipitation Quality in a Southcentral Pennsylvania Watershed

Richard H. Shertzer
Pennsylvania Department of Environmental Protection

David W. Hall
United States Geological Survey

Scott A. Steffey
Alliance for the Chesapeake Bay

Rodney A. Kime
Pennsylvania Department of Environmental Protection

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INTRODUCTION

Background

Atmospheric deposition has emerged as a major environmental problem throughout the northeastern United States. Primary causes have been identified as emissions of sulfur and nitrogen oxides (SO_x and NO_x) resulting from fossil fuel combustion (Lynch, 1990). Emissions of SO_x in the United States totaled 23.21 million short tons (mst) in 1990, while NO_x emissions were listed at 21.36 mst (U.S. EPA, 1992). Although these figures reflect a slight decrease from 1985 levels (23.89 and 21.37 mst respectively), they represent significant environmental loadings.

A review of air emission trends presented by the U.S. Environmental Protection Agency (EPA) geographic regions indicates that Region III (mid-Atlantic - including Pennsylvania) reports emissions of these compounds at or above the national average of all 10 EPA regions ($\text{NO}_x \sim 2.2$ mst/ $\text{SO}_x \sim 3.2$ mst). Region V, an industrial and heavily populated area upwind from Pennsylvania reports levels of these emissions at over twice the national average ($\text{NO}_x \sim 4.0$ mst/ $\text{SO}_x \sim 5.5$ mst) (U.S. EPA, 1992). Pennsylvania contributed 0.56 mst of NO_x and 1.27 mst of SO_x toward these 1990 national and regional emissions (Rodosky, 1993). These figures, combined with those from upwind Region V states (Ohio, Indiana and Illinois) make Pennsylvania precipitation some of the most acidic and nitrogen/sulfate laden in the country.

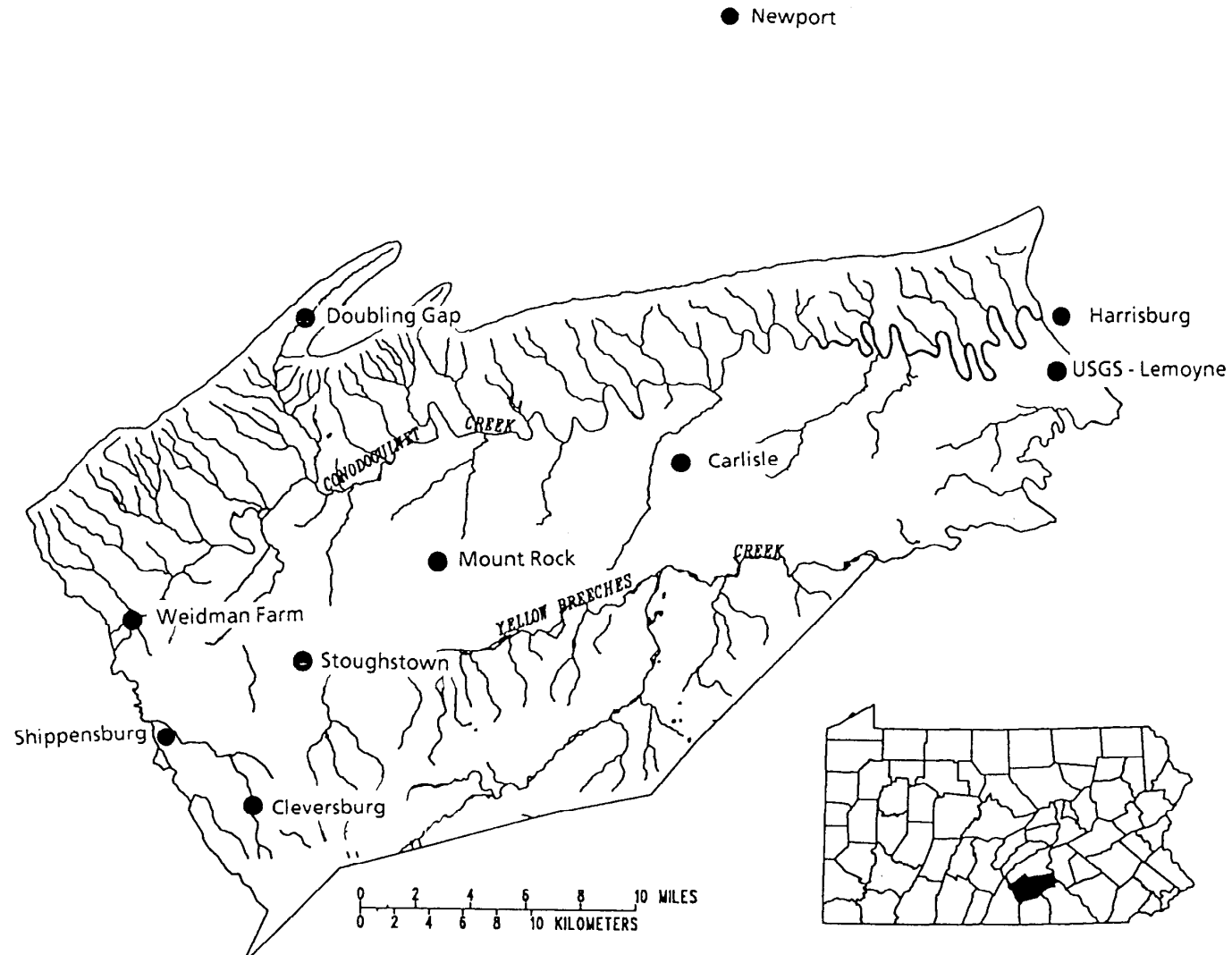
Atmospheric deposition of nitrogen in both precipitation and dryfall is estimated to contribute as much as 25 percent of the annual anthropogenic nitrogen load entering the Chesapeake Bay (Fisher, *et al.* 1988). Other studies indicate that the atmosphere could account for 30-40 percent of the total nitrogen input to the Chesapeake Bay, (STAC, 1994). Nitrogen concentrations in precipitation have been monitored on national and regional scales by the National Atmospheric Deposition Program (NADP) and the Pennsylvania Acid Deposition Monitoring Network (PADMN) but little information exists on local variability or the effects of local sources on precipitation quality. Herbicides are also deposited in precipitation and dryfall but there is very limited information on local variations in atmospheric transport and deposition of such organic contaminants.

Given these national and regional patterns and the paucity of information relating local land use to precipitation quality, a study was designed to monitor nitrogen and herbicide concentrations in precipitation falling on agricultural, forested, and urban areas within or adjacent to the Conodoguinet Creek watershed (a tributary to the Chesapeake Bay via the Susquehanna River) in southcentral Pennsylvania (Figure 1).

The Commonwealth of Pennsylvania, a signatory to the Chesapeake Bay Agreement, is committed to improving Bay water quality and living resources by reducing both nutrient and toxic loads delivered to the Bay via the Susquehanna and Potomac Rivers. This study, a cooperative effort between the Alliance for the Chesapeake Bay (ACB), the Pennsylvania Department of Environmental Protection (DEP) and the United States Geological Survey (USGS), utilized trained citizen volunteers in a data collection effort designed to characterize the spatial and temporal variations in nutrients, major ions, and triazine herbicide concentrations in precipitation. Eight study sites were selected in order to better understand the relationship of these contaminants to prevailing land uses and their potential pathways to the Chesapeake Bay.

An overview of the history of precipitation-quality investigations from the eighteenth century through 1990 is presented by Bowersox (1990). Bowersox summarized precipitation-quality monitoring in the United States, from the first regional effort during the 1950's, through establishment of the National Atmospheric Deposition Program in 1977.

**Figure 1 - Conodoguinet Creek Location Map
and Sampling Sites Cumberland County, PA.**



Research performed by universities and various federal, state and local agencies through 1990 is also discussed. The Environmental Resources Research Institute at Penn State University has also published extensive annual reports since 1982 describing precipitation quality in Pennsylvania.

Precipitation data collected in the northeastern United States during the past 40 years have documented the effects of anthropogenic activities on precipitation quality. Data from the NADP network, the PADMN network, and others (Bowersox and de Pena, 1980) indicate declining rainfall pH, the phenomenon known as "acid rain." Decreased pH in precipitation samples has also been linked to increased concentrations of nitrogen and sulfur, and decreased alkalinity in precipitation samples (Bowersox and de Pena, 1980; Lynch, 1990). Additional data have demonstrated that precipitation samples collected in the northcentral and northeastern United States contain measurable concentrations of pesticides (Stanley et al., 1971; Eisenreich et al., 1981; Richards et al., 1987; Goolsby, 1991; Hatfield et al., 1993; Nations et al., 1993).

While investigations cited above have documented the occurrence and seasonality of pesticides in precipitation over regional and state levels, few data exist describing spatial and temporal variations in precipitation quality within relatively small basins (Berndtsson 1993). Nations et al. (1993) reported slightly lower concentrations of pesticides in precipitation samples collected at urban and undeveloped sites, relative to agricultural areas, and attributed slight differences in numbers of pesticide detections across Iowa to differences in local use of pesticides.

Purpose and Scope

This report provides information on the spatial and temporal variability in concentrations of nutrients, major ions, and herbicides in precipitation collected from 10 stations located at eight sites in the Conodoguinet Creek Basin, Pennsylvania, from 1991-93. Additionally, data from an eleventh station co-located with a site which is part of the PADMN were used to assess comparability of analytical results. Precipitation quality in forested, urban, and agricultural areas is compared and related to local and regional land use patterns. Samples from two stations located adjacent to a manure-storage facility describe localized deposition of ammonium originating from manure-storage facilities.

Description of the Study Area

Conodoguinet Creek originates in the shale and limestone formations of the Great Valley Section of Pennsylvania, approximately 100 miles from its confluence with the Susquehanna River near Harrisburg, Pennsylvania (Figure 1). The Conodoguinet Creek Basin is located in the Chesapeake Bay watershed and comprises approximately 506 square miles of the Valley and Ridge Province in Pennsylvania (U.S. EPA, 1994). Land-surface elevations range from about 1,900 ft in the mountainous headwater areas to approximately 400 ft near the mouth. Headwater reaches (approximately 20 stream miles) drain mountainous, forested terrain until the stream emerges into the fertile Cumberland Valley where it flows for 50 miles through rolling farmland. The final 30 miles drain urban/suburban areas where lands are rapidly being converted to more intense uses (Wilderman, 1989).

Approximately 189.0 square miles (37.3 percent) of the basin is forested (Figure 2). Of the forested land, approximately 179.2 square miles (35.4 percent) is classified as deciduous, 6.3 square miles (1.2 percent) evergreen, and 3.5 square miles (0.7 percent) mixed.

Approximately 34.6 square miles (6.8 percent) of the basin is urban area with 31.2 square miles (6.2 percent) low intensity developed land and 3.4 square miles (0.6 percent) high intensity developed land.

**Figure 2 - Conodoguinet Creek Land Uses
Cumberland County, PA 1994.**



Agricultural land use is classified as herbaceous in the EPA database. Approximately 279.3 square miles (55.2 percent) of the basin is agricultural area. The remaining basin area consists of 3.0 square miles (0.6 percent) water surface, 0.10 square miles (0.02 percent) wetlands, and 0.29 square miles (0.08 percent) exposed rock surfaces.

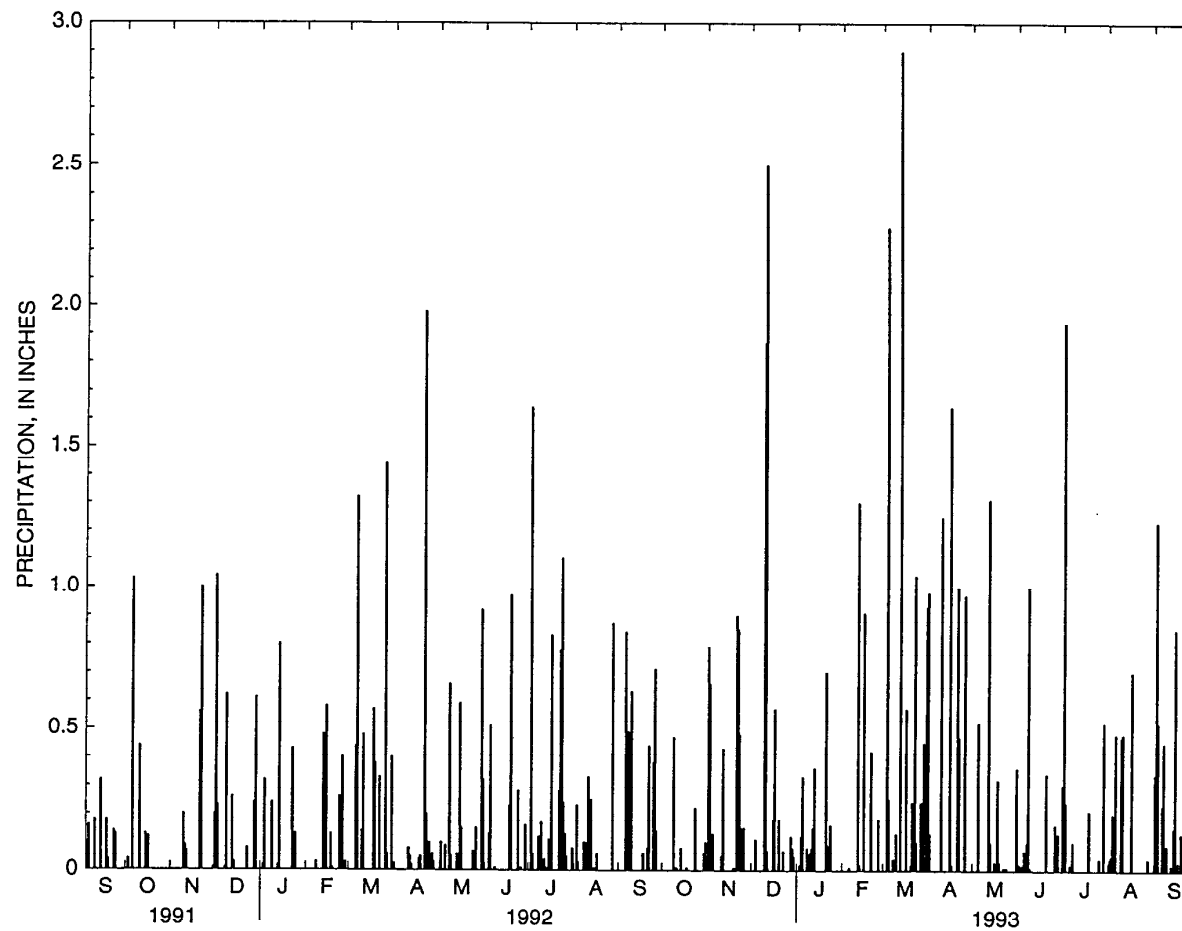
The climate of Pennsylvania is classified as Humid Continental on the Koppen-Geiger Climate Areas map (Yarnel, 1989). However, in the ridge and valley pattern of central Pennsylvania, ridgetops experience more extreme climates than valley bottoms. On average, the mountaintops have lower temperatures, higher winds, and more total precipitation than the valley bottoms.

Most precipitation-producing weather fronts move through Pennsylvania from west to east. In doing so, these systems are lifted by the Allegheny Plateaus forcing much of the moisture to be deposited in the higher elevations to the west of the study area. Average annual precipitation amounts of less than 40 inches per year are common along the western border of Pennsylvania. These averages rise to 42 inches in the western plateau due to the orographic lift described above and then drop to less than 38 inches per year in parts of the Ridge and Valley Region before recovering to higher amounts farther east.

Average annual precipitation in the study area ranges from 40 inches per year in the western parts of the watershed to 42 inches per year in the central and eastern portions. Daily precipitation measured during the study period at the National Oceanic and Atmospheric Administration gage in Shippensburg, Pennsylvania is displayed in Figure 3.

These data indicate that the fall of 1991 was relatively dry (-4.03 inches - compared to long-time average precipitation at this site), March - November of 1992 was wetter than average (+3.34 inches) and March - September of 1993 was also wet (+6.34 inches) making the total departure from established normal rainfall +5.65 inches for the study period. (NOAA 1991, 1992, 1993).

Figure 3 - Daily Precipitation, September 1991 - September 1993
National Oceanic and Atmospheric Administration Gage
Shippensburg, PA.



Description of the Project

Precipitation samples were collected from September 1991 to September 1993 at 10 stations located in the Conodoguinet Creek Basin (Figure 1). Spring, summer, and fall precipitation events were sampled. Winter samples were not collected because rainfall froze in the collection apparatus and because samplers were not designed to sample snowfall. Two precipitation-monitoring stations were located in forested areas, two in urban areas, two in agricultural areas, two were located adjacent to (~50 ft.) a manure-storage facility and two stations were located adjacent to the Lemoyne urban site for quality control. Paired stations were placed in each land-use area to ensure that at least one sample representing each land-use type would be collected during sampled precipitation events and to provide data to assess variability within each area.

Additionally, one station was located in Little Buffalo State Park near Newport, Pennsylvania, adjacent to a precipitation station of the PADMN to provide data for quality control.

Specific study objectives include the following:

1. Define nutrient, major ion, and triazine herbicide concentrations in precipitation samples from the Conodoguinet Creek basin.
2. Compare nutrient, major ion, and triazine herbicide concentrations in precipitation samples from agricultural, forested, and urban areas in the Conodoguinet Creek Basin.
3. Assess the potential for manure-holding facilities to contribute to atmospheric deposition of nitrogen.
4. Test the capacity for precipitation collection stations to preserve the chemical integrity of nutrient, major ion, and triazine herbicide samples for varying time intervals.
5. Assess the practicality of using volunteer citizen monitors in an intensive and extensive scientific study.

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Forested Sites

- | | |
|-------------------------------------|--|
| 1. Cleversburg | Mark and Arlene Lipper/
Janet Adams |
| 2. Doubling Gap (Col Denning St Pk) | Ken Boyles/Steve Mell |

Agricultural Sites

- | | |
|---------------------------------|-------------------|
| 3. Mount Rock (Main Farm) | Herb Auhlenbacher |
| 4. Stoughstown (Stambaugh Farm) | Tom McCarty |

Urban Sites

- | | |
|----------------------------------|----------------------------|
| 5. Carlisle (Linah's Auto Sales) | Bill Turner |
| 6. Lemoyne (USGS building) | Bob Diethorn/Walter Wilson |

Manure Storage Sites

- | | |
|---------------------|---------------------------|
| 7 & 8. Weidman Farm | Dave Smythe/Kim Van Fleet |
|---------------------|---------------------------|

Quality Assurance Sites

- | | |
|-----------------------------------|----------------------------|
| 9. Newport (Little Buffalo St Pk) | Walt Griffith |
| 10. Lemoyne (USGS building) | Walter Wilson/Bob Diethorn |

Fixed-Interval Site

- | | |
|-----------------------------|----------------------------|
| 11. Lemoyne (USGS building) | Walter Wilson/Bob Diethorn |
|-----------------------------|----------------------------|

METHODS

Data Collection

Precipitation was monitored during spring, summer, and fall for a two year period (September 1991 – September 1993) from the sites listed in Table 1 and illustrated in Figure 1. Quality assurance was provided by co-locating a collector at an existing PADMN site north of the watershed (Little Buffalo State Park near Newport) and by analyzing replicate storm samples from a second collector located at the Lemoyne urban site.

A third collector was located at the Lemoyne urban site from which weekly fixed interval samples were collected during the first year of the study. This was done to evaluate the capacity of the sampling equipment to preserve the chemical integrity of the precipitation samples over time. During the course of the study, weekly intervals with only one precipitation event provided an opportunity to analyze and compare the results of samples collected immediately after cessation of a rainfall event with samples of the same event retrieved from the collector between 1 and 8 days later.

TABLE 1
Sampling Sites - Conodoguinet Creek Watershed

Site Description	Elev. (ft)	USGS Quad.	Lat./Long.		Prevailing Land Use
Cleversburg, South Mountain	880	Walnut Bottom	400136	772750	Forested
Doubling Gap, Col Denning St Pk	780	Andersonburg	401631	772529	Forested
Mount Rock, Main Farm	620	Plainfield	400859	771959	Agricultural
Stoughstown, Stambaugh Farm	630	Walnut Bottom	400559	772540	Agricultural
Shippensburg, Weidman Farm (E)	540	Shippensburg	400717	773248	Manure storage
Shippensburg, Weidman Farm (N)	540	Shippensburg	400717	773248	Manure storage
Carlisle, Linah's Auto Sales	470	Carlisle	401155	770951	Urban
Lemoyne, USGS Office	420	Lemoyne	401436	765414	Urban
Newport, Little Buffalo State Park	480	Newport	402749	770859	Q/A Site
Lemoyne (replicate), USGS Office	420	Lemoyne	401436	765414	Q/A Site
Lemoyne (fixed interval) * USGS Office	420	Lemoyne	401436	765414	Q/A Site

* Fixed Interval collector at Lemoyne urban site established to test the capacity of collector to preserve the chemical integrity of samples over varying time intervals.

At each sampling site, collectors were located to accommodate the following requirements which were modified from NADP criteria.

- No structure, tree or wire bisecting a 45° angle extending from the top of the collector.
- No structure within 100 feet of collector
- No road within 100 feet of collector
- Maintain annual vegetation height <2 feet

- Top of funnel set at 5 feet above ground surface
- Rain gage attached to opposite side of support pole from collector and far enough below the lip of the collector funnel to preclude the possibility of sample contamination by splash from the gage.

Precipitation collectors were designed to minimize cost while promoting accuracy and simplicity of use. Figure 4 depicts the design of the collector used at each site. Silicon caulk provided a seal between the funnel and the plexiglass base plate. The stem of the funnel extended into the mouth of the sample bottle and bottle caps (when not in use) were stored in plastic bags inside the PVC cylinder which formed the body of the collector.

Citizen volunteers were recruited and trained to collect samples from significant rainfall events (>0.1 inches) occurring at or near their homes in accordance with the procedures described in Appendix A. The entire effort was orchestrated by the “project coordinator” who provided training, maintained equipment and supplies, supervised quality assurance, performed field measurements, and monitored weather forecasts to coordinate sampling of “significant” rainfall events at multiple locations. Glass collection funnels were exposed to the atmosphere no longer than 8 hours prior to and 12 hours after a rainfall event (except at the fixed interval site). Samples were collected in 1 liter brown glass bottles which were sealed with teflon lined caps and refrigerated or iced within 12 hours of the rainfall event. Because of the need to analyze samples for pesticides, funnels were rinsed with hexane and deionized water and stored in sealed plastic bags between uses. Sample bottles were baked at 300°C for a minimum of 8 hours before use to remove organic residues. Rainfall amounts were recorded for each sample.

Samples collected by volunteers were packed in ice and transported by the project coordinator to the USGS laboratory in Lemoyne where “field analyses” were completed and sample aliquots were prepared/preserved for shipment to the USGS Laboratory in Denver as described below. Additionally, a small aliquot (20–40 ml) was removed and analyzed for triazines at Lemoyne using immunoassay methods (Goolsby et al., 1990). Triazine screening results were verified by analyzing 15 percent of the samples with solid phase extraction performed by the USGS Denver Laboratory. Samples scheduled for triazine analysis in Denver were filtered by the project coordinator in Lemoyne prior to shipment. A list of the analyses performed in the Denver laboratory and their detection limits is presented in Table 2.

Figure 4 - Rainfall Collector Assembly.

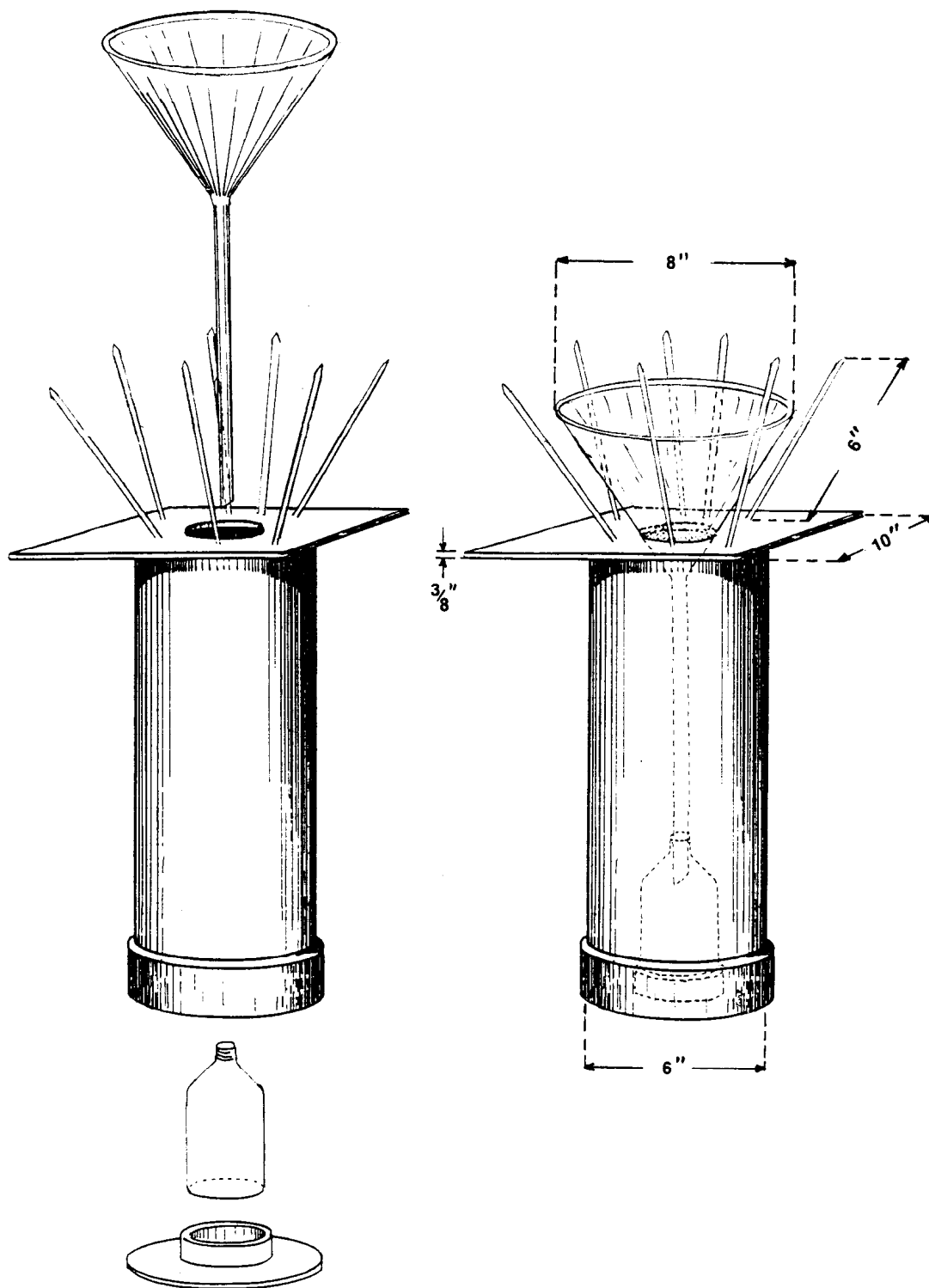


TABLE 2
Analytical Methods and Detection Limits

<u>Parameter</u>	<u>USGS WATSTORE Code</u>	<u>Method Description</u> ^{1,2}	<u>Method Detection Limit</u>
<u>Dissolved Nutrients</u>			
Ammonium (as NH ₄)	71846	Autoanalyzer	0.01 mg/L
Ammonia (as N)	00608	Autoanalyzer	0.01 mg/L
NO ₂ +NO ₃ (as N)	00631	Autoanalyzer	0.01 mg/L
pH	00400	Electrometric-Ross probe	0.01 pH units
Alkalinity	00410	Gran titration	0.1 mg/L
Hardness	00900	Calculated value	
Specific conductance	00095	Electrometric	1 us/cm
Nitrate (total as N)	00620	Ion exchange chromatographic	0.01 mg/L
Orthophosphate (dissolved as P)	00671	Ion exchange chromatographic	0.001 mg/L
Silica (dissolved)	00955	Inductively coupled plasma	0.009 mg/L
<u>Dissolved Anions</u>			
Bromide	71870	Ion chromatography	0.01 mg/L
Chloride	00940	Ion chromatography	0.01 mg/L
Fluoride	00950	Ion chromatography	0.01 mg/L
Nitrate (as N)	00618	Ion chromatography	0.01 mg/L
Orthophosphate (as PO ₄)	00660	Ion chromatography	0.01 mg/L
Sulfate	00945	Ion chromatography	0.01 mg/L
<u>Dissolved Cations</u>			
Calcium	00915	Inductively coupled plasma	0.02 mg/L
Magnesium	00925	Inductively coupled plasma	0.001 mg/L
Manganese	01056	Inductively coupled plasma	0.001 mg/L
Iron	01046	Inductively coupled plasma	0.003 mg/L
Sodium	00930	Inductively coupled plasma	0.2 mg/L
Potassium	00935	Atomic absorption spectrophotometric	0.01 mg/L
Triazines	34757	Immunoassay	0.1 µg/L

¹ Methods for determination of inorganic substances in water described in Fishman and Friedman, 1989.

² Immunoassay techniques for triazine analysis described in Vanderlaan and others (1990), Thurman et al. (1990), and Goolsby et al. (1990).

Sample handling and analysis were dependent on the volume of rainwater collected. All samples received “field analyses” for pH, alkalinity, and specific conductance. In addition, the triazine screening using immunoassay was performed on 50 samples. Laboratory analyses were performed according to the schedule presented in Table 3. Numbers in parentheses in the second column of Table 3 indicate the priority of analysis for samples with limited volume.

TABLE 3
Laboratory Analysis Schedule
Conodoguinet Creek Study

Sample Size	Analyses	Sample Handling
250 mL	(1) <u>Dissolved Nutrients</u> Ammonia Nitrite & Nitrate	125 mL filtered (0.1µ), preserved w/HgCl ₂ and iced
	(2) pH (2) Alkalinity (2) Hardness (2) Specific Conductance (2) Nitrate (total) (2) Orthophosphate (as P) (2) Silica	125 mL iced
375 mL	(1) <u>Dissolved Nutrients</u> Ammonia Nitrite & Nitrate	125 mL filtered (0.1µ), preserved w/HgCl ₂ and iced
	(2) pH (2) Alkalinity (2) Hardness (2) Specific Conductance (2) Nitrate (total as N) (2) Orthophosphate (as P) (2) Silica	125 mL iced
	(3) <u>Dissolved Anions</u> Bromide Chloride Fluoride Nitrate Orthophosphate (as PO ₄) Sulfate (3) <u>Dissolved Cations</u> Calcium Magnesium Manganese Iron Sodium Potassium	125 mL filtered (0.1µ), preserved with H ₂ NO ₃ and iced

The major ion analyses listed above were performed on approximately 10 percent of the samples in order to calculate an ionic balance for QA/QC purposes.

Data Analysis

Monitoring stations were located to enable statistical analysis of data within and between land-use areas. Basic statistics (number of samples, mean, range) were calculated using the Statistical Analysis System (SAS Institute Inc., 1989) to characterize the physical/chemical quality of precipitation samples from the Conodoguinet Creek basin (Objective 1), while a nested analysis of variance was used to test for differences in rainfall parameter concentrations within and between land use types (Objective 2). SAS/LAB (SAS Institute Inc., 1992) software diagnostics were first applied to determine if data transformation or censoring of extreme values was appropriate. Time-series plots were used to test for seasonality in constituent concentrations.

To assess the potential for manure-holding facilities to contribute to atmospheric deposition of nitrogen (Objective 3), T-tests were used, also preceded by SAS diagnostics for data transformation. The same approach was used to evaluate the capacity of the fixed interval collector to maintain the physical/chemical integrity of precipitation samples up to seven days (Objective 4).

Replicate samples collected at the urban site and comparison samples collected from the Newport site provided quality assurance checks on sample and sampler handling/transport. Ion balance and conductance balance calculations were also used to assess the quality of the data. This information was used to help assess the efficacy of the volunteer monitoring effort (Objective 5).

RESULTS & DISCUSSION

Characterization of Precipitation Quality

Table 4 presents summary statistics for the results of chemical analyses completed during this study. Values for dissolved silica are not listed because all 46 analyses were reported as <0.1 mg/L.

TABLE 4
Summary Statistics

pH - UNITS (field)

LAND USE	#OBS.	MEAN	STD. DEV.	MEDIAN	MIN.	MAX.
1. Forest	40	5.8	-	4.6	3.7	7.0
2. Agriculture	36	5.9	-	4.6	3.7	6.8
3. Urban	35	5.2	-	4.5	3.7	6.7
4. Manure Pit	31	6.6	-	4.9	3.7	8.0
5. Overall	142	6.1	-	4.6	3.7	8.0

TOTAL ALKALINITY - MG/L as CaCO₃ (field)

LAND USE	#OBS.	MEAN	STD. DEV.	MEDIAN	MIN.	MAX.
1. Forest	7	1.9	0.90	2	1	3
2. Agriculture	7	2.9	2.79	2	1	9
3. Urban	6	1.2	0.41	1	1	2
4. Manure Pit	7	2.1	2.03	1	1	6
5. Overall	27	2.0	1.80	1	1	9

CONDUCTIVITY - US/CM (field)

LAND USE	#OBS.	MEAN	STD. DEV.	MEDIAN	MIN.	MAX.
1. Forest	13	51.4	36.2	53	5	127
2. Agriculture	15	46.1	23.2	50	5	88
3. Urban	14	50.2	41.6	47	5	173
4. Manure Pit	9	90.2	80.4	48	27	260
5. Overall	51	56.4	47	48	5	260

TOTAL HARDNESS - MG/L as CaCO₃

LAND USE	#OBS.	MEAN	STD. DEV.	MEDIAN	MIN.	MAX.
1. Forest	12	0.9	0.29	1	0	1
2. Agriculture	12	0.9	0.79	1	0	3
3. Urban	12	1.2	1.02	1	0	4
4. Manure Pit	5	0.8	0.45	1	0	1
5. Overall	41	1.0	0.72	1	0	4

DISSOLVED CALCIUM - MG/L

LAND USE	#OBS.	MEAN	STD. DEV.	MEDIAN	MIN.	MAX.
1. Forest	13	0.25	0.12	0.29	0.10	0.46
2. Agriculture	14	0.25	0.18	0.21	0.10	0.84
3. Urban	12	0.37	0.39	0.26	0.11	1.50
4. Manure Pit	7	0.21	0.10	0.18	0.10	0.33
5. Overall	46	0.27	0.24	0.22	0.10	1.50

DISSOLVED MAGNESIUM - MG/L

LAND USE	#OBS.	MEAN	STD. DEV.	MEDIAN	MIN.	MAX.
1. Forest	13	0.04	0.03	0.04	0.01	0.09
2. Agriculture	14	0.04	0.04	0.03	0.01	0.17
3. Urban	12	0.06	0.05	0.05	0.01	0.18
4. Manure Pit	7	0.03	0.02	0.03	0.02	0.06
5. Overall	46	0.05	0.04	0.04	0.01	0.18

DISSOLVED POTASSIUM - MG/L

LAND USE	#OBS.	MEAN	STD. DEV.	MEDIAN	MIN.	MAX.
1. Forest	13	0.12	0.08	0.10	0.04	0.34
2. Agriculture	14	0.29	0.6 0	0.08	0.03	2.30
3. Urban	12	0.28	0.51	0.08	0.02	1.60
4. Manure Pit	7	0.24	0.31	0.10	0.04	0.76
5. Overall	46	0.23	0.44	0.08	0.02	2.30

DISSOLVED FLUORIDE - MG/L

LAND USE	#OBS.	MEAN	STD. DEV.	MEDIAN	MIN.	MAX.
1. Forest	13	0.03	0.02	0.02	0.01	0.08
2. Agriculture	14	0.04	0.03	0.03	0.01	0.09
3. Urban	12	0.07	0.05	0.06	0.01	0.19
4. Manure Pit	7	0.03	0.02	0.02	0.01	0.05
5. Overall	46	0.04	0.04	0.03	0.01	0.19

DISSOLVED IRON - UG/L

LAND USE	#OBS.	MEAN	STD. DEV.	MEDIAN	MIN.	MAX.
1. Forest	13	11.5	5.5	9.0	6	25
2. Agriculture	14	9.5	3.4	9.5	3	14
3. Urban	12	10.2	4.5	9.0	4	19
4. Manure Pit	7	8.6	2.9	8.0	6	14
5. Overall	46	10.1	4.3	9.0	3	25

DISSOLVED MANGANESE - UG/L

LAND USE	#OBS.	MEAN	STD. DEV.	MEDIAN	MIN.	MAX.
1. Forest	13	2.8	1.2	3.0	1	5
2. Agriculture	14	2.2	1.1	2.0	1	4
3. Urban	12	2.8	1.8	3.0	1	6
4. Manure Pit	7	2.9	1.5	2.0	1	5
5. Overall	46	2.6	1.4	3.0	1	6

DISSOLVED BROMIDE - MG/L

LAND USE	#OBS.	MEAN	STD. DEV.	MEDIAN	MIN.	MAX.
1. Forest	13	0.012	0.01	0.01	0.01	0.04
2. Agriculture	14	0.02	0.02	0.01	0.01	0.10
3. Urban	12	0.02	0.03	0.01	0.01	0.13
4. Manure Pit	7	0.02	0.03	0.01	0.01	0.09
5. Overall	45	0.017	0.03	0.01	0.01	0.13

DISSOLVED SODIUM - MG/L

LAND USE	#OBS.	MEAN	STD. DEV.	MEDIAN	MIN.	MAX.
1. Forest	2	-	-	-	0.2	0.2
2. Agriculture	2	-	-	-	0.2	0.3
3. Urban	2	-	-	-	0.3	0.3
4. Manure Pit	2	-	-	-	0.3	0.3
5. Overall	8	0.26	0.05	0.30	0.2	0.3

DISSOLVED SULFATE- MG/L

LAND USE	#OBS.	MEAN	STD. DEV.	MEDIAN	MIN.	MAX.
1. Forest	13	2.00	1.23	1.90	0.42	4.8
2. Agriculture	14	2.19	1.42	2.05	0.47	5.3
3. Urban	12	2.77	1.55	2.70	0.52	4.8
4. Manure Pit	7	2.55	1.41	2.70	0.66	4.2
5. Overall	46	2.36	1.41	2.30	0.42	5.3

DISSOLVED CHLORIDE - MG/L

LAND USE	#OBS.	MEAN	STD. DEV.	MEDIAN	MIN.	MAX.
1. Forest	13	0.58	0.53	0.41	0.01	1.60
2. Agriculture	14	0.32	0.18	0.34	0.01	0.57
3. Urban	12	0.60	0.46	0.45	0.24	1.90
4. Manure Pit	7	0.38	0.24	0.28	0.11	0.76
5. Overall	46	0.48	0.40	0.39	0.01	1.90

DISSOLVED ORTHOPHOSPHATE - MG/L AS PO₄

LAND USE	#OBS.	MEAN	STD. DEV.	MEDIAN	MIN.	MAX.
1. Forest	21	0.05	0.05	0.03	0.01	0.20
2. Agriculture	21	0.16	0.34	0.05	0.00	1.60
3. Urban	18	0.06	0.07	0.04	0.00	0.29
4. Manure Pit	17	0.07	0.05	0.01	0.01	0.20
5. Overall	77	0.09	0.19	0.04	0.00	1.60

DISSOLVED ORTHOPHOSPHATE - MG/L AS P

LAND USE	#OBS.	MEAN	STD. DEV.	MEDIAN	MIN.	MAX.
1. Forest	25	0.016	0.014	0.010	.002	0.065
2. Agriculture	24	0.050	0.109	0.013	.001	0.537
3. Urban	20	0.020	0.024	0.010	.001	0.096
4. Manure Pit	19	0.022	0.018	0.014	.002	0.066
5. Overall	88	0.027	0.060	0.012	.001	0.537

DISSOLVED AMMONIA - MG/L AS N

LAND USE	#OBS.	MEAN	STD. DEV.	MEDIAN	MIN.	MAX.
1. Forest	21	0.42	0.32	0.31	0.04	1.3
2. Agriculture	21	0.58	0.37	0.56	0.09	1.6
3. Urban	18	0.62	0.41	0.57	0.06	1.5
4. Manure Pit	15	0.70	0.38	0.79	0.20	1.2
5. Overall	75	0.57	0.38	0.46	0.04	1.6

DISSOLVED AMMONIUM - MG/L AS NH₄

LAND USE	#OBS.	MEAN	STD. DEV.	MEDIAN	MIN.	MAX.
1. Forest	21	0.55	0.43	0.40	0.05	1.7
2. Agriculture	21	0.75	0.49	0.72	0.11	2.1
3. Urban	18	0.80	0.53	0.74	0.08	1.9
4. Manure Pit	15	0.90	0.48	1.00	0.26	1.5
5. Overall	75	0.73	0.49	0.59	0.05	2.1

DISSOLVED NITRATE - MG/L AS N

LAND USE	#OBS.	MEAN	STD. DEV.	MEDIAN	MIN.	MAX.
1. Forest	13	0.32	0.12	0.30	0.10	0.56
2. Agriculture	14	0.36	0.12	0.33	0.21	0.58
3. Urban	11	0.39	0.20	0.42	0.01	0.72
4. Manure Pit	7	0.35	0.14	0.38	0.13	0.49
5. Overall	45	0.34	0.15	0.34	0.01	0.72

TOTAL NITRATE - MG/L AS N

LAND USE	#OBS.	MEAN	STD. DEV.	MEDIAN	MIN.	MAX.
1. Forest	21	0.42	0.25	0.40	0.08	1.00
2. Agriculture	21	0.42	0.22	0.39	0.16	0.98
3. Urban	18	0.53	0.32	0.51	0.09	1.30
4. Manure Pit	17	0.64	0.45	0.47	0.10	1.50
5. Overall	77	0.50	0.32	0.44	0.08	1.50

DISSOLVED NITRITE + NITRATE - MG/L AS N

LAND USE	#OBS.	MEAN	STD. DEV.	MEDIAN	MIN.	MAX.
1. Forest	21	0.42	0.25	0.40	0.08	1.00
2. Agriculture	21	0.43	0.22	0.39	0.16	0.98
3. Urban	18	0.54	0.32	0.52	0.09	1.30
4. Manure Pit	17	0.64	0.45	0.47	0.10	1.50
5. Overall	77	0.50	0.32	0.44	0.08	1.50

TRIAZINE - UG/L

LAND USE	#OBS.	MEAN	STD. DEV.	MEDIAN	MIN.	MAX.
1. Forest	39	0.23	0.49	0.1	0.1	3.0
2. Agriculture	33	0.25	0.47	0.1	0.1	2.0
3. Urban	35	0.15	0.13	0.1	0.1	0.6
4. Manure Pit	30	0.18	0.18	0.1	0.1	0.8
5. Overall	137	0.21	0.36	0.1	0.1	3.0

Major Ions

Analyses of samples collected during the study period confirm that rainfall is a relatively pure solution, low in dissolved solids. Specific conductance of all samples collected during the study period ranged from 5 to 260 $\mu\text{S}/\text{cm}$ with a median value of 48 $\mu\text{S}/\text{cm}$ (Table 4). Dissolved phosphate values were low (median = 0.04 mg/L) while total nitrate and dissolved ammonium levels were relatively high (median = 0.44 mg/L and 0.59 mg/L respectively). Dissolved calcium ranged from 0.1–1.5 mg/L with a median value of 0.22 mg/L and sulfates were present in dissolved concentrations between 0.42 mg/L and 5.3 mg/L (median=2.3 mg/L). Hardness never exceeded 4 mg/L.

Quality Assurance

Over 50 samples were collected and analyzed for major ions to provide information on precipitation quality and for project quality control. Because rainfall is a dilute, low-ionic strength solution, trace cations and anions that are insignificant components of typical surface or groundwater ion balance may be important in rainfall chemistry. Therefore, a complete ion balance is difficult to attain in rainfall-sample analysis. This problem is compounded by the fact that, in this study, only a limited number of samples contained sufficient volume to allow for a complete analysis of major ions.

Table 5 illustrates the ionic strength and composition of a sample collected during the study period. The alkalinity value used in this calculation is the field value measured at the time of sample collection. All other concentrations (except sodium) were obtained from laboratory analyses. Sodium was absent from the lab analyses performed during the first year of the study but was estimated using the median value of all sodium samples collected during the second year. When sodium is included in the calculation, the balance between positive and negative electrical charges in solution is off by 0.4 percent. This is well within the 20 percent range normally considered acceptable for evaluating the precision of rainfall chemical analyses.

TABLE 5
Typical Partial Ion Balance
Southcentral Pennsylvania Rainfall
September 25, 1992

DISSOLVED CATIONS	CONCENTRATION (MG/L) (MEQ/L)	DISSOLVED ANIONS	CONCENTRATION (MG/L) (MEQ/L)
Calcium	0.220 0.011	Chloride	0.570 0.016
Magnesium	0.090 0.007	Sulfate	0.590 0.012
Potassium	2.300 0.059	Fluoride	0.080 0.004
Iron	0.013 0.0005	Nitrate (as N)	0.480 0.034
Manganese	0.003 0.0001	Alk. (Tot. as CaCO_3)	1.450 0.029
Ammonium (as NH_4)	0.200 0.011	Phosphate	0.240 0.007
Sodium*	0.300 0.013		
TOTAL	0.101	TOTAL	0.102

Percent Difference = 0.4

*generic value representing the mean of all sodium analyses conducted

Among the cations present in rainfall, calcium, magnesium, potassium, ammonium, and sodium have proportionally greater effects on sample ion balances than the small concentrations of iron and manganese. All anions have a substantial effect on sample ion balances but phosphate and fluoride, exert the least influence because they are present in relatively low concentrations.

Fifteen samples were found to have analytical results complete enough to allow for ion balance calculations as displayed in Table 5. The percent difference between positive and negative charge attributable to ionic constituents in these samples as well as the percent difference between measured and calculated conductance is illustrated in Table 6. Eight of the 15 samples demonstrate ion balances with less than a 20 percent difference and, 13 of 15 samples are within 30 percent. Conductance balance calculations are more difficult to interpret. Where field conductivity measurements are available, comparisons between those values and conductivity calculated from the sum of major ions are acceptable (within 20 percent) 88 percent of the time. Comparisons made to laboratory conductivity measurements are acceptable 73 percent of the time.

TABLE 6
Partial Ion Balance and Conductance Balance Calculations
Southcentral Pennsylvania Rainfall
1991 - 1993

Date	Location	ION Balance (meq/L)			Conductance Balance (µs/cm)				
		ΣCations	ΣAnions	Percent Difference	Calculated Conductivity	Measured Conductivity		Percent Difference	
						Field	Lab	Field	Lab
4/21/92	Mount Rock	0.048	0.078	24	10.9	-	8	-	15
4/21/92	Cleversburg	0.042	0.044	2	5.5	-	6	-	4
6/18/92	Lemoyne	0.139	0.173	11	24.1	-	21	-	7
8/27/92	Stoughstown	0.102	0.116	6	11.2	-	16	-	18
8/28/92	Weidman E	0.043	0.070	24	9.0	-	12	-	14
8/28/92	Weidman N	0.067	0.047	17	9.2	-	5	-	29
9/9/92	Lemoyne (Fixed Interval)	0.109	0.088	11	13.4	19	19	17	17
9/25/92	Stoughstown	.028	.061	37	4.7	5	5	3	3
9/25/92	Mount Rock	0.102	0.105	1	15.4	15	17	1	5
9/25/92	Carlisle	0.079	0.056	17	10.5	11	11	2	2
9/25/92	Lemoyne	0.026	0.046	28	4.1	5	8	10	32
9/25/92	Lemoyne (replicate)	0.027	0.052	32	5.2	6	9	7	27
9/25/92	Doubling Gap	0.046	0.073	23	8.6	5	11	26	12
9/25/92	Cleversburg	0.035	0.065	30	6.5	6	11	4	26
9/25/92	Newport	0.042	0.057	15	7.5	6	9	11	9

To further evaluate the quality of analytical results, comparisons are made between results from samples collected at Newport during this study and ongoing PADMN monitoring at the same location. This comparison is difficult to make because PADMN values previously reported by Lynch (1992, 1993 and 1994) at the Newport (Little Buffalo State Park) PADMN site represent fixed interval collections expressed as precipitation weighted means while the results of this study were obtained from individual storm events. Table 7 compares Lynch's raw data (weekly unweighted values) from the PADMN site at Newport with individual storms monitored at this site during the same time frame. Although these two methods of monitoring differ and the sites were not precisely co-located (~400 yds. apart), the data display reasonable agreement with major ion concentrations for 51 of 76 data pairs falling within approximately 25 percent of each other. Agreement between the data sets was best for pH, conductance, sulfate, nitrate, ammonium, and magnesium and worst for calcium, potassium, and chlorides. Larger differences, such as those noted during the weeks of June 16, August 25 and September 22, 1992 are probably due either to the fact that the PADMN site collected multiple rainfall events which are being compared to a single storm sampled for this study, or single storm events captured at the PADMN collector changed in physical/chemical composition due to biological activity within the sample as it was held in the collector during the week.

Another way to assess the quality of data generated during this study is to compare the true replicate samples collected at Lemoyne (Table 8). These data show very minimal variation with 95 percent of the paired results falling within the 25 percent range for acceptability.

The results of replicate samples collected at Lemoyne, PADMN vs. study collectors deployed at Newport and the ion balance/conductance balance calculations discussed earlier indicate that the data collected during this study are of acceptable accuracy and precision for the purposes of this report.

TABLE 7
Comparison of Mean Concentrations of Major Dissolved Ions
found in Rainfall at Newport, Pennsylvania 1991-1993 *

PARAMETER CONCENTRATIONS (mg/L)

Date	Ca	Mg	K	Na	NH ₄	NO ₃	Cl	SO ₄	pH	Sp Cond
Week of Sep 3, 1991	0.08	0.01	0.02	0.03	0.31	1.73	0.15	3.58	4.15	30
Sep 4-5, 1991	-	-	-	-	-	-	-	-	4.3	-
Week of Sep 17, 1991	0.09	0.01	0.03	0.03	0.29	2.26	0.16	3.81	4.05	42
Sep 18-19, 1991	-	-	-	-	-	-	-	-	4.1	63
Week of Sep 24, 1991	0.10	0.02	0.02	0.05	0.99	5.10	0.30	7.72	3.82	75
Sep 24-25, 1991	-	-	-	-	1.00	3.66	-	-	4.1	69
Week of Oct 1, 1991	0.14	0.02	0.04	0.10	0.47	2.02	0.13	2.49	4.27	30
Oct 5-7, 1991	0.12	0.01	0.05	-	0.35	1.68	0.15	1.70	4.3	28
Week of Mar 10, 1992	0.14	0.01	0.01	0.05	0.21	2.03	0.22	2.05	4.25	29
Mar 10-11, 1992	-	-	-	-	0.37	-	-	-	4.8	-
Week of Jun 16, 1992	0.07	0.02	0.02	0.03	0.27	1.73	0.15	2.93	4.23	31
Jun 18-20, 1992	0.24	0.04	0.07	-	0.37	<0.04	1.1	3.40	4.3	-
Week of Jul 7, 1992	0.22	0.04	0.03	0.10	0.21	2.39	0.17	3.68	4.04	44
Jul 8-9, 1992	-	-	-	-	-	-	-	-	4.0	-
Week of Aug 25, 1992	0.17	0.03	0.01	0.05	0.21	1.23	0.12	3.14	4.28	27
Aug 27-29, 1992	0.36	0.06	0.16	-	0.29	1.51	0.43	2.5	4.4	-
Week of Sep 22, 1992	0.01	0.001	0.004	0.02	0.056	0.35	0.053	0.67	4.88	8
Sep 25-27, 1992	0.24	0.06	0.06	-	0.18	1.33	0.39	0.85	5.8	6
Week of Mar 23, 1993	0.03	0.01	0.02	0.04	0.27	1.56	0.19	2.03	4.24	27
Mar 23-24, 1993	0.14	0.02	0.06	-	0.31	1.86	0.17	2.3	4.8	25
Week of Apr 20, 1993	0.04	0.01	0.03	0.01	0.20	1.10	0.09	1.88	4.36	21
Apr 26-27, 1993	0.15	0.02	0.03	0.3	0.31	1.33	0.48	2.3	4.7	-
Week of May 18, 1993	0.37	0.07	0.04	0.02	1.44	5.55	0.28	6.50	3.86	71
May 18-19, 1993	-	-	-	-	1.3	-	-	-	4.1	-
Week of Jun 29, 1993	0.04	0.01	0.01	0.04	0.24	1.57	0.17	3.03	4.10	34
Jul 1-3, 1993	0.15	0.03	0.05	-	0.36	1.73	<0.01	3.4	4.3	35
Week of Aug 3, 1993	0.08	0.01	0.05	0.04	0.46	2.06	0.29	3.48	4.09	37
Aug 6-7, 1993	-	-	-	-	0.53	-	-	-	-	-

* First row of each pair - Weekly PADMN data
 Second row of each pair - Individual storm from this study.
 Paired data points in **bold face** type differ by > 25 percent.

TABLE 8
Results of Replicate Samples
Lemoyne Urban Site
1991 - 1993*

PARAMETERS

Date	Field pH (units)	Conduc- tivity (µs/cm)	Dissolved Ammonia (mg/L as N)	Total Nitrate (mg/L as N)	Dissolved Ortho- phosphate (mg/L)	Dissolved Calcium (mg/L)	Dissolved Magne- sium mg/L	Dissolved Potas- sium mg/L	Dissolved Chloride mg/L	Dissolved Sulfate mg/L	Dissolved Fluoride mg/L	Dissolved Iron (µg/L)	Dissolved Mangan- ese (µg/L)	Triazine Herbicides (Screening) (µg/L)
10/5/91	4.5	173	0.171	0.183	0.01	0.11	0.01	0.03	0.40	1.4	<0.10	6	1	<0.1
Replicate	4.5	173	0.142	0.183	0.02	<0.10	0.01	0.03	0.10	1.4	<0.10	9	<1	<0.1
4/21/92	5.1	42	0.134	0.173	0.02	0.24	0.04	0.04	0.50	1.3	<0.10	4	<1	0.1
Replicate	4.8	-	0.113	0.157	0.02	0.13	0.03	0.04	0.59	1.0	0.04	74	<1	0.5
6/18/92	5.2	-	0.485	0.545	-	1.5	0.18	0.07	0.39	4.3	0.15	7	5	0.4
Replicate	4.8	-	0.524	0.555	0.01	0.99	0.11	0.08	0.53	4.1	0.12	11	3	0.4
9/25/92	5.5	5	0.059	0.092	0.01	0.12	0.02	0.02	0.44	0.52	0.07	5	1	<0.1
Replicate	5.6	6	0.082	0.090	0.02	<0.10	0.02	0.04	0.66	0.52	0.05	5	<1	<0.1
3/23/93	4.6	26	0.561	0.538	0.03	0.69	0.13	0.16	1.9	3.6	0.07	13	6	<0.1
Replicate	4.5	29	0.505	0.564	0.05	0.65	0.06	0.06	0.45	3.2	0.03	15	3	<0.1
7/1/93	4.1	53	0.583	0.553	0.02	0.28	0.04	0.04	0.46	4.8	0.05	19	4	<0.1
Replicate	4.1	51	0.615	0.539	0.02	0.28	0.08	0.05	0.60	4.9	0.08	23	4	<0.1

*Paired data points in **bold face** type differ by >25 percent

Herbicides

Immunoassays were performed in the field on selected samples to test for the presence or absence of triazine herbicides and metabolites (Table 9). Solid-phase extraction analyses were also performed in the laboratory on 15 percent of these samples to determine the utility of the immunoassay as a screening tool and to determine the specific herbicides and metabolites present in those samples that tested positive in the screening. These solid-phase extraction data (Table 10) indicate:

- 1) Positive results obtained with the immunoassay screening procedure very reliably predict the presence of quantifiable amounts of atrazine in the sample.
- 2) Positive results from the immunoassay screening test generally underestimate the total concentration of herbicides in the sample.
- 3) Negative results from the immunoassay procedure generally indicate (78 percent of the time) that herbicides are not present in detectable amounts.
- 4) The immunoassay screening test did not detect (on two occasions) the presence of herbicides (simazine and prometon) in the absence of atrazine.

General Relationships Between Rainfall Parameters

Pearson correlation coefficients (at $\alpha = 0.05$) were calculated for all parameters in rainfall samples after the data were normalized using SAS/LAB® software (SAS Institute, 1992). Many correlations are highly significant and are discussed below.

Field pH is highly, negatively correlated with dissolve sulfate ($r = -0.816$, $p = 0.0001$, $n = 46$) and total nitrate ($r = -0.671$, $p = 0.0001$, $n = 64$) and is significantly negatively correlated with ammonium ($r = -0.324$, $p = 0.01$, $n = 62$) and dissolved nitrate ($r = -0.352$, $p = 0.02$, $n = 45$). These relationships indicate that rainfall pH declines as concentrations of sulfates, nitrates and ammonium (a precursor of nitrate) increase. This is not surprising given that oxides of sulfur and nitrogen are the principle components of acid precipitation (see introduction). Correlation between pH and all other rainfall components (except iron) were insignificant. Field pH was significantly, negatively correlated with iron ($r = -0.420$, $p = 0.004$, $n = 46$) indicating that perhaps the NO_x and SO_x were originally bound with iron, a theory supported by strong positive correlations between iron and both sulfate and dissolved nitrate ($\text{SO}_4 - r = 0.447$, $p = 0.002$, $n = 46$; $\text{NO}_3 - r = 0.488$, $p = 0.0007$, $N = 45$).

Several hardness correlations were strongly significant but very erratic. Positive correlations were demonstrated with ammonium ($r = 0.393$, $p = 0.02$, $n = 33$), magnesium ($r = 0.742$, $P = 0.0001$, $n = 41$), manganese ($r = 0.565$, $p = 0.0001$, $n = 41$, sulfate ($r = 0.348$, $p = 0.02$, $n = 41$) and chloride ($r = 0.401$, $p = 0.009$, $n = 41$). However, calcium and potassium were both negatively correlated with hardness ($\text{Ca } r = -0.818$, $p = 0.0001$, $n = 41$; $\text{K } r = -0.339$, $p = 0.03$, $n = 41$). Since hardness relates directly to the calcium and magnesium concentrations of the sample, the negative correlation with calcium is illogical. An examination of the raw data illustrates the both calcium and magnesium concentrations increase and decrease with corresponding positive and negative changes in hardness levels. However, the statistical analysis is unable to detect the relationship because of the limitations of the data set which include 61 hardness measurements consisting of 39 values equal to 1.0 mg/L, 10 measurements reported as zero and only 12 measurements above 1.0 mg/L. This phenomenon probably also explains the fact that conductivity correlated only with sulfate ($r = 0.429$, $p = 0.03$, $n = 26$) and alkalinity showed no correlation to any other measured parameter.

TABLE 9
Triazine Concentrations in Precipitation Samples
Based on Immunoassay Screening Tests
Cumberland County, PA 1991 - 1993*

	1991				1992																1993					
	9/4	9/18	9/24	10/5	3/10	4/15	4/16	4/21	5/4	6/18	6/19	7/7	7/8	7/17	8/7	8/8	8/13	8/27	9/25	9/27	3/23	4/25	7/1	7/19	8/6	8/16
Doubling Gap	<0.1	<0.1	<0.1	<0.1	<0.1	0.2		<0.1	0.8	0.2			0.1				<0.1	0.1	<0.1		<0.1	<0.1	<0.1	<0.1	<0.1	
Cleversburg									1.0																	
Stoughstown	<0.1			<0.1			2.0		2.0	0.7								<0.1	<0.1		<0.1	0.1	0.1	<0.1	<0.1	<0.1
Mount Rock	<0.1	<0.1	<0.1	<0.1				0.1		0.3		0.3	<0.3		<0.1		<0.1	<0.1		<0.1	<0.1	0.1	<0.1	<0.1	<0.1	<0.1
Lemoyne	<0.1	<0.1	<0.1	<0.1				0.1	0.5	0.4			0.1	0.2		<0.1	<0.1		<0.1		<0.1	0.2	<0.1	<0.1	<0.1	<0.1
Carlisle		<0.1	<0.1		<0.1	0.6		<0.1		0.5			0.1			<0.1	<0.1	<0.1	<0.1		<0.1	0.1	<0.1	0.2	<0.1	<0.1
Weidman East	<0.1	<0.1	<0.1						0.8													0.1	<0.1	0.3	<0.1	<0.1
Weidman North		<0.1	<0.1		<0.1				0.7		0.3		0.3			<0.1	<0.1	<0.1			<0.1	0.1	<0.1	0.4	<0.1	<0.1
Lemoyne (QA)	<0.1	<0.1	<0.1	<0.1				0.5	0.5	0.4			0.2	0.2		<0.1	<0.1		<0.1		<0.1	0.1	<0.1		<0.1	<0.1
Lemoyne (fixed)	<0.1	<0.1	<0.1	<0.1		<0.1			0.6	0.5				<0.1	<0.1	<0.1	<0.1		<0.1	<0.1						
Newport (QA)	<0.1	<0.1	<0.1	<0.1	<0.1				1.0	0.4			0.3			0.3	0.6	<0.1	<0.1		<0.1	<0.1	<0.1	0.1	<0.1	<0.1

* All results in µg/L
< = less than detection limit
Bold Face entries = greater than detection limit

TABLE 10
Herbicide Concentrations in Precipitation Samples Analyzed
Using Immunoassay vs Solid Phase Extraction
Cumberland County, PA 1991-1993*

Station Name	Land Use	Date	Immuno-assay Screening (Triazines)	Atrazine	Simazine	Cyan-azine	Prop-azine	Deiso-propyl-atrazine	Deethyl-atrazine	Meto-lachlor	Alachlor	Ametryn	Prom-etyrn	Prom-eton	Metri-buzin
Doubling Gap	Forest	Sep 4, 1991	<0.1	<0.05	<0.05	<0.2	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.17	<0.05
		Jul 19, 1993	<0.1	<0.05	<0.05	<0.2	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Cleversburg	Forest	May 4, 1992	1.0	0.64	<0.05	<0.2	<0.05	<0.05	0.12	1.1	0.13	<0.05	<0.05	<0.05	<0.05
		Jul 19, 1993	--	0.05	<0.05	<0.2	<0.05	<0.05	<0.05	0.06	0.03	<0.05	<0.05	<0.05	<0.05
Stoughstown	Agriculture	Sep 4, 1991	<0.1	<0.05	<0.05	<0.2	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
		Jul 19, 1993	<0.1	<0.05	<0.05	<0.2	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Mount Rock	Agriculture	Jun 18, 1992	0.3	0.1	<0.1	<0.4	<0.1	<0.1	<0.1	0.2	<0.1	<0.4	<0.1	<0.1	<0.1
		Jul 19, 1993	<0.1	<0.05	<0.05	<0.2	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Lemoyne	Urban	Sep 4, 1991	<0.1	<0.05	<0.05	<0.2	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
		May 4, 1992	0.5	0.33	<0.05	<0.2	<0.05	<0.05	0.05	0.64	0.12	<0.05	<0.05	<0.05	<0.05
		Jul 19, 1993	<0.1	<0.05	<0.05	<0.2	<0.05	<0.05	<0.05	0.02	0.05	<0.05	<0.05	<0.05	<0.05
Carlisle	Urban	Jun 18, 1992	0.5	0.2	<0.1	<0.4	<0.1	<0.1	0.1	0.3	<0.1	<0.1	<0.1	<0.1	<0.1
		Jul 19, 1993	0.2	0.05	<0.05	<0.2	<0.05	<0.05	<0.05	<0.05	<0.05	0.20	<0.05	<0.05	<0.05
Weidman East	Manure Pit	May 4, 1992	0.8	0.46	<0.05	<0.2	<0.05	<0.05	0.07	1.3	0.17	<0.05	<0.05	<0.05	<0.05
Weidman North	Manure Pit	May 4, 1992	0.7	0.48	<0.05	<0.2	<0.05	<0.05	0.05	1.0	0.14	<0.05	<0.05	<0.05	<0.05
Lemoyne (QC)	QA	Sep 4, 1991	<0.1	<0.05	<0.05	<0.2	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Newport	QA	Sep 4, 1991	<0.1	<0.05	0.15	<0.2	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
		May 4, 1992	1.0	0.61	<0.05	<0.2	0.05	<0.05	0.08	0.59	2.10	<0.05	<0.05	<0.05	<0.05
		Jun 18, 1992	0.4	0.10	0.20	<0.4	<0.10	<0.10	<0.10	0.10	0.10	<0.10	<0.10	<0.10	<0.10

* All results in µg/L
< = Less than detection limit
Bold face = Greater than detection limit

Finally, ammonium and phosphate concentrations were strongly positively correlated ($r = 0.448$, $p = 0.0001$, $n = 72$) indicating that their concentrations rise and fall in unison. Since both are plant nutrients and components of commercial chemical fertilizers, this relationship is not surprising.

Relation of Precipitation Quality to Local and Regional Land Use

Major Ions

Concentrations of major ions appeared to be related more to regional than local influences. When evaluated using an analysis of variance, the null hypothesis that there were no differences in rainfall quality between the varying land uses could not be rejected (Table 11). Thus, with the possible exception of iron ($p = 0.06$), differences in mean ion concentrations between samples collected in forested, urban, and agricultural areas were not statistically significant ($p \leq 0.05$). This is most probably due to the overwhelming regional influences of the Ohio Valley and other upwind activities discussed in the introduction. The relatively small, localized areas of forest cover, agricultural lands, or urban uses involved in this study are not capable of influencing prevailing conditions.

TABLE 11
Analysis of Variance Comparing Rainfall Quality
between Forested, Agricultural and Urban Sites
Cumberland County, PA
1991-1993

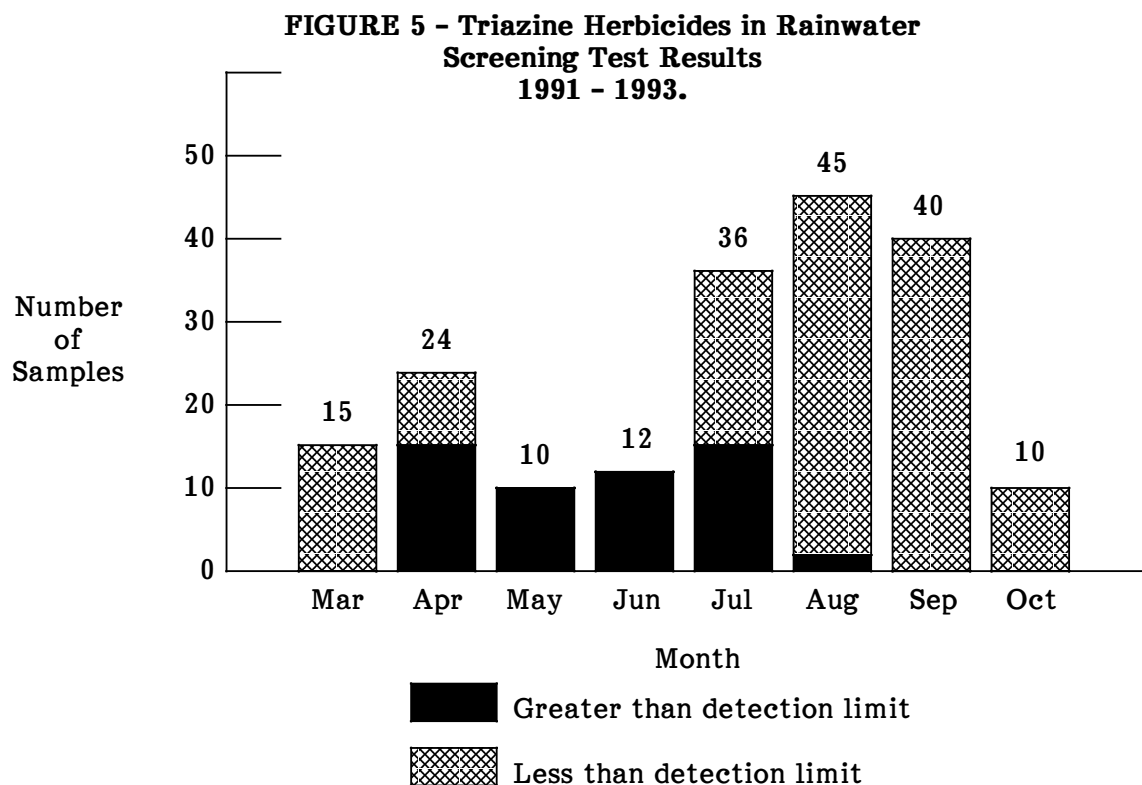
Parameter	p-value
pH, field	0.44
Hardness	0.87
Conductivity	0.99
Calcium, dissolved	0.52
Magnesium, dissolved	0.16
Potassium, dissolved	0.39
Fluoride, dissolved	0.59
Iron, dissolved	0.06
Manganese, dissolved	0.68
Sulfate, dissolved	0.84
Chloride, dissolved	0.22
Orthophosphate, dissolved as PO_4	0.97
Orthophosphate, dissolved as P	0.97
Ammonia, dissolved as N	0.28
Ammonia, dissolved as NH_4	0.29
Nitrate, total as N	0.99
Nitrate, dissolved as N	0.67
Nitrate + nitrite, total as N	0.99

Herbicides

Concentrations of herbicides in rainfall may be affected by both regional and local influences. Compounds like atrazine, deethylatrazine, propazine, simazine, metalochlor, alochlor, ametryn, and prometon were frequently present in detectable concentrations in rainfall (Tables 4, 9, and 10). These detections were more common during the spring and most probably resulted from agricultural activities related to row crops (see below).

Seasonality

A seasonal pattern was evident in the data for a number of measured parameters including herbicides, pH, nitrogen, and sulfate. Peaks in herbicide detections occurred in late spring with lower, but detectable amounts persisting sporadically throughout the summer (Tables 9 and 10; Figure 5). This pattern is consistent with that reported by Waite et al. (1995). These occurrences are not restricted to samples collected at agricultural sites but rather seem to reflect the regional influence of agricultural weed control activities related to corn production. The exception is the detection of prometon at Doubling Gap (forest land-use). This detection may have resulted from a local application of this non-selective herbicide used to control many broadleaf weeds and grasses (Sine, 1993).



Concentrations of nitrogen (ammonia and nitrate) and sulfate build in rainfall through the spring and summer and decrease in the fall of 1992 while rainfall pH does the opposite (Figures 6-9). These observations are not surprising since pH was negatively correlated with nitrogen and sulfate. However, a close inspection of field data reveals that one event, tropical storm Danielle, is responsible for most of this effect in the fall of 1992 (September 25-27). This storm yielded relatively good quality rainfall because it tracked up the Atlantic coast and “backed in” on central Pennsylvania from the east. Concentrations of dissolved ammonia nitrogen, total nitrates, and dissolved sulfates measured during Danielle were approximately 50 percent of values recorded from storms moving with prevailing westerly winds. Values for pH were also about 1 unit higher than “typical” westerly storms.

Other parameters that demonstrate more subtle seasonal patterns are presented in Figures 10 - 15. In these graphs, tropical storm Danielle, appears to exert less influence on the 1992 data distribution. Four metals (calcium, iron, manganese, and magnesium), one nutrient (orthophosphate) and one major ion (chloride) all demonstrate similar seasonal patterns with concentrations peaking in mid summer of 1992.

Patterns for 1993 data, are more erratic and many of the parameters measured, peak in the spring and decline through the summer months. Unfortunately there are fewer data points for 1993 and it is difficult to illustrate a pattern.

FIGURE 6 - Rainfall pH, 1991 - 1993.*

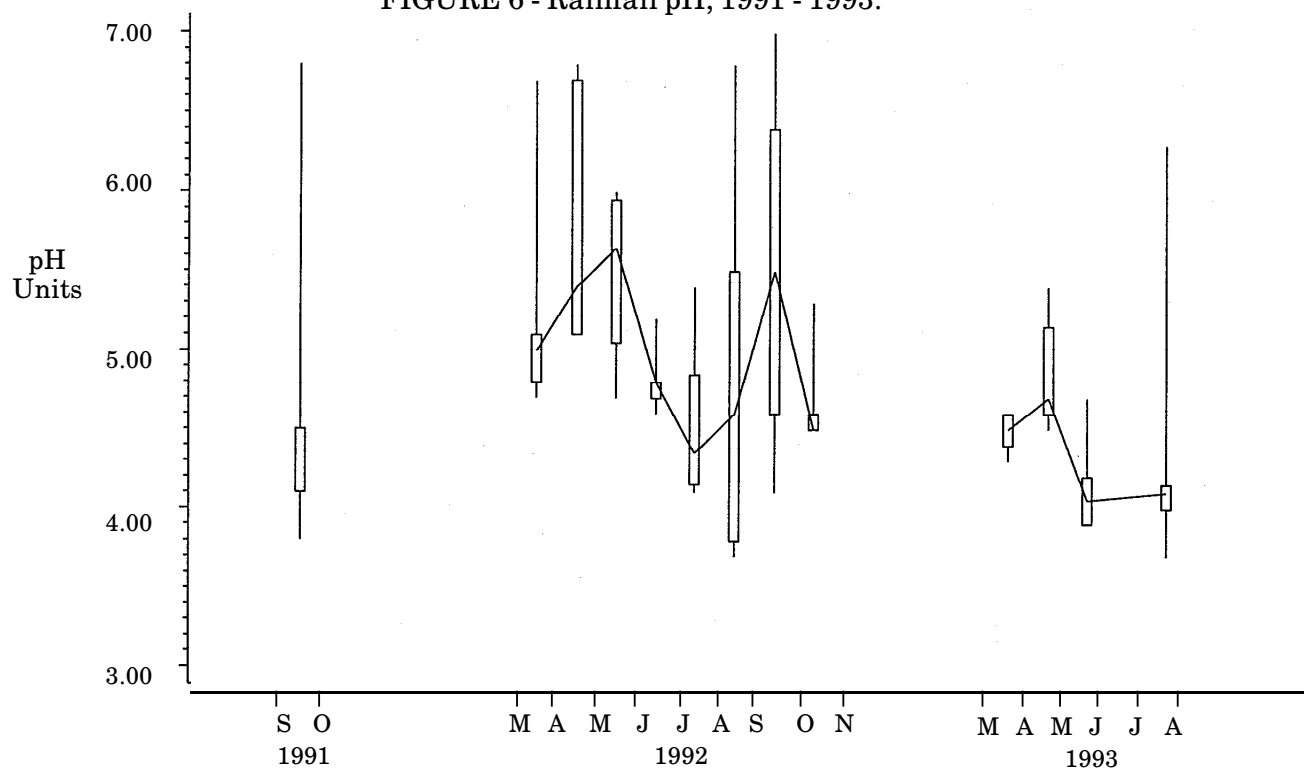
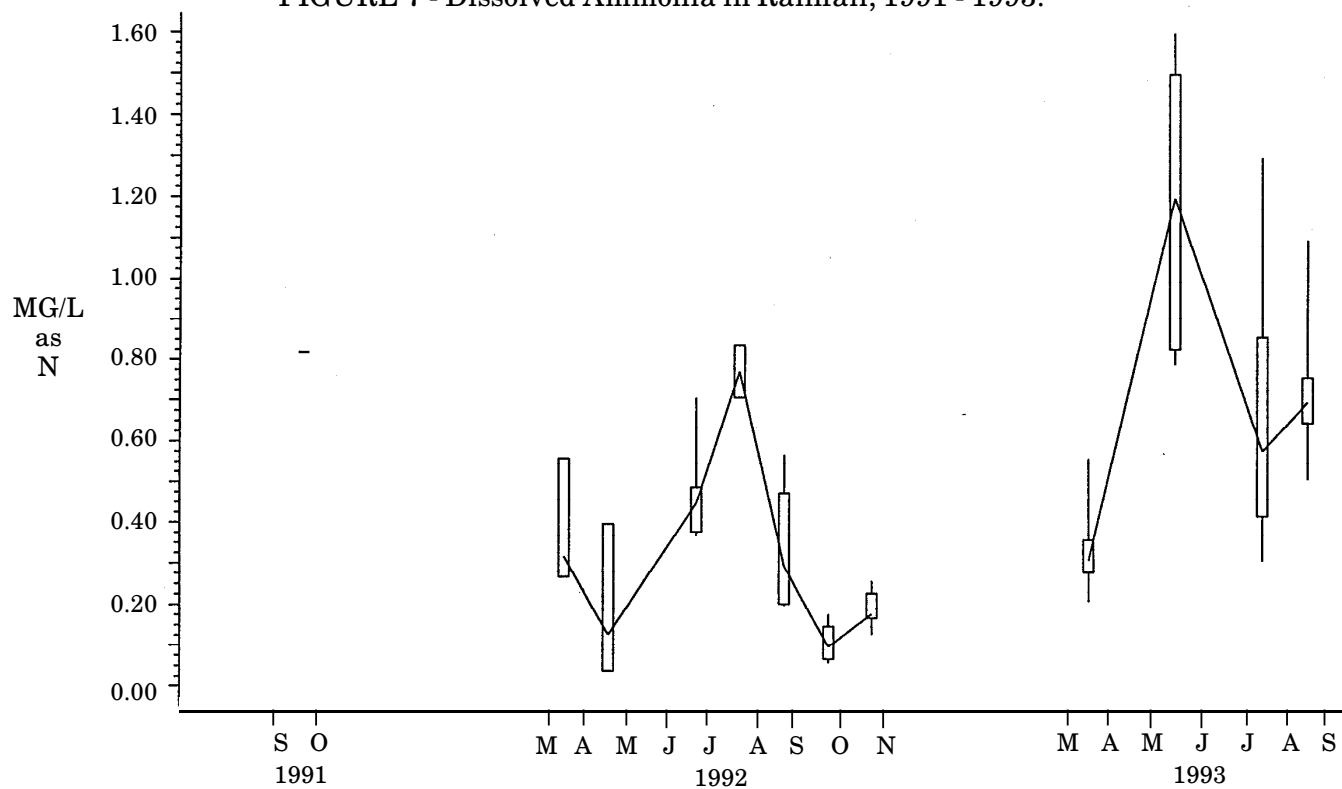


FIGURE 7 - Dissolved Ammonia in Rainfall, 1991 - 1993.*



* Graphed line connects median values. Top and bottom of boxes represent 75th and 25th percentiles, respectively. Whiskers indicate complete range of data.

FIGURE 8 - Total Nitrate in Rainfall, 1991 - 1993.*

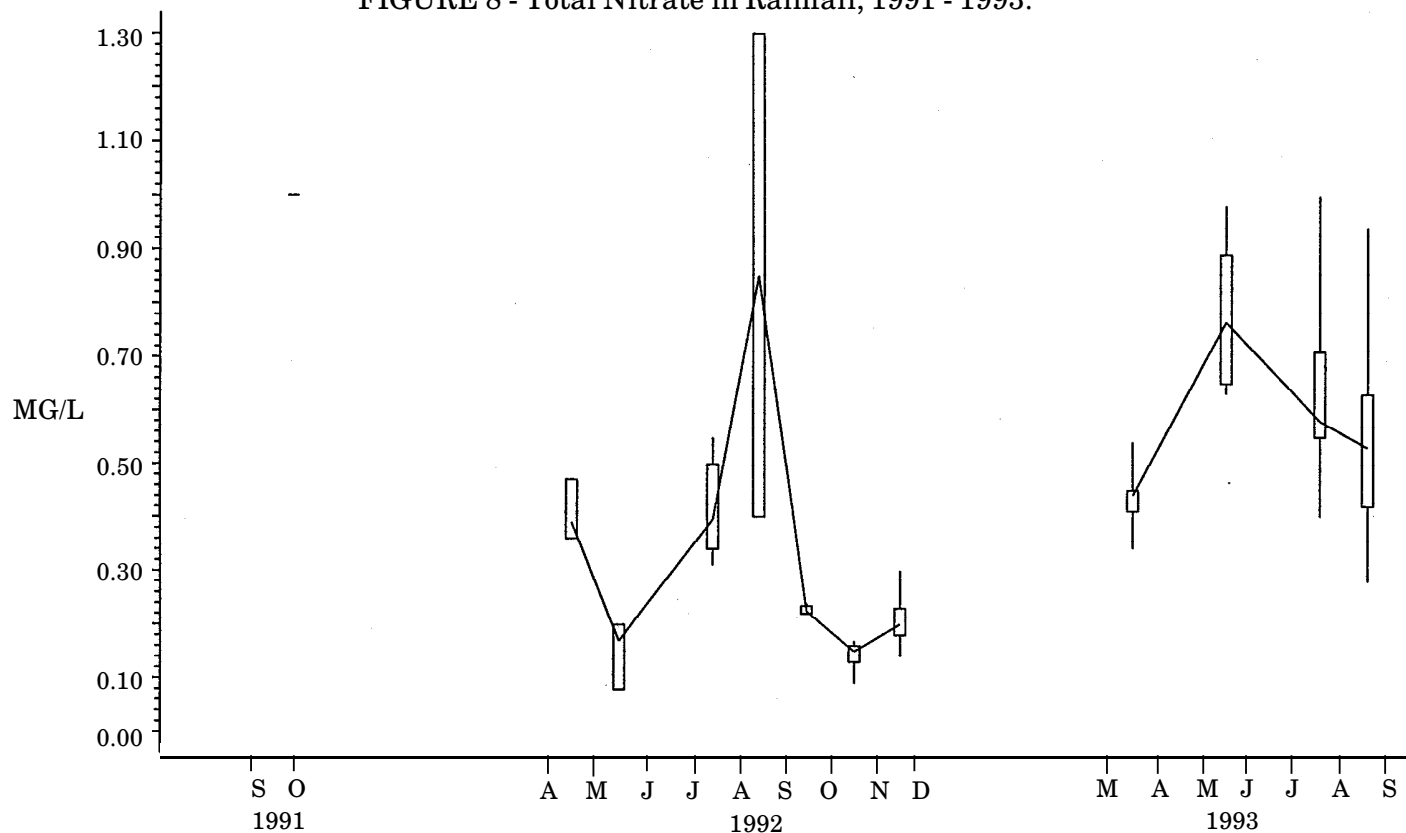
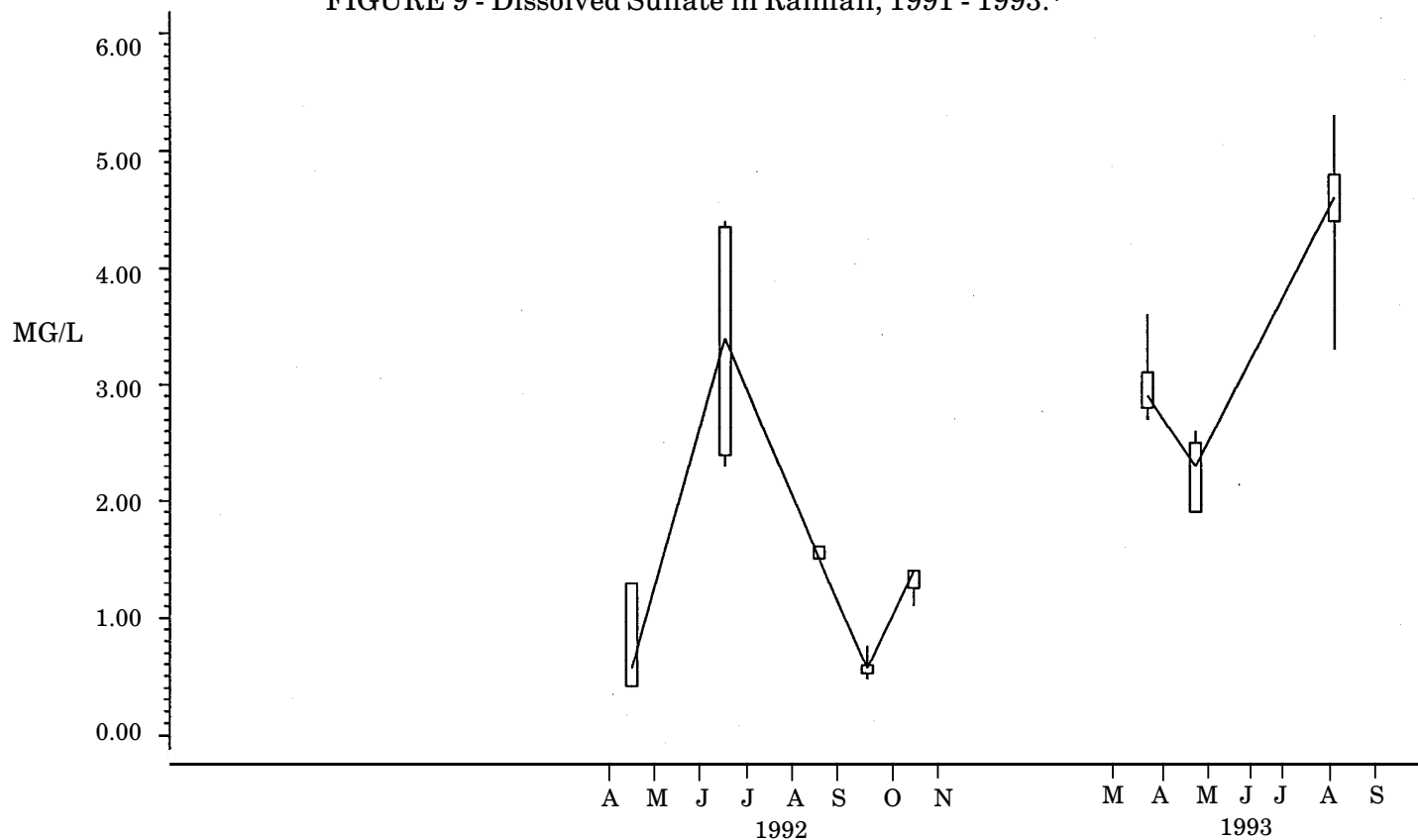


FIGURE 9 - Dissolved Sulfate in Rainfall, 1991 - 1993.*



* Graphed line connects median values. Top and bottom of boxes represent 75th and 25th percentiles, respectively. Whiskers indicate complete range of data.

FIGURE 10 - Dissolved Calcium in Rainfall, 1991 - 1993.*

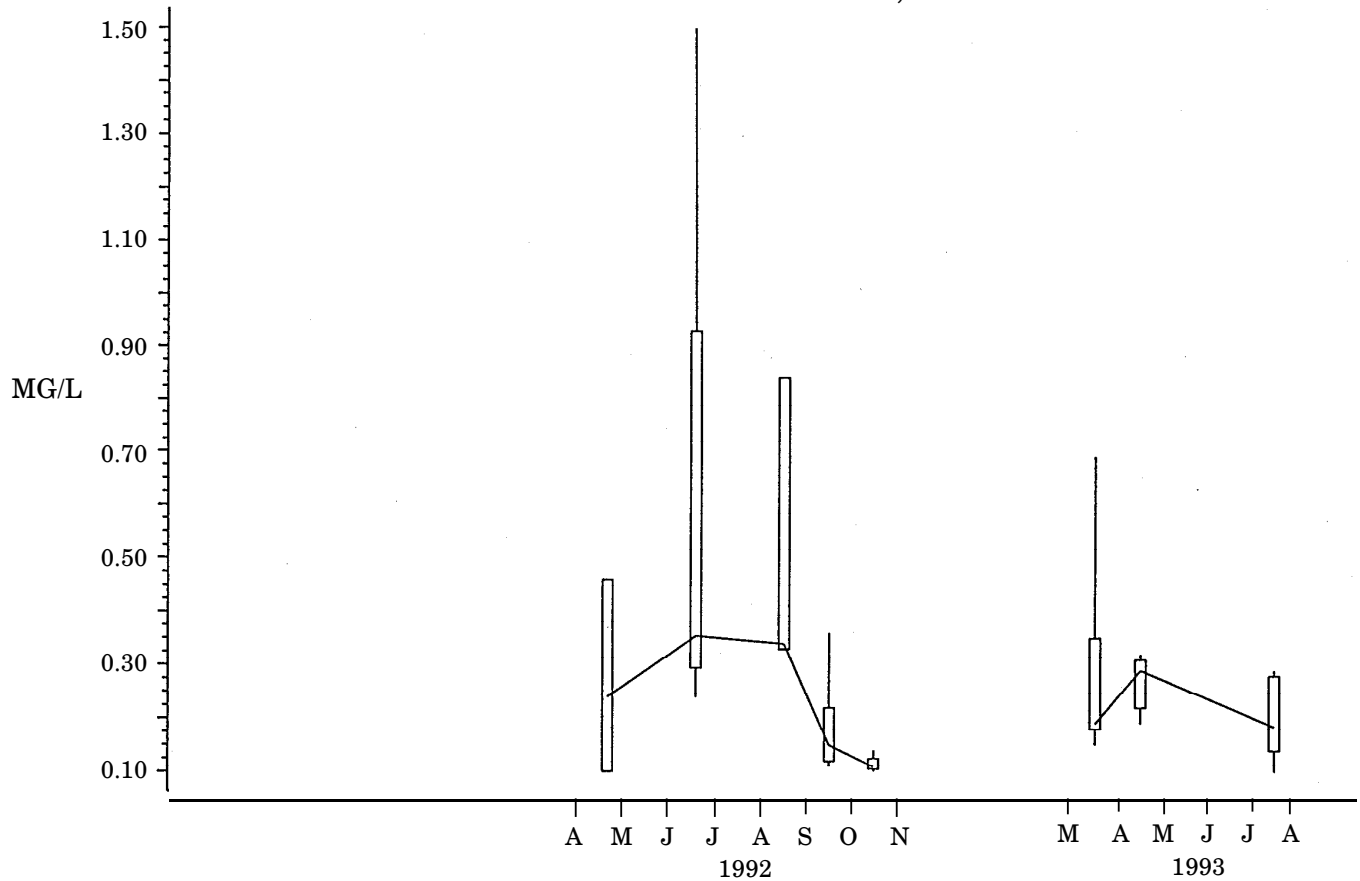
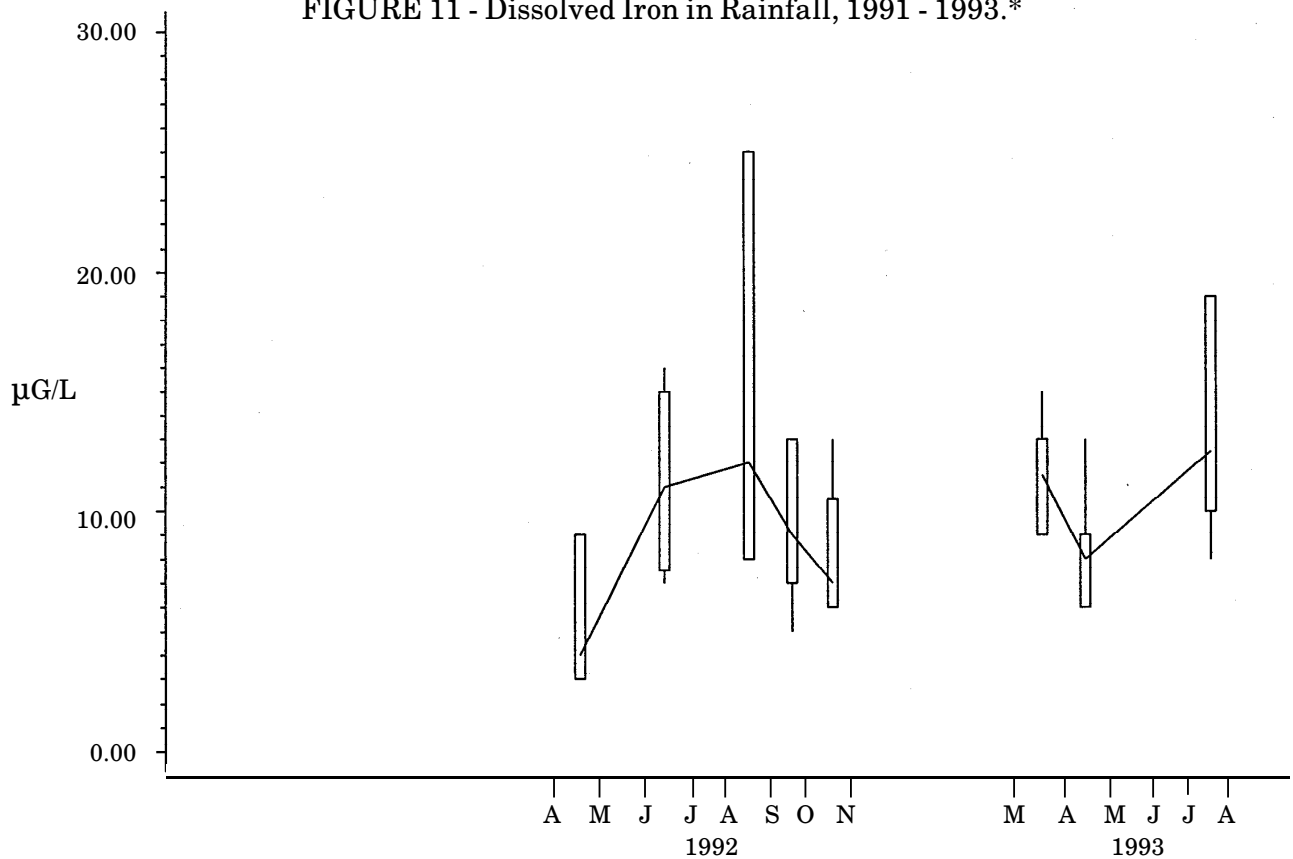


FIGURE 11 - Dissolved Iron in Rainfall, 1991 - 1993.*



* Graphed line connects median values. Top and bottom of boxes represent 75th and 25th percentiles, respectively. Whiskers indicate complete range of data.

FIGURE 12 - Dissolved Manganese in Rainfall, 1991 - 1993.*

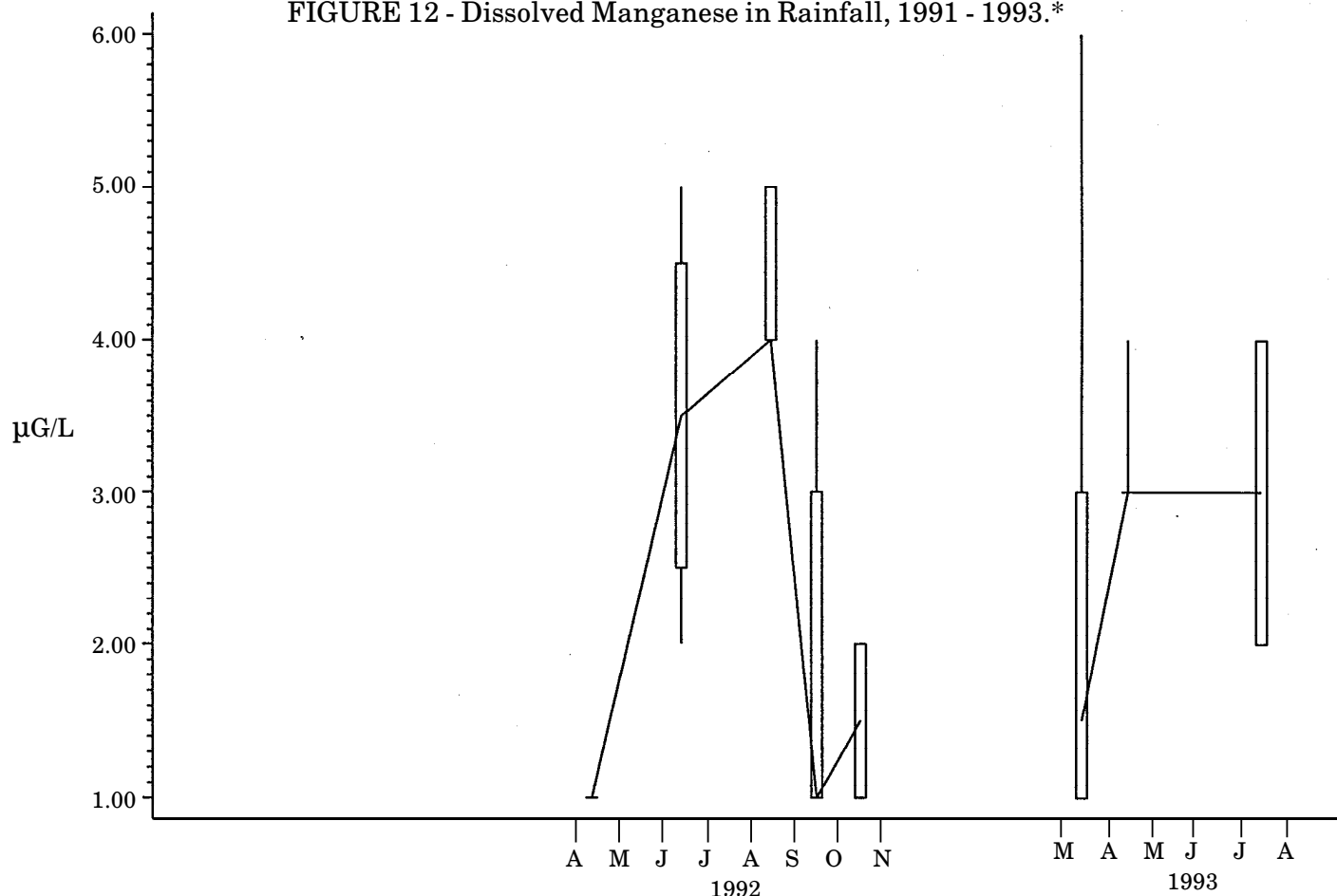
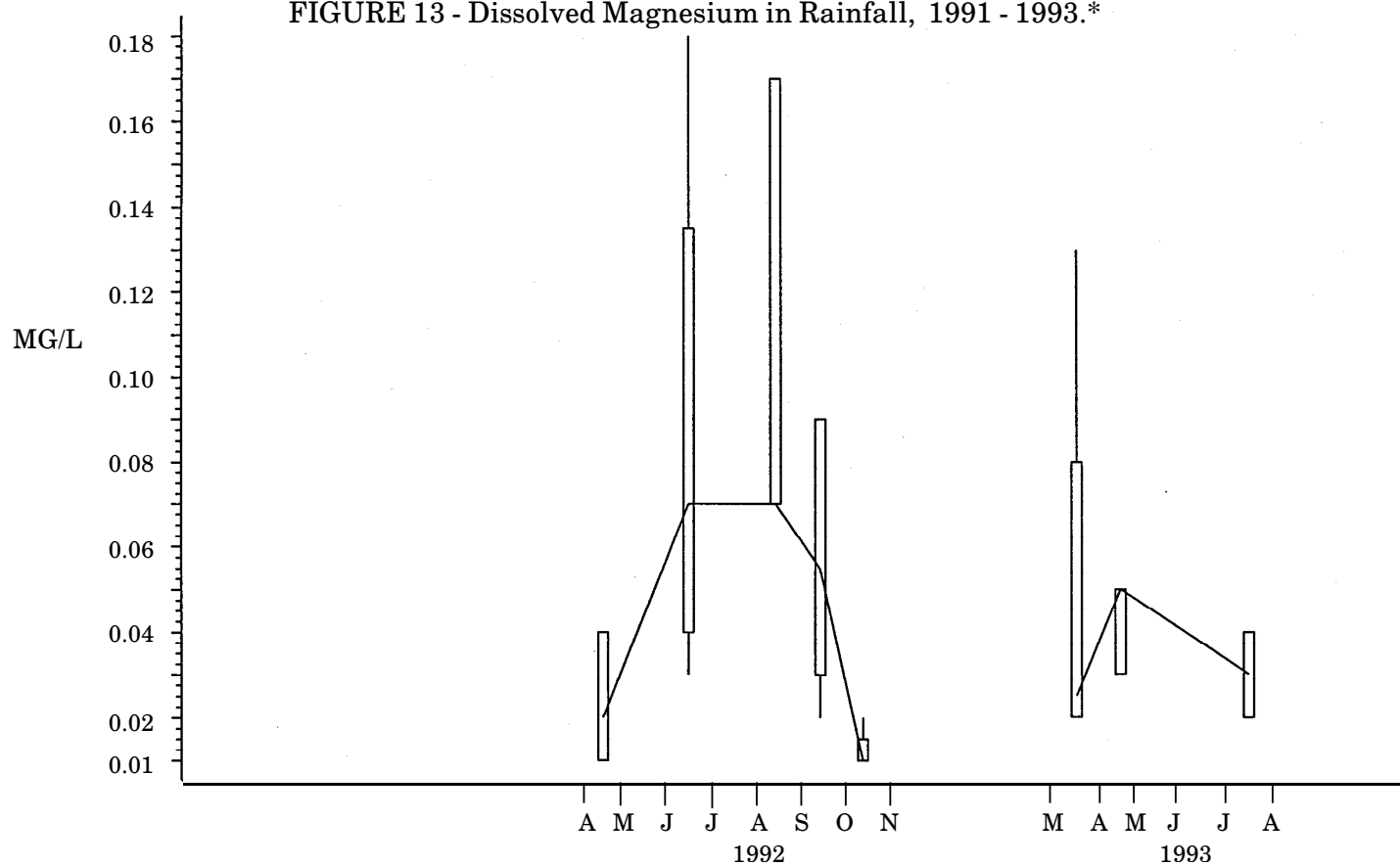


FIGURE 13 - Dissolved Magnesium in Rainfall, 1991 - 1993.*



* Graphed line connects median values. Top and bottom of boxes represent 75th and 25th percentiles, respectively. Whiskers indicate complete range of data.

FIGURE 14 - Dissolved Orthophosphate in Rainfall, 1991 - 1993.*

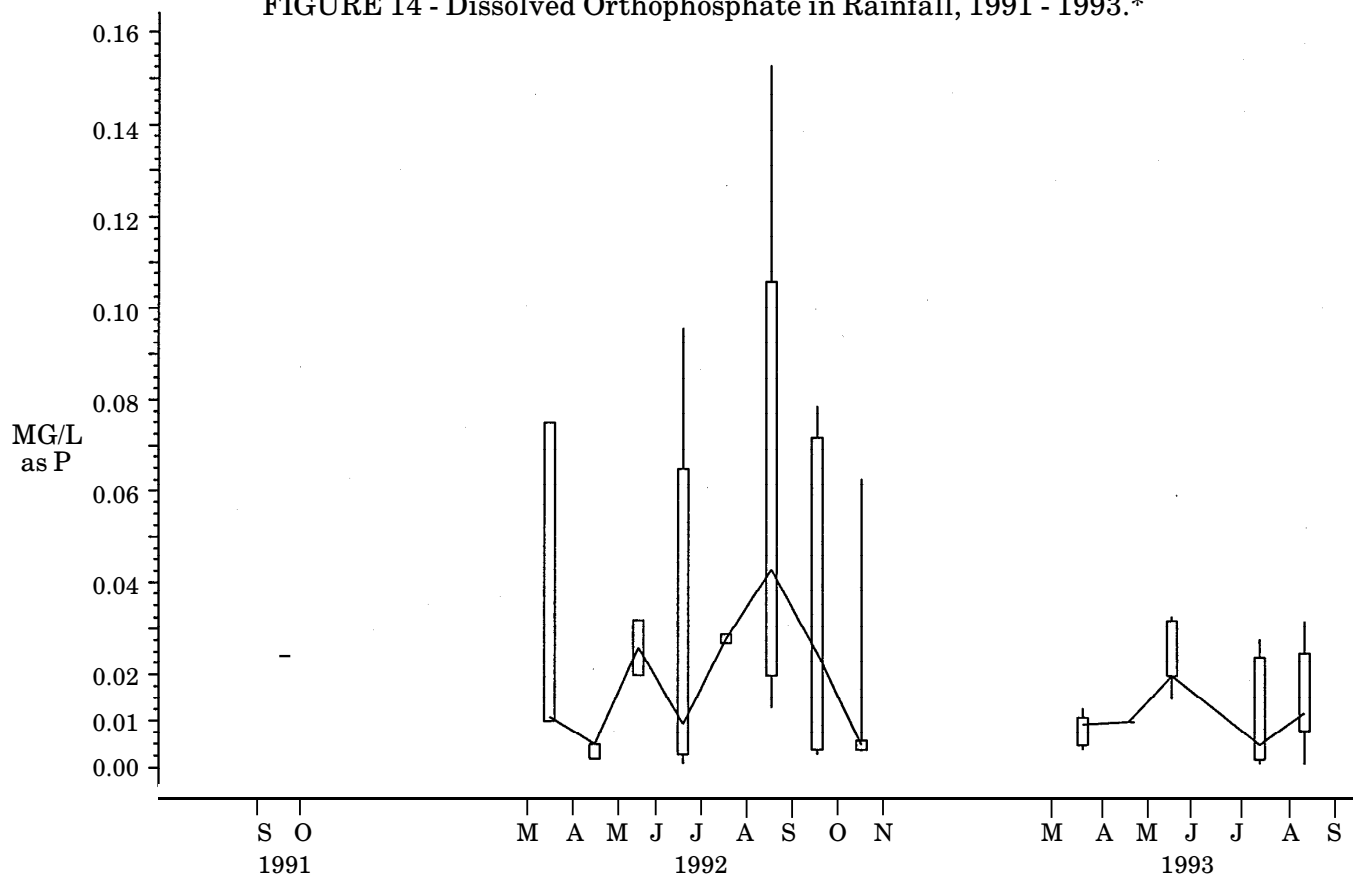
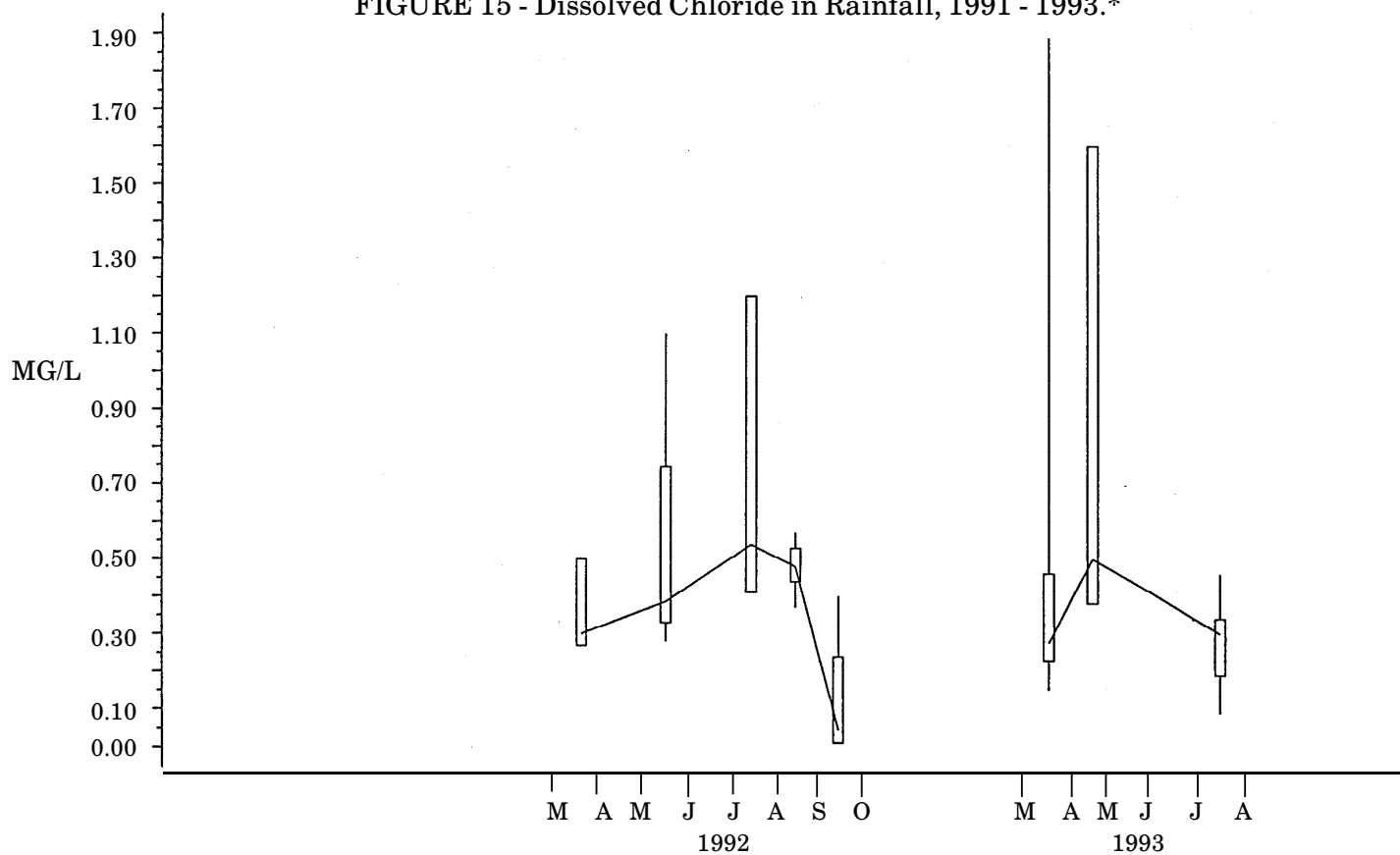


FIGURE 15 - Dissolved Chloride in Rainfall, 1991 - 1993.*



* Graphed line connects median values. Top and bottom of boxes represent 75th and 25th percentiles, respectively. Whiskers indicate complete range of data.

Manure-Holding Facilities

Results of samples collected from two sites adjacent to a manure holding pit at the Weidman Farm are included in Table 4. Mean values for nitrogen in precipitation collected downwind from the manure-pit suggest a localized effect when compared to upwind values (Table 12). However, a comparison (paired T-tests) of mean values for these selected parameters between the two sites illustrates that there was no significant difference ($p=0.05$) in precipitation quality upwind or downwind of the holding pit. This contradicts the findings of Langland (1992) who, in a more rigorous study, conducted immediately south of the Conodoguinet Creek basin, documented significant volatilization and localized redeposition of ammonia from a manure-storage lagoon. It is likely, given the apparent trend of these data, that more stations located in the vicinity of this manure storage pit or more samples from the two existing sites may have increased the rainfall sample population size enough to document a statistically significant difference between upwind and downwind nitrogen concentrations.

TABLE 12
Mean Values for Nitrogen in Precipitation
Measured Upwind and Downwind
from a Manure Storage Pit

Parameter	n (pairs)	Upwind Site	Downwind Site	T-test P-value
Ammonium, dissolved as NH_4	7	0.84	0.97	0.66
Ammonia, dissolved as N	7	0.65	0.75	0.66
Nitrate, dissolved as N	3	0.35	0.34	0.97
Nitrate, total as N	8	0.60	0.69	0.72
Nitrite plus Nitrate, dissolved as N	8	0.60	0.69	0.73

An analysis of variance between the pit sites and other land use areas for all parameters is presented in Table 13. Again, the null hypothesis that there is no difference in rainfall quality between varying land use areas cannot be rejected at the “p” values presented. Therefore, it was concluded that precipitation quality between the manure pit sites and other collection sites in the study were not significantly different ($p \leq 0.05$) for the parameters measured. Iron is, again, very close to significance at $p = 0.06$.

TABLE 13
Analysis of Variance Comparing Rainfall Quality
between Forested, Agricultural, Urban and Manure-Storage Sites
Cumberland County, PA
1991-1993

Parameter	p-value
pH, field	0.43
Hardness	0.54
Conductivity	0.99
Calcium, dissolved	0.51
Magnesium, dissolved	0.16
Potassium, dissolved	0.40
Fluoride, dissolved	0.59
Iron, dissolved	0.06
Manganese, dissolved	0.68
Sulfate, dissolved	0.84
Chloride, dissolved	0.68
Orthophosphate, dissolved as PO ₄	0.95
Orthophosphate, dissolved as P	0.97
Ammonia, dissolved as N	0.28
Ammonium, dissolved as NH ₄	0.28
Nitrate, total as N	0.99
Nitrate, dissolved as N	0.67
Nitrate + Nitrite, total as N	0.99

Chemical Integrity of Samples

Table 14 illustrates the relationship between the Lemoyne (urban) sampling site and the Lemoyne Fixed Interval site. Since the Lemoyne (urban) site was sampled immediately after cessation of rainfall events and the fixed interval site was collected weekly, there were times during the study when a rainfall event was sampled and analyzed immediately (urban site) and that same rainfall sample was allowed to remain in the fixed interval collector for one to 8 days before sampling/analysis. These circumstances provide an opportunity to evaluate the ability of the collector to preserve sample integrity over time.

No pattern or trend could be identified between parameter concentrations in rainfall sampled and processed immediately after cessation of the event versus samples left in the collector and processed on a weekly basis. However, the fact that the results were highly variable with respect to both magnitude and direction (loss or gain) in concentration over time, indicates that the collectors were not suitable for fixed interval use. In some instances parameter concentrations increased in samples held in the collector for all or part of the next week presumably due to evaporative water loss or additional deposition. In other cases constituents were lost over time probably because of volatilization or biological conversion.

TABLE 14
Differences in Major Ion Concentrations with Increasing Elapsed Time
between Rainfall Event and Sample Collection
Lemoyne, PA - September 1991 - September 1993

Parameter Analyzed	Elapsed Time Between Samples (days)										
	0	0	0	0	1	2	2	5	5	5	8
Dissolved ammonia (mg/L as N)	•	0.00	-0.02	0.40	•	-0.39	•	•	0.00	0.42	0.09
Total nitrate (mg/L as N)	•	0.00	-0.54	0.78	•	-0.89	•	•	0.00	0.61	0.22
Diss. orthophosphate (mg/L as P)	•	0.00	-0.01	0.06	•	-0.03	0.00	•	0.00	0.05	0.00
Field pH (units)	0.50	2.70	0.30	0.20	0.60	1.30	-0.30	0.70	-0.10	0.20	-1.00
Conductivity (µs/cm)	45	99	0	0	0	13	0	0	0	-144	71
Dissolved sulfate (mg/L)	•	•	•	•	•	•	•	•	•	2.10	1.18
Dissolved chloride (mg/L)	•	•	•	•	•	•	•	•	•	-0.07	2.96
Dissolved calcium (mg/L)	•	•	•	•	•	•	•	•	•	0.82	0.66
Dissolved iron (µg/l)	•	•	•	•	•	•	•	•	•	20	8
Dissolved manganese (µg/l)	•	•	•	•	•	•	•	•	•	3	1

Volunteer Monitors

Well trained volunteer monitors were critical to the successful completion of this study. They consistently collected what proved to be good quality rainfall data at no cost, in a very timely manner. Their attention to detail and adherence to protocol is evidenced by the acceptable quality control data discussed earlier in this report including partial ion balance calculations conductivity balance calculations and replicate results. Without their willingness to deploy collectors immediately before storms and recover samples immediately afterwards, this study could not have proceeded. Employees of state or federal agencies or the Alliance for the Chesapeake Bay working regular hours could not have provided, even with overtime, similar areal coverage in a way that was flexible enough to respond to the rainfall events that occurred over the two year study period.

SUMMARY AND CONCLUSIONS

Objectives 1 & 2: Characterize precipitation quality and assess differences related to varied land use.

- As indicated in previous studies, sulfate and nitrogen concentrations in precipitation are linked to sample pH.
- Concentrations of major ions in precipitation appear to relate more to regional influences rather than local influences.
- Concentrations of herbicides in precipitation may be effected by both regional and local use which caused compounds like atrazine, deethylatrazine, propazine, simazine, metolachlor, alachlor, ametryn, and prometon to be present in detectable concentrations in rainfall.
- Seasonality was evident in nitrogen, sulfate, pH, and herbicide data and was suggested in calcium, iron, manganese, magnesium, orthophosphate, and chloride data. Agricultural weed control activities were probably responsible for the seasonal pattern in pesticide data which peaked in May and June. Tropical storm Danielle may have caused the apparent seasonal patterns for the other nine parameters. This storm did not follow the typical west to east movement pattern and consequently produced rainfall of relative high quality.

Objective 3: Assess the potential for manure-holding facilities to contribute to the atmospheric deposition of nitrogen.

- Localized effects of manure storage facilities on nitrogen concentrations in precipitation was suggested but not statistically supported by data collected upwind and downwind from the manure-storage facility.

Objective 4: Test the capacity of the collection device to preserve the chemical integrity of precipitation for variable time intervals.

- Collectors were adequately designed for rainfall-event sampling. However, the simple design of sample collectors permitted water to evaporate from collection bottles and air-borne contaminants to deposit over time. Therefore, they were not well suited for collection of weekly (fixed interval) precipitation samples.

Objective 5: Assess the practicality of using volunteer citizen monitors in this intensive and extension scientific study.

- A variety of quality assurance checks indicate that trained volunteer citizen monitors were successful participants in this intensive and extensive scientific study, collecting good quality samples in a timely manner. Without this kind of volunteer help, it is extremely difficult to complete studies that require sampling in response to natural events, such as rainfall.

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APPENDIX A

ATMOSPHERIC DEPOSITION CITIZEN MONITORING INSTRUCTION MANUAL

Prepared by

Scott Steffey
Project Coordinator

QC INFORMATION FOR MONITORS

- 1) Monitors will attend a 2-3 hour training workshop which will cover the following topics:
 - overview of project
 - site selection strategy
 - operation of project
 - construction of rainfall collectors
 - operation of rainfall collectors
 - quality control measures
 - potential importance of findings
- 2) Keep equipment e.g. bottles, funnels without contamination.
- 3) Receive call from Monitoring Coordinator to activate collector before event.
- 4) Monitor activates collector placing funnel and bottle in their perspective location a maximum of 8 hours prior to event, collection must take place a maximum of 12 hours after event.
- 5) If event does not occur within 8 hours, then monitor retrieves funnel/bottle and stores this equipment until replacement. A new funnel and bottle are used for next event.
- 6) Monitor reads, records and empties rain gauge upon sample collection.
- 7) Monitor completes data sheet which is turned in with sample.
- 8) Upon collection, sample must be capped and returned to a refrigerator, funnel is removed and stored until it can be cleaned at time of sample pick-up.
- 9) Monitor should collect the screw-in bottom to the collector so as to minimize vandalism to collector.
- 10) After monitor stores sample, he/she phones Monitoring Coordinator so sample, used equipment and data sheet can be collected.

AFTER THE RAIN EVENT

Try to retrieve the sample as soon as possible after the event. The maximum amount of time that bottles should be left in collectors after a rain event is 12 hours. It is desirable to collect the sample as soon as possible after the rain for several reasons:

1. Lower risk of changes in composition of the rainfall that may take place over time.
2. Lower risk of contamination.
3. Lower risk of vandalism.

Step 1. Return to your collector.

Step 2. Very carefully unscrew the base of the collector and lower it until you can grasp and support the sample bottle with your other hand. Screw the lid on the sample bottle immediately. If the sample bottle contains more than a “trace” amount and if the rain gauge reads that more than 0.1 inch of rain fell, proceed with the next step. If not, see instructions for “false run.”

Step 3. Lift funnel out of collector. Carefully place it back in the bag. At this point contamination is not an issue, but try to protect the funnel from breakage.

Step 4. Read rain gauge (see rain gauge instructions). Record amount on field data sheet.

Step 5. Record time and date sample was retrieved on data sheet.

Step 6. Return home. Refrigerate the sample promptly, and phone the ACB office (236-8825) to arrange for sample pick-up. If you will not be home for the arranged pick-up, please place sample in a cooler, on ice, at a pre-arranged safe place outside of your home.

RAIN GAUGE INSTRUCTIONS

Installation

- Step 1. Place a gauge on the opposite side of the post so that the top of the gauge sticks up approximately 2 inches above the top of the post.
- Step 2. Use the three screws accompanying the gauge to mount the gauge onto the post.

Operation

The top funnel catches the rain and delivers it to the measuring tube. the measuring tube has a capacity of 1.00 inch. Rainfalls of less than one inch can be read directly from the measuring tube.

- Step 1. Stand the measuring tube on a level surface.
- Step 2. Read the amount to the nearest 0.01 inch. Be careful to read the level at the bottom of the meniscus.
- Step 3. If rainfall exceeds 1.00 inch, the excess flows into the outer cylinder. To measure this extra amount, empty the measuring tube containing the first 1.00 inch.
- Step 4. Place the funnel into the measuring tube and pour carefully the excess rain water until the outer cylinder is empty.
- Step 5. Add the amount from the first measuring tube to the amount measured from the outer cylinder (ex. 1.00 inch + 0.45 inch = 1.45 inch).
- Step 6. Record the amount measured on the field data sheet.