

**ATMOSPHERIC DEPOSITION OF SELECTED CHEMICALS AND  
THEIR EFFECT ON NONPOINT-SOURCE POLLUTION IN  
THE TWIN CITIES METROPOLITAN AREA, MINNESOTA**

By R. G. Brown

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### FACTORS FOR CONVERTING INTERNATIONAL SYSTEM OF UNITS (SI) TO INCH-POUND UNITS

For the convenience of readers who may want to use inch-pound units, the data may be converted using the following factors:

<u>Multiply SI unit</u>	<u>By</u>	<u>To obtain inch-pound unit</u>
millimeter (mm)	0.03937	inch (in.)
meter (m)	3.281	foot (ft)
square meter (m <sup>2</sup> )	10.7642	square foot (ft <sup>2</sup> )
hectare (ha)	2.471	acre
liter (L)	0.2642	gallon (gal)
milligram (mg)	35.27	ounce (oz)
kilogram (kg)	2.205	pound (lb)
milligrams per liter (mg/L)	133.49	ounces per gallon (oz/gal)
kilograms per hectare (kg/ha)	0.8924	pounds per acre (lb/acre)
kilograms per hectare per day [(kg/ha)/d]	0.8924	pounds per acre per day [(kg/ha)d]

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**ABSTRACT**

Atmospheric deposition and subsequent runoff concentrations of total Kjeldahl nitrogen, dissolved nitrite-plus-nitrate nitrogen, total phosphorus, total sulfate (only for atmospheric deposition), total chloride, and total lead were studied from April 1 to October 31, 1980, in one rural and three urban watersheds in the Twin Cities Metropolitan Area, Minnesota. Seasonal patterns of wetfall and dryfall generally were similar for all constituents except chloride in both rural and urban watersheds. Similarity between constituents and between rural and urban watersheds suggested that regional air masses transported from the Gulf of Mexico by frontal storm movements influence seasonal patterns of atmospheric deposition in the metropolitan area. Local influences such as industrial, agricultural, and vehicular air pollutants were found to influence the magnitude or rate of atmospheric deposition rather than the seasonal pattern. Chloride was primarily influenced by northwest frontal storms laden with coastal chloride. Local influences such as dust from road deicing salt dust are thought to have caused an increase in atmospheric chloride during June.

The atmospheric contribution to nonpoint-source-runoff pollution of nitrogen, in the form of nitrite-plus-nitrate, and lead was extremely high contributing as much as 84 percent of the runoff load. In contrast, phosphorus and chloride inputs were low averaging of 6 percent of the total runoff load. Future investigations of nonpoint-source pollution in runoff might include collection of data on atmospheric deposition of nitrite-plus-nitrate nitrogen and lead because of the importance of that source of these constituents in runoff.

**INTRODUCTION**

**Background**

Deposition of numerous chemical constituents from the atmosphere is becoming a serious and widespread problem throughout Europe and the northeastern United States (Likens and others, 1979; Cogbill and Likens, 1974; Galloway and others, 1976; Gjessing and others, 1976). Various contaminants that are emitted into the atmosphere by human activities enter natural geochemical atmospheric cycles and are returned to terrestrial and aquatic ecosystems through wet precipitation and dry fallout. This input of contaminants to both terrestrial and aquatic ecosystems can be detrimental (Driscoll, 1980; Johnson, 1979; Swank and Henderson, 1976). Deposition of airborne contaminants is considered to be nonpoint-source pollution, which contributes to the nonpoint-source pollution problem throughout the United States and the world (Lewis and Grant, 1980; Ritter and Brown, 1981).

Nonpoint-source pollution in the Twin Cities Metropolitan Area, Minnesota, as in many areas throughout the United States, contributes significantly to degradation of the quality of streams, rivers, and lakes (Federal Water Pollution Control Administration, 1969). However, the contribution of contaminants from the atmosphere to nonpoint-source pollution in rural and urban runoff is not well documented. Little information is available on the percentage of pollution in runoff caused by atmospheric deposition as compared to pollutants derived from terrestrial or aquatic sources. Data have been collected on contaminants associated with acid rain in the Boundary Waters Canoe Area of northeast Minnesota (Eisenreich and others, 1978; 1981; Glass and Loucks, 1980), but these data have not been analyzed with respect to contaminants in nonpoint-source runoff. Similar data have not been collected in a highly urbanized part of the state such as the Twin Cities Metropolitan Area.

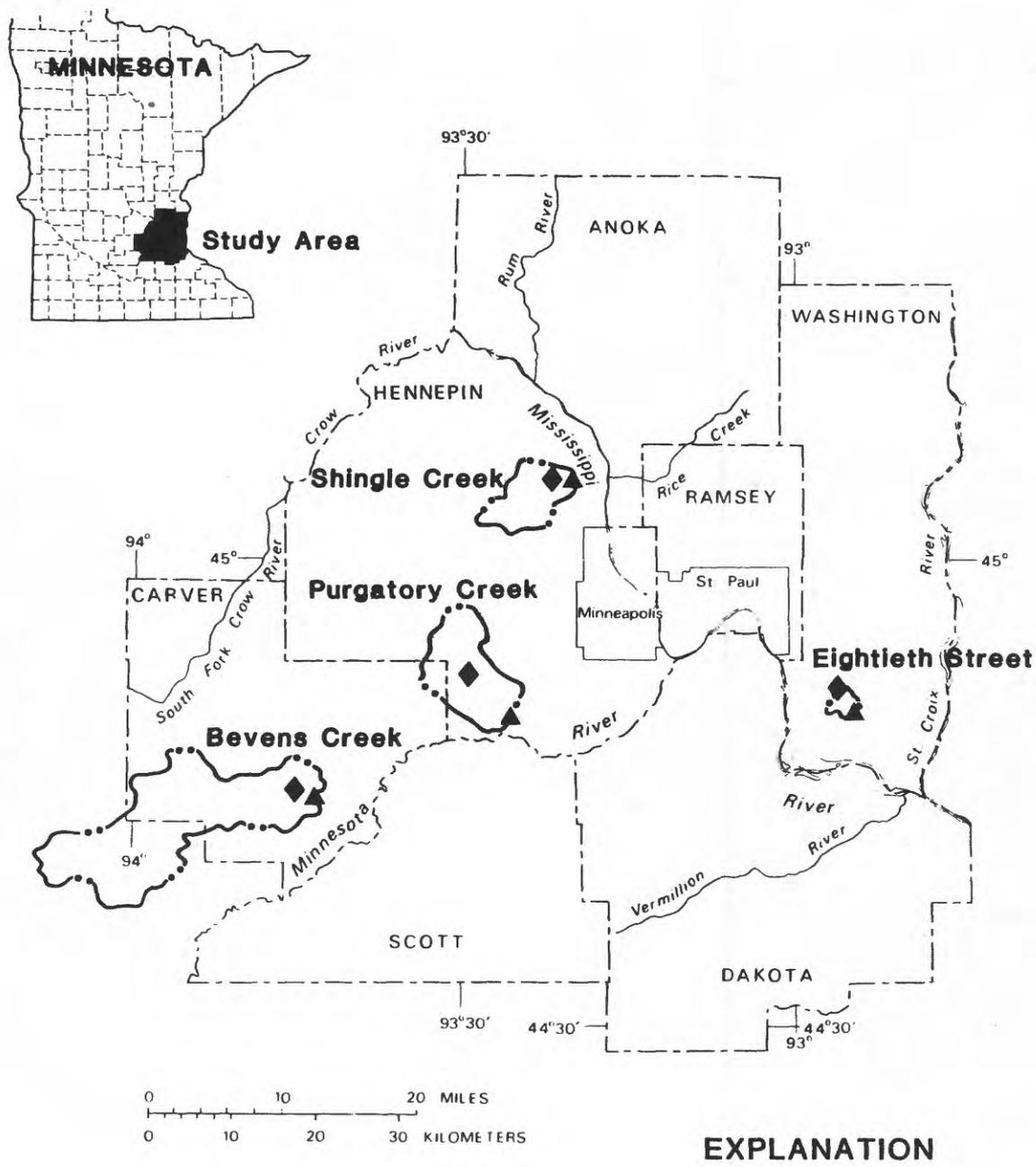
### Purpose and Scope

A study by Ayers and others (1980) investigated nonpoint-source pollution in the Twin Cities Metropolitan Area in terms of urban and rural runoff. Atmospheric-deposition data, including wetfall and dryfall, were also collected during the study. Results presented here are based on both the year-long (January to December 1979) study of nonpoint-source pollution in runoff and a 7-month (April to October 1979) period in which additional data were collected on atmospheric deposition of selected chemical constituents. The objectives of collecting atmospheric data in addition to runoff data were to: (1) determine seasonal variations in atmospheric deposition of nitrogen, phosphorus, sulfate, chloride, and lead, (2) evaluate the contribution of these contaminants to nonpoint-source pollution in the Twin Cities Metropolitan Area, and (3) examine how local emissions and regional air masses affect atmospheric-deposition rates.

This report is primarily concerned with the methods and results of determining atmospheric deposition and the effect on nonpoint-source-runoff pollution. The methods and more detailed interpretations of the nonpoint-source-runoff pollution study is described in Payne and others (1982). The discussion of runoff in this report will be restricted to interpreting the contribution of atmospheric deposition to nonpoint-source pollution.

### Description of the Study Area

The Twin Cities Metropolitan Area encompasses about 777,000 hectares in Anoka, Carver, Dakota, Hennepin, Ramsey, Scott, and Washington Counties (fig. 1). This study of the metropolitan area does not include combined-sewered areas in Minneapolis, St. Paul, and South St. Paul that are being studied by the MWCC (Metropolitan Waste Control Commission) under a Section 201 Facilities Planning grant.



**Figure 1.--Location of runoff and rain quality sampling sites for rural and urban watersheds in the Twin Cities Runoff Study**

Land use in the metropolitan area is 43 percent agricultural, 27 percent urban, and 30 percent open space (Oberts and Jouseau, 1979). Urban growth is concentrated around the Minneapolis and St. Paul metropolitan centers, with the most growth to the north, south, and west. Major agricultural areas are to the south and west in Dakota, Scott, and Carver Counties.

The climate is one of generally mild, humid summers and relatively long, severe winters. Normal annual precipitation is 686 millimeters with 1,118 millimeters of snow in winter (Kuehnast and Baker, 1978). May and June are generally the wettest months and February the driest. Most rain comes as frontal storms and some as warm-weather convective storms.

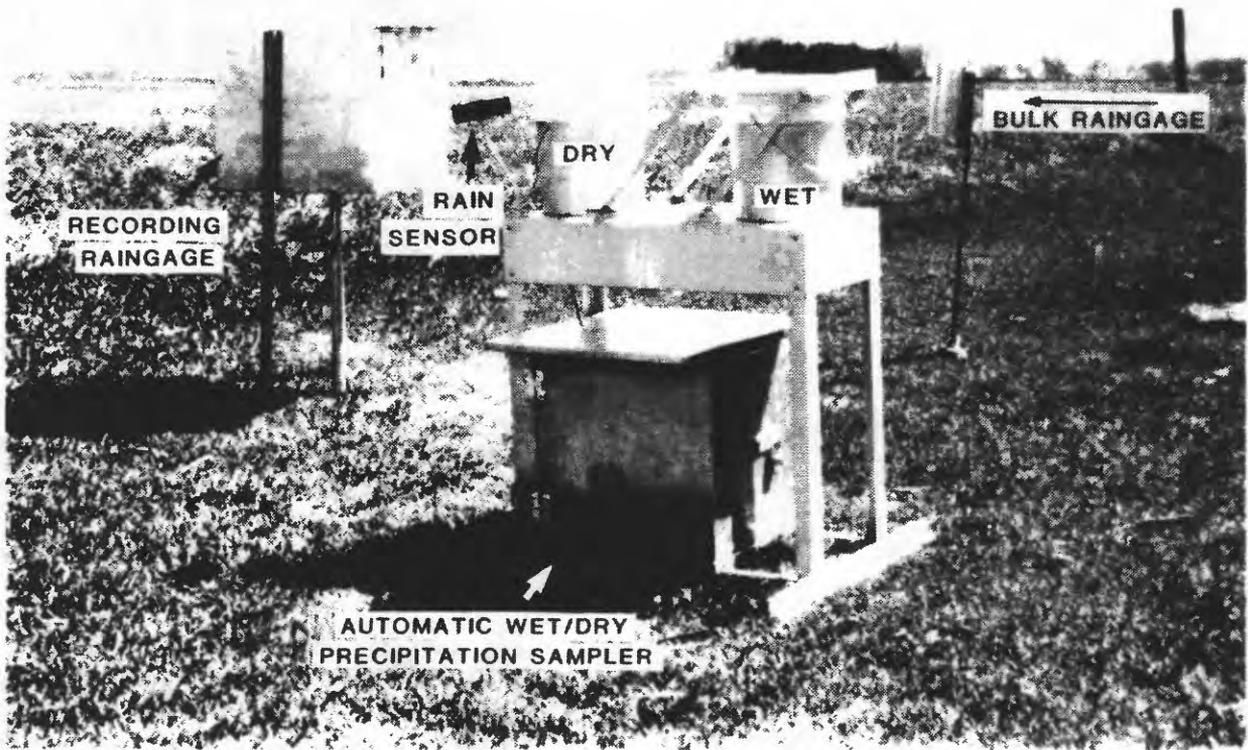
### Methods and Approach

Four automatic samplers that collected both wetfall and dryfall were placed in the metropolitan area to obtain data representative of regional variability in atmospheric deposition (fig. 1). The samplers were placed near 4 runoff monitoring sites: Bevens, Purgatory, and Shingle Creeks, and Eightieth Street storm-sewer watersheds. The sites were selected to typify different localized land use as well as to obtain satisfactory areal distribution of data points in the metropolitan area. Only one rural site was selected—Bevens Creek—because previous literature (Kramer, 1978) indicates that there is more variability in locally generated atmospheric deposition in urban areas than in rural areas. Shingle and Purgatory Creeks and Eightieth Street storm-sewer watersheds were chosen as representative of urban areas. Table 1 summarizes the characteristics of the rural and urban watersheds monitored for both atmospheric deposition and runoff quality and quantity.

Each of the four sampling sites was equipped with an automatic-sensing wet-dry precipitation collector (fig. 2). The collector is designed to collect: (1) rain and snow in a container open only during storms and (2) dry-deposited material in a second container open only between storms (Likens and Galloway, 1976). A sensor detects the occurrence of precipitation, activating a motor that removes the cover from the wet collector and transfers it to the dry collector. When precipitation ceases, the cycle is reversed.

Table 1.—Characteristics of rural and urban watersheds

Site location and drainage area	Letter designation (fig. 1)	County	General watershed characteristics
Bevens Creek at County Road 41, 21,472 hectares.	B	Carver	About 70 percent of watershed in farms. Principally dairy or feetlot operations and associated cropping. Most intensive agriculture is in lower two-thirds of watershed. Stream free flowing or channelized through lower part. Large series of wetlands and shallow lakes in headwaters. Loamy, well-drained, dark-colored soils.
Shingle Creek at Noble Avenue 5,931 hectares.	S	Hennepin	Upper third of watershed partly developed with low- to medium-density residential areas; urbanization continuing. Drains into several lakes. Lower part fully developed, medium-density residential with mixed commercial areas. Storm sewers drain directly into creek. Well-drained soils, loamy, light colored in upper part and sandy, dark colored in lower,
Purgatory Creek below Staring Lake, 6,216 hectares.	P	Hennepin	Partly urbanized in the upper part of the watershed. Rapid urbanization occurring in the middle and lower parts of the watershed. Lakes common, wetlands and open areas plentiful, especially along the channel system. Holding ponds common in existing storm-sewer systems. Loamy, well-drained, light-colored soils.
Eightieth Street storm sewer, 401 hectares	H	Washington	Fully developed medium-density residential areas 1 to 10 years old. Watershed is storm sewered with two wet and six dry in-line-holding ponds. Well-drained soils grade from loamy, dark colored in upper end of watershed to sandy, light colored in lower.



**Figure 2.--Bevens Creek automatic wet/dry precipitation installation**

A 15,240-millimeter-diameter bulk rain gage also was installed at each site to determine precipitation volumes associated with the wetfall collection. A recording tipping-bucket rain gage was installed at the Bevens Creek site in conjunction with the bulk gage for calibration purposes (fig. 2).

The location of each installation differed among the sites. The collector at Bevens Creek was near a farming operation, the Shingle Creek collector was in a large residential lot about 15 meters from the runoff gage, the Purgatory Creek collector was on the roof of a city government building, and the Eightieth Street storm-sewer collector was on top of a fire department building.

The collectors were visited every 2 to 4 weeks for sample collection, depending on the frequency of precipitation (table 2). Wetfall was collected by thoroughly mixing and pouring the sample from the precipitation collector into a polyvinylchloride sample bottle. Any large debris, such as twigs, grass, bark, insects, and litter were discarded before the sample was taken. Dryfall was collected by pouring 1 liter of deionized water into the dryfall collection bucket and, after mixing thoroughly, pouring the sample back into a sample bottle. If the precipitation collector's sensor malfunctioned, causing the dryfall sample to be contaminated with wetfall, the samples were combined into a composite atmospheric-deposition sample.

Table 2.--Sample collection periods and types of samples collected for the four atmospheric-deposition sampling sites from April 1 to October 31, 1980

[W/D, separate samples of wetfall and dryfall components;  
C, composite sample of wetfall and dryfall components]

Date	Bevens Creek	Shingle Creek	Purgatory Creek	Eightieth Street storm sewer
April 1-17 (18 days).....	W/D	W/D	W/D	W/D
April 17-May 19 (33 days).....	W/D	W/D	W/D	W/D
May 20-June 2 (14 days).....	W/D	W/D	W/D	W/D
June 3-16 (14 days).....	W/D	W/D	W/D	W/D
June 17-July 16 (30 days).....	W/D	C	W/D	C
July 17-August 13 (28 days).....	W/D	C	W/D	C
August 14-September 4 (22 days).....	W/D	C	W/D	C
September 5-18 (14 days).....	W/D	C	W/D	C
September 19-October 31 (44 days)...	W/D	W/D	W/D	W/D

The dryfall, wetfall, and composite samples were analyzed for total Kjeldahl nitrogen (TKN), dissolved nitrite-plus-nitrate nitrogen (NN), total phosphorus (TP), total sulfate (SO<sub>4</sub>), total chloride (Cl), and total lead (Pb) at the U.S. Geological Survey Laboratory in Atlanta, Ga. Further discussion on laboratory analyses and data-collection procedures are described in Payne and others (1982).

Atmospheric deposition, in kilograms per hectare, of TKN, NN, TP, SO<sub>4</sub>, Cl, and Pb were calculated for each of the four sites for the entire collection period, April 1 to October 31, 1980. The inputs of wetfall, dryfall, and composite were calculated by the equation:

Average daily atmospheric deposition =

$$\frac{\text{Concentration} \times \text{volume} \times \text{weight conversion}}{\text{Collection period} \times \text{bucket area} \times \text{area conversion}}$$

where

Average daily atmospheric deposition = wetfall, dryfall, or composite atmospheric deposition of constituent, in kilograms per hectare.

Concentration = concentration of constituent in wetfall, dryfall, or composite as reported from the laboratory, in milligrams per liter.

Volume = the total precipitation in collection bucket for wetfall and composite inputs, and for dryfall input the volume is the total amount of water added to the sample for hydration, both in liters,

Weight conversion = the conversion of milligrams to kilograms ( $1.0 \times 10^{-6}$ ),

Collection period = the number of days in the collection period,

Bucket area = the area of the collection bucket, in square meters, and

Area conversion = the conversion of square meters to hectares ( $1.0 \times 10^{-4}$ ).

The relationship between total deposition input and localized land uses in the four watersheds was tested by both linear- and multiple-regression models. The statistical models incorporated localized land uses as independent variables and annual deposition loads as dependent variables. Regression analysis was performed using the SAS procedure PROC STEPWISE (Barr and others, 1976). The procedure develops a model by adding one independent variable at a time to the regression model, using F-statistics and significant levels as selection criteria, until an acceptable model is produced. Regression analysis was performed on each of the constituents determined in the analyses of atmospheric deposition: Kjeldahl nitrogen, nitrite-plus-nitrate nitrogen, phosphorus, sulfate, chloride, and lead.

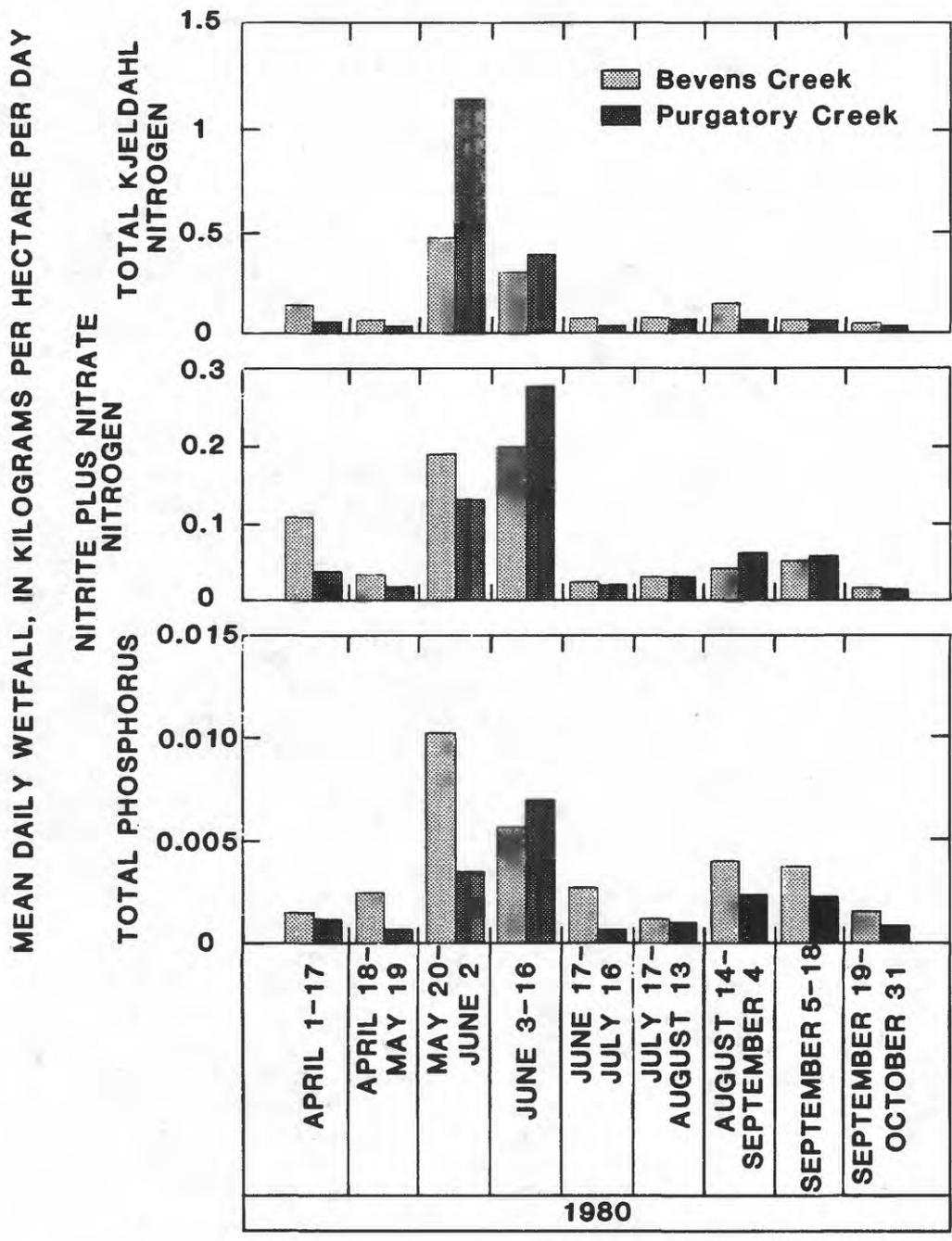
## RESULTS AND DISCUSSION

### Wetfall and Dryfall

Mean daily wetfall and dryfall concentrations in kilograms per hectare for Kjeldahl nitrogen, nitrite-plus-nitrate nitrogen, phosphorus, sulfate, chloride, and lead for Bevens and Purgatory Creeks watersheds from April 1 to October 31, 1980, are plotted in figures 3, 4, 5, and 6. Bevens and Purgatory Creeks watersheds were the only watersheds with both wetfall and dryfall samples throughout the collection period. The other two sites both had equipment failure, causing the wetfall and dryfall samples to be mixed into bulk samples from June 17 to September 18, 1980. Therefore, a discussion of the differences between wetfall and dryfall components in atmospheric deposition is limited to Bevens and Purgatory Creeks watersheds.

Wetfall-deposition rates for the six constituents in Bevens and Purgatory Creeks watersheds had similar seasonal patterns but differed in actual yield (figs. 3 and 4). The similarity in seasonal patterns between a rural watershed, Bevens Creek, and an urban watershed, Purgatory Creek, is an indication that the atmospheric deposition of Kjeldahl nitrogen, nitrite-plus-nitrate nitrogen, total phosphorus, sulfate, and lead are primarily controlled by regional weather systems. However, the deposition-rate differences between sites are a reflection of the local influences (industrial emissions, agricultural practices, etc.) on yield from the atmosphere. Similar seasonal variations for nitrogen, phosphorus, sulfate, and lead have also been noted in northern Minnesota and other parts of the United States (Eisenreich and others, 1978; Glass and Loucks, 1980; Hendry and Brezonik, 1980). The peak during early June is due to the difference in storm patterns (Hendry and Brezonik, 1980). Late spring (June) storms are generally frontal movements associated with large regional air masses, whereas convective storms in summer are generally associated with local air masses. A peak during late spring or June is caused by both the increased deposition of atmospheric contaminants from regional air masses and by conditions of persistent low-lying inversion layers that reduce atmospheric dispersion while increasing atmospheric deposition in the local area. Late summer peaks of chloride, also noted in Minnesota, are probably due to frontal movements caused by northwesterly winds transporting chloride in regional air masses from the northwest coastal regions (Eisenreich and others, 1978). The deposition rates of chloride from these frontal storms are dependent on precipitation and wind speed, which vary between watersheds.

Deposition rates are also affected by frontal air masses that originate in the southwestern coastal region of the United States. The transport of chloride from the coastal region to Minnesota covers a great distance and, therefore, the characteristics of the frontal movement become important. If the moisture-laden front moves rapidly to Minnesota, input of chloride will be high. Conversely, if frontal movement is slow, most of the coastal moisture is lost before the front reaches Minnesota and the deposition of chloride is less. This is a simplified example, because other frontal-storm characteristics also affect the deposition of chloride for any one geographical area.



**Figure 3.--Histograms of mean daily wetfall for total Kjeldahl nitrogen, nitrite plus nitrate nitrogen, and total phosphorus for Bevens Creek and Purgatory Creek watersheds from April 1 to October 31, 1980**

MEAN DAILY WETFALL, IN KILOGRAMS PER HECTARE PER DAY

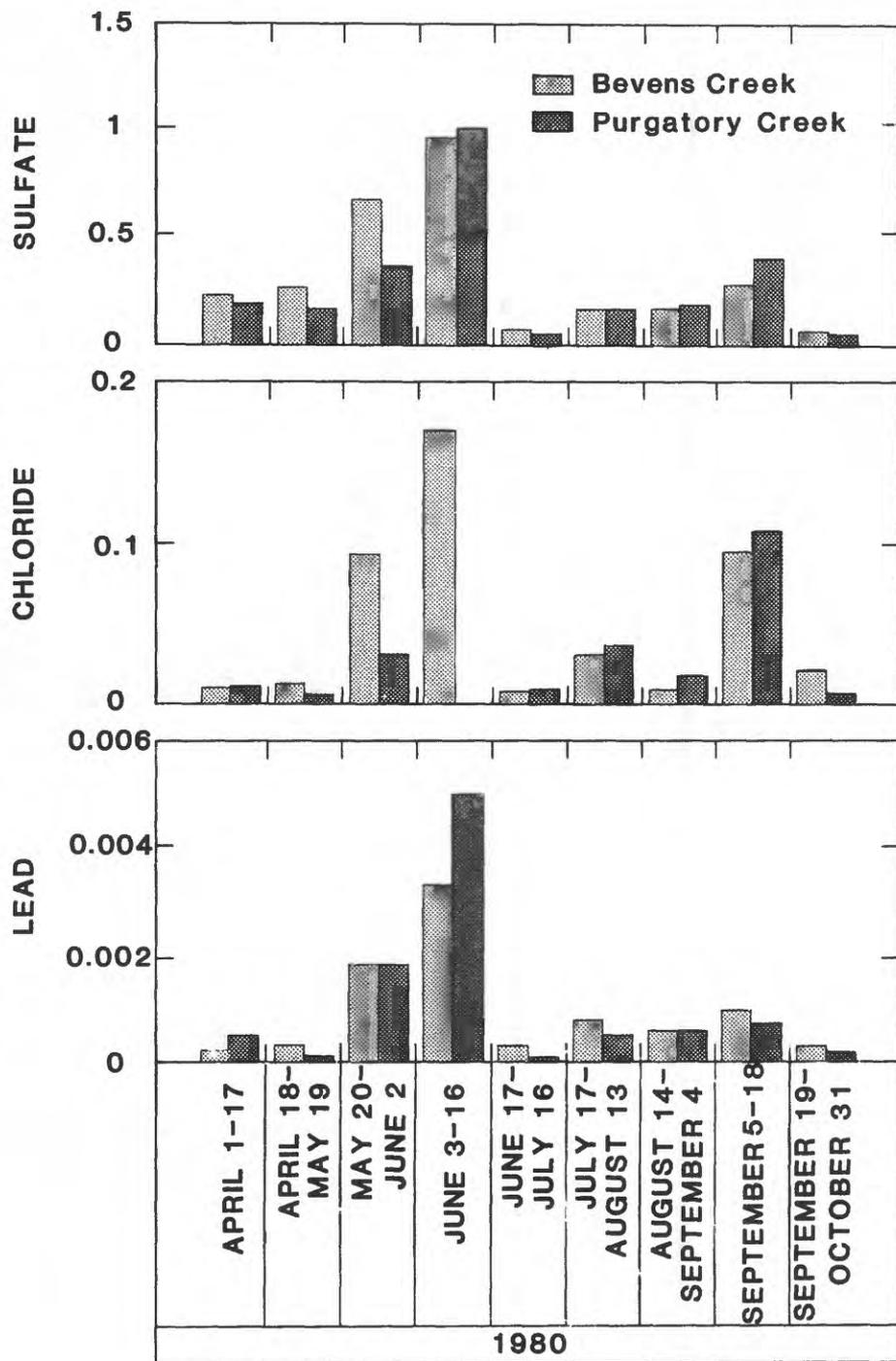


Figure 4.--Histograms of mean daily wetfall for sulfate, chloride, and lead for Bevens Creek and Purgatory Creek watersheds from April 1 to October 31, 1980

MEAN DAILY DRYFALL, IN KILOGRAMS PER HECTARE PER DAY

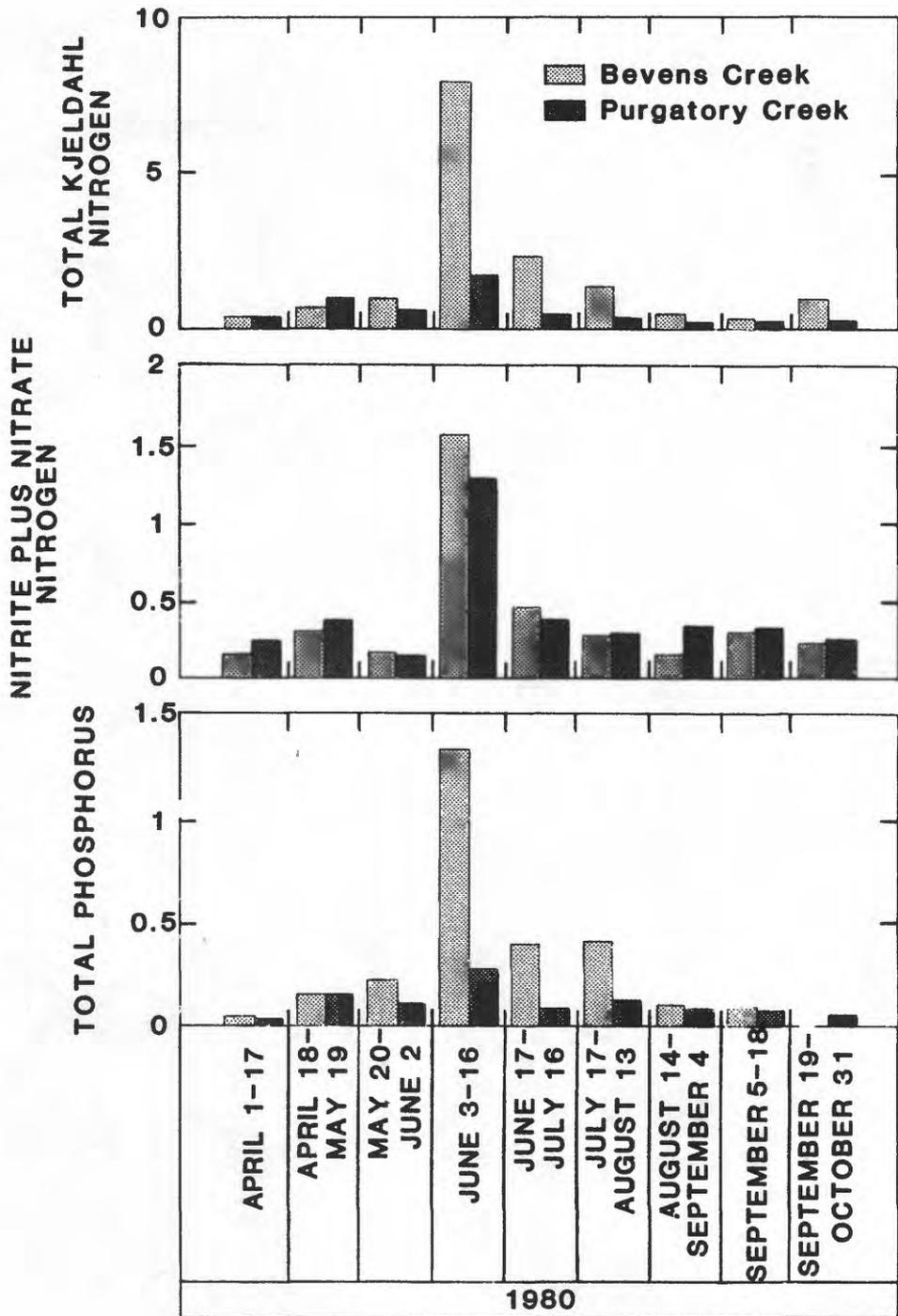


Figure 5.--Histograms of mean daily dryfall for total Kjeldahl nitrogen, nitrite plus nitrate nitrogen, and total phosphorus for Bevens Creek and Purgatory Creek watersheds from April 1 to October 31, 1980

MEAN DAILY DRYFALL, IN KILOGRAMS PER HECTARE PER DAY

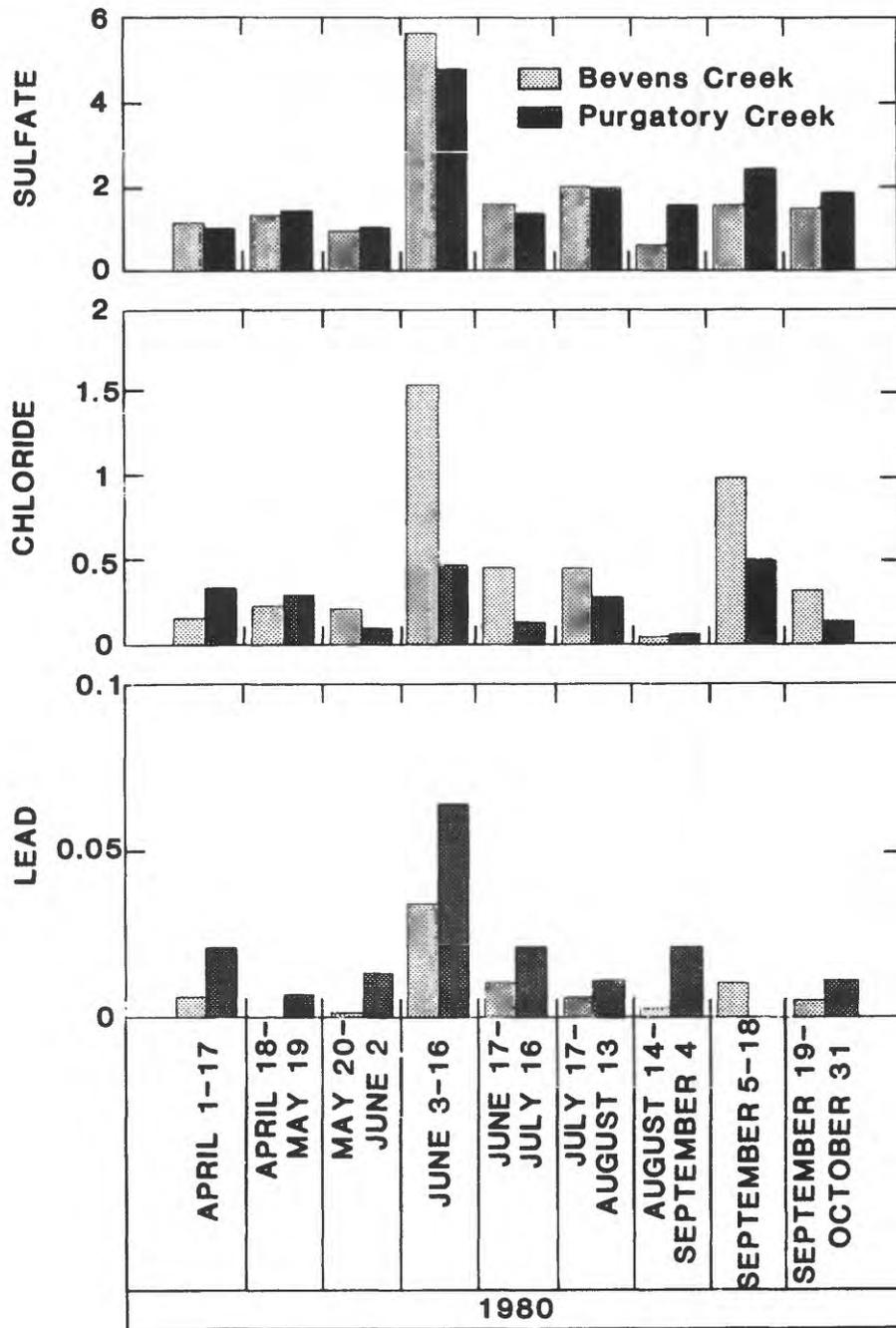


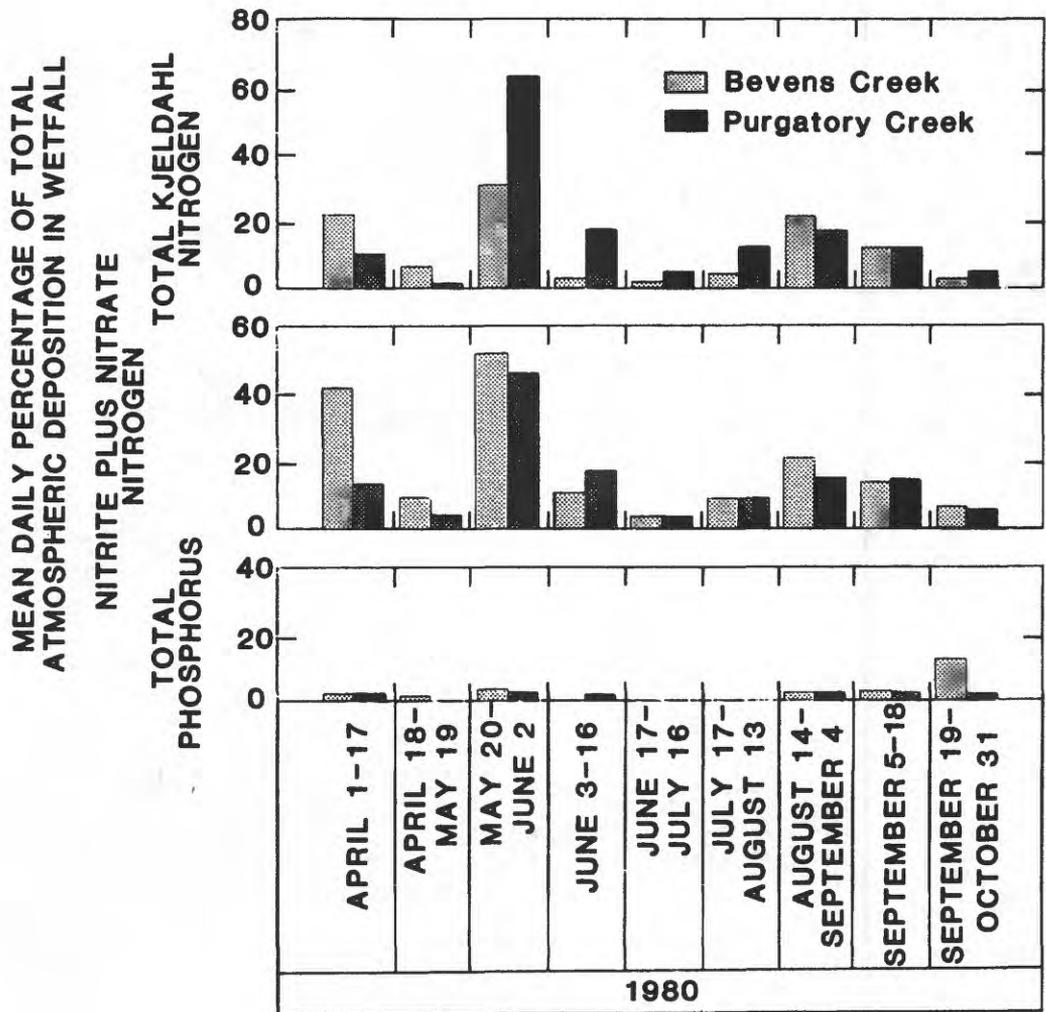
Figure 6.--Histograms of mean daily dryfall for sulfate, chloride, and lead for Bevens Creek and Purgatory Creek watersheds from April 1 to October 31, 1980

In late spring, winds generally are southerly and regional air masses transport atmospheric contaminants from the lower Mississippi valley, which has extensive industrial areas, to the Twin Cities (Baker and others, 1979). Minnesota is effectively cut off from Gulf air masses by August when the winds become northwesterly, passing over areas in which land use is primarily agricultural. The peak during June for all constituents is primarily caused by southerly winds, laden with atmospheric contaminants, that move from the Gulf to Minnesota. These southerly winds gradually decrease during summer and northwesterly winds predominate during autumn and winter. The gradual decrease in southerly winds is evident by the gradual decrease in atmospheric deposition throughout summer. Smaller peaks during summer are caused by occasional large convective storms.

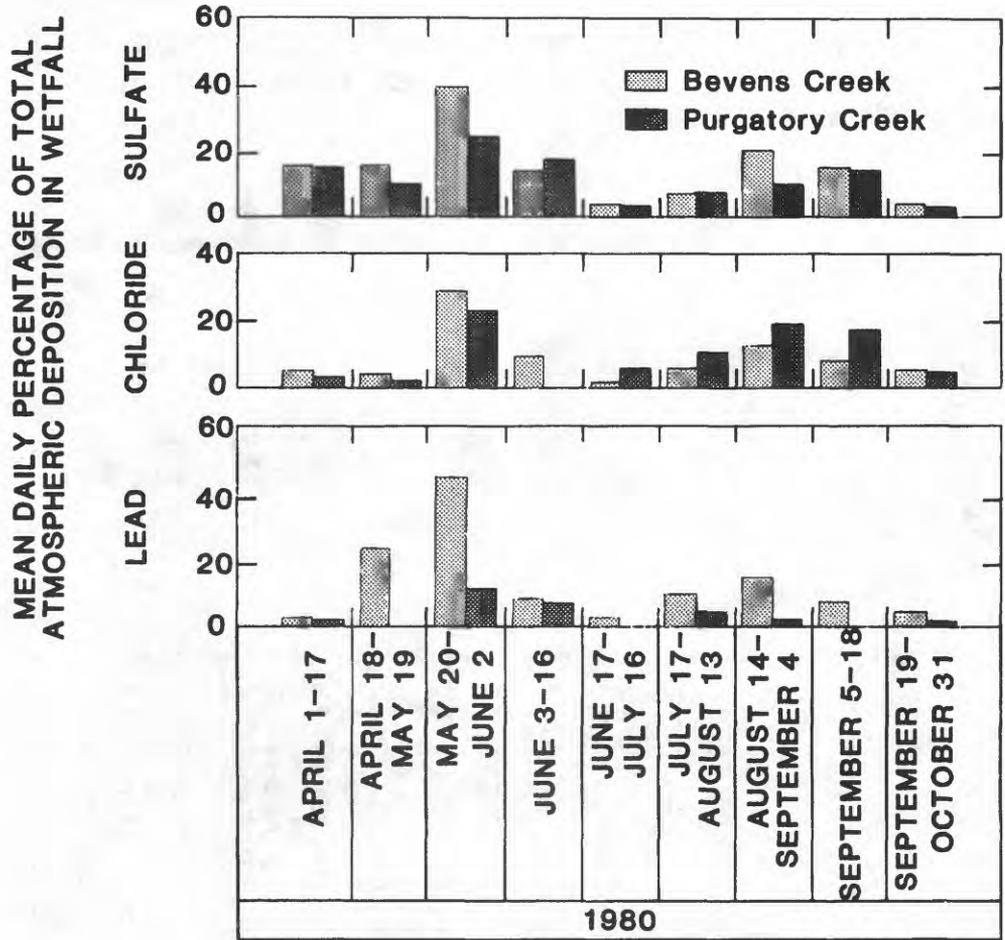
Local influence on wetfall is indicated by the differences between deposition rates at Bevens and Purgatory Creek watersheds. Large differences between sites in atmospheric deposition of Kjeldahl nitrogen, phosphorus, and chloride may be caused by differences in land use between the two watersheds. However, there were no significant correlations found between land use and atmospheric deposition of any constituent. These insignificant correlations suggest that land use is not entirely responsible for atmospheric-deposition differences. In contrast, similarity of nitrite-plus-nitrate nitrogen, sulfate, and lead atmospheric-deposition rates between sites suggests regional influences rather than local influences.

Seasonal patterns of dryfall concentrations in Bevens and Purgatory Creeks are similar to the wetfall patterns, as illustrated in figures 5 and 6. Kjeldahl nitrogen showed the only difference between wetfall- and dryfall-deposition rates. This difference may be caused by the origins of wetfall and dryfall. Kjeldahl nitrogen dryfall at Purgatory Creek was about equal to the wetfall rate. In contrast, Bevens Creek dryfall was approximately twentyfold that of wetfall. Agricultural practices, such as plowing and planting, that promote wind erosion may have contributed to the high dryfall rates in Bevens Creek watershed. Purgatory Creek, an urban watershed, had lower dryfall rates, possibly because paved industrial and residential areas are more common than open-land agricultural areas. However, these cause-and-effect relationships are theoretical and not based on any statistical analysis.

The percentages of atmospheric deposition in wetfall for all six constituents in Bevens and Purgatory Creek watersheds are shown in figures 7 and 8. Generally, the atmospheric deposition was comprised of 20 percent wetfall; however, the phosphorus was extremely low in wetfall, mostly under 5 percent, whereas Kjeldahl nitrogen at Purgatory Creek was 67 percent wetfall during one sampling period.



**Figure 7.--Histograms of mean daily percentage of atmospheric deposition in wetfall for total Kjeldahl nitrogen, nitrite plus nitrate nitrogen, and total phosphorus for Bevens Creek and Purgatory Creek watersheds from April 1 to October 31, 1980**



**Figure 8.--Histograms of mean daily percentage of atmospheric deposition in wetfall of sulfate, chloride, and lead for Bevens Creek and Purgatory Creek watersheds from April 1 to October 31, 1980**

### Total Atmospheric Deposition

Total atmospheric deposition (the sum of wetfall and dryfall) in kilograms per hectare per day, (kg/ha)/d, for each constituent in the four watersheds from April 1 to October 31, 1980, is illustrated in figures 9 and 10. The mean daily atmospheric deposition of all constituents in all four watersheds followed similar seasonal patterns and peaked in June, except for chloride. Shingle Creek watershed had an extremely high yield of chloride, 1,526 (kg/ha)/d during June, compared to the other sites in which yields ranged from 246 to 616 (kg/ha)/d. This high yield was probably due to the great amount of urbanization in the watershed. The other three watersheds have less urbanization and more residential and agricultural areas (table 1). The difference between Shingle Creek and the other three watersheds in peak total deposition of chloride was also evident for the other constituents except phosphorus. Bevens Creek, a rural watershed, had the highest daily phosphorus load, which was due to the high concentration of phosphorus in dryfall (figs. 5 and 6), possibly resulting from agricultural activities. The consistently high peaks for the other five constituents in Shingle Creek watershed could be attributed to commercial development because that is the single major land-use difference between the four watersheds. The peaks were also an indication that atmospheric loads are locally being influenced during early summer to a greater degree in Shingle Creek watershed than in the other three watersheds, which may result from the extensive commercial development in the Shingle Creek watershed.

Peak deposition of atmospheric chloride was variable among watersheds. Deposition of chloride in the Shingle Creek watershed peaked in June only, following the same pattern of the other constituents in that watershed. Atmospheric deposition of chloride in Purgatory Creek watershed peaked both in August and September, similar to Eightieth Street. Atmospheric deposition of chloride in Bevens Creek watershed peaked in June, August, and September. The differences between seasonal patterns may have been caused by variation in frontal-storm characteristics between watersheds, such as precipitation and wind patterns.

Linear multiple-regression analyses indicate there was no significant relationship (95 percent confidence interval) between total atmospheric deposition and land use within each watershed. However, there did appear to be some relationship between local land use and the magnitude of atmospheric deposition within any one month. The small sample size and overriding influence of seasonal patterns may have masked any significant trends present in the regression analyses. The influence of weather patterns seems to dominate the overall seasonal pattern for all the constituents except chloride, but local emissions seem to influence the magnitude of atmospheric deposition. Therefore, local emissions of contaminants contribute to the atmospheric deposition but do not dominate it; thus, the atmospheric deposition is influenced by both local and regional contaminant emissions as they are transported by large regional weather patterns.

MEAN DAILY TOTAL ATMOSPHERIC DEPOSITION,  
IN KILOGRAMS PER HECTARE PER DAY

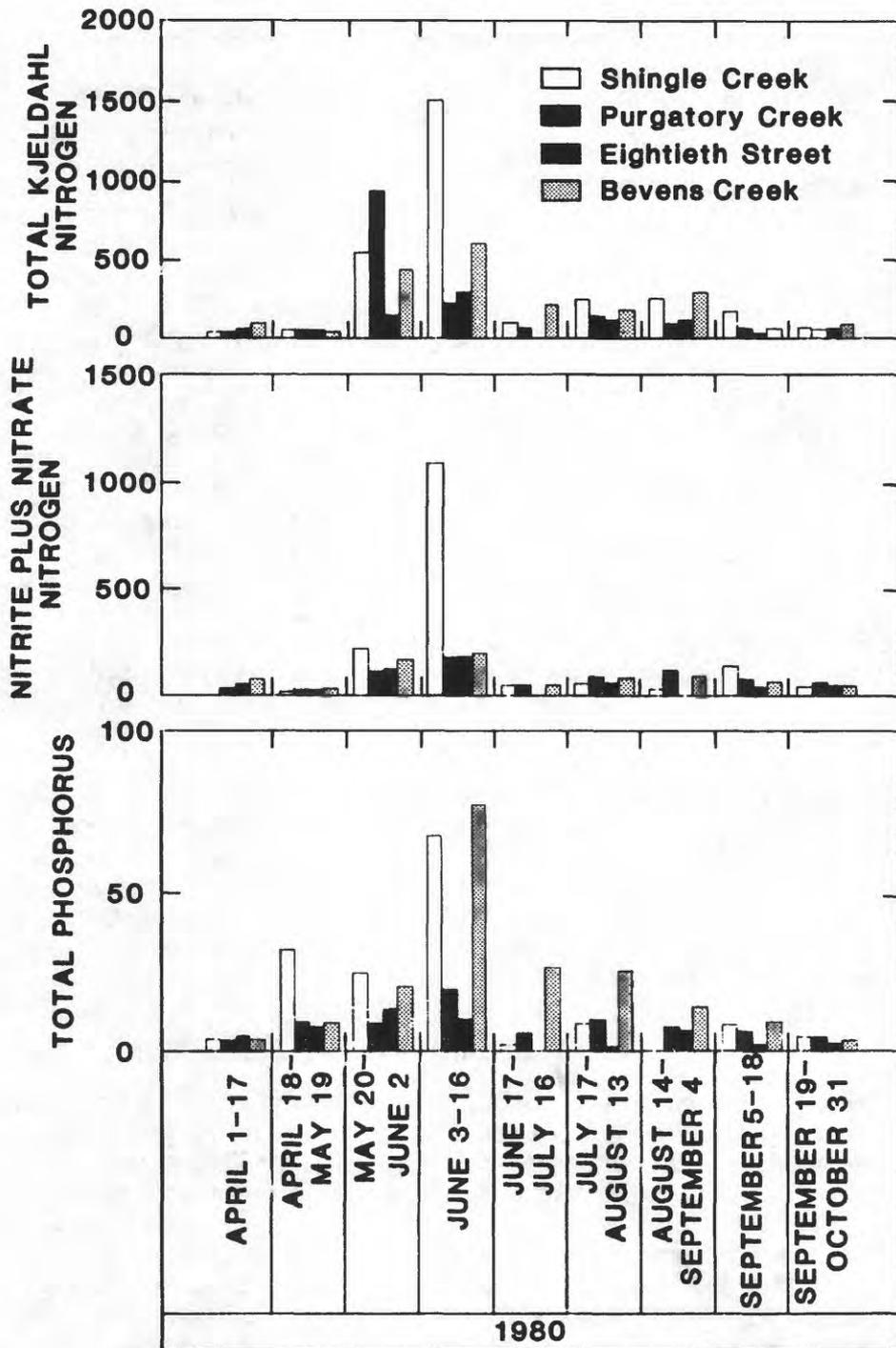
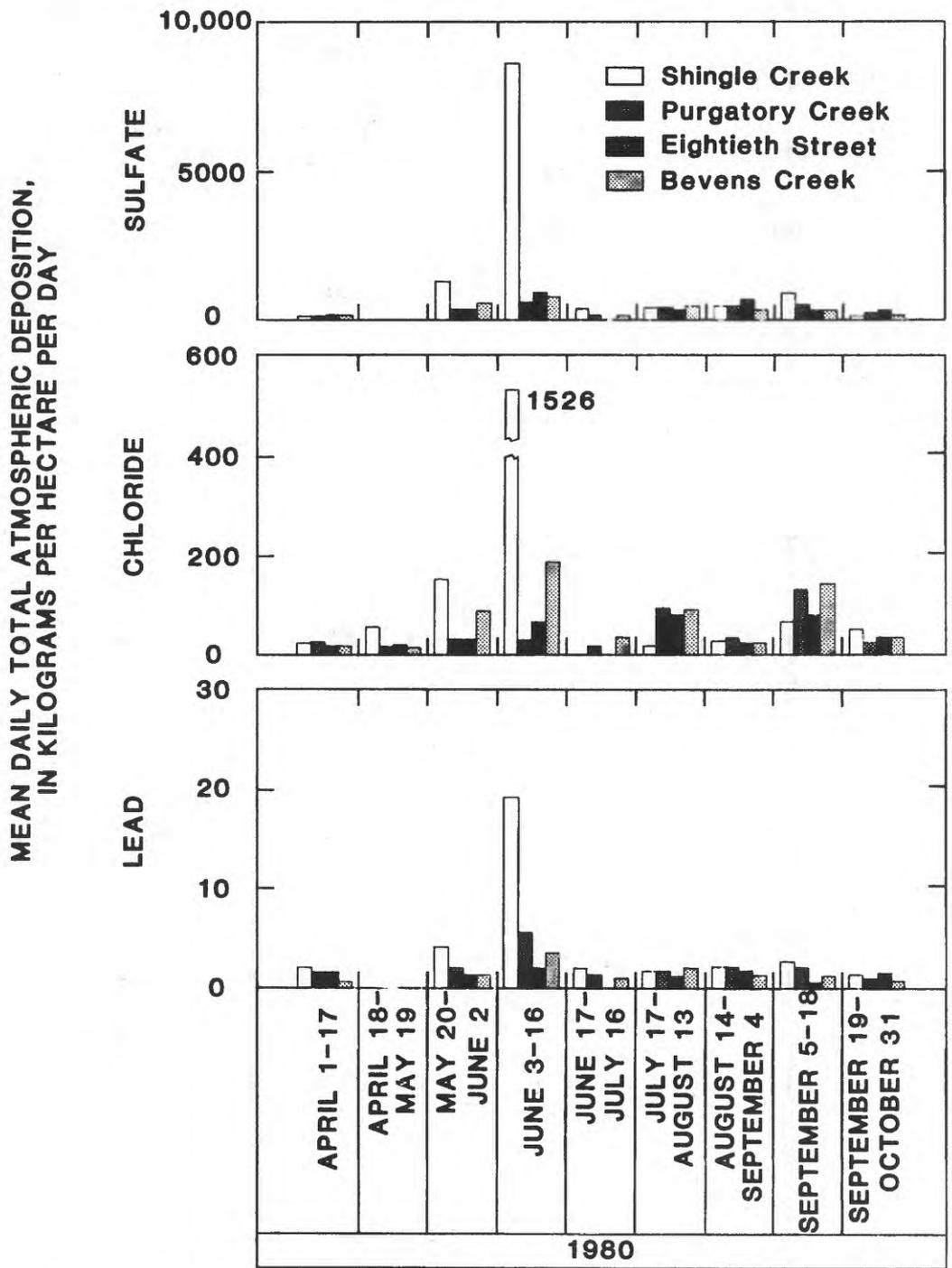


Figure 9.--Histograms of mean daily total atmospheric deposition of total Kjeldahl nitrogen, nitrite plus nitrate nitrogen, and total phosphorus for Shingle Creek, Purgatory Creek, Eightleth Street, and Bevens Creek watersheds from April 1 to October 31, 1980



**Figure 10.--Histograms of mean dally total atmospheric deposition of sulfate, chloride, and lead for Shingle Creek, Purgatory Creek, Eightieth Street, and Bevens Creek watersheds from April 1 to October 31, 1980**

## Contribution to Urban Runoff

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Atmospheric deposition in the Twin Cities Metropolitan Area is a likely source of some constituents in nonpoint-source pollution runoff, as indicated in table 3. The atmospheric-deposition data given in the table are the amounts of input only to open-water areas in the watershed, such as lakes, ponds, and stream channels, and impervious areas such as streets, roof tops, and parking lots. Deposition to areas other than open water and impervious parts of the watershed may have a significant impact on nonpoint-source pollution, but is not readily quantifiable. The calculated total atmospheric deposition load to the entire watershed does not take into account the effects of vegetation uptake on atmospheric deposition rates, ion absorption and adsorption in soils, and the resuspension of atmospheric deposition from nonvegetated surfaces such as streets and bare fields. The deposition to impervious areas was assumed to be a direct input to receiving waters via storm-sewer drainage.

The influence of atmospheric deposition on nonpoint-source runoff generally was higher in Shingle and Purgatory Creek watersheds than in Bevens Creek and Eightieth Street storm-sewer watersheds. The difference is due to a combination of higher atmospheric loads in more urbanized areas and more extensive open-water and impervious areas in Shingle and Purgatory Creek watersheds. Shingle and Purgatory Creek watersheds both have approximately 8 percent open-water and impervious areas, and Bevens and Eightieth Street storm-sewer watersheds have about 3 and 4 percent open-water and impervious areas, respectively.

The relative contribution of atmospheric contaminants to runoff loads is similar for both Shingle and Purgatory Creek watersheds, with  $NN > Pb > TKN > TP > Cl$ . Relative contributions in Bevens Creek and Eightieth Street storm-sewer watersheds differed with  $Pb > TKN > TP > NN > Cl$  and  $NN > TKN > TP > Pb > Cl$ , respectively. The percentage of runoff loads contributed by atmospheric deposition of all five constituents was generally greatest in Purgatory Creek watershed. However, the total atmospheric-deposition load to open-water and impervious areas for all five constituents was greatest in Shingle Creek watershed, which may be due to extensive urbanization that includes commercial and industrial developments.

The contributions of nitrite-plus-nitrate nitrogen and lead from atmospheric deposition to runoff loads are high, an average of 40 and 27 percent, respectively, whereas contributions of phosphorus and chloride are low, 10 percent and 1 percent, respectively. Studies of nonpoint-source pollution in runoff that includes determinations of nitrite-plus-nitrate nitrogen and lead should be concerned with the impact of atmospheric deposition. A significant part of the runoff load may come not from the basin but from atmospheric deposition. In contrast, phosphorus and chloride loads in runoff probably are not as influenced by atmospheric input.

Table 3.--Approximate contribution of atmospheric deposition to runoff loads of total Kjeldahl nitrogen, dissolved nitrite-plus-nitrate nitrogen, total phosphorus, total chloride, and total lead for Bevens, Shingle, and Purgatory Creeks, and Eightieth Street storm-sewer watersheds from April 1 to October 31, 1980

[Atmospheric deposition loads are to open-water and impervious areas in the watershed, and runoff loads are in kilograms per hectare. Percentage of runoff loads are the loads estimated to be contributed by atmospheric deposition]

Site	Total Kjeldahl nitrogen	Dissolved nitrite plus-nitrate nitrogen	Total phosphorus	Total chloride	Total lead
<b>Bevens Creek</b>					
Atmospheric deposition <sup>1</sup> ..	37	14	4	13	.22
Runoff load <sup>2</sup> .....	836	709	189	9,292	2.5
Percent of runoff load <sup>3</sup> ..	4	1.9	2.1	.1	9
<b>Shingle Creek</b>					
Atmospheric deposition...	176	101	14	843	4.1
Runoff load.....	982	147	128	25,059	20
Percent of runoff load...	18	69	11	4	21
<b>Purgatory Creek</b>					
Atmospheric deposition...	167	46	11	86	1.46
Runoff load.....	627	55	41	17,254	1.92
Percent of runoff load...	27	84	27	.5	76
<b>80th Street storm sewer</b>					
Atmospheric deposition...	28	14	2	18	.26
Runoff load.....	1,068	315	253	18,473	28
Percent of runoff load...	3	4	1	.1	.9

<sup>1</sup>Atmospheric deposition loads to open-water and impervious areas in the watershed, in kilograms per hectare.

<sup>2</sup>Runoff loads in kilograms per hectare.

<sup>3</sup>Estimated percent of runoff loads contributed by atmospheric deposition.

#### SUMMARY AND CONCLUSIONS

Atmospheric deposition in terms of both wetfall and dryfall was studied in one rural and three urban watersheds for six chemical constituents from April 1 to October 31, 1980. The seasonal patterns of both wetfall and dryfall concentrations of total Kjeldahl nitrogen, nitrite-plus-nitrate nitrogen, phosphorus,

sulfate, and lead are similar in both rural and urban watersheds. Chloride seasonal patterns were varied due to frontal storm influences. Total atmospheric deposition, wetfall and dryfall combined, for all four watersheds also has similar seasonal patterns for each constituent, except chloride, indicating a prominent regional influence. Local influence on the distribution of atmospheric-deposition loadings was also evident from the differences in input rates between watersheds for each constituent.

Regression analyses of the relationships between atmospheric loadings of the six constituents and individual land-use and basin characteristics failed to identify any significant trends. The findings suggest that atmospheric deposition loadings in the metropolitan area are a complicated mix of local and regional mechanisms and sources.

Atmospheric deposition for all six constituents at Shingle Creek, the most urbanized watershed, had significantly higher peaks, as much as ninefold higher, than the other three watersheds. These higher peaks are likely the result of local influences from urbanization such as traffic flow and industrial emissions. Atmospheric contaminants from these urban sources are mixed with regional air masses during early summer and, due to persistent low-lying inversion layers, the atmospheric dispersion of the contaminants is reduced and deposition is increased in the local area, particularly in Shingle Creek watershed. Deposition in the Shingle Creek watershed peaked during this period in all constituents, as follows: Kjeldahl nitrogen 1,500 (kg/ha)/d; nitrite-plus-nitrate nitrogen 1,000 (kg/ha)/d; phosphorus 71 (kg/ha)/d; sulfate 8,900 (kg/ha)/d during June, chloride 410 (kg/ha)/d, and lead 21 (kg/ha)/d.

In the rural watershed, Bevens Creek, phosphorus may have been influenced by local activities, peaking during June at 79 (kg/ha)/d. Agricultural activities such as plowing, bare fields, and harvesting could have produced the high concentrations of phosphorus in dryfall. The urban areas were lower in phosphorus, ranging from 9 to 71 (kg/ha)/d. Phosphorus levels in Shingle Creek watershed were higher than in other urban watersheds, perhaps due to greater use of lawn fertilizer and commercial detergents.

Atmospheric contributions of nitrogen, in the form of dissolved nitrite plus nitrate, and lead to nonpoint-source runoff loads were high, as much as 84 percent of the runoff load. In contrast, atmospheric contributions of phosphorus and chloride were not as significant. The average relative contributions of the five constituents were nitrite-plus-nitrate nitrogen (40 percent of runoff loadings), lead (27 percent), Kjeldahl nitrogen (13 percent), phosphorus (10 percent), and chloride (1 percent). Relative contributions of atmospheric deposition input to runoff were twofold higher in Purgatory Creek watershed than in the other three watersheds.

Future investigations of nonpoint-source pollution in runoff should include the impact of nitrite-plus-nitrate nitrogen and lead from atmospheric deposition because the origin of these constituents may not be directly from terrestrial sources.

## REFERENCES

- Baker, D. G., Nelson, W. W., Kuehnast, E. L., 1979, Climate of Minnesota: Part XII - The hydrologic cycle and soil water: University of Minnesota Agricultural Experiment Station, University of Minnesota Technical Bulletin 322, 23 p.
- Barr, A. J., Goodnight, J. H., Sall, J. P., and Helvig, J. T., 1976, A user's guide to SAS 76: SAS Institute, Inc., Raleigh, N.C., 329 p.
- Cogbill, C. V., and Likens, G. E., 1974, Acid precipitation in the north eastern United States: Water Resources Research, v. 10, p. 1133-1137.
- Driscoll, C. T., 1980, Chemical characterization of some dilute acidified lakes and streams in the Adirondack region of New York state: Thesis, Cornell University, Ph. D., 62 p.
- Eisenreich, S. J., Hollod, G. J., and Langevin, S., 1978, Precipitation chemistry and atmospheric deposition of trace elements in northeastern Minnesota: Report to the Minnesota Environmental Quality Council.
- Eisenreich, S. J., Looney, B. B., and Thornton, J. D., 1981, Airborne organic contaminants in the Great Lakes ecosystem: Environmental Science and Technology, v. 15, no. 1, p. 30-38.
- Federal Water Pollution Control Administration, 1969, Water-pollution aspects of urban runoff: Water pollution Control Series WP-20-15, 272 p.
- Galloway, J. N., Likens, G. E., and Edgerton, E. S., 1976, Acid precipitation in the northeastern United States: pH and acidity: Science, v. 194, p. 722-724.
- Gjessing, E. T., Henriksen, A., Johannessen, M., and Wright, R. F., 1976, Effects of acid precipitation on freshwater chemistry, in Braekke, F. H., ed., Impact of acid precipitation on forest and freshwater ecosystems in Norway: SNNF-project, Oslo.
- Glass, F. E., and Loucks, O. L., 1980, Impacts of airborne pollutants on wilderness areas along the Minnesota-Ontario border: U.S. Environmental Protection Agency Report 600/3-80-044.
- Hendry, C. D., and Brezvnik, P. L., 1980, Chemistry of precipitation at Gainsville, Florida: Environmental Science and Technology, v. 14, no. 7, p. 843-849.
- Johnson, N. M., 1979, Acid rain: neutralization within the Hubbard Brook ecosystem and regional implications: Science, v. 204, p. 497-499.
- Kramer, J. R., 1978, Acid precipitation, in Nriagu, J. D., ed., Sulfate in the environment: New York, Wiley and Sons.
- Kuehnast, E. L., and Baker, D. G., 1978, Climate of Minnesota, part X, precipitation normals of Minnesota: 1941-1970: University of Minnesota, Agricultural Experiment Station, 15 p.
- Lewis, W. M., Jr., and Grant, M. C., 1980, Acid precipitation in the western United States: Science, v. 207, p. 176-177.
- Likens, G. E., and Galloway, J. N., 1976, Calibration of collection procedures for the determination of precipitation chemistry: Water, Air, and Soil Pollution, no. 6, p. 241-258.
- Likens, G. E., Wright, R. F., Galloway, J. N., and Butler, T. J., 1979, Acid rain: Scientific American, v. 241, p. 43-50.
- Oberts, G. L., and Jouseau, Marcel, 1979, Water pollution from non-point sources: an assessment and recommendations: Metropolitan Council of the Twin Cities Area, publication no. 62-79-008, 194 p.

- Payne, G. A., Ayers, M. A., and Brown, R. G., 1982, Quality of runoff from small watersheds in the Twin Cities Metropolitan Area, Minnesota—Hydrologic data for 1980: U.S. Geological Survey Open-File Report 82-504, 293 p.
- Ritter, J. R., and Brown, A. E., 1981, An evaluation of the effects of acid rain on low conductivity headwater streams in Pennsylvania: U.S. Geological Survey Open-File Report 81-1025, 53 p.
- Swank, W. T., and Henderson, G. S., 1976, Atmospheric input of some cations and anions to forest ecosystems in North Carolina and Tennessee: Water Resources Research, v. 12, no. 3, p. 541-546.