

WRC RESEARCH REPORT NO. 92

SOURCES OF PHOSPHORUS INPUTS FROM THE ATMOSPHERE  
AND THEIR  
SIGNIFICANCE TO OLIGOTROPHIC LAKES

Thomas J. Murphy  
Department of Chemistry  
De Paul University

F I N A L   R E P O R T

Project No. A-065-I11.

The work upon which this publication is based was supported by funds provided by the U. S. Department of the Interior as authorized under the Water Resources Research Act of 1964, P. L. 88-379 Agreement No. 14-31-0001-4013

UNIVERSITY OF ILLINOIS  
WATER RESOURCES CENTER  
2535 Hydrosystems Laboratory  
Urbana, Illinois 61801

September, 1974

## Table of Contents

Objectives	1
Procedures and Methods	4
Procedures	4
Chemical Analysis	5
Neutron Activation Analysis	8
Sources of Particulate Matter to the Atmosphere	9
Calculations	12
Results and Discussion	14
Phosphorus in Rainfall	14
Particulate Matter	14
Atmospheric Distribution of Phosphorus	17
Sources of Phosphorus Containing Particulate Matter	24
Total Inputs of Phosphorus to the Atmosphere	31
The Significance of Atmospheric Inputs of Phosphorus	35
Conclusions	39
References	40
Appendix A	43

## ABSTRACT

Precipitation in the Chicago area was analysed and found to contain .034 mg/l. of phosphorus with about one half of this present as ortho phosphate. Because of the small amounts of phosphorus needed to stimulate the growth of organisms in bodies of water which are phosphorus limited, these inputs from the atmosphere are important to many natural bodies of water. From one-fifth to one-third of the phosphorus going into Lake Michigan is from precipitation.

The sources of this phosphorus were investigated and found to be almost all sources of particulate matter. With the exception of emissions from the fertilizer industry these were found to contain a relatively consistent 0.1 percent phosphorus. Since the discharge of particulates to the atmosphere are being controlled, contributions of phosphorus to bodies of water from the atmosphere would also be controlled.

Murphy, Thomas J.

SOURCES OF PHOSPHORUS INPUTS FROM THE ATMOSPHERE AND THEIR SIGNIFICANCE TO OLIGOTROPHIC LAKES

This is the final report of project A-065-111 to the Office of Water Research and Technology.

Keywords: Phosphorus; Precipitation; Particulate Matter; Oligotrophic Lakes; Lake Michigan; Atmospheric Inputs; Nutrients; Smoke.

## ACKNOWLEDGEMENTS

The work reported on here was supported principally through OWRT Annual Allotment Project Number A-065-ILL. The author wishes to express his thanks for this support to the Office of Water Research and Technology and to the University of Illinois Water Resources Center.

This project would have accomplished little without the competent assistance of Dennis Cesarotti, Charles Rzeszutko, Paul Doskey and Larry O'Connor, the contributions of the burn samples by Dr. Ellis F. Darley, and of the air particulate samples by the Department of Environmental Control of the City of Chicago, and the help and guidance of Dr. Donald F. Gatz of the Illinois State Water Survey, with the air particulate methodology. The author would like to express his special gratitude to these people.

The project was supported through its initial stages by DePaul University and the neutron activation analysis work was supported through the Thesis Part Program of Argonne National Laboratory. The author would like to express his appreciation to these two sources, and to Dr. David Edgington of Argonne National Laboratory for his help.

Some of the work reported herein will serve as a masters thesis for Mr. Cesarotti. A preliminary report of the results of this project was presented in a paper to the 37th Annual Meeting of the American Society of Limnology and Oceanography in June 1974. Additionally, this work will shortly be submitted for publication.

OBJECTIVES

This project had three objectives. They were:

- 1) to determine the amount of phosphorus in particulate matter washed out of the atmosphere by precipitation.
- 2) to determine the source of this particulate matter to the atmosphere.
- 3) to evaluate the significance of this source of nutrient to oligotrophic lakes.

The first objective was accomplished by the collection and measurement of precipitation in Chicago and determining the concentration and forms of the phosphorus present in the precipitation.

The second objective required the major amount of effort of the project. It was directed to an important area where little had been done in the past and significant progress was made.

In accomplishing this second objective, three different approaches were taken. In the first, a number of sources of phosphorus to the atmosphere in the Chicago area were evaluated by collecting samples of the particulate matter present in the atmosphere and determining the concentrations of a number of the elements present in the samples. Since some particulates are unique or very concentrated sources of a particular element, by determining the amount of these tracer elements, and knowing the composition of the sources, the amount of particulates from these sources was found. About 45% of the particulate matter was identified as to its source. Knowing the phosphorus content of these sources, the importance of different sources of phosphorus to the atmosphere was determined. These identifiable sources accounted for 48% of the phosphorus present in the atmospheric samples.

The second approach was to look at the problem on a national scale and see if there might be a good input-output correlation for phosphorus in the atmosphere. Inputs to the atmosphere from a variety of sources were compared to output values determined in this report and elsewhere.

The maximum values of inputs to the atmosphere were found to be several times the minimum values of phosphorus determined to be coming from the atmosphere. There thus seems to be basic inconsistencies in the data and these indicate an important lack of knowledge or understanding of the atmospheric phosphorus cycle.

The third approach was to locate local sources of phosphorus containing particulates by analyzing particulate matter samples collected at a number of sites in the Chicago area by the City of Chicago. The results indicate that there were sources of phosphorus containing particulate matter in the City but that they were diffuse and there were no sources with high concentrations or large amounts.

The third objective was accomplished by comparing the amounts of phosphorus found in precipitation with the amounts going into Lake Michigan from other sources. This objective was fully achieved. It was found that precipitation is now contributing a significant percentage of the phosphorus going into the south end of the Lake. When effluent restrictions on discharges to the Lake and its tributaries are fully implemented, the importance of the inputs from the atmosphere will increase.

DEFINITIONS

All of the phosphorus analyzed for or discussed in this report was present chemically as phosphate. All of the values included and discussed here, however, have been converted and are reported as the element phosphorus. To convert from phosphorus to phosphate, one multiplies by 95/31 or 3.06. To convert to phosphorus pentoxide, one multiplies the phosphorus values by 142/62 or 2.3.

The term "ortho phosphate" refers to phosphorus present in solution or in a sample as the free phosphate ion,  $\text{PO}_4^{---}$ . Of course, there will always be three equivalents of cations present to balance the charge. In solution, the phosphate ion will have from zero to three protons associated with it, depending on the pH of the solution. The analytical method used for phosphorus in this study was sensitive only to phosphorus present as ortho phosphate. Phosphorus present in all other forms was first converted to the ortho phosphate ion by standard procedures and then analyzed.

The term "total phosphorus" refers to all of the phosphorus present in a sample, regardless of its chemical identity.

The term "filtered sample", unless otherwise designated, refers to a sample filtered through a 0.45 micrometer cellulose nitrate membrane filter (Sartorius; #113 06). Unlike some other membrane filters, these are free of extractable phosphorus.

## PROCEDURES AND METHODS

### Procedures

Precipitation was collected in open plastic or glass containers exposed about one meter above the roof of a building. The roof was about 10 meters above street level. The building ( $41^{\circ} 55' 25''$  N,  $87^{\circ} 39' 19''$  W) was in a densely populated urban area about 5 km north of the central area of Chicago and about 2 km west of the shore of Lake Michigan. There was also light manufacturing in the immediate vicinity.

Clean containers were placed out before a storm and brought in as soon as practical after the rainfall ended. This was done to minimize the amount of dry fallout collected. The location of the collector, about 11 m above street level, probably decreased the amount of traffic-related particles incorporated with the samples. The samples were preserved by immediate freezing in a polyethylene container. In a few cases, 40 mg/l. of mercuric chloride was used as a preservative.

The precipitation was measured in a standard rain gauge adjacent to the precipitation collector.

Air particulate samples were collected by using a high volume air sampling pump (General Metal Works, Cleves, Ohio, Model GMWL 2000) with an 18 x 23 cm filter holder in an outdoor shelter. A sample was collected for 24 hours. The initial and final flow rates through the filter were measured with a calibrated flow meter. The flow for the duration of the collection period was assumed to be the average of the initial and final measurements.

Whatman No. 41 filter paper was used for most of the sampling. This cellulose paper is particularly low in trace concentrations of elements other than carbon, hydrogen and oxygen. A back-up filter was used for all samples.



Before and after weighing, the filters were equilibrated in a desiccator over a drying agent for 24 hours. The weight of the air particulate sample collected was the difference between the initial and final weight of the filter paper.

Air particulate samples on glass fiber paper were obtained from the City of Chicago. These samples were collected by the City from their routine air sampling network. We analyzed these filters for phosphorus and carbon. Particulate matter samples on glass fiber paper from the burning of plant material were obtained from Dr. Ellis P. Darley of the University of California at Riverside.

The amount of particulate used for an analysis was determined by weighing the portion of the filter paper to be used and by multiplying this by a previously determined ratio of the particulate/total weight of the collection area of the filter. Samples sizes were usually about 100 mg for neutron activation analysis and 50 mg for other chemical analysis. This typically included 1-3 mg of particulate matter.

The ratio of the particulate to the total weight of the collection area was calculated as follows. The total weight of the paper before the sample was collected was divided by the total area of the paper,  $509.04 \text{ cm}^2$ , to give  $W_1$ , the weight of the paper/ $\text{cm}^2$ . The total weight of the particulate matter, then was divided by the collection area of the paper,  $407 \text{ cm}^2$ , to give  $W_2$ , the weight of particulate matter/ $\text{cm}^2$  of collection area. The total weight of a portion of the collection area of filter paper is then  $W_1 + W_2$  and the ratio of particulate/total weight of a portion of the collection area of the paper is  $W_2 / (W_1 + W_2)$ .

#### Chemical Analyses

A standard analytical procedure for phosphorus<sup>1</sup> which utilizes the molybdenum-antimony-ascorbate method of Murphy and Riley was used for the

water and air particulate samples. Ortho phosphate was often determined on a filtered as well as an unfiltered sample. Persulfate digestion was used for the total phosphorus analysis. Most phosphorus determinations as ortho phosphate were done on 12.5 ml samples while 25 or 50 ml was used for total phosphorus samples.

The intensity of the color developed in the phosphorus determination was measured in a 25 mm test tube using a Bausch and Lomb Spectronic 20 spectrophotometer. To minimize variability among sample tubes, one tube was used for all the samples readings. A set of six standards was run each day and a least squares line determined from these standards was used to calculate the results for the samples run that day.

On occasion, for samples of low concentration, a Beckman DK-2a spectrophotometer was used with absorption cells of 10 cm path length. Several control experiments were run. On a number of occasions, precipitation samples were re-analyzed. Usually, there was close correspondence between the new and old values for the samples. There was no change or difference during long-term storage in two series of synthetic samples with different preservation conditions. One was preserved by freezing, the other by the addition of 40 mg/l. of mercuric chloride. The reproducibility of the sampling was checked on two occasions by putting out multiple buckets and analyzing each one separately. They indicated that the ortho phosphate results are very reproducible while there is variation in the total phosphate results.

The Whatman and glass fiber filter paper samples were analyzed by placing approximately 0.05 gm ( $7 \text{ cm}^2$ ) of the paper to be analyzed in a 125 ml flask with a magnetic stir bar and 50 ml of deionized water, and stirring for

30-60 minutes to disrupt the structure of the paper. If a total phosphate analysis was to be done, 0.6 gm of ammonium persulfate was then added and the slurry was digested for one hour. If an ortho phosphate analysis was being done, or after the persulfate digestion on a total phosphate analysis, the slurry was filtered. In the case of an ortho phosphate determination the filtered solution was directly analysed.

The gasoline and crude oil samples were analyzed for phosphorus by an ASTM procedure. This involved combustion of the sample and the use of molybdate, with hydrazine as the reducing agent, to produce the color for analysis.

The low level chemical oxygen demand procedure of the EPA<sup>1</sup> was used without alteration.

Total carbon and its apparent equivalent weight was determined on air particulate samples by quantitatively collecting in a barium hydroxide solution the carbon dioxide liberated from the chemical oxygen demand experiment. The precipitated barium carbonate was collected and weighed. In one of these experiments then, the chemical oxygen demand part gave the number of equivalents of oxidant consumed and the barium carbonate part gave the amount of carbon present. If all of the oxidant is consumed in oxidizing the carbon, then one can use these two experiments to calculate an equivalent weight for the carbon present.

Arsenate gives the same color reaction with the Murphy-Riley reagent as does phosphate. Therefore, if there is arsenate present in the precipitation samples its presence could lead to high results. The amount of arsenate present in the samples was determined by the method of Johnson.<sup>3</sup> It involved analyzing duplicate samples for phosphorus, one where the arsenate had been reduced with thiosulfate, the other where the arsenate had not been reduced.

The arsenate present then was the difference between the two determinations. The arsenate correction averaged less than .001 ppm as phosphorus and was neglected.

#### Neutron Activation Analysis

Neutron activation analysis was used to determine the concentration of most of the tracer elements in the air particulate samples. A portion of the filter to be analysed was carefully cut, weighed and placed in a zip-locked polyethylene container which had been previously rinsed with dilute nitric acid and de-ionized water. The samples were irradiated in the rapid irradiation facility (RABBIT) of the CP-5 research reactor at Argonne National Laboratory for about 30 seconds at a thermal neutron flux of about  $2 \times 10^{13}$  n/cm<sup>2</sup>/sec. Both the actual irradiation time and the flux were determined for each irradiation. The counter consisted of a solid-state, Ge(Li) diode detector coupled to a 4,000 channel analyser with computer-compatible output to tape.

The first count of 400 seconds was started three minutes after the termination of the irradiation. And the second count, of 1,000 seconds, was begun 15 minutes after the end of the irradiation. The actual counting time, 400 or 1,000 seconds, did not include the dead time of the detector. The counter increased the counting time to compensate for this deadtime, the amount of time the detector was not able to accept counts. Thus the clock time for the count was longer than the reported counting time. The dead time was proportional to the activity of the sample and ranged from 20 to 40% for the air particulate samples.

A vanadium flux monitor was irradiated with each sample and was counted 35 minutes after the irradiation for 100 seconds.

Standards were prepared to relate the count-rate of each isotope to the amount of element present. Aqueous solutions of the elements to be determined

were prepared from analytical grade reagents. Sections of Whatman No. 41 filter paper were then spotted with the appropriate amount of the solutions and dried. Trace impurities in the Whatman 41 filters were determined on blank pieces. The papers containing the standards and the blank papers were irradiated and counted using the same procedures as for the actual samples. The counting rates of all samples, standards and blanks were corrected for differences in the irradiation time and conditions. All calculations were done on disintegration rates, corrected for decay, to the end of the irradiation period.

#### Sources of Particulate Matter to the Atmosphere

In order to determine the sources of particulate matter to the atmosphere at the collection site, the method of Miller<sup>4</sup> and Gatz<sup>5</sup> was used. This involved determining the concentration of specific elements in the atmosphere which served as tracers for different sources, finding or determining the compositions of these different sources of particulates, and then using this information to determine the concentration of the different sources in the atmosphere. The elemental compositions for the different sources which were used in the following calculations are shown on Table 1.

For instance, automobile fuel additives are the only significant source of bromine to the atmosphere. It has been determined<sup>7</sup> that bromine comprises 7.9% of the exhaust particulates of autos. For the samples collected with the wind direction from the southwest, bromine composed 0.53% of the particulate matter. Thus, for these samples, particulates from automobile exhausts must be  $.0053/.079$  or 6.7% of the total particulate matter in the atmosphere.

In similar manner, the following tracer elements were used to calculate the contributions of different sources of particulate matter to the atmosphere:

	Sea Salt	Auto	Fuel Oil	Iron <sup>5</sup> Steel	Cement	Soil	Coal & Coke <sup>2</sup>
Aluminum	--	--	0.8	1.62	2.4	6.6	9.4
Bromine	0.19	7.9	--	0.77	--	--	--
Carbon	--	40.3	--	1.4	--	0.02	--
Calcium	1.16	--	1.3	4.7	46.0	1.5	4.0
Chlorine	55.0	6.8	--	--	--	--	--
Copper	--	--	0.2	--	--	0.008	--
Magnesium	3.7	--	0.06	--	0.48	1.4	--
Manganese	--	--	0.06	0.20	--	0.11	0.001
Sodium	30.6	--	5.0	1.03	0.4	2.5	0.6
Phosphorus <sup>12</sup>	--	--	0.4	0.15	0.017	0.042	0.074
Vanadium	--	--	7.0	0.053	--	0.006	--

All values are from reference 7, except where noted.

Table 1. Percent elemental composition of different sources of particulates to the atmosphere.

Bromine	Automobile exhaust
Calcium	Cement
Aluminum	Soil
Sodium	Sea Salt
Manganese	Iron and Steel
Vanadium	Fuel Oil
Aluminum	Coal and Coke

Since many of the tracer elements were contributed by more than one of the sources, the calculations were done a second or third time, incorporating corrections for sources of the elements other than the one being traced for. Also, since aluminum was used to trace for both soil, and coal and coke, the best agreement of secondary tracer elements was used to apportion the aluminum between these two sources. For instance, for the samples with the wind from the southwest, the best accounting for aluminum, sodium and calcium occurred with a soil contribution of 19% and with a contribution from coal and coke of 8%.

A fundamental drawback of this method, however, is that the data being used are only marginally adequate. This is for several reasons:

- 1) The compositions of the sources are averages. For instance, it is obvious that not all stack emissions of the iron and steel industry have the same composition. The assumption is that if there are enough different sources of this industry in the area, that their average is close to the numbers used in the calculations.
- 2) It is assumed that one source is the only, or at least the major source of its tracer element. For some elements, such as bromine or vanadium, which have only one major source, this is a good approximation. For other elements which are more ubiquitous in their distribution, and are not particularly concentrated in any one source, such as aluminum and silica,

this is less useful approximation.

- 3) Normal analytical errors in determining elemental concentrations, particularly of elements present in low concentrations.

In fact, a more sophisticated calculational method introduced by Friedlander<sup>7</sup> was tried. But, using our data, it was not possible to obtain a set of meaningful numbers from the internally consistent set of simultaneous equations.

The input of phosphorus in kg/ha from each rainfall sample was calculated by multiplying the concentration of phosphorus in mg/l. by the amount of precipitation which was measured for that sample and converting this number (mg/1000 cm<sup>2</sup>) to kg/ha by multiplying by 10<sup>-1</sup>. To determine the average phosphorus concentrations which are shown for all of the samples, the sum of the inputs in kg/ha was divided by the total amount of precipitation represented by those samples. This number was converted to mg/l. by multiplying by 10. Inputs in kg/ha/yr can be converted to lbs/acre/yr by multiplying by .89.

Evaporation of water from the sample container would concentrate the phosphorus in the sample. Therefore, after analysis, when the input was determined by multiplying the concentration of the phosphorus in the sample by the amount of precipitation, a high value would be obtained. Therefore, for many of the samples, a correction was applied for evaporation. Since the open area of the collection container was known and, knowing the amount of precipitation of a particulate sample, it could then be calculated how much water should be in the collector. If less was present when the sample was taken in, the final concentration of the phosphorus was multiplied by the ratio of how much was in the bucket divided by how much should have been in the container.



## RESULTS AND DISCUSSION

### Phosphorus Concentration in Rainfall

The results of the analysis for ortho, filtered ortho and total phosphorus of the rainfall samples collected in Chicago are shown on Table 2. Values are shown for precipitation weighted concentrations and inputs in kg/ha/yr (for precipitation of 74 cm/yr). Figure 1 is a plot of the phosphorus concentrations determined plotted versus the amount of precipitation. This illustrates the scattering between the different samples of the concentrations. But it also demonstrates that there is some rational to it. In general, the smaller the amount of precipitation, the higher the concentrations tend to be. This is a result which is generally found in precipitation scavenging. The factors which affect this are several and have been discussed by Gatz and Dingle.<sup>8</sup>

Samples of snowfall were also collected and analysed. The concentrations of phosphorus found in these samples are shown on Table 3. The turbulent nature of the winds in the area of the collection site due to the many buildings in the vicinity, including a taller one immediately to the west, led to uneven deposition of snow. Therefore, the amount of snow which fell was not able to be determined and the inputs of phosphorus in kg/ha could not be calculated for these samples. However, it can be seen from the data in Table 3 that the concentrations of phosphorus found in these samples are similar to those found in the rainfall samples and thus the inputs from snow are probably not a lot different.

### Particulate Matter

The size of a particulate matter in the atmosphere is very important because, for similarly shaped particles, the depositional velocity is related to the mass which is related to the size. The smaller the size, the lower

	Phosphorus		
	Total	Ortho	Ortho (filtered)
Number of Samples	89	79	52
Total Amount of Precipitation (cm)	110.4	93.7	61.3
Sum of Inputs (kg/ha)	0.38	.169	.0713
Weighted Average Concentration (mg/l.)	.034	.018	.012
Annual Inputs for 74 cm Precipitation (kg/ha/yr)	.25	.13	.09

Table 2. Inputs of phosphorus from the atmosphere in Chicago.

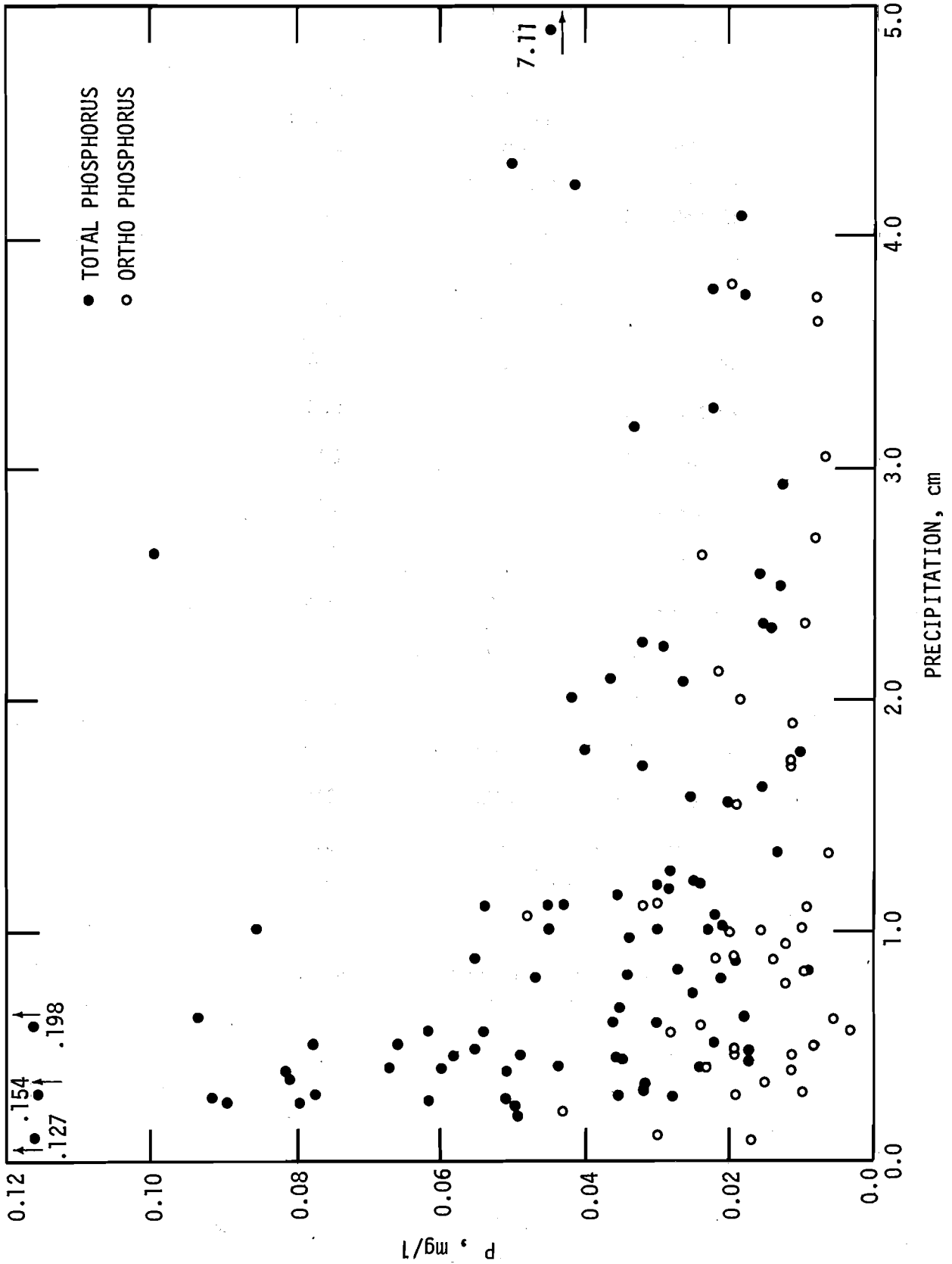


Figure 1. Concentration of phosphorus in precipitation vs. the amount of precipitation

Date	Total phosphorus mg/l	Ortho phosphate mg/l
23 Feb. 72		.041
13 Mar. 72	.051	.012
27 Mar. 72	.051	.017
29 Mar. 72	.036	.020
22 Nov. 72		.026
1 Dec. 72		.026
6 Dec. 72		.196
8 Dec. 72		.018
12 Dec. 72	.025	.054
15 Feb. 73	.021	.006
17 Feb. 73		.026
17 Mar. 73	.021	.009
19 Dec. 73	.016	.016
22 Feb. 74	.054	.016

Table 3. Concentrations of phosphorus  
in snow samples.

the settling velocity and the further a particle may be transported by the atmosphere before impinging on the ground.

Particles with diameters greater than about 20  $\mu$ , giant particles, have a short atmospheric residence time and are removed from the atmosphere chiefly by impacting on the surface. They are a major contributor to dry fallout and are chiefly of local origin. Particles with diameters less than 10  $\mu$ , large particles, have long atmospheric residence times and are removed chiefly by precipitation scavenging. They may be of local or very distant origin. They also may have very different mechanisms of formation, with the giant particles formed in erosional processes and the large particles formed in combustion processes and from condensation and scavenging of the smaller particles in the atmosphere.<sup>9</sup>

There are two reports of the determination of the particle size of phosphorus containing particulate matter.<sup>10, 11</sup> Both show the average size of a few microns and therefore of long atmospheric residence time. This indicates that the phosphorus being scavenged by precipitation in an area may very likely be of distant origin.

To the extent that the material scavenged by precipitation is of distant origin, the results from the analysis of precipitation samples collected in one area, will be independent of the collection site and should be able to be extrapolated to adjacent areas. Dry fallout, on the other hand, should be dominated by local inputs of large particles and is probably only representative of the immediate area. This is one of the reasons that dry fallout collection and analysis was not a part of this project.

#### Atmospheric Distribution of Phosphorus

An unavoidable criticism of the results obtained in this study is that the precipitation is being collected on one of the largest manufacturing and

residential areas of the country and therefore, the results may have no bearing on phosphorus inputs from the atmosphere in other areas. Several procedures were used to try and measure these local effects.

The first of these is to try to determine how the phosphorus content of the atmospheric aerosol varies with the wind direction and also to determine if there are large local inputs of phosphorus to the atmosphere in the area.

To do this, we obtained portions of air particulate samples, collected by the City of Chicago's Department of Environmental Control, for three different days. Each day was chosen because it was a week day, it had relatively steady winds, and the winds for each of the days were from a different direction. We obtained samples from an average of 23 locations for each day. Figures 2, 3 and 4 show the concentration of particulate matter, total phosphorus and ortho phosphate for each day. Also shown on the plots are the location of the sampling site at DePaul University ( $\oplus$ ) and of Midway (M) and O'Hare (O'H) airports which are the sources for the meteorological information.

As can be seen, concentration gradients exist over the city for all of these days. Keeping in mind that even materials for which there are no known local sources vary in concentration by about a factor of four, it can be seen that most of the values are within this range.

The days with the winds out of the southeast and from the west, show the highest concentrations of total phosphorus in the atmosphere. The day with the winds out of the north shows the lowest values. This is understandable since the heavy industrial areas are to the south, and the major farm areas are to the west and south of the city. The plots of the concentration of the total phosphorus indicate the presence of one definite source in the southwest corner of the city and several other possible sources of phosphorus to the atmosphere within the city. The plots of the ortho phosphate concentrations







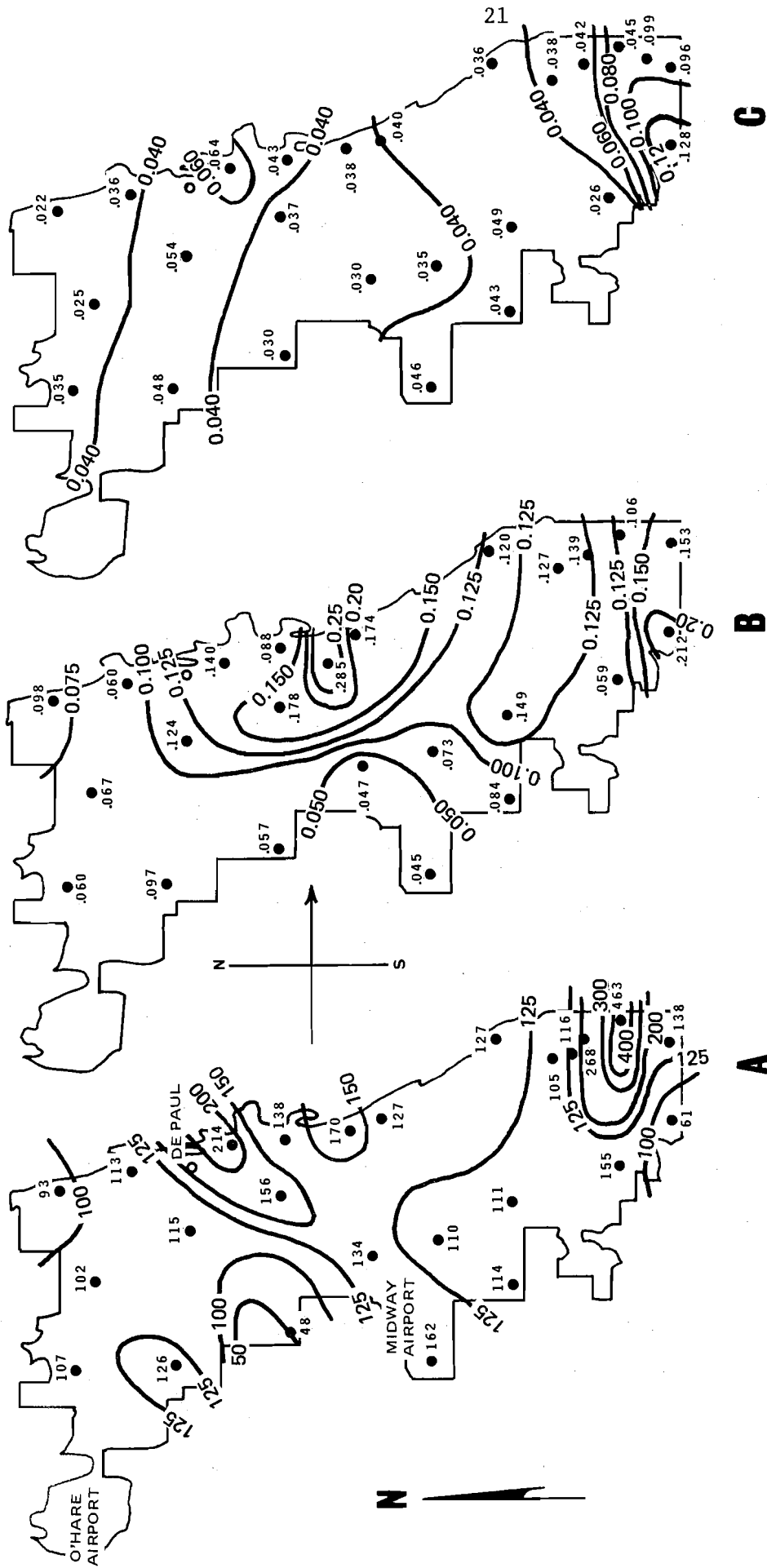


Figure 4. Thursday May 10, 1973. Winds out of the West.

- A. Concentration of particulate matter  $\mu\text{g}/\text{m}^3$
- B. Concentration of total phosphorus  $\mu\text{g P}/\text{m}^3$
- C. Concentration of ortho phosphate  $\mu\text{g P}/\text{m}^3$

show that some of the sources are high in ortho phosphorus, while others are low.

Statistical data from the City of Chicago samples is shown on Table 4. Interestingly, the ortho phosphate means for the three days all are close to one another and the standard deviations of the values from the mean are low. The means for the total phosphorus samples show greater variability and their standard deviations are much greater.

It is not clear if there is any significance to the close similarity of the ortho phosphate mean values. One could be tempted to infer that the inputs of phosphorus from the City are chiefly of the unavailable total phosphorus while the ortho phosphate present has chiefly been transported from more distant areas. This is certainly an over simplification, but may have some validity.

Some support for this speculation is the fact that precipitation samples collected by the Canada Centre for Inland Waters on board their research vessels on Lake Superior, and immediately analysed, show that a high proportion of the phosphorus is present as ortho phosphate.<sup>31</sup>

The correlation coefficients between the concentration of particulate matter in the atmosphere at each sampling point and the amount of phosphorus in each sample are also on Table 4. For the samples of March 29, with the north winds (Figure 3), there was a positive correlation, significant at the 10% level, for the particulate matter versus the total phosphorus concentration. For the other two days, neither the particulate matter versus the ortho phosphate, nor the particulate matter versus the total phosphorus correlations were significant at the 10% level. In fact, one of these correlations was negative.

## Arithmetic Means and Their Standard Deviations

	Particulate Matter	Total Phosphorus	Ortho Phosphorus
October 10, 1972	130 ± 48	.134 ± .056	.047 ± .023
March 29, 1973	78 ± 23	.072 ± .028	.041 ± .016
May 10, 1973	143 ± 80	.114 ± .058	.047 ± .025

Logarithmic Means and their Standard Deviations  
Geometric Means

	Particulate Matter	Total Phosphorus	Ortho Phosphorus
October 10, 1972			
Mean of the logarithms	2.0884	-.9147	-1.3754
Std. Dev. of the logarithms	.147	.204	.194
Geometric Mean	122.6	.122	.042
March 29, 1973			
Mean of the logarithms	1.8734	-1.1314	-1.42545
Std. Dev. of the logarithm	.136	.226	.177
Geometric mean	74.7	.074	.038
May 10, 1973			
Mean of the logarithms	2.1111	-.9931	-1.3663
Std. Dev. of the logarithms	.188	.215	.186
Geometric Mean	129.2	.102	.043

## Correlation Coefficients

	Particulate Matter vs Total Phosphorus	Particulate Matter vs Ortho Phosphorus
October 10, 1972	.143 n = 23	-.213 n = 23
March 29, 1973	.421* n = 22	.342 n = 21
May 10, 1973	.124 n = 24	.328 n = 25

\*Significant at the 10% confidence level

Table 4. Statistical data for the City of Chicago air particulate samples.

These statistical data are helpful in interpreting Figures 2-4. Thus, the March 29 day (Fig. 3), with the winds out of north, should show the least effect of the industrial areas of the city. Therefore, the particulate should be more homogenous and be representative of a single source, background to the north, and a positive correlation of the phosphorus with the particulate matter could be anticipated. While the other two days should show the effects of numerous sources of particulate matter to the atmosphere, which contain varying amounts of phosphorus. Therefore little or no positive correlation between the particulate and the phosphorus concentration would be expected. This is what is found.

#### Sources of the Phosphorus Containing Particulate Matter

As discussed earlier, a second means of determining the effect of the Chicago area on the precipitation samples collected there is to learn the source of the phosphorus containing particulate matter in the atmosphere. To do this, high volume air particulate samples were collected on Whatman 41 cellulose filter paper on ten different days at the same site where the precipitation samples were collected. Bromine and the metals were analysed by neutron activation analysis. Phosphorus was determined colorimetrically. While carbon could not be determined directly on these papers due to the blank of the paper itself, an average value of 18.4% was obtained from analysis of the City of Chicago samples and this value was used in these calculations.

The results of these ten samples were grouped on the basis of the prevailing wind observed at O'Hare airport, 21 km distant, during the time of collection of the samples. An average concentration of each element was calculated for each of the groups of samples. These are shown on Table 5. Also, an average composition for the atmosphere, using the compositions for the different wind directions found above and weighted using a National Weather

Service wind rose, was calculated. This is also shown on Table 5.

The average elemental composition of a number of sources of particulate matter have been determined. The ones of interest are shown on Table 1. These source compositions, along with the atmospheric compositions shown on Table 5 were used to determine the amount of particulate matter contributed to the atmosphere in Chicago from the different sources. The calculational method of Miller<sup>4</sup> and Gatz<sup>5</sup> as outlined on pages 9-12, were used. The results of these calculations are shown on Table 6.

Included on Table 6 is a value of 6% for the composition contribution of particulate matter to the atmosphere from natural and agricultural fires. This value was determined as follows. A value for the concentration of carbon in the atmosphere of 18% of  $15.8 \mu\text{g}/\text{m}^3$  has been determined from the City of Chicago samples. The sources of automobiles, soil, and iron and steel whose atmospheric contributions were taken from Table 6 accounted for  $3.63 \mu\text{g}/\text{m}^3$  of this carbon. In carrying out similar calculations for Los Angeles, Friedlander had used values of 1.8% carbon from diesel emissions and 2.7% for emissions from aircraft. These values were increased by 50% and accounted for an additional  $5.76 \mu\text{g}/\text{m}^3$ . This left  $6.4 \mu\text{g}/\text{m}^3$  still unaccounted for. Friedlander attributed this remaining carbon to particulate matter formed from the reaction and condensation of gases in the atmosphere. In this report, only one half of the carbon is attributed to this source. The other half,  $3.2 \mu\text{g}/\text{m}^3$ , or 3.7% is arbitrarily attributed to particulate matter from fires. Our analysis of filter papers from burn samples indicate that they are about 60% carbon. Therefore, this source contributes about  $5 \mu\text{g}/\text{m}^3$  of particulate matter to the atmosphere in Chicago.

The source contributions to the atmosphere were then multiplied by their average phosphorus concentration to find the amount of phosphorus each contributed to the atmosphere. These results are shown on Table 7. It can be seen

	WIND DIRECTION				City Composite
	NE-E	S-SW	W	NNW	
Aluminum	1.85	2.98	2.35	1.46	2.30
Bromine	0.30	0.53	0.56	0.75	0.49
Calcium	2.00	2.73	1.64	1.93	1.96
Copper	0.19	0.45	0.12	0.56	--
Manganese	0.02	0.39	0.19	0.19	0.165
Sodium	0.33	0.66	0.67	0.48	0.53
Vanadium	0.10	0.02	0.013	0.11	0.05
Phosphorus	0.053	0.064	0.017	0.08	0.07
Carbon	--	--	--	--	18.0
Total Particulate Matter ( $\mu\text{g}/\text{m}^3$ )	84	103	94	63	86
Number of Samples	1	4	2	3	10

Table 5. Average percent composition of particulate matter by wind direction.

	WIND DIRECTION				City Composite
	NE-E	S-SW	W	NNW	
Auto	3.8	6.7	7.1	9.5	6.2
Fuel Oil	1.4	0.3	0.2	1.6	0.7
Iron & Steel	2.1	12.5	8.3	7.9	6.9
Cement	3.2	2.3	1.3	2.8	2.2
Soil	12.0	19.0	18.0	14.0	18.0
Sea Salt	0.1	0.13	0.6	0.13	0.1
Coal & Coke	7.3	8.0	4.2	0.33	6.9
Natural and Agricultural Fires					5.8

Table 6. Percent source contributions to the atmosphere in Chicago by wind direction.

Source	$\mu\text{g}/\text{m}^3$	% P	$\mu\text{g p}/\text{m}^3$ contributed to atmosphere
Auto	5.3	0	-
Fuel Oil	0.6	0.4	.00024
Iron & Steel	5.9	0.15	.00883
Cement	1.9	0.017	.00032
Soil	15.4	0.042	.00648
Sea Salt	0.1		-
Coal & Coke	5.9	0.074	.0044
Fires	5	0.15	.0075
			<hr/>
			.028

Table 7. Source contributions of phosphorus to the atmosphere for city composit sample.



that for the composite city sample, about 48% of the phosphorus is accounted for. With the exception of the contributions from the soil and the fires, this phosphorus probably has its origin within the immediate urban area.

No contribution of phosphorus is attributed to automobile usage although tricresol phosphate and other phosphorus containing compounds have been used as gasoline additives. However, when some samples of gasoline, of the brands known to use these additives, were analysed, no phosphorus was found. Subsequently, an oil company representative confirmed that these additives were no longer in use.

There are a number of possible explanations to account for the remainder of the phosphorus. They include:

- 1) If the phosphorus content of the remaining unidentified particulate matter would average the same as that particulate which has been accounted for, this could account for the remaining phosphorus.
- 2) The identified sources of particulate matter which contain phosphorus and have been evaluated, may be underestimated.
- 3) The phosphorus content of these sources may be too low.
- 4) There may be significant sources of phosphorus to the atmosphere which have not been evaluated.
- 5) There may be sources which have not yet been identified.

For instance, under item three above, emissions from the fertilizer industry are known to be an important source of phosphorus to the atmosphere. Contributions from this source could not be determined due to the lack of a tracer element for them. Since it is reported<sup>12</sup> that 8%, or  $11.3 \times 10^6$  kg, of the emissions from this industry occur in Environmental Protection Agency Region V, which includes Chicago, this source would account for some of the deficiency. If controls on phosphorus emissions to the atmosphere are ever considered, this is the one source where they might be able to be justified.

In addition, there are two potentially large sources of phosphorus to the atmosphere which were unable to be evaluated. These are organisms and plant material, and spray from bodies of water.

The atmosphere always contains some algae, viruses, bacteria, etc. which have been eroded or ejected into the atmosphere, as well as large amounts of pollen, during some seasons. The organisms and the pollen can be expected to have phosphorus concentrations of about 0.2%. MacIntyre<sup>13</sup> has shown that breaking bubbles at the surface of the ocean ejects material from the uppermost surface layers into the atmosphere. The concentration of materials in the water at the sea-air interface is known to be considerably different from the bulk of the sea. Baylor<sup>14</sup> et al. and MacIntyre and Winchester<sup>15</sup> have shown that this spray is probably quite enriched in phosphorus. Unfortunately, neither the amount of this material nor its phosphorus content have been determined. This would be an input which would be correlated with the sea salt input from the atmosphere. The primary objective for trying to determine the sources of phosphorus to the atmosphere was to evaluate the influence of the urban area on the concentration of phosphorus in precipitation collected in Chicago. Some tentative conclusions may now be drawn. In determining the sources of particulate matter to the atmosphere and their phosphorus concentrations, it was not anticipated that every source investigated from agricultural fires to meteorites would be found to contain some phosphorus. The proportion, with the exception of the emissions of the fertilizer industry, was never large but usually fell within the range of 0.02 to 0.2%. The fact that the % phosphorus accounted for in the atmosphere in Chicago was close to the percent particulate matter accounted for, supports this ubiquitous distribution of a low concentration of phosphorus.

If this distribution is uniform, it permits one to readily estimate the

effect of Chicago and developments around the entire Lake on the phosphorus going into the Lake in precipitation. The effect would be proportional to the increase in particulate matter in the atmosphere over that normally present. Ludwig et al.<sup>18</sup> determined that the average concentration of particulate matter in the atmosphere of urban locations was  $102 \mu\text{g}/\text{m}^3$ , that in proximate areas (suburban?) was  $45 \mu\text{g}/\text{m}^3$ , that in nonurban intermediate areas (farming) was  $40 \mu\text{g}/\text{m}^3$  and that in remote areas (isolated from man's normal activity) was  $20 \mu\text{g}/\text{m}^3$ .

The land use around Lake Michigan would be predominantly in the categories of proximate and nonurban intermediate. There would be some remote areas in the northern part and a lot of urban areas in the southern part. The average would probably be about  $50 \mu\text{g}/\text{m}^3$  of particulate matter in the atmosphere. This would indicate that the concentrations of phosphorus in precipitation in Chicago would be high by a factor of two. It further suggests that the effect of man on the Lake has been to increase the inputs of phosphorus from the atmosphere by a factor of 2.5.

#### Total Inputs of Phosphorus to the Atmosphere

An attempt was then made to approach the problem from the other direction, hoping that this would give some insight to the problem. This was done by determining all the known sources of phosphorus to the atmosphere, finding an average depositional rate and comparing this to the depositional rates which have been measured.

The EPA report<sup>12</sup> was the principal source of information. It did, however, contain one serious error and it did not consider several important sources. The error was in using a conversion factor of 4.58 instead of 2.29 for converting phosphorus to  $\text{P}_2\text{O}_5$ . This caused the refuse incineration and coal combustion sources, and perhaps others, to be overestimated by a factor of two.

Additional sources considered which were not included in the EPA report, were meteoric inputs, which are quite small, inputs from agricultural and natural fires and wind-blown soil. The inputs and the phosphorus concentration of meteoric material was found in the literature.<sup>16</sup> The inputs from agricultural and natural fires from 1968 were reported in an earlier report.<sup>17</sup> The phosphorus content of this material was estimated from the analysis of samples obtained from Dr. Ellis Darley (Appendix A) and the input of wind-blown soil was estimated from literature values.<sup>35</sup> The phosphorus content of a large number of soil samples taken eight inches below the surface has been reported in a USGS publication.<sup>19</sup>

The data in the 1973 EPA report along with the additional data, and with the error corrected for those data where the incorrect factor was known to be used, are shown on Table 8. It can be seen that the contributions from the fertilizer industry, soil, and fuel are large.

If one takes the total discharges to the atmosphere as identified on Table 8 and divides by the area of the U.S., one gets an average input of about .08 kg/ha/yr. This is about one-third the value found earlier (Table 1) for inputs from precipitation scavenging without considering dry fallout. Other investigators in widely scattered areas and in some remote areas have found even higher inputs of phosphorus from the atmosphere.<sup>20,21</sup>

A possible rationalization of this low result is that there is considerable re-entrainment of material deposited from the atmosphere. If the material is re-entrained an average of two or three times, this would bring into reasonable balance the input-output numbers for those sources to the atmosphere must still be found and/or the contributions of present sources must be reevaluated.

It should be noted that even if considerable re-entrainment does occur,

	Emissions $\times 10^{-3}$ Metric Tons per year	Percent Phosphorus	Input of Phosphorus Metric Tons per year
<b>Phosphorus Industry</b>			
Phosphate Rock Mining	68	7.8	5,300
Phosphoric Acid Manufacturing	21	13.0	2,180
Fertilizer Manufacture	167	25	41,700
Other Chemicals	26.5	25	6,600
<b>Inadvertant Sources</b>			
Iron Manufacture	1,830	0.15	2,800
Steel Manufacturing	183	0.15	280
Cement	1,030	0.017	175
Wind-Blown Soil <sup>35, 19</sup>	15,000	0.042	6,300
Meteoric <sup>16</sup>	50	0.02	10
Refuse Incineration	88	0.05	44
Fuel Oil Combustion	400	0.4	1,600
Coal Combustion	6,100	0.074	4,320
Agricultural Burning	2,400	0.15*	3,600
Forest Fires	6,700	0.10*	6,700
Total			81,609

\*Appendix A

All other values from Ref. 12.

Table 8. Sources and amounts of phosphorus inputs to the atmosphere.

the values in Table 5 of the sources to the atmosphere determined in Chicago would not be affected. Since, even if material is re-entrained, it should still retain its source identity and would automatically have been considered.

If phosphorus containing particulate matter is entrained in the atmosphere several times before being permanently scavenged, this has serious implications for bodies of water. This is because the surface of a body of water should be a sink for particulate matter. If this is so, then bodies of water are recipients for a disproportionate share of atmospheric particulate matter.

THE SIGNIFICANCE OF ATMOSPHERIC INPUTS OF PHOSPHORUS TO OLIGOTROPHIC BODIES OF WATER

The most important question then is what is the significance of these atmospheric phosphorus inputs, do they make any difference to receiving waters?

First, the role of phosphorus should be considered. It is an essential component of DNA and RNA--the hereditary material, of ATP--the principle energy source for organisms and of numerous other phosphorylated compounds which are essential components of the biochemical pathways of living organisms and it is also a component of some structural materials and tissues. Thus it is one of the elements absolutely necessary for the existence of life from the most primitive to the most advanced organisms which exist on the earth.

In any natural system, there is some necessary factor for life whose shortage exerts the greatest controls over the amount of living bio-mass which can exist. This factor can be a physical limitation such as light or temperature or a nutrient as nitrogen, phosphorus, sulfur, ascorbic acid, etc. For our purposes, only those systems or times will be considered where the limiting factor is a nutrient. This nutrient then, which is present in the smallest amount, is called the 'limiting nutrient'. Inputs of this one material will permit corresponding increases in bio-mass since all other necessary materials are present in some excess. Large inputs of the limiting nutrient will permit the bio-mass to increase until some other factor becomes limiting.

In individual cases, a wide variety of nutrients have been shown to be limiting.<sup>22</sup> These include nitrogen in the oceans, and nitrogen, iron, molybdenum and phosphorus in different lakes.

Phosphorus has been found to be the most common limiting nutrient for oligotrophic lakes, those lakes least affected by cultural pollution

and which have the lowest concentrations of nutrients present.

The most important factor about phosphorus, however, is the fact that it usually comprises much less than one per cent by weight of an organism. Thus only a small amount is needed for a large increase in the number of organisms able to grow.

Of the three upper Great Lakes, Lake Michigan is subjected to the largest culturally related inputs of phosphorus and the most studies of the effects of phosphorus additions to date have been made on Lake Michigan.

Miller et al.<sup>23</sup> have shown that phosphorus is limiting in Lake Michigan and other similar work has confirmed this for Lakes Superior and Huron.<sup>24, 25</sup> The addition of phosphorus to Lake Michigan has led to a number of changes in the Lake which have been documented and interpreted by Schelske and Stoermer.<sup>26, 27</sup>

That phosphorus was probably the limiting nutrient in Lake Michigan was recognized at the Lake Michigan Enforcement Conference of 1968. As a result, the states bordering on Lake Michigan developed programs to remove phosphorus from sewage effluents, the largest and most easily controlled source. These programs were to be fully implemented by January 1, 1973. Most of them are now in operation.

Phosphorus inputs from the atmosphere, of course, are not a part of this program. However, as a contribution to the phosphorus budget of the Lake, their magnitude may be important in determining the effects to be expected of the phosphorus removal programs and in the evaluation of the results of these programs.

In 1972, the Phosphorus Technical Committee determined the phosphorus inputs to the Lake in 1971. These are shown on Table 9. The 1973 inputs of Lake Michigan as determined by the International Joint Commission are also on Table 9. The expected results of the phosphorus removal program when



	1971 <sup>32</sup> (kg x 10 <sup>-6</sup> ) kg/ha	1973 <sup>34</sup> (kg x 10 <sup>-6</sup> ) kg/ha	Future <sup>33</sup> (kg x 10 <sup>-6</sup> ) kg/ha	Precipitation* kg/ha Total Ortho
Waste water				
Discharges to the Lake	1.7	.31	0.35	.063
Discharges to Tributaries	4.2	.73	0.8	.14
Combined Sewer Overflows	0.35	.063		
Erosion	1.35	.24	1.35	.24
Totals	7.7	1.33	4.7	0.81
			2.5	.44
				.25
				.13

\*Figure 1, page 13

Table 9. Estimated and Projected Inputs Present and projected inputs of phosphorus to Lake Michigan.

completed, were estimated by the Phosphorus Technical Committee<sup>32</sup> and Lee.<sup>33</sup> These predictions are shown on Table 9. The inputs are shown as total amounts and in kg/ha/yr averaged over the surface of the Lake.

In comparing these values, inputs of total phosphorus from precipitation (Table 9) should be compared to the values determined by the Lake Michigan Enforcement Conference and the International Joint Commission<sup>34</sup> since these are also total phosphorus values. The problem here is, however, that it is ortho phosphate, not total phosphorus, which determines the effects of phosphorus inputs to the Lake. Much of the phosphorus which is discharged to tributaries of the Lake, and some of that discharged to the Lake itself, enters the Lake in a form where it will never become available to the organisms in the Lake. Thus, much of the phosphorus included in the inputs shown on Table 9, has no effect on the Lake, while the precipitation inputs are about 50% ortho phosphate.

A further complication is that under the low pH (0.4 N H<sub>2</sub>SO<sub>4</sub>) conditions of the ortho phosphate determination, some unavailable phosphorus is hydrolysed to ortho phosphate. However, Walton and Lee<sup>29</sup> have shown, at least for Lakes Mendota and Wingra in Madison, Wisconsin, that the ortho phosphate determination is a good measure of biologically available phosphorus. Presumably, that phosphorus which is hydrolysed during the determination then, is easily hydrolysable and would also be hydrolysed under natural conditions. Thus, the ortho phosphate values are probably the best measure of available phosphorus.

The precipitation weighted mean hydrogen ion concentration of the precipitation in Chicago corresponds to a pH of 3.8.<sup>30</sup> This is reasonably acidic and could lead to the hydrolysis of some phosphorus compounds on the particulate matter in precipitation before it falls into the higher pH Lake waters.

CONCLUSIONS

- 1) Almost all sources of particulate matter to the atmosphere contain a small but relatively constant amount of phosphorus. In Chicago, the particulates in the atmosphere contain about 0.1% phosphorus.
- 2) This particulate matter, when scavenged from the atmosphere by precipitation, can be an important component of the phosphorus budget of natural bodies of water which are low in this essential nutrient.
- 3) Since the phosphorus content of particulate matter is relatively constant, then, to a first approximation, the amount of phosphorus scavenged by precipitation is proportional to the amount of particulate scavenged, or to the amount of particulates in the atmosphere.
- 4) This source is presently contributing one-fifth to one-third of the phosphorus going into Lake Michigan. Of this amount, about 40% is "natural", the rest can be attributed to the effects of man. As contributions to bodies of water from other sources are eliminated, the contributions from the atmosphere will become more significant.
- 5) Of the phosphorus coming from the atmosphere, about one half of it is in the form of ortho phosphate, the form most readily available to organisms.
- 6) Since phosphorus is so universally distributed in the atmosphere, specific efforts to control these emissions would not be judicious, with the possible exception of the fertilizer industry. Programs well underway to control particulate emissions in general, should be reducing the emissions of phosphorus.

## BIBLIOGRAPHY

1. U.S. EPA (1971). Methods for Chemical Analysis of Water and Wastes. U.S. Gov't. Printing Ofc., 5501-0067; \$3.00.
2. Ruch, R. R., H. J. Gluskoter and N. F. Shimp (1973). Occurrence and Distribution of Potentially Volatile Trace Elements in Coal: An Interim Report. Ill. State Geol. Survey; Envir. Geol. Note #61.
3. Johnson, D. L. (1971). Simultaneous Determination of Arsenate and Phosphate in Natural Waters. Envir. Sci. and Tech. 5, 411.
4. Miller, M. S., Friedlander, S. K. and Hidy, G. M. (1972). A Chemical Element Balance for Pasadena Aerosol. J. Coll. and Inter. Sci. 39, 165.
5. Gatz, D. F. (1974). Relative Contributions of Different Sources of Urban Aerosols. Atm. Envir. to be published.
7. Friedlander, S. K. (1973). Chemical Element Balances and Identification of Air Pollution Sources. Env. Sci. & Tech. 7. 235.
8. Gatz, D. F. and A. N. Dingle (1971). Trace Substances in Rain Water: Concentration Variations During Convective Rains, and Their Interpretation. Tellus 23, 14.
9. Whitby, K. T., R. B. Husar and B. Y. H. Liu (1972). The Aerosol Size Distribution of Los Angeles Smog. J. Coll. and Inter. Sci. 39, 177.
10. Cunningham, P. T., S. A. Johnson and R. T. Yang (1974). Variations in Chemistry of Airborne Particulate Matter with Particulate Size and Time. Envir. Sci. and Tech. 8, 131.
11. Lee, R. E. and R. K. Patterson (1969). Size Determination of Atmospheric Phosphate, Nitrate, Chloride and Ammonium Particulate in Several Areas. Atmos. Envir., 3, 249.
12. U.S. EPA (1973). National Emissions Inventory of Sources and Emissions of Phosphorus. EPA-450/3-74-013. Air Pollution Technical Information Center, Research Triangle Park, North Carolina 27711.
13. MacIntyre, F. (1968). Bubbles: A Boundary Layer "Microtome" for Micron-thick Samples of a Liquid Surface. J. Phys. Chem. 72, 589.
14. Baylor, E. R., Sutcliff, W. H. and Hirschfeld, D. S. (1962). Adsorption of Phosphate onto Bubbles. Deep Sea Res. 9, 120.
15. MacIntyre, F. and Winchester, J. (1969). Phosphate Ion Enrichment in Drops from Breaking Bubbles. J. Phys. Chem. 73, 2163.
16. Moore, C. B. (1973). Phosphorus in Meteorites and Lunar Samples. In Environmental Phosphorus Handbook, C. E. Griffith et al. Ed. Wiley. Chap. 1.

17. U.S. Dept. of HEW (1970). Nationwide Inventory of Air Pollutant Emissions 1968. U.S. Government Printing Office. \$0.30.
18. Ludwig, J.H., G. B. Morgan and T. B. McMullin (1971). In Trends in Urban Air Quality, In Man's Impact on the Climate, MIT Press, p. 321.
19. Shacklette, H. T., Hamilton, J. C., Boerngent, J. G. and Bowles, J. M. (1971). U.S. Geol. Sur. Prof. Paper 574-D.
20. Shiomi, M. T. and Kuntz, K. W. (1973). Great Lakes Precipitation Chemistry. Proc. 16th Conf. on Great Lakes Res., Huron, Ohio p. 581.
21. Kramer, J. R. (1973). Fate of Atmospheric Sulfur Dioxide and Related Substances as Indicated by Chemistry of Precipitation. Report to the Ministry of the Environment, Air Management Branch, Canada.
22. Likens, G. F., Ed. (1972). Nutrients and Eutrophication. Proceedings of the Symposium on Nutrients and Eutrophication. Allen Press, Lawrence, Kansas 66044.
23. Miller, W. E., T. E. Maloney and J. C. Greene (1974). Algal Productivity in 49 Lake Waters. Water Res., 8, 667.
24. Schelske, C. L., L. E. Feldt, M. A. Santiago and E. F. Stoermer (1972). Nutrient Enrichment and its Effect on Phytoplankton Production and Species Composition in Lake Superior. Proc. of the 15th Conf. on Great Lakes Res., April 1972, p. 149.
25. Schelske, C. L., L. E. Feldt, M. A. Santiago and E. F. Stoermer (1974). Fall Phytoplankton and Nutrients in Saginaw Bay and Western Lake Huron. Paper presented to the 17th Conf. of Great Lakes Res. Aug. 1974, Hamilton, Ont., Canada.
26. Schelske, C. L. and Stoermer, E. F. (1972). Phosphorus, Silica and Eutrophication of Lake Michigan. In Nutrients and Eutrophication. G. F. Likens, Ed. Allen Press, Lawrence, Kansas 66044, p. 157.
27. Schelske, C. L. and Stoermer, E. F. (1971). Eutrophication, Silica and Predicted Changes in Algal Quality in Lake Michigan. Sci. 173, 423.
28. Natusch, D. E. S., J. R. Wallace and C. A. Evans (1974). Toxic Trace Elements: Preferential Concentration in REspirable Particles. Science 183, 202.
29. Walton, C. P. and Lee, G. F. (1972). A Biological Evaluation of the Molybdenum Blue Method for Orthophosphate Analysis. Verh. Inter. Verein. Limnol., 18 676.
30. Murphy, T. J., unpublished results.
31. Matheson, D. L. Canada Centre for Inland Waters. Personal communication.
32. Phosphorus Technical Committee (1972). Report of the Phosphorus Technical Committee to the Lake Michigan Enforcement Conference. Chicago, Ill., Sept.

33. Lee, G. F. (1972). Phosphorus, Water Quality and Eutrophication of Lake Michigan. Presented to the Lake Michigan Enforcement Conference, Sept., Chicago, Ill.
34. Great Lakes Water Quality Board (1974). Draft Report. International Joint Commission, 100 Oulette Ave. Windsor, Ont. N9A 623.
35. Peterson, J. T. and C. E. Junge (1971). Sources of Particulate Matter in the Atmosphere. In Man's Impact on the Climate, Matthews et al. Ed. MIT Press, p. 310.

APPENDIX A

In accumulating available information on the source of phosphorus to the atmosphere, and their phosphorus content, there was one conspicuous void. This was the area of the phosphorus content of smoke from burning plant material. The 1968 EPA report on emissions to the atmosphere<sup>17</sup> stated that 25% of the total amount of particulates emitted to the atmosphere were from agricultural and forest fires. Since all living material contains phosphorus, one would expect that some of this would be included in the smoke. However, no information on the phosphorus content of this type of smoke could be found in the literature.

Dr. Ellis F. Darley at the University of California at Riverside was determining the amount of particulate emitted by different types of plant material upon combustion. Dr. Darley generously made available to us samples of smoke from a variety of fuels which were collected on glass fiber papers. With the exception of the samples from sugar cane, the smoke from each burn was sampled isokinetically and filtered through two filters arranged in series. For the sugar samples, only a single filter was used.

These samples were analysed for their phosphorus and carbon content. The results of the phosphorus analyses are shown on Table 10. The results shown for those samples where the particulate was collected on two filters in series are calculated on the basis of the phosphorus content and the amount of particulate on each paper. One difficulty in analysing these samples was the small amount of particulate on many of the samples. This affected the accuracy of those determinations and was probably the reason several of the ortho phosphate determinations were higher than the total phosphorus determinations. A series of samples was run where additional phosphorus was added to the filters. This additional phosphorus was recovered in the analysis, indicating that all of the phosphorus in the samples was being recovered.

Sample	Weight of Particulate Collected (gm)	Pounds of Particulate per Ton of Fuel	Percent Phosphorus in Particulate		Phosphorus Emitted from Fuel (gm/kg)	
			TOTAL	ORTHO	TOTAL	ORTHO
Sugar Cane, (leaves)	.01625	5.5	.22	.17	.006	.0047
" (leaves)	.01800	6.8	.09	.085	.0031	.0029
" (whole cane)	.02535	7.3	.24	.22	.0088	.008
" (whole cane)	.3170	7.1	.27	.16	.0096	.0057
Asparagus Fern	.11665 .03135	28.6 7.6	.016	.014	.0029	.0025
Citrus (green) (branches and leaves)	.1197 .02955	10.8 2.9	.003	.001	.0002	.00007
" (dry)	.04445 .01530	4.0 1.4	.001	.002	.00003	.00005
Pineapple (trash)	.03625 .01220	8.7 2.9	.007	.012	.0004	.0007
Russian Thistle (tumbleweed)	.05595 .00870	20.4 3.2	.018	.011	.0021	.0013
Grape Vines	.03375 .01035	5.2 1.6	.005	.002	.0002	.00007
Peach tree (prunings)	.02805 .00830	3.6 1.1	.004	.0025	.0001	.00006
Ponderosa Pine (flame period) (needles and duff)	.05550 .01425	27.1 6.9	.11	.066	.019	.011
" (smolder per.)	.04480 .01110	38.3 9.5	.11	.029	.026	.0069
Giant Sequoia (flame period) (needles and duff)	.06900 .01480	23.1 5.0	.043	.02	.006	.028
" (smolder period)	.07110 .01235	59.3 10.3	.031	.007	.011	.0024

Table 10. Results of the analysis of particulate matter samples collected from the combustion of different fuels.



Interestingly, the phosphorus content of the samples fell into two categories, those with a high content of phosphorus and those with a low content. The reasons for this are not clear. However, there are enough of the samples in each category that the existence of the two groups is established.

The sugar cane, the ponderosa pine and the giant sequoia samples were the most important. This is because the burning of sugar cane fields is widely practiced and the tree samples should be indicative of the contributions from forest fires. On the basis of these analyses, it was conservatively estimated that the phosphorus content of the smoke from agricultural fires contained 0.15% phosphorus while that from forest fires contained 0.10% phosphorus.

It is interesting that, with one exception, the second filter from all of the tree burns had a higher concentration of phosphorus. This could indicate that the smaller particulate particles are enriched in phosphorus. A similar enrichment of some metals in smaller particulates has been reported.<sup>28</sup>