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**ALKALINE AEROSOLS:
AN INITIAL INVESTIGATION OF
THEIR ROLE IN DETERMINING PRECIPITATION ACIDITY**

Final Report

Grant **ATM 77-24294**

The Role of Airborne Alkaline Materials
in Determining Precipitation Acidity

*Donald F. Gatz
Gary J. Stensland
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Sponsored by:
Atmospheric Chemistry Program
Division of Atmospheric Sciences
National Science Foundation

Principal Investigators: D. F. Gatz and G. J. Stensland

Champaign, Illinois
September 1984



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SUMMARY

This research was an initial attempt to increase our knowledge of airborne alkaline materials and their role in precipitation chemistry—subjects generally ignored in favor of studies of the acidic components of precipitation. Three questions motivated this work:

1. Which elements abundant in the earth's crust are also abundant in airborne particles and precipitation?
2. What fraction of air and precipitation impurities comes from crustal sources?
3. What are the chemical mechanisms linking crustal materials in air and precipitation? Specifically, what fractions of alkaline aerosols dissolve in water as a function of time, dilution ratio, and pH?

The approach to research on this highly interdisciplinary subject was observational, involving measurement of ionic composition of soil and unpaved road dust source materials, as well as aerosols and precipitation.

Field sampling was conducted primarily in the vicinity of our rural Bondville Road field site, which also serves as a sampling site for NADP, MAP3S, and other regional and local projects. Source sampling of soils and road dust was also carried out in other areas of Illinois within about 100 km of Champaign-Urbana. At Bondville, precipitation and aerosols were sampled during a 6-week observational period in October-November 1978. Six separate aerosol samplers were compared at ground level, and four of these were operated on a nearby 30-m tower as well.

Analytical quality assurance measures included 1) analysis of certain soil standards, 2) comparison of results from analyses performed with air/acetylene and N_2O /acetylene flames, and 3) comparison of multiple analytical methods.

Several exploratory mineralogical analyses were carried out to assess their utility in identifying and apportioning soil and unpaved road sources. Comparison of the mineral composition of soils and unpaved road materials showed differences sufficient to suggest that apportionment of these sources in aerosol samples may be possible. Calcite and dolomite would be the tracers for unpaved roads, and one of the clay minerals, perhaps montmorillonite/vermiculite, would be the soil tracer. Such calculations would be complicated by the observation of aerosol minerals in such high abundances that distant sources are likely, and the observation that local aerosols lack montmorillonite/vermiculite, even in situations where clay-rich local soil was seen to be blowing. The mineralogical observations also provided some evidence that gypsum detected on the filters may have been formed by the reaction of SO_2 or H_2SO_4 with airborne or collected calcite particles (perhaps wet with haze or fog droplets).

A major component of this work was the elemental analysis of soil and unpaved road materials to characterize their mean composition and variability. Local unpaved roads are spread with either crushed limestone rock or crushed or natural washed gravel derived from glacial deposits. Champaign county uses about 85% limestone, and most of our analyses were on this material.

The limestone samples contained high concentrations of both Ca and Si. The washed gravel samples contained less Ca, but still relatively high concentrations. (Si was not measured on washed gravel.) Variabilities (coefficient of variation) of the various elements ranged from 16-76%.

For two limestone samples, and two samples of limestone mixed with the underlying soil, the mean Mg, K, and Ca extractable by shaking 25 mg of dust in 25 mL of pH 3 nitric acid for 20 minutes were 2.2%, 1.8%, and 16.6% of the respective elements present in the samples.

Local surface soils were sampled from the 1 square km surrounding the Bondville Road field site. Soil samples were from the Drummer, Flanagan, and Elburn series, which are nearly identical in terms of the physical characteristics of near-surface material.

Comparison of analytical methods for the soil samples showed fusion/atomic absorption spectrophotometry to be somewhat more accurate than x-ray diffraction and neutron activation analysis. For total element mass, soils showed smaller variabilities than unpaved road samples, with coefficients of variation ranging from 3-33%. Si had the highest mass fraction (abundance) in the soil samples, followed by Al, Fe, K, Na, and Ca, but Ca had the largest ratio of abundance in road dust to that in soils.

Considerable effort was devoted to measuring mean values and spatial variability of extractable elements in soils from near the Bondville Road field site. Samples of 0.1 g were shaken in 100 mL of pH 3.3 simulated rainwater (nitric and sulfuric acids) for 20 min. No significant differences in Ca, Mg, or K results were found for "bulk" samples (that passed through a 2000 μm sieve), as compared to "sieved" samples (that passed through a 53 μm sieve), and the spatial distributions of bulk and sieved Ca and Mg were similar. No significant differences were found between soil series for soil pH or extractable Ca, but some of the differences found for Mg were significant.

Soil pH varied from 4.66-7.78 over the Bondville Road field site sampling grid. Fine scale transects confirmed the major variations noted in the larger-scale (150 m) grid. On a regional scale (100 km) we found no significant differences in soil pH between soil associations.

On the question of earth's crust elements in air and precipitation, of the 12 most abundant elements in average crustal rock, we detected all but P in aerosols and/or precipitation. Element ratios to K and factor analyses strongly suggested that the earth's crust was the major source of airborne Si, Al, Fe, Ca, K, Mg, Ti, and Mn, at least among coarse particles (2.5-15 μm aerodynamic diameter) at our Bondville Road field site. The same source appears to be responsible for the Ca, Mg, and K in precipitation. Other work indicates that Al and Fe in precipitation are mostly of crustal origin as well.

The second major motivating question concerned apportionment of the relative contributions of various sources to aerosols and precipitation. Approximate contributions of unpaved road and soil materials to Bondville aerosols were calculated from a simple chemical element balance (CEB) model, assuming that Ca and K were from these two sources only. Results indicated that soil contributed at least 85% of the aerosol mass of Al, Si, K, Ti, and Fe during a summer sampling period, but that road materials were responsible for 92% of the Ca. The Si results must be viewed with caution, since its total calculated concentrations exceeded those observed by a factor of more than 2.

A method was described whereby aerosols from major crustal source types may be identified in a series of short period (2 hour) ambient samples. The method uses variations in Ca, Al, and the Ca/Al ratio in simultaneous sequential samples at two widely spaced (by 10's of km) sampling sites. The method is promising for (at least) identifying wind erosion aerosols and road dust aerosols.

A CEB calculation on a series of Bondville Road event precipitation samples yielded estimates of source contributions to the total mass of impurities in precipitation of 2% from sea salt or road deicing salt, 32% from sulfates and ammonium compounds, 16% from nitrates, 11-24% from road dust (mean 12%), and 0-22% from soils (mean 15%). The results of a CEB calculation based on extracted (as opposed to total) soil and road dust compositions were physically unreasonable—the combined total contributions from soils and road dust alone exceeded 100%. An alternative method of accounting for insoluble matter in precipitation samples was more successful.

In pursuit of answers to the third question, considerable effort was devoted to an investigation of soil extraction methods and the variation of Ca and Mg extractability with extraction conditions. We examined the effects of varying the liquid/solids ratio (the dilution ratio), the extraction time, and the extractant pH. Extraction of Ca and Mg from soils increased with increasing dilution ratio and decreasing pH. The maximum fractions of these two elements extracted by any combination of dilution ratio and pH were 69% and 46% for Ca and Mg, respectively.

Data on soluble fractions of Ca and Mg in precipitation are rather few, but those that are available indicate that Ca is typically >90% soluble in precipitation, and Mg is often >80% soluble. The pH values of our extractants were typical of precipitation in the eastern U.S., so pH would not explain the differences between our extraction results and solubility in typical precipitation. However, dilution ratios in typical precipitation samples would be much larger than those of our experiments, and contact times would typically be longer. Based on the observed trends toward increasing solubility with increasing dilution ratio and contact times, it appears feasible that >80% solubilities of Ca and Mg could be achieved in precipitation with soil as their source.

The size distribution of windblown soil particles likely to enter precipitation would probably be systematically smaller than those used in our extraction experiments (<53 μm), and would thus be more susceptible to leaching in solution, as well. This has not yet been checked experimentally, however.

Proper sampling of particles larger than a few micrometers diameter, a size range typical of crustal dust particles, is still difficult. Results of an intercomparison of 6 ambient aerosol samplers showed that one type of sampler gave significantly larger, and another gave significantly smaller, concentrations of Ca and Mg. The reasons for this behavior are not clear, but the results do not correspond to expected differences in ranges of particle sizes sampled efficiently by the various samplers.

1 INTRODUCTION

Acidic precipitation is a subject of much current concern, both in the scientific literature (e.g., Likens et al., 1979) and the popular press.

Much of the current research into the nature of the acidic precipitation phenomenon is concerned, and rightly so, with the sources of acidic materials in precipitation. Elementary principles of chemistry tell us, however, that the net acidity of an aqueous solution results from the interactions of both acids and bases in the solution. Little attention has been paid thus far to the basic, or alkaline substances in precipitation. The research effort reported here was a first attempt to provide some rudimentary information about the role of alkaline materials in precipitation. We have examined one major source of alkaline materials in the atmosphere and in precipitation--dust from the earth's surface.

Considerable research has already been carried out to describe the physics of soil wind erosion (Bagnold, 1965; Bisal and Nielsen, 1962; Chepil, 1945a,b,c, 1946a,b, 1956, 1957a,b, Chepil and Milne, 1941; Chepil et al., 1962; Chepil and Woodruff, 1963; Gillette, 1974; Gillette et al., 1972; Lyles and Krauss, 1971; Lyles et al., 1974; Woodruff and Armburst, 1968; Woodruff and Siddoway, 1965; Zingg, 1954). More recently, concern over sources of airborne dust from large-scale non-point sources stimulated research into methods of estimating emissions of fugitive dust from unpaved roads (Cowherd and Englehart, 1982; Cowherd et al., 1974; Cowherd and Mann, 1976). Using emission rates from the literature, Evans and Cooper (1980) have calculated emissions from a wide variety of open (i.e., non-point) sources, by state, for the United States.

For the purposes of assessing the role of these aerosols from the earth's surface in precipitation chemistry, however, these earlier studies lack some vital information: the elemental or chemical composition of the emitted materials. It was the goal of this study to begin to supply information on the elemental composition of soil and road dust aerosols, and to explore their interactions with precipitation.

The basic approach of the investigation, and one appropriate to such an initial exploration, was one of field observations of the elemental and ionic composition of source materials, aerosols, and precipitation.

The subject matter of this investigation is highly interdisciplinary. It includes such scientific disciplines as meteorology, chemistry, geology, and agronomy, and many of their sub-disciplines. In such studies, communication across disciplines is often a barrier that must be overcome before significant progress is possible. Time is a necessary commodity in the overcoming of such obstacles.

2 EXPERIMENTAL METHODS

Our approach to this investigation was largely observational, involving the collection and analysis of both aerosols and precipitation for their content of alkaline materials, as well as collection and analysis of samples of the sources expected to be dominant, namely soils and unpaved road materials. In this chapter we describe the experimental methods used in 1) sample collection, 2) sample handling and preparation, and 3) sample analysis.

2.1 FIELD SAMPLING PROCEDURES

Aerosol and precipitation samples were collected at our rural Bondville Road field site (Figure 1), located approximately 10 km southwest of Champaign-Urbana, Illinois. This site is also used as a precipitation sampling site for the National Atmospheric Deposition (NADP) network and the Multistate Atmospheric Power Production Pollutant Study (MAP3S) network. In addition, it is the site of daily aerosol filter sampling and event precipitation sampling for other research grants and contracts in the Atmospheric Chemistry Section and one of six sites in a network of solar radiation and wind measurements in Illinois. Soil and road material samples were collected both locally and as far away as 100 km from the atmospheric sampling site.

2.1.1 Source Samples

Samples of unpaved road materials were collected (after brushing away the loose rocks) by scraping the top 1-2 cm of fine road dust from several spots within a 5 m radius circle. Both crushed limestone and washed gravel roads, the dominant types of unpaved road surfaces in the vicinity of the sampling site, were sampled. The sampling sites are shown in Figure 1.

A soil sampling grid with 160 m (approximately 0.1 mi) intervals between grid points was established surrounding the aerosol sampling sites (Figure 2). At 74 locations in this grid, surface soil material was collected to a depth of about 4 cm from several points in a circle 0.5 m in radius from the grid point. Samples were mixed in a plastic bucket and poured into double plastic bags for transport and temporary storage. Subsequent sampling at 45 m intervals along two transects of the original sampling grid employed the same methods as the original collections.

After the local variability of the soil surface composition at the Bondville site had been assessed, the next logical step was to obtain some rudimentary information on a regional scale. Published information was lacking or not of practical value for our needs. Thus, we decided to sample on a regional scale. When time and resource constraints were considered, it was apparent that only a limited number of samples could be gathered and that the pH of the samples would have to serve as the initial indicator of variability. To limit the investigation, we

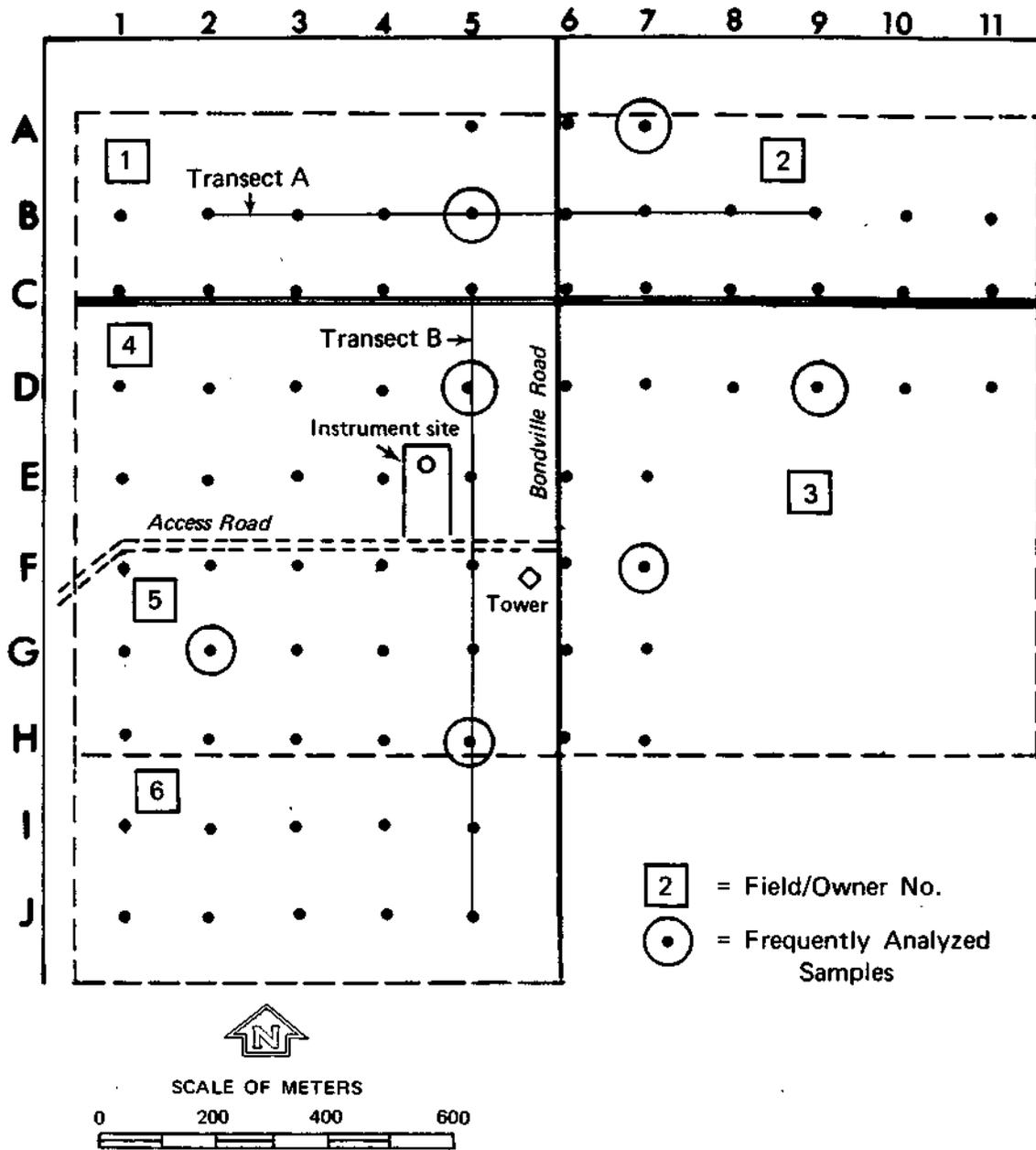


Figure 2. Map showing atmospheric sampling site and soil sampling grid (dots).

sampled only upwind of our aerosol sampling site in the directions of the two dominant wind directions during our October-November, 1978, sampling period. Winds were predominantly from the southwest or northeast during this period. A line through the Bondville site in a southwest/northeast direction was used as a base line for sampling purposes. Sampling was limited to a distance of about 100 km in both directions from the Bondville site, and took place between November 29 and December 11, 1979.

The soil association map given by Fehrenbacher et al. (1967) was transferred as an overlay to county maps that were used as base maps and guides for sampling. Reconnaissance by automobile was used to choose a minimum of 5 sampling sites for each soil association. The sites were chosen to represent the range of drainage conditions in the area and to provide even spacing across the association along the sampling line. Figure 3 shows the sampling locations.

Two areas away from the line were also sampled. These are enclosed by dashed lines in Figure 3. Association X (following the notation of Fehrenbacher et al., 1967), north of the main sampling line, represents sandy soils with little loess cover. Associations F and Q, south of our main sampling line, represent an older pre-Wisconsinan surface. Most of the area between these extremes is covered by 12-18 m of loess and thus would be expected to present a surface that is quite uniform in terms of the material subject to wind erosion, even though it is classified into many different soil series and associations. Soil series are defined by characteristics of multiple layers of the soil column, so that different series may still have the same surface material.

At each site we sampled either the varying drainage conditions along a slope or a 0.5 - 0.8 km line on a level surface. When a slope was present, we collected samples from the poorly drained, somewhat poorly drained, and well drained portions. If the site was devoid of slopes, 4 to 5 spots along the line were sampled. At each sampling site, 5-10 trowels-full of surface material from an area approximately 6 m in diameter were collected in a plastic bucket. Each sample was mixed in the bucket, transferred to a plastic bag, and brought to the laboratory, where it was air dried, crushed, and passed through a 2 mm sieve. Approximately 400 g of each sample was subsampled by a sample splitter to serve as a working sample. The remaining portion of each sample is stored for future use.

The following is a list of the associations sampled and the samples collected. No series description or identification was attempted for individual samples. Series names with listed associations are included only for completeness and possible future reference.

Soil Association A. Joy-Tama-Muscatine-Ipava-Sable Soils.

Samples: 83,84,85,86,87.

Dark-colored soils developed under prairie from loess more than 4 to 5 ft thick. The majority of the area is nearly level to moderately sloping and is found on the broader upland divides where drainage systems are not well developed.

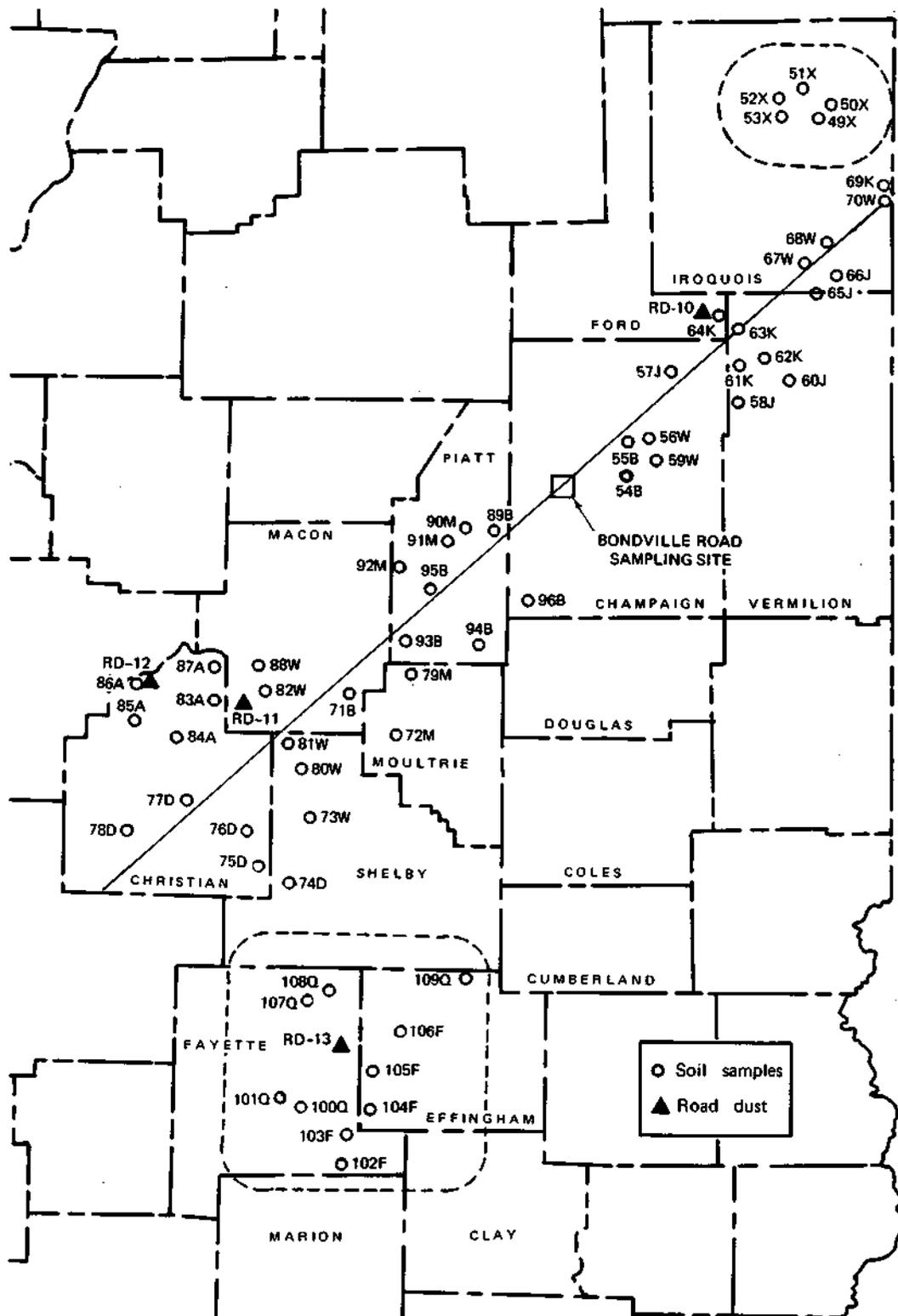


Figure 3. Map of east central Illinois showing sampling locations for soil and unpaved road materials within counties. Letter suffixes on soil samples match soil associations as given by Fehrenbacher et al. (1967).

Soil Association B. Sidel-Catlin-Flanagan-Drummer Soils.

Samples: 54,55,71,89,93,94,95,96.

Dark-colored soils developed under prairie on nearly level to strongly sloping upland area. Loess can vary from 1 to 5 ft thick with till generally under the loess.

Soil Association D. Harrison-Herrick-Virden Soils.

Samples: 74, 75, 76, 77, 78.

Dark-colored soils developed under grass from 5 to 7 ft of loess on weathered Illinoisan till. These soils occur on nearly level to strongly sloping uplands.

Soil Association F. Hoyleton-Cisne-Huey Soils.

Samples: 102, 103, 104, 105, 106.

Moderately dark-colored soils developed under grass from 2.5 to 4 ft of loess on weathered Illinoisan till. These soils occur on nearly level to moderately sloping uplands.

Soil Association J. Elliot-Ashkum-Andres Soils.

Samples: 57, 58, 60, 65, 66.

Dark-colored soils developed under grass in medium-textured material underlain by silty clay loam till at depths of less than 3 to 4 ft. These soils occur on nearly level to strongly sloping uplands. Topography is generally rolling with relatively short slopes interrupted by potholes and depressions.

Soil Association K. Swygert-Bryce-Clarence-Rowe Soils.

Samples: 61, 62, 63, 64, 69.

Dark-colored soils developed under grass from medium-textured material 2 to 4 ft thick over silty clay, clay till, or drift. These soils occur on nearly level to strongly sloping uplands.

Soil Association M. Birkbeck-Ward-Russell Soils.

Samples: 72, 79, 90, 91, 92

Light-colored to moderately dark-colored soils developed under forest or mixed prairie and forest vegetation from 3 to 5 ft of loess. These soils occur on nearly level to steep slopes and are underlain by loam to silty clay loam till.

Soil Association Q. Ava-Bluford-Wynoose Soils.

Samples: 100, 101, 107, 108, 109.

Light-colored soils formed under forest vegetation from 1.5 to 4 ft of loess on Illinoisan drift. These soils occur on nearly level to steep uplands.

Soil Association W. Littleton-Proctor-Plano-Camden-Hurst-Ginat Soils.
Samples: 56, 59, 67, 70, 73, 80, 81, 82, 88.

Light-, moderately dark- and dark-colored soils developed from medium- and fine-textured water-deposited materials with some areas having loess present above the water-deposited materials. These soils occur over a wide range of slopes—from nearly level to very steep on upland and stream terraces.

Soil Association X. Hagener-Ridgeville-Bloomfield-Alvin Soils.
Samples 49, 50, 51, 52, 53.

Light- to dark-colored soils developed in sandy materials over a variety of subsoil materials. These soils occur on nearly level to strongly sloping topography.

Four samples of road materials were also gathered at the same time as these soils. Samples were collected by mixing several spot samples gathered from the road surface along an 0.8 km stretch of road. The sampling sites are shown in Figure 3. Samples Rd-10 and Rd-12 are crushed limestone, while Rd-11 and Rd-13 are water-washed glacially deposited gravel.

2.1.2 Aerosols

Airborne particles were collected with a variety of sampling devices operated, for the most part, simultaneously. The reason for using several different samplers was partly to compare them and partly to maximize our chances of sampling both large and small particles properly, i.e., isokinetically, or nearly isokinetically. Thus, samples were collected:

1. On Nuclepore™ filters under rain shields,
2. On Nuclepore filters in vane samplers,
3. On Nuclepore filters in "streaker" samplers,
4. On Teflon™ filters in dichotomous virtual impactors,
5. On quartz filters exposed under rain shields and in vane samplers, and
6. On Whatman-41 filters used as impaction surfaces in Casella impactors.

The following paragraphs give the details of sample collection by these methods. Table 1 provides a summary of the various aerosol sampling methods used, any sample extractions performed, and the sample analysis methods used.

Table 1. Summary of aerosol sampling, handling, and analysis procedures, Bondville Road field site, October - November, 1978.

<u>Sampler type</u>	<u>Sampling schedule</u>	<u>Sampling height</u>	<u>Filter type (pore diam, um)</u>	<u>Extraction method*</u>	<u>Analytical laboratory**</u>	<u>Analysis method***</u>
Wat Surv funnel	12 hr sa, 1/day	Ground	Nuclepore (0.8)	pH 3	Wat Survey	Flame AA
Wat Surv vane	12 hr sa, 1/day	Ground Tower	Nuclepore (0.8) Nuclepore (0.8)	pH 3 pH 3	Wat Survey Wat Survey	Flame AA Flame AA
NCAR vane	12 hr sa, 1/day	Ground Tower	Nuclepore (0.8) Nuclepore (0.8)	DI, pH 3 DI, pH 3	Wat Survey Wat Survey	Flame AA Flame AA
FSU streaker	Continuous, 2 hr resol	Ground Tower	Nuclepore (0.4) Nuclepore (0.4)	---- ----	FSU FSU	PIXE PIXE
Dichotomous	24 or 12 hr 1 or 2/day	Ground Tower	Teflon (1.0) Teflon (1.0)	---- ----	EPA EPA	XRF XRF
Casella impactor	24 or 48 hr	Ground Tower	Whatman-41 Whatman-41	pH 3 pH 3	Wat Survey Wat Survey	Flame AA Flame AA
Funnel	48 to 96 hr	Ground	Quartz	----	SDSM	XRD
Wat Surv vane	48 to 96 hr	Ground	Quartz	----	SDSM	XRD

* All extractions in 25 mL pH 3 HCl, shaken 4 days (funnel samples shaken only 2 days). NCAR vane samples extracted first in 25 mL of deionized water for 4 days.

** FSU = Florida State University, Tallahassee; EPA = U.S. Environmental Protection Agency, Research Triangle Park, NC; SDSM = South Dakota School of Mines, Rapid City.

*** Flame AA = flame atomic absorption spectrophotometry (for K, Ca, Mg); PIXE = proton-induced X-ray emission (for Al, Si, P, S, Cl, K, Ca, Ti, Fe, Cu, Zn, Br, and Pb); XRF = X-ray fluorescence (for Al, Si, P, S, Cl, K, Ca, Ti, Mn, Fe, Cu, Zn, Br, and Pb in most samples, and Co, Ni, As, Se, Rb, Sr, Sn, Sb, Ba, and W in some samples; total mass by beta attenuation).

Daily 12-hr filter samples were collected on preweighed 37 mm diameter Nuclepore filters with 0.8 μm diameter pores. One series of these filters was exposed in open-face plastic cartridges, face down under an inverted funnel rain shield, about 1.5 m over grass. Two more Nuclepore series were exposed in vane samplers that always face into the wind. The objective of both types of vane samplers was to provide quasi-isokinetic sampling of large particles, and to avoid the under-sampling of large particles that could occur on the face-down filter if particles were unable to follow the air when it makes a sharp bend from horizontal to vertical motion to enter the filter.

One type of vane sampler was built following the plans for the National Center for Atmospheric Research (NCAR) sampler described by Gillette *et al.* (1974). This sampler uses an airtight vacuum rotation joint to enable the filter to be mounted vertically, so it always faces into the wind. Another main feature of this sampler is its use of any one of a variety of sampling nozzles of different diameters. The nozzle to use at any given time is chosen to provide approximately isokinetic sampling for the ambient wind speed. The pumping rate is also adjusted to match the nozzle in use. However, in our case this variation in flow rates may have caused an error of up to 10-20% in our sample volume determinations. The filters used in this sampler were reweighed after sampling to obtain the mass of the sample collected.

The other vane sampler was designed and constructed at the Water Survey (Gatz, 1981). It consists of a plastic tube with a gradual 90° bend ahead of a horizontally-mounted filter, and a constricted opening. These features were designed to turn the particles gradually from horizontal to vertical motion so as to avoid their overshooting the filter, and to slow them to approximately the face velocity of the filter, so as to provide quasi-isokinetic sampling of particles at wind speeds of 4 m/s. The sampler is provided with a tail and is free to rotate about a vertical axis, so it always faces into the wind. In a comparison of the vane and funnel samplers (Gatz, 1981) the vane sampler was found to measure 20% to 35% higher concentrations of soil-derived elements, which are expected to occur on relatively large ($>5 \mu\text{m}$) particles. However concentrations of S and Zn, which are commonly found preferentially on submicrometer particles, were about the same in both samplers. Both types of vane samplers were operated near ground level and also on top of a 35 m tower located 360 m to the southeast of the ground site (Figure 2).

Florida State University streaker samplers (Nelson, 1977) were also operated at both ground and tower sites. These samplers draw air through a strip of 0.4 μm Nuclepore filter exposed face downward. The sampler uses a vacuum orifice which moves the length of the filter strip at a rate of 1 mm/h, thus providing a week's sample in a "streak" 168 mm long.

Beckman automatic dichotomous samplers were also operated on the tower and at the ground site. These samplers collected aerosol in two size ranges (less than 2.5 μm , and 2.5-15 μm) on 1 μm pore diameter Teflon filters. The dichotomous samplers were loaned to the Water

Survey, and the samples were analyzed, by the U.S. EPA Environmental Sciences Laboratory, Research Triangle Park, North Carolina, through the courtesy of Dr. Tom Dzubay.

Samples for mineralogical analysis were collected at about 1 m above grass at the ground site only, using 37 mm diameter Pallflex type 2500-QAST "Tissue Quartz" filters, mounted in open-face plastic cartridges and exposed under an inverted funnel or in the Water Survey vane sampler described above.

Size-segregated samples were collected on uncoated Whatman-41 filter paper impaction substrates in Casella impactors, at both tower and ground sites. No backup filter was used. Samples were collected continuously over periods of 24 or 48 h using Gelman/Gast diaphragm pumps and a critical orifice giving a constant flow of 17.5 L/min, under ambient conditions. Sample volumes have not been corrected to standard conditions. The impactors were operated with a tail to keep them facing into the wind, and with a 6.0 cm diameter, 11.5 cm long cylindrical metal "guard tube" surrounding the inlet and parallel to the airflow, as recommended by May et al. (1976).

2.1.3 Precipitation

Precipitation samples were collected in duplicate on both the ground and the tower using wet/dry samplers of the U.S. Department of Energy Health and Safety Laboratory (now Environmental Measurements Laboratory) design (Volchok and Graveson, 1975). Samples were collected as soon as possible after each rain event, but not later than the following morning.

2.2 SAMPLE PREPARATION PROCEDURES

Sample preparation includes all the various operations used in preparing samples for analysis. These operations generally consist of sample dissolution, extraction, or filtration to yield samples free of solids.

Sample bags of soil and road materials were opened to the atmosphere and allowed to air dry. The air dried soils were crushed with a common wooden rolling pin to break up clods or chunks. Road samples were not crushed. For both soils and road materials the next step was to hand sieve the materials through a 2 mm sieve, retaining the fine materials that passed through the sieve and discarding the portion of the sample larger than 2 mm. The sample retained at this point is referred to in this report as the "bulk" sample. Laboratory working samples were acquired by subsampling the bulk surface materials with a sample splitter and passing the subsample through a 53 μ m sieve. Again, the materials left on the sieve were discarded, and the <53 μ m material that passed through the screen was retained as the working sample for further processing. No quantitative determination of the mass fraction obtained from the sieving was attempted. The only intent of the sieving was to obtain samples for laboratory use.

A few words of explanation are needed here regarding particle size terminology. Any of the dry sieving techniques separate what we refer to as "environmental" particles into various groups according to their size. These environmental particles would be termed agglomerates by agronomists, because they are composed of agglomerations of "true" particles. True particles are those measured by wet sieving techniques, involving the use of wetting agents or detergents to break up the agglomerates into their component true particles.

Further separation of the surface materials (both soils and road materials) into smaller size classes was carried out using an ATM Corporation Model L3P "Sonic Sifter" with a series of electroformed nickel sieves having 5, 10, 20, and 45 μm openings.

The sonic sifter procedure was not intended at this point to separate environmental particles quantitatively and to yield mass fractions for the various size classes. The intent was simply to obtain representative materials in given size classes for further analyses and characterization. Therefore the procedure was arranged to yield sample with no regard to sample mass, except to provide enough to split so that multiple analyses could be performed.

The $<53 \mu\text{m}$ material was first loaded onto the 5 μm screen in 4-7 g portions and sieved in 15 min increments until no sample passed the screen in successive time increments. The $>5 \mu\text{m}$ material was saved and loaded onto the 10 μm sieve in 4-7 g portions and sieved in the same manner as before. The material was transferred to screens with successively larger openings until the full set of screens was used. The materials that passed each screen were put into glass vials labeled by particle size and stored for later use. At the end of the sonic sifting procedure we had samples of particles in the following size ranges: <5 , 5-10, 10-20, 20-45, and 45-53 μm .

An alternate method of separating bulk soil and road materials according to environmental particle size is the laboratory airjet device at the University of Wisconsin Water Chemistry Laboratory. Samples of soils and road materials in four size classes were generated with this device. Approximately 1-2 g of sieved ($<53 \mu\text{m}$) soil or road dust was placed into a 5-gal polyethylene chamber and suspended by directing two jets of filtered air on the sample. The suspended particles were collected on 37 mm diameter Whatman-41 filter substrates on stages 2, 4, and 6, and an 8 cm diameter backup filter of a 6-stage Delron Model DCI-6 cascade impactor. Before reaching these stages, the particles passed through two stage-1 (16 μm diameter 50% cutoff) collectors equipped with Apiezon-L-coated Nuclepore filter substrates. These stage-1 collections were discarded.

Source samples were either extracted by water or a dilute acid solution, or they were completely dissolved by fusion. Details of the various extraction methods are given later in the text when the results are presented.

The fusion technique used to completely dissolve samples of various kinds prior to analysis is a combination of techniques reported previously by Suhr and Ingamells (1966) and Van Loon and Parissis (1969). The procedure follows:

1. Weigh a 0.0250 g sample to the nearest 0.0001 g.
2. Add approximately 0.125 g of LiBO_2 to the weighing paper and mix well with the sample.
3. Transfer the sample and LiBO_2 to a clean graphite crucible and fire in a muffle furnace for 15 min at 960 C.
4. Pour the molten sample into 80 mL of 1:24 water/concentrated HNO_3 in a precleaned 125 mL widemouth plastic bottle.
5. Tightly cap the plastic bottle and shake the sample in a horizontal position at 180 cycles min on a reciprocal shaker for 24 h.
6. Transfer the sample mixture to a 250 mL volumetric flask and bring to volume with deionized water.

Filter samples collected in the Water Survey vane or funnel samplers, the NCAR vane sampler, and the Casella impactor were extracted by shaking for 2 or 4 days in 25 mL of pH 3 HNO_3 (see Table 1). After extraction the samples were filtered through 0.45 μm Millipore HA filters preleached with 200 mL of pH 3 HNO_3 . In a test of the procedure, the NCAR vane filters were pre-extracted by shaking for 4 days in 25 mL of deionized water and filtered through the same Millipore filter as mentioned above. In the case of the deionized water extraction, however, the leached filters were rinsed with two 200 mL portions of deionized water before filtering the filter extract.

Precipitation samples were filtered within 48 h of collection through 0.45 μm Millipore HA filters preleached with two 200 mL portions of deionized water.

2.3 SAMPLE ANALYSIS PROCEDURES

A summary of analysis procedures used for aerosol samples is included in Table 1. Extracts from the Water Survey vane and funnel filters, the NCAR vane filters, and the Casella impaction substrates were analyzed at the Water survey for Mg, K, and Ca, using standard flame/AAS techniques (Stensland et al., 1979).

The FSU streaker samples were analyzed in 2-h time increments using proton-induced X-ray emission (PIXE) (Johansson et al., 1975).

The Teflon filters from the dichotomous samplers were analyzed for multiple elements by the U.S. EPA, Research Triangle Park, North Carolina, using X-ray fluorescence techniques. Details of the procedure were given by Dzubay et al. (1980). The quartz filters were analyzed for minerals by Dr. Briant Davis at Brigham Young University and at the South Dakota School of Mines using methods documented elsewhere (Davis and Cho, 1977; Davis, 1978; Davis, 1980). Precipitation filtrates were analyzed by the Water Survey Analytical Chemistry Laboratory, using the same methods applied to samples from the National Atmospheric Deposition Program (Stensland et al., 1979).

The surface materials samples (soils and road materials) were measured for pH and also for various elements, using several different analytical methods, as discussed in the following paragraphs.

Soil pH was measured using a glass electrode and a Calomel reference electrode. The sample was prepared by mixing 20 g of a soil or road material sample with 20 mL of deionized water, stirring three times at 10 min intervals, and allowing the mixture to stand for 30 min.

The LiBO_2 fusion samples were analyzed for Na, Mg, Al, K, Ca, Mn, and Fe using standard AAS procedures (Stensland et al., 1979), except that a N_2O /acetylene flame was used instead of the conventional air/acetylene flame to avoid interferences (see discussion below). Other types of surface materials extracts were analyzed for the same elements using the same techniques.

Surface materials were also analyzed for Al, Si, K, Ca, Ti, and Fe at the Illinois State Geological Survey using X-ray fluorescence methods (Rose and Flanagan, 1962). Some surface materials samples were also analyzed at the University of Illinois Institute of Environmental Studies. Na, Mg, Al, K, Ca, Ti, Mn, Fe, and other elements were measured by INAA. The procedure involved a series of irradiations, delay periods, and counts, to obtain a multielement analysis. For the first irradiation, samples or standards were irradiated one at a time for 30-60 s in the pneumatic tube facility of the Illinois Advanced TRIGA reactor Facility, along with a nickel foil flux monitor. The samples were counted for 200 s after a 60 s delay, using a 10% efficient Ge(Li) gamma ray spectrometer. The spectra were accumulated in a 4096-channel analyzer and recorded on computer compatible magnetic tape. The spectral data were then reduced to elemental concentrations by a series of programs described by Maney et al. (1977). For the second irradiation, the standards and approximately 10 samples were irradiated simultaneously for 30-60 min and counted twice. A 15 min count was made after a 1-3 h delay and a 1 h count after a 16-20 h delay. A similar procedure was employed for the third irradiation. This irradiation lasted 6-8 h and the samples were counted for 1.5 h after an 8-12 day delay. This system has been evaluated using National Bureau of Standards No. 1633 Coal Fly Ash standards and U.S. Geological Survey Standard Rocks No. AGV-1 and G-2. Results were found to agree within reported uncertainties with the values certified by the respective agencies.

3 ANALYTICAL COMPARISONS, QUALITY ASSURANCE, AND EXPLORATORY INVESTIGATIONS

A continuing concern of this research was the validity of sample analyses. This is a worthy concern in any research, but is especially important when a laboratory analyzes a particular kind of sample for the first time or begins using a new analysis procedure. Both of these events occurred during this research; hence, a number of steps were taken to insure analytical accuracy. These steps included 1) analysis of certified soil standards, 2) comparison of results from analyses performed with air/acetylene and N_2O /acetylene flames in AAS, and 3) comparison of three analytical methods—atomic absorption spectrophotometry (AAS), X-ray fluorescence (XRF), and instrumental neutron activation analysis (INAA). The following sections report the results of these efforts. In addition to these analytical comparisons and quality assurance measures, we carried out exploratory investigations in two subject areas. The first of these concerned methods for extracting Na, Mg, K, and Ca from soil and road dust. Further, some exploratory mineralogical analyses were carried out by a consultant, Dr. Briant Davis, who performed some of the analyses at the Thermochemical Institute of Brigham Young University, Provo, Utah, and some at his home institution, the South Dakota School of Mines, Rapid City, South Dakota.

3.1 CANADIAN CERTIFIED SOIL STANDARDS

Inquiries to various sources indicated that no standard soil samples for total element analyses were available from U.S. agencies, although we understand that the National Soil Survey Laboratory, Soil Conservation Service, Lincoln, Nebraska, is preparing such a set of samples. Our inquiries brought out, however, that a set of standard soil samples with certified elemental content was available from the Canada Centre for Mineral and Energy Technology (Bowman *et al.*, 1979). We purchased a set of four of these standard soils, and analyzed them to provide assurance of analytical accuracy for Na, Mg, Al, K, Ca, Mn, and Fe analyses by AAS.

Duplicate samples of each of the four standard soils were dissolved using the $LiBO_2$ procedure and analyzed by N_2O /acetylene flame AAS, as described earlier. Results are shown in Table 2, which lists the measured and certified values for each sample, as well as the deviation from the certified value in both absolute and relative terms. The table shows mean deviations from certified values over all 8 analyses, as follows: Na, 3.7%; Mg, 2.1%; Al, 2.1%; K, 4.3%; Ca, 1.8%; Mn, 6.6%; and Fe, 4.3%. Comparing the means of the duplicate samples to the certified values produced mean deviations of: Na, 3.6%; Mg, 1.7%; Al, 2.2%; K, 4.2%; Ca, 1.8%; Mn, 5.6%; and Fe, 3.3%. Thus, by either measure, $LiBO_2$ fusion followed by N_2O /acetylene flame AAS yielded analyses of Na, Mg, Al, K, Ca, Mn, and Fe with mean errors of less than 7%. The N_2O /acetylene flame was found to be necessary for accurate Ca analysis on soils, as shown in the following section.

Table 2. Comparison of measured and certified elemental concentrations in Canadian soil samples.

Element	Soil sample	Repli- cation	A	B	A-B		
			Measured value* %	Recommended value** %	Deviation		
					A-B, %	(A-B)/B, %***	
Na	SO-1	1	1.99	(1.90)	0.09	4.7	
		2	1.99		0.09	4.7	
	SO-2	1	1.85	(1.74)	0.11	6.3	
		2	1.80		0.06	3.4	
	SO-3	1	0.80	0.74	0.06	8.1	
		2	0.74		0.00	0.0	
	SO-4	1	0.99	(0.97)	0.02	2.1	
		2	0.97		0.00	0.0	
						Mean = 3.7	
	Mg	SO-1	1	2.34	2.31	0.03	1.3
			2	2.34		0.03	1.3
		SO-2	1	0.56	0.54	0.02	3.7
2			0.54		0.00	0.0	
SO-3		1	5.03	(5.11)	-0.08	1.6	
		2	5.19		0.08	1.6	
SO-4		1	0.54	0.56	-0.02	3.6	
		2	0.54		-0.02	3.6	
					Mean = 2.1		
Al		SO-1	1	9.21	9.38	-0.17	1.8
			2	9.31		-0.07	0.7
		SO-2	1	8.09	8.07	0.02	0.2
	2		7.79		-0.28	3.5	
	SO-3	1	3.06	3.05	0.01	0.3	
		2	3.09		0.04	1.3	
	SO-4	1	5.69	5.46	0.23	4.2	
		2	5.74		0.28	5.1	
						Mean = 2.1	

Table 2 (continued)

Element	Soil sample	Repli- cation	A	B	A-B	
			Measured value* %	Recommended value** %	Deviation	
					A-B,	(A-B)/B, %***
K	SO-1	1	2.57	2.68	-0.11	4.1
		2	2.57		-0.11	4.1
	SO-2	1	2.36	2.45	-0.09	3.7
		2	2.33		-0.12	4.9
	SO-3	1	1.14	1.16	-0.02	1.7
		2	1.13		-0.03	1.6
	SO-4	1	1.61	1.73	-0.12	6.9
		2	1.62		-0.11	6.3
					Mean = 4.3%	
Ca	SO-1	1	1.71	1.80	-0.09	5.0
		2	1.74		-0.06	3.3
	SO-2	1	1.94	1.96	-0.02	1.0
		2	1.92		-0.04	2.0
	SO-3	1	14.81	(14.8)	0.0	0.0
		2	14.57		-0.2	1.4
	SO-4	1	1.10	1.11	-0.01	0.9
		2	1.10		-0.01	0.9
					Mean = 1.8	
Mn	SO-1	1	0.091	0.089	0.002	2.2
		2	0.103		0.014	15.7
	SO-2	1	0.072	0.072	0.000	0.0
		2	0.079		0.007	9.7
	SO-3	1	0.052	0.052	0.000	0.0
		2	0.061		0.009	17.3
	SO-4	1	0.062	0.060	0.002	3.3
		2	0.057		-0.003	5.0
					Mean = 6.6	

Table 2 (continued)

Element	Soil sample	Repli- cation	A	B	A-B	
			Measured value* %	Recommended value** %	Deviation	
					A-B, %	(A-B)/B, %***
Fe	SO-1	1	5.72	6.00	-0.28	4.7
		2	5.70		-0.30	5.0
	SO-2	1	5.49	5.56	-0.07	1.2
		2	5.34		-0.22	4.0
	SO-3	1	1.74	1.51	-0.23	15.2
		2	1.53		-0.02	1.3
	SO-4	1	2.36	2.37	-0.01	0.4
		2	2.31		-0.06	2.5
					Mean = 4.3%	

* Units are % element in oven-dried sample.

** Values in parentheses were determined in the same way as others, but assignment of a recommended value was considered unjustified (Bowman et al., 1979).

*** Absolute value.

3.2 COMPARISON OF AIR/ACETYLENE AND N₂O/ACETYLENE FLAMES FOR AAS

Inconsistent Ca analyses obtained using an air/acetylene flame on a variety of samples prompted us to compare air/acetylene and N₂O/acetylene flames on analyses of standard soils dissolved by LiBO₂ fusion. Results are presented in Table 3, which shows anomalous results for Ca by air/acetylene. Although not apparent in the table, the direction of the error was toward underestimation of the true Ca concentration. This problem had not occurred in previous analyses of aerosol and rain water samples in our laboratory, which suggests that the error lies in an interference caused by something in the soil matrix.

3.3 COMPARISON OF ANALYSES OF SOURCE MATERIALS BY INAA, XRF, AND FUSION/AAS

In addition to AAS, two other methods, namely INAA and XRF, were used for analyses of soils and road materials. INAA and XRF have the advantage of providing the multielement analyses that are required for modern source identification methods. This section compares results of the three analytical methods applied to the same samples.

Results of analyses of Na, Mg, Al, Si, S, K, Ca, Ti, Mn, and Fe by one or more of the three methods appear in Tables 4 and 5. Table 4 covers soil samples and Table 5 unpaved road material. A few elements were measured by only one method; for those elements comparison of results is not possible.

Comparison of results against certified values for standard soil samples was carried out only for the LiBO₂ fusion/AAS method. As shown earlier (Section 3.1) our results were very close to the recommended value in each case; therefore, the fusion/AAS method serves as the standard in this comparison. This applies only to Na, Mg, Al, K, Ca, Mn, and Fe; no standards of comparison are available for Si, S, or Ti.

The samples used in the fusion/AAS method were oven dried (105 C) before analysis, whereas those used in the other two methods were air dried. Since the element masses were compared with total sample masses that included approximately 2 to 5% water in the cases of INAA and XRF, the results of those analyses should be expected to be lower by approximately 2 to 5% than the fusion/AAS results.

Table 4 shows sample-to-sample variabilities of elemental concentrations, even within analysis methods, greater than the respective analytical uncertainties. Furthermore, the degree of variability is different for different elements. This spatial variability of element concentrations in surface soils is discussed further in a later section.

Examination of Table 5 quickly reveals an even greater sample-to-sample variation for road materials than for soil, for a given element and method. Observations in the field suggest that this could occur

Table 3. Comparison of analytical results using air/acetylene and N₂O/acetylene flames for analyses of Canadian standard soils by AAS.

<u>Element</u>	<u>Mean deviation from certified values, %</u>	
	<u>N₂O/acetylene</u>	<u>Air/acetylene</u>
Ca	1.8	22.8
Mg	2.1	1.6
Na	3.7	4.3
K	4.3	6.4

Table 4. Comparison of analytical results for soil samples, using three different analyses methods. Units are % element in sieved (<53 μm) air dried soil for INAA and XRF, % element in oven dried soil for fusion/AAS.

Element	Sample number	INAA			XRF			Fusion/AAS*		
		N	\bar{X}	S.E.	N	\bar{X}	S.E.	N	\bar{X}	S.E.
Na	2G	1	0.76					2	0.78	0.02
	5B	2	0.74	0.02				2	0.76	0.01
	5D	2	0.76	0.00				2	0.75	0.00
	5H	1	0.65							
	7A	2	0.74	0.02				2	0.78	0.04
	7F	1	0.70					2	0.72	0.02
	9D	1	0.70					2	0.76	0.02
Mg	2G	1	1.69		1	0.20		2	0.34	0.00
	5B	2	2.48	0.54	2	0.38	0.03	2	0.63	0.01
	5D	2	2.58	0.07	2	0.30	0.10	2	0.58	0.01
	5H	1	2.43							
	7A	2	2.16	0.18	2	<0.02	>0.00	2	0.36	0.02
	7F	1	2.52		1	0.12		2	0.44	0.00
	9D	1	2.77		1	0.30		2	0.50	0.00
Al	2G	1	2.71		1	5.06		2	4.46	0.00
	5B	2	2.86	0.44	2	5.68	0.01			
	5D	2	3.24	0.08	2	5.57	0.10	2	5.63	0.15
	5H	1	2.84							
	7A	2	2.68	0.02	2	4.80	0.00			
	7F	1	3.01		1	3.81		2	4.83	0.03
	9D	1	3.17		1	5.59		2	5.24	0.00
Si	2G				1	37.25				
	5B				2	31.62	0.10			
	5D				2	31.40	0.25			
	7A				2	35.80	0.04			
	7F				1	36.46				
	9D				1	35.52				
S	5B				1	0.06				
	5D				1	0.03				
	7A				1	0.05				

Table 4 (continued)

Element	Sample number	INAA			XRF			Fusion/AAS*			
		\bar{X}	S.E.	N	\bar{X}	S.E.	N	\bar{X}	S.E.		
K	2G	1	1.61		1	1.72		2	1.68	0.00	
	5B	2	1.62	0.00	2	1.50	0.00	2	1.67	0.04	
	5D	2	1.78	0.04	2	1.54	0.00	2	1.77	0.03	
	5H	1	1.45								
	7A	2	1.66	0.08	2	1.56	0.00	2	1.75	0.08	
	7F	1	1.64		1	1.78		2	1.84	0.02	
	9D	1	1.64		1	1.80		2	1.80	0.00	
	Ca	2G	1	1.81		1	0.62		2	0.60	0.00
		5B	2	2.02	0.08	2	0.84	0.02	2	0.92	0.00
5D		2	1.88	0.12	2	0.76	0.02	2	0.84	0.00	
5H		1	1.82								
7A		2	1.81	0.05	2	0.47	0.01	2	0.52	0.02	
7F		1	1.88		1	0.58		2	0.65	0.03	
9D		1	1.63		1	0.76		2	0.68	0.00	
Ti		2G	1	0.44		1	0.45				
		5B	2	0.33	0.10	2	0.39	0.00			
	5D	2	0.38	0.03	2	0.40	0.00				
	5H	1	0.44								
	7A	2	0.43	0.01	2	0.42	0.00				
	7F	1	0.33		1	0.45					
	9D	1	0.48		1	0.41					
	Mn	2G	1	0.0231					2	0.027	0.001
		5B	2	0.0158	0.0002						
5D		2	0.0198	0.0004				2	0.030	0.002	
5H		1	<0.0113								
7A		2	0.0220	0.0006							
7F		1	0.0275					2	0.034	0.002	
9D		1	0.0202					2	0.022	0.009	
Fe		2G	1	1.42		1	1.99		2	1.56	0.02
		5B	2	2.18	0.07	2	2.65	0.04			
	5D	2	1.94	0.04	2	2.26	0.00	2	2.24	0.00	
	5H	1	1.73								
	7A	2	1.54	0.05	2	1.82	0.00				
	7F	1	1.77		1	2.12		2	1.86	0.04	
	9D	1	1.82		1	2.41		2	2.25	0.11	

* N₂O/acetylene flame used for Ca analyses, air/acetylene for other elements.

Table 5. Comparison of analytical results for road materials samples, using three different analysis methods. Units are % element in air dried sample for INAA and XRF, % element in oven dried sample for fusion/AAS.

Element	Sample number*	INAA**	XRF**	Fusion/AAS***		
				N	X	S.E.
Na	1a			2	0.56	0.02
	3			2	0.21	0.02
	5			2	0.33	0.00
	6	0.33		2	0.36	0.02
	7			2	0.23	0.01
	8			2	0.24	0.00
	9	0.54		2	0.58	0.02
	9c			2	0.53	0.06
	Mg	1a		0.32	2	0.42
3			1.29	2	1.41	0.02
5			1.45	2	1.54	0.01
6		2.93	1.34	2	1.53	0.00
7				2	3.70	0.06
8				2	0.42	0.00
9		4.55		2	3.76	0.16
9c				2	3.15	0.18
Al		1a		3.04	2	3.12
	3		0.75	2	1.12	0.02
	5		1.30	2	1.31	0.05
	6	1.19	1.84	2	1.72	0.05
	7			2	1.29	0.00
	8			2	1.58	0.01
	9	1.65		2	2.90	0.13
	9c			2	1.70	0.14
	Si	1a		23.83		
3			7.07			
5			14.89			
6			17.42			
K	1a		1.14	2	1.22	0.01
	3		0.32	2	0.38	0.00
	5		0.54	2	0.57	0.03
	6	0.74	0.67	2	0.72	0.01
	7			2	0.56	0.00
	8			2	0.56	0.00
	9	1.27		2	1.34	0.05
	9c			2	0.78	0.06

Table 5. (continued)

Element	Sample number*	INAA**	XRF**	Fusion/AAS***		
				N	X	S.E.
Ca	1a		14.42	2	11.90	1.77
	3		31.84	2	28.90	0.80
	5		24.36	2	22.39	0.36
	6	13.9	20.53	2	19.79	0.03
	7			2	23.56	0.46
	8			2	26.14	0.09
	9	6.85		2	10.25	0.44
	9c			2	12.01	0.86
	Ti	1a		0.26		
3			0.05			
5			0.09			
6		0.16	0.10			
9		0.20				
Mn	1a			2	0.081	0.003
	3			2	0.113	0.002
	5			2	0.116	0.004
	6	0.0906		2	0.104	0.008
	7			2	0.091	0.003
	8			2	0.126	0.005
	9	0.0725		2	0.086	0.007
	9c			2	0.040	0.002
Fe	1a		1.58	2	1.46	0.02
	3		0.83	2	0.94	0.00
	5		1.26	2	1.24	0.10
	6	1.37	1.78	2	1.56	0.00
	7			2	1.00	0.02
	8			2	1.08	0.00
	9	1.82		2	2.08	0.06
	9c			2	1.31	0.13

* Sample 9c was prepared by crushing and grinding rocks from sample 9.
 ** All analyses were of single samples (i.e., N=1).
 *** N₂O/acetylene flame used for Ca analyses, air/acetylene for other elements.

because, 1) different materials, namely crushed limestone and washed glacially-deposited gravel, were sampled on different roads, and 2) individual road sampling sites would likely vary in the fraction of soil from beneath the road that has been mixed upward into the road materials.

The information in Tables 4 and 5 comparing the results of INAA and XRF analyses with those of fusion/AAS has been summarized in Table 6 for Na, Mg, Al, K, Ca, Mn, and Fe. Table 6 shows mean relative deviations from fusion/AAS results for Na, Mg, Al, K, Ca, Mn, and Fe measured by INAA or XRF. The table shows mean deviations of less than 10% for Na and K in both soils and road materials analyzed by INAA and for K in soil and road materials, Ca in soil, and Fe in road materials measured by XRF. For these elements and methods, the biases were predominantly negative (i.e., fusion/AAS concentrations higher), as expected from the fact that the fusion/AAS samples were oven dried and the others air dried.

In addition, Fe in soil, and Mn and Fe in road materials, had mean errors of less than 15% by INAA. Al and Fe in both soil and road materials had mean errors between 10 and 15% for XRF measurements.

Thus, the XRF method gave reasonably good agreement with the fusion/AAS results for all the measured elements (Na and Mn were not measured) in both soil and road materials, except for Mg in soil.

INAA, on the other hand, agreed with the fusion/AAS method within 15% only for Na, K, and Fe in soil and Na, K, Mn, and Fe in road materials. The other elements measured by INAA (Mg, Al, and Ca in both materials, and Mn in soils) compared rather poorly to fusion/AAS. Summary tables of source composition measurements are presented in Chapter 4.

3.4 EXPLORATORY EXTRACTIONS OF SOURCE SAMPLES

3.4.1 Dependence of Extractability on Dilution Ratio and pH

Precipitation samples are very dilute solutions. Figure 4 shows the distributions of both insoluble residue and total (soluble and insoluble) residue concentrations in precipitation at our Bondville Road sampling site. Median concentrations were 4.16 and 10.6 $\mu\text{g/mL}$ for insoluble and total residue, respectively. These values are equivalent to dilution ratios of 240,400 and 94,300 g of water/g of residue, respectively. Since extractions of soils or other source materials are likely to involve samples of perhaps 0.1 - 1.0 g of solids in, say, 100 g of solute (dilution ratios of 100 - 1000) it is of interest to know whether the amounts of elements extracted from the solid samples depend on the dilution ratio.

The experiments described here were designed to look for effects of varying the dilution ratio on source material extractions. atmospheric

Table 6. Summary table: Comparison of Na, Mg, Al, K, Ca, Mn, and Fe results by INAA and XRF against fusion/AAS results.

Soil					Road materials				
	Mean relative				Mean relative				
N*	deviation. %	S.D.	Bias**		N*	deviation. %	S.D.	Bias**	
Neutron activation									
Na	6	3.7	2.4	5 of 6 negative	2	7.6	1.0	both negative	
Mg	6	Results erratic, mostly < detection limit			2	38.2	37.5	one positive one negative	
Al	4	39.8	1.9	all negative	2	37.0	8.7	both negative	
K	6	5.4	3.8	5 of 6 negative	2	4.0	1.7	one positive one negative	
Ca	6	170	51	all positive	2	31.5	2.4	both negative	
Mn	4	18.9	11.0	all negative	2	14.3	2.0	both negative	
Fe	4	11.9	6.3	all negative	2	12.4	0.2	both negative	
X-ray fluorescence									
Na		no analyses				no analyses			
Mg	6	>56.0	22.6	all negative	4	12.6	7.9	all negative	
Al	4	10.6	8.6	2 of 4 negative	4	10.8	15.0	3 of 4 negative	
K	6	5.4	3.8	5 of 6 negative	4	8.4	5.0	all negative	
Ca	6	9.0	3.0	4 of 6 negative	4	11.0	7.4	all positive	
Mn		no analyses				no analyses			
Fe	4	11.9	6.3	all negative	4	8.9	5.4	3 of 4 positive	

* Number of samples analyzed.

Positive bias means concentrations by INAA or XRF were higher than those by fusion/AAS.

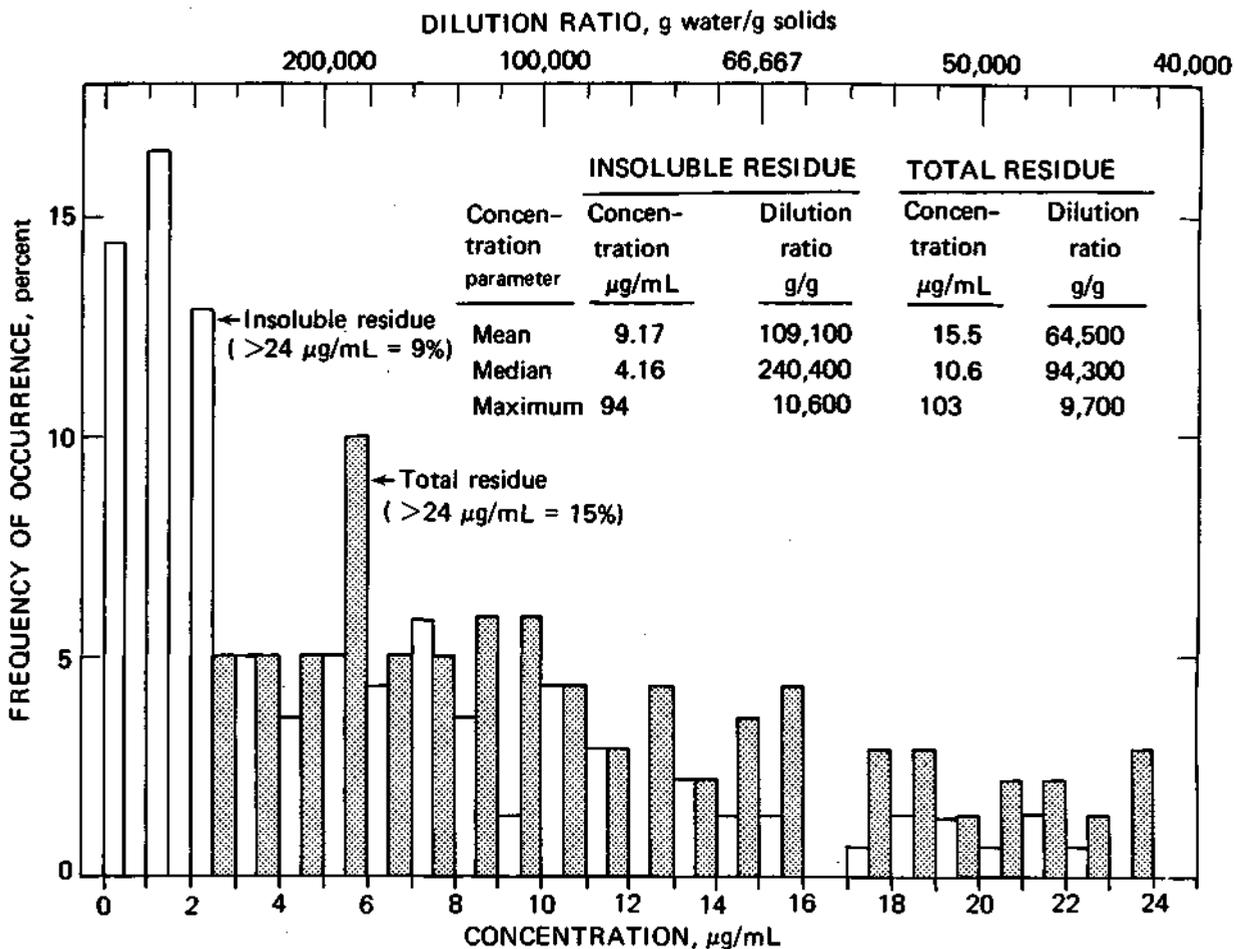


Figure 4. Frequency of occurrence of concentrations and dilution ratios for total residue and insoluble residue in 137 event precipitation samples from the Bondville Road sampling site.

Rain water samples from east of the Mississippi River have a pH range of 3.0 to 6.0 with median values of 4.0 - 4.5 occurring over much of the area. Thus, the range of extractant pH values used in the soil sample extractions was chosen to match that which soil particles would encounter in rain. With respect to dilution ratios, Figure 4 shows that our highest feasible experimental ratio, 20,000, was at the lower end of the range of naturally-occurring ratios in central Illinois precipitation.

Soil samples of approximately 0.005, 0.1, and 1.0 g were added to 100 mL volumes of dilute HNO₃ of varied pH. These mixtures correspond to dilution ratios of 20,000, 1000, and 100, respectively. Duplicate samples were shaken for 20 min on a wrist-action shaker, filtered through pre-leached 0.4 μm pore diameter Millipore type HA filters, and stored at room temperature in clean plastic bottles until analysis. The samples were analyzed for Ca and Mg by atomic absorption spectrophotometry.

For large dilution ratios (very dilute solutions), the sample blank correction values were relatively large, and this was a limiting factor in designing the experiment. This is illustrated by the results for the extraction of Ca from site soil 7A in Table 7, where extractant pH values are those of the solution before soil was added. All the Ca concentrations in Table 7A were less than 1 mg/L for the samples with the highest dilution ratios; thus the blank was relatively large compared to the measured concentrations. For the larger soil sample size (0.10 g - Table 7B), the blank values were relatively smaller, ranging from 3 to 30% of the concentrations measured in the soil solutions. The other three soils used in these experiments released more Ca, so Table 7 illustrates the worst case of the problem with large blanks.

The agreement between duplicate samples was usually quite good. Differences between duplicate analyses are given in Table 8 for both of the elements and both soil samples. The largest differences occurred with the smallest (0.005 g) samples, as expected. In the figures to follow, we have plotted the means of duplicate samples.

Extractable fractions of Ca and Mg for four different soil samples (all from the area of the Bondville Road sampling site) and four extractant pH values are shown as a function of dilution ratio in Figures 5 and 6, respectively. Except for Ca at pH 2.1, almost all of the extractable fractions of Ca and Mg increased with dilution ratio. Thus, a major conclusion is that Ca and Mg in these soils were generally more extractable as the dilution ratio increased. This effect was largest at pH 4.1 (Figure 5b), where the Ca extractable in the most dilute solutions was higher by a factor of about 10 than that in the least dilute solution.

The major exception to the general trend for extractable fractions of Ca and Mg to increase with increasing dilution ratio occurred in the extraction of Ca at pH 2.1 (Figure 5d). The same behavior was not found for Mg extractions at the same pH (Figure 6d). Section 3.2 of this report discusses errors in the measurement of Ca by AAS when using an

Table 7. Calcium concentrations (mg/L) after extraction of duplicate samples of Soil 7A at two dilution ratios and a variety of extractant pH values. The detection limit for Ca was 0.02 mg/L.

A. Dilution ratio = 20,000 (0.005 g of soil in 100 mL of extractant)

	Extractant pH						
	5.6*	4.4	4.1	3.8	3.3	3.0	2.1
Replicate A	0.15	0.19	0.28	0.16	0.24	0.27	0.17
Replicate B	0.13	0.13	0.20	0.33	0.29	0.38	0.18
Mean	0.14	0.16	0.24	0.24	0.26	0.32	0.18
Blank**	0.11	0.11	0.11	0.11	0.11	0.11	0.11
Mean minus blank	0.03	0.05	0.13	0.13	0.15	0.21	0.07

B. Dilution ratio = 1,000 (0.1 g of soil in 100 mL of extractant)

	Extractant pH						
	5.6*	4.4	4.1	3.8	3.3	3.0	2.1
Replicate A	0.61	0.64	1.27	1.61	2.98	3.19	3.40
Replicate B	0.36	0.66	1.36	1.61	2.76	3.19	3.40
Mean	0.48	0.65	1.32	1.61	2.87	3.19	3.40
Blank**	0.11	0.11	0.11	0.11	0.11	0.11	0.11
Mean minus blank	0.37	0.54	1.21	1.50	2.76	3.08	3.29

*Deionized water, with pH approximately 5.6.

**For 28 blank samples, mean = 0.112, median = 0.105, and S.D. = 0.067 mg/L. The blanks were samples treated like the other samples, except that no soil was added to them. The blanks included extraction solutions of several different pH values, but since the blank values did not appear to be related to solution pH, all 28 values were used to calculate a single mean value.

Table 8. Differences (%) in measured concentrations between duplicate soil extraction solutions.

Soil sample	Extractant pH						
	5.6**	4.4	4.1	3.8	3.3	3.0	2.1
A. Calcium, soil 7A							
1.0	4.8	1.1	3.0	0.8	3.6	1.7	1.3
0.10	7.7	3.7	2.4	4.2	2.2	1.6	9.9
0.005	20.0	16.7	3.5	14.3	14.3	8.7	23.1
B. Calcium, Soil 6A							
1.0	3.5	3.6	1.7	2.8	0.0	1.1	1.8
0.10	10.5	9.6	5.2	0.5	40.0	45.0	0.0
0.005	0.0	25.9	360	18.0	21.6	4.4	9.4
C. Magnesium, soil 7A							
1.0	18.1	4.5	0.1	0.0	0.0	0.5	1.2
0.10	28.1	4.1	5.4	1.5	4.7	4.0	5.3
0.005	31.7	53.5	71.1	39.7	30.0	13.5	1.7
D. Magnesium, soil 6A							
1.0	4.2	2.5	1.8	2.9	1.1	0.0	0.9
0.10	14.2	4.6	3.5	0.0	46.8	45.3	4.9
0.005	17.4	23.4	139	16.1	8.8	24.5	15.9

* Percent difference = $100(|A-B|)/A$, where the "A" values were selected randomly from the data pairs.

** Deionized water with pH approximately 5.6.

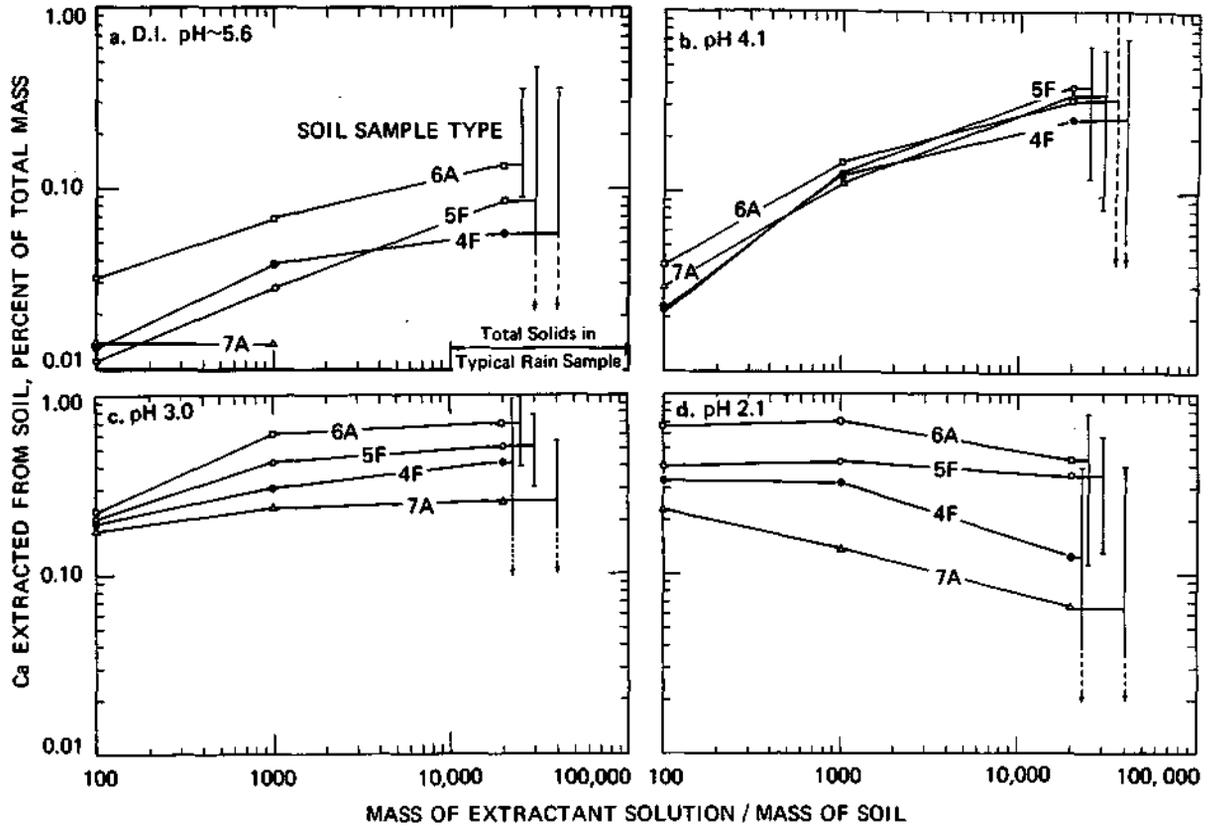


Figure 5. Variation of Ca abundance extracted from soils as a function of extractant pH and dilution ratio (mass of extractant/mass of soil).

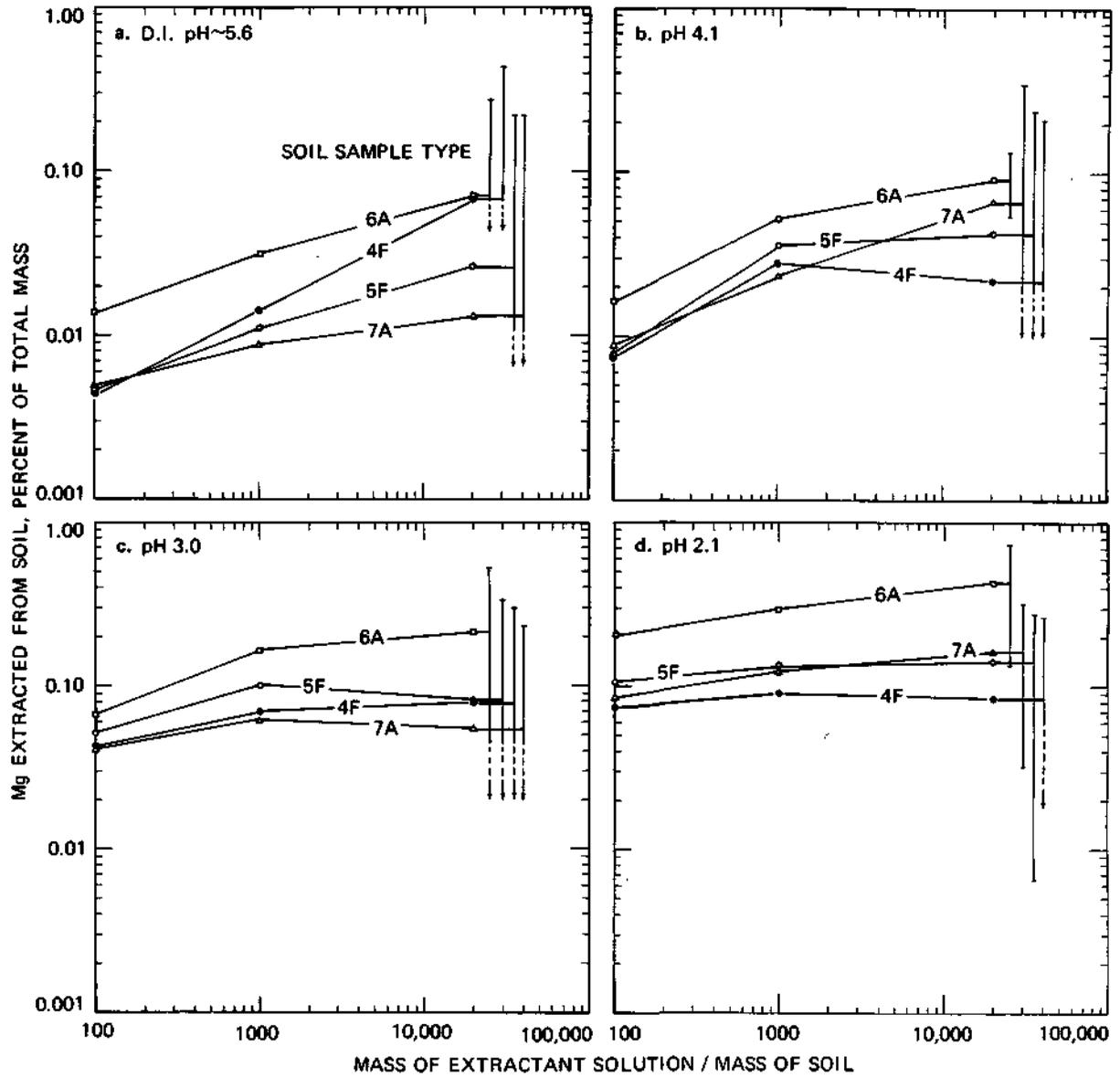


Figure 6. Variation of Mg abundance extracted from soils as a function of extractant pH and dilution ratio (mass of extractant/mass of soil).

i.e., those produced by total dissolution of a soil sample by LiBO_2 fusion. Such effects have not been observed by our laboratory in many previous analyses of precipitation and of filters extracted with pH 3 nitric acid, and our hypothesis is that there is a matrix effect of some kind. If such an error produced the trends plotted in Figure 5d, however, the relative error must have been greater at the higher dilution ratios. In any case, we are skeptical of the results plotted in Figure 5d. Additional research will be necessary to evaluate the effect of dilution ratio for low-pH extractions.

The error bars shown on the highest dilution ratio results are + the sum of the standard errors of the blanks and the duplicate analyses. The errors shown emphasize that the total uncertainties were relatively large for the highest dilution ratios. The relative errors were much smaller for the lower dilution ratios. This, combined with the consistency of the trends of the curves for the various extractants in Figures 5 and 6, clearly demonstrates that the trends are real. The fractions of Ca and Mg extractable from soil samples clearly depend on the pH of the extractant and the dilution ratio of the extraction, for a constant 20 min extraction time. Experiments were also carried out to investigate the dependence of the element mass fraction extracted on the duration of the extraction, and the results of these experiments are reported next.

3.4.2 Dependence of Extractability on Duration and pH

Figures 7 and 8 show how the extracted mass fractions of Ca and Mg, respectively, varied with extraction duration and pH. Figure 7 shows that both dilute and 4 N nitric acid were much more effective than deionized water in extracting Ca from soil. In the water extraction, the Ca removed from the soil nearly doubled in the first few hours of contact, and then increased very gradually out to 12 days. At pH 3, the extracted Ca increased significantly over the first 4 days, but then remained approximately constant out to 12 days. With 4 N nitric acid, Figure 7 shows that the extracted Ca actually decreased over the first 4 days, but we again suspect that these results are erroneous due to interferences in the air/acetylene flame.

Figure 8 shows similar results for Mg, except for two important differences. First, the fractions extracted at pH 3 were smaller for Mg than for Ca, relative to those extracted by the 4 N nitric acid. Second, with 4 N nitric acid, the amounts of Mg extracted continued to increase with time out to 12 days, while at lower acidities, and at all acidities for Ca, the extracted fractions all remained nearly constant beyond 4 days.

Figure 9 shows the variation of Ca mass fractions extracted at pH 3, as a function of time, for three different soils of varying pH, all collected near the Bondville Road sampling site. The results were similar to those for the pH 3 extractant in Figure 7 - extractable Ca

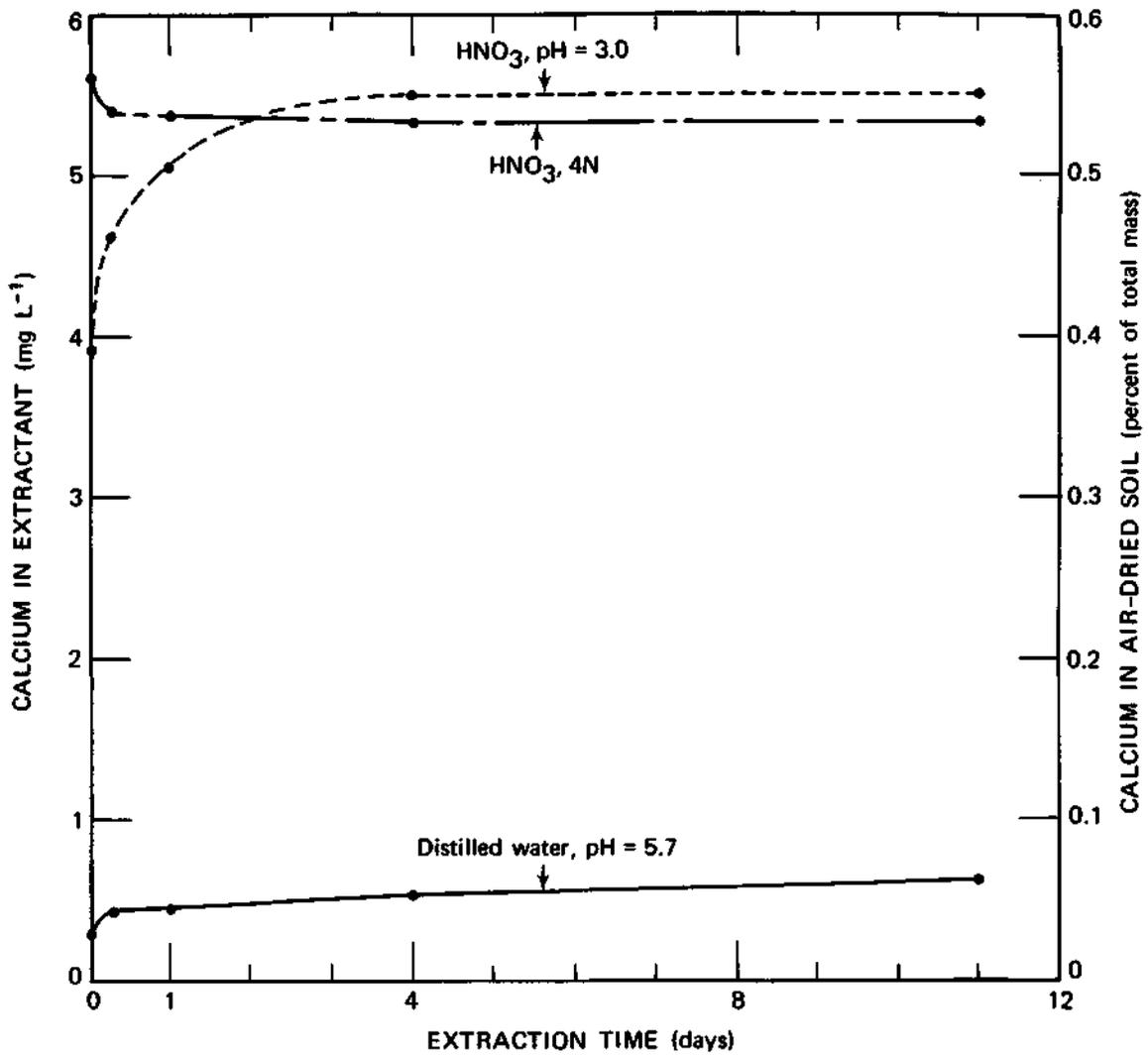


Figure 7. Variation of abundance of Ca extracted from soil 5B as a function of time and extractant pH.

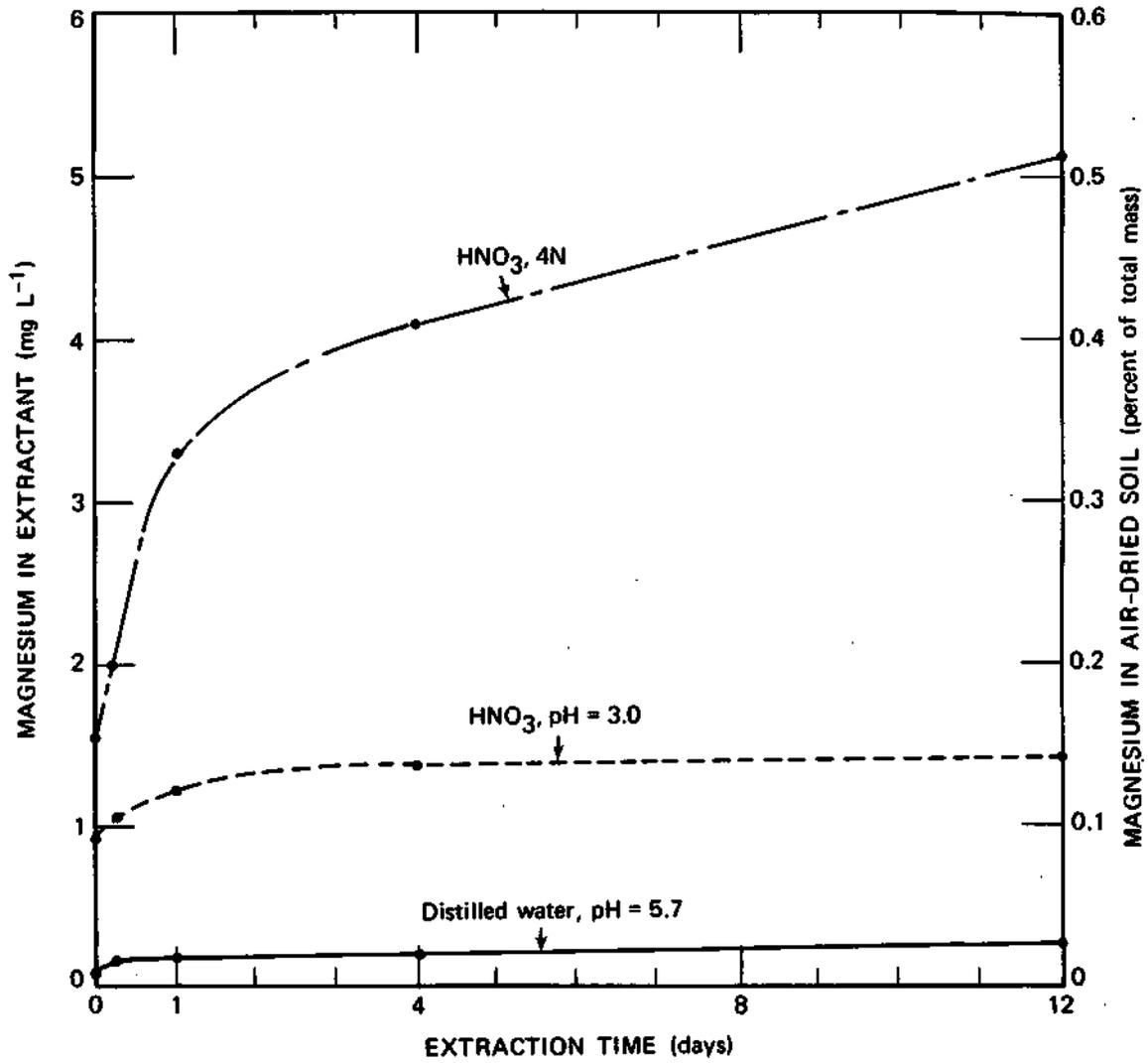


Figure 8. Variation of abundance of Mg extracted from soil 5B function of time and extractant pH.

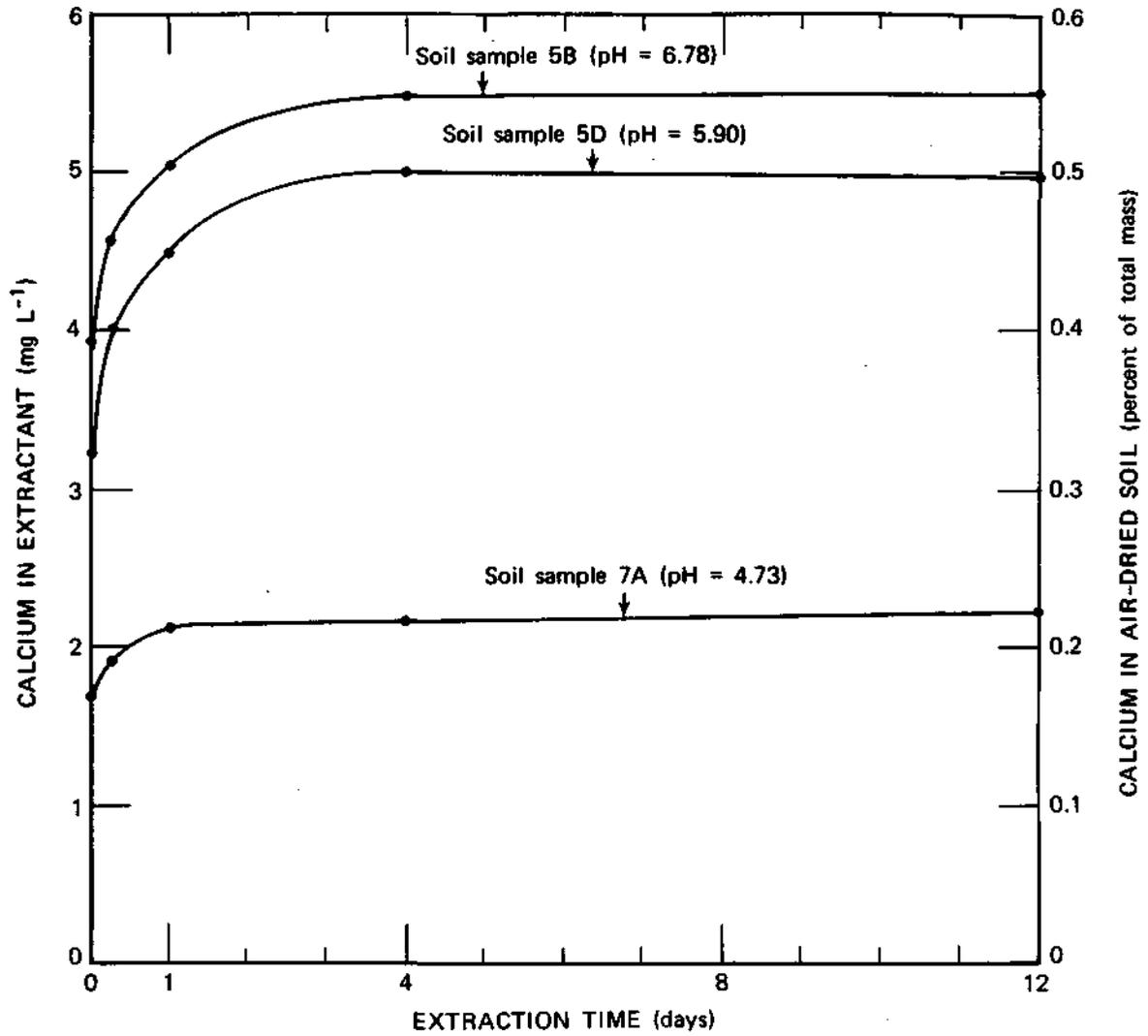


Figure 9. Variation of abundance of Ca extracted from 3 Bondville area soil samples at pH 3 as a function of time.

reached a constant value after 4 days, at the most. However, it is clear that the amounts that could be extracted varied considerably between samples. The mass fractions of extractable Ca varied directly with the soil pH, as one might expect.

Thus, it is clear that time is also an important factor in the extraction of source materials. For pH values typical of precipitation, constant values of the fractions of Ca and Mg removed were reached after about 4 days on the sources samples extracted. For ambient soil dust in rain, the equilibrium values might possibly be reached sooner, however, since the size distribution of the ambient aerosol would very likely include many more smaller, more rapidly extracted particles, than those in the soil samples extracted, which were <53 μm by dry sieving.

3.5 X-RAY DIFFRACTION MINERALOGY OF BONDVILLE AREA SURFACE MATERIAL SAMPLES AND AEROSOL FILTERS

In an exploratory effort to characterize local crustal sources and aerosols, various source samples and aerosol samples were analyzed by X-ray diffraction for their crystalline mineral composition.

Aerosol, soil, and road materials samples were analyzed on two different occasions. The first batch of samples was analyzed in spring, 1980, and consisted of all the soil and road material samples, plus aerosol filters Q1 and Q2. The remaining aerosol filters were analyzed in February, 1981. The samples are described as follows:

1. Aerosol filters.

1. Q1(D1) and Q1(D2): Filters collected simultaneously, 27-29 May 1980.
2. Q2(D1) and Q2(D2): Filters collected simultaneously, 29 May - 2 June 1980,
3. Q11(S1) and Q11(S2): A single filter collected 2-5 Sept 1980, and divided into two parts for analysis.
4. Q14(S1) and Q14(S2): A single filter collected 7-10 Oct 1980. and divided into two parts for analysis.
5. Q17: A single filter collected 20-24 Oct 1980.
6. Q19: A single filter collected 4-7 Nov 1980.
7. Q21: A single filter collected 18-21 Nov 1980.

2. Unpaved road surface material.

1. Rd 7: Crushed limestone, <53 μm diameter fraction.
2. Rd 9: Washed gravel, <53 μm diameter fraction.

3. Soil surface material.
 1. 7A(S1) and 7A(S2): Subsamples of soil sample 7A, <53 μm fraction.
 2. 5B(S1) and 5B(S2): Subsamples of soil sample 5B, <53 μm fraction.
 3. M-50: A sandy soil from approximately 100 km northeast of Champaign-Urbana, <53 μm fraction.
4. Soil 7A separated into approximate size classes by Sonic Sifter.
 1. 7A1: <5 μm diameter.
 2. 7A2: 5-10 μm diameter.
 3. 7A3: 10-20 μm diameter.
 4. 7A4: 20-45 μm diameter.
 5. 7A5: 45-53 μm diameter.

In presenting results we will emphasize differences between the major types of samples: soils, road materials, and aerosols. This emphasis on differences between sample types stems from our main reasons for pursuing this exploratory mineralogical investigation. These objectives were: 1) to search for minerals having sufficiently different abundances in source materials that they might be useful in aerosol source apportionment using mass balance techniques (see the review of these techniques by Gordon, 1980), and 2) to compare aerosol mineral composition with that of local soils and unpaved roads.

Table 7 shows all results, in units of percent of each mineral in the total mass of each sample. As in any preliminary investigation, especially where only a few samples of any given type were analyzed, the results should be interpreted with much caution. This point is amplified by consideration of the duplicate sample results given in Table 7. For the duplicate soil samples, the abundances of individual samples differ from the mean by about 10% for most of the mineral groups. However, differences of more than 25% occurred for sample 7A duplicates on the montmorillonite/vermiculite and oligoclase/andesine groups. This is greater variation than expected from the precision of the method (Davis, personal communication, 1981), which suggests that it may have been caused by problems in subsampling.

Substantial differences between duplicates also occurred in the aerosol samples. Recall that Q1/Q2 and Q3/Q4 were duplicate filters collected simultaneously, whereas Q11(S1)/Q11(S2) and Q14(S1)/Q14(S2) were split filters. For both types of duplicates, deviations of 50% or more from the mean were common for some minerals; however, deviations of less than 15% were found for quartz, calcite, dolomite, and gypsum.

With these overall precisions in mind, we may examine the results for evidence of differences in mineral abundances between sample types. Table 7 shows clear differences between soils and road materials for calcite and dolomite, and to a lesser (extent when taken as a group) the clay mineral suite illite/muscovite, kaolinite, and montmorillonite/

vermiculite. The latter group is clearly higher in abundance in soils than in road materials, but the other two would be judged higher in soil only as part of the clay mineral suite.

Care must be taken in the use of calcite and dolomite to identify road sources because farmers fertilize with crushed limestone ("lime"), and if soil is blown into the air soon after application of this material it could contain abnormal amounts of calcite and dolomite. However, agronomists expect all carbonate particles less than 250 μm in diameter to be totally reactive (dissolved) approximately one year after application (Pearson and Adams, 1981).

Results for two road dust samples are also shown in Table 7. Sample Rd 7 was collected from a crushed limestone road and sample Rd 9 from a washed gravel road. Despite the fact that only a single sample of each road type was analyzed, observed differences in mineral abundances are sufficient to suggest that these two types of unpaved road materials might be distinguishable in aerosol samples. The limestone appears to have greater abundances of calcite and dolomite, and lesser of all the other mineral groups, than the washed gravel.

Table 7 also shows mineral abundances for a series of soil fractions separated by size. The size separation was done with the ATM Sonic Sifter, as described earlier, so that the particles were separated based on their environmental (aggregate) sizes, as distinguished from the usual agronomic size distributions, i.e., distributions of the sizes of true particles. The subsample representing the largest particles (45-53 μm diameter) is labelled 7A-5 and that representing the smallest (<5 μm) 7A-1.

The variations of mineral abundance with particle size are shown in Figure 7. Contrary to the notion that clay minerals should occur in clay-sized (less than 2 μm diameter) particles, we see generally increasing abundances of the total clay mineral suite (illite/muscovite, kaolinite, and montmorillonite/vermiculite) with particle size. This variation was actually determined by the montmorillonite/vermiculite fraction; the abundances of illite/muscovite and kaolinite showed little variation with aggregate size. Quartz, on the other hand, was most abundant on 10-20 μm particles, and the smallest abundances occurred on the largest particles. This was also unexpected, based on the idea that quartz should be abundant in sand-sized (>50 μm) particles. The other minerals showed relatively minor variation of abundance with size.

The mineral composition of the aerosol samples in Table 6 was quite different than that of any of the surface materials. The following characteristics are apparent:

1. Some quartz and illite/muscovite abundances were greater than could be expected from local sources.
2. Expandable clay minerals (i.e., montmorillonite/vermiculite) were absent on any of the aerosol filters.

3. Various sulfate minerals were present on the filters—gypsum on all filters and the ammonium and calcium sulfates on aerosol filters Q1 and Q2. These compounds were discussed in some detail by Davis et al. (1982).

We now consider whether these observations allow us to meet the objectives of this exploratory investigation.

The first objective was to identify marker minerals for soil and dust from unpaved roads. The analyses of bulk source materials suggests calcite and dolomite as potential markers for road dust, and montmorillonite/vermiculate for soils. Quartz was also present in varying abundance in both soil and road material, and the calcite/quartz ratio appears, from these few samples, to possibly be diagnostic. Table 10 shows that the calcite/quartz ratio was approximately 0.1 in soils, 1.0 in washed gravel road dust, and 10 in limestone road dust. However, these values are based on bulk source samples; any fractionation that takes place as particles become airborne could change them significantly in the respective aerosols.

The aerosol (X) samples listed in Table 9 were all collected in a rural location (Figures 1 and 2), near sources of both soil dust and dust from unpaved roads. Yet, the results in Table 9 are very clear: none of the aerosol samples contained detectable montmorillonite/vermiculite, and fewer than half contained detectable calcite. The absence of the marker mineral for soils is particularly puzzling, since soil dust plumes from tilling operations were observed while several of the samples were being collected. Further, the measured illite/muscovite compositions of most of the aerosol samples exceeded by a wide margin the illite abundance in local soils. Several of the aerosol samples had quartz abundances greater than the local soils as well. Thus by comparison with bulk soil compositions, it appears that the measured aerosol compositions reflect aerosols transported from distant sources. This is supported by the observation that several of the samples with high abundances of the illite were collected on days with southerly winds. Soils containing high concentrations of illite are located to the south of Illinois.

There are several reasons why these findings should be considered preliminary. First, the number of samples involved is relatively small. Second, the reproducibility of the combined subsampling and analysis steps was less than one would like in some "duplicate" samples, so any individual analysis must be considered to have a relatively large uncertainty. Third, detection limits for most minerals were rather high - about 5% of sample mass.

The absence of the bulk soil marker montmorillonite/vermiculite on any of the aerosol filters is a potentially important finding in that it may be evidence of fractionation during soil aerosol mobilization. This may be simply the results of the relatively high detection limits. That is, even though montmorillonite/vermiculite constitutes perhaps 25% (Table 9) of the local soil mass, soil may contribute only 25%, say, of the aerosol mass. Thus, montmorillonite/vermiculite would amount to only about 6% of the aerosol mass, a barely detectable amount.

Table 9. X-Ray Mineralogy of Aerosols and Surface Materials Expressed as Percent of Total Sample Mass

Sample	Illite/ muscovite (I/M)	Kaolinite (K)	Montmorillonite/ vermiculite (M)	Quartz (Q)	Orthoclase/ microcline (O/M)	Oligoclase/ andesine (O/A)	Hornblende (H)	Calcite (C)	Dolomite (D)	Gypsum (G)	AS ³	ACS ⁴
Q1(D1)	31.5	3.1	--	41.3	--	--	--	--	--	10.1	5.0	8.9
Q2(D2)	20.8	1	--	31.1	--	--	--	--	--	10.0	8.3	29.8
Q3(D1)	--	--	--	51.7	--	--	--	--	--	21.7	20.0	6.7
Q4(D2)	9.3	--	--	52.4	--	--	--	--	--	25.9	12.3	--
Q11(S1)	25.34	--	--	1.11	--	3.55	--	--	--	10.01	--	--
Q11(S2)	18.41	--	--	1.72	4.04	3.80	--	--	--	12.04	--	--
Q14(S1)	2.42	0.94	--	22.94	1.10	2.54	--	9.81	7.32	7.94	--	--
Q14(S2)	10.84	--	--	22.75	1.54	3.66	--	9.06	8.64	6.82	--	--
Q17	9.66	--	--	11.16	--	--	--	1.23	--	47.95	--	--
Q19	10.84	--	--	27.02	6.78	14.60	--	12.69	12.64	5.43	--	--
Q21	20.34	--	--	20.09	--	--	--	--	--	49.56	--	--
5B(S1)	4.4	3.2	32.2	33.6	12.7	12.4 ²	1.4	--	--	--	--	--
5B(S2)	5.4	3.2	27.3	39.2	10.0	14.1 ²	0.9	--	--	--	--	--
7A(S2)	3.0	0.7	26.0	44.4	15.0	10.8	--	--	--	--	--	--
7A(S1)	3.4	1.5	14.8	45.9	15.9	18.4	--	--	--	--	--	--
7A5	6.8	2.7	35.5	27.9	13.7	13.3	--	--	--	--	--	--
7A4	6.3	2.2	24.6	38.1	16.4	12.5	--	--	--	--	--	--
7A3	3.5	2.1	14.4	47.2	15.8	15.3	1.7	--	--	--	--	--
7A2	8.0	2.2	14.2	42.8	15.3	16.2	1.4	--	--	--	--	--
7A1	4.7	1.9	18.2	40.6	18.4	13.0	3.2	--	--	--	--	--
M-50	4.8	3.1	20.1	39.0	15.1	17.3	0.6	--	--	--	--	--
Rd 7	1.8	0.4	1.6	6.6	2.3	2.7	--	65.4	19.2	--	--	--
Rd 9	4.6	2.1	3.9	23.6	10.2	10.2	--	22.2	4.6	--	--	--

1. -- Below Detection Limits
2. Labradorite

3. $(\text{NH}_4)_2\text{SO}_4$
4. $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Ca}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$

Table 10. Calcite/quartz ratios for soil and two types of road dust samples.

<u>Source</u> <u>type</u>	<u>Sample</u> <u>number</u>	<u>No. of</u> <u>replicates</u>	<u>Mean</u> <u>percent</u> <u>calcite</u>	<u>Mean</u> <u>percent</u> <u>quartz</u>	<u>calcite</u> <u>quartz</u>
soil	5B	2	<5	36.4	<0.14
soil	7A	2	<5	45.2	<0.11
soil	M-50	1	<5	39.0	<0.13
road (limestone)	RD-7	1	65.4	6.6	9.9
road (washed gravel)	RD-9	1	22.2	23.6	0.94

On the other hand, the lack of montmorillonite/vermiculite in the aerosol samples could be real, which would indicate fractionation of the soil composition during aerosol mobilization. Fractionation could perhaps account, at least partially, for the high illite/muscovite and quartz abundances on the aerosol filters, and would thus influence the interpretation of a distant source for the sampled aerosol.

As an expandable clay, montmorillonite/vermiculite is likely to develop a substantial static surface charge. This would favor aggregation into or with larger, heavier, particles in the soil, which could limit mobilization. The increased montmorillonite/vermiculite abundances in the larger particle size fractions shown in Figure 10 support this possibility. The possibility also exists, of course, that these large particles could actually become airborne, but be improperly undersampled because of their high inertia.

The exploratory mineralogical measurements have provided useful mineral compositions of soil, road dust, and aerosols, but interpretation is still uncertain, and additional measurements will be necessary to answer some of the questions raised.

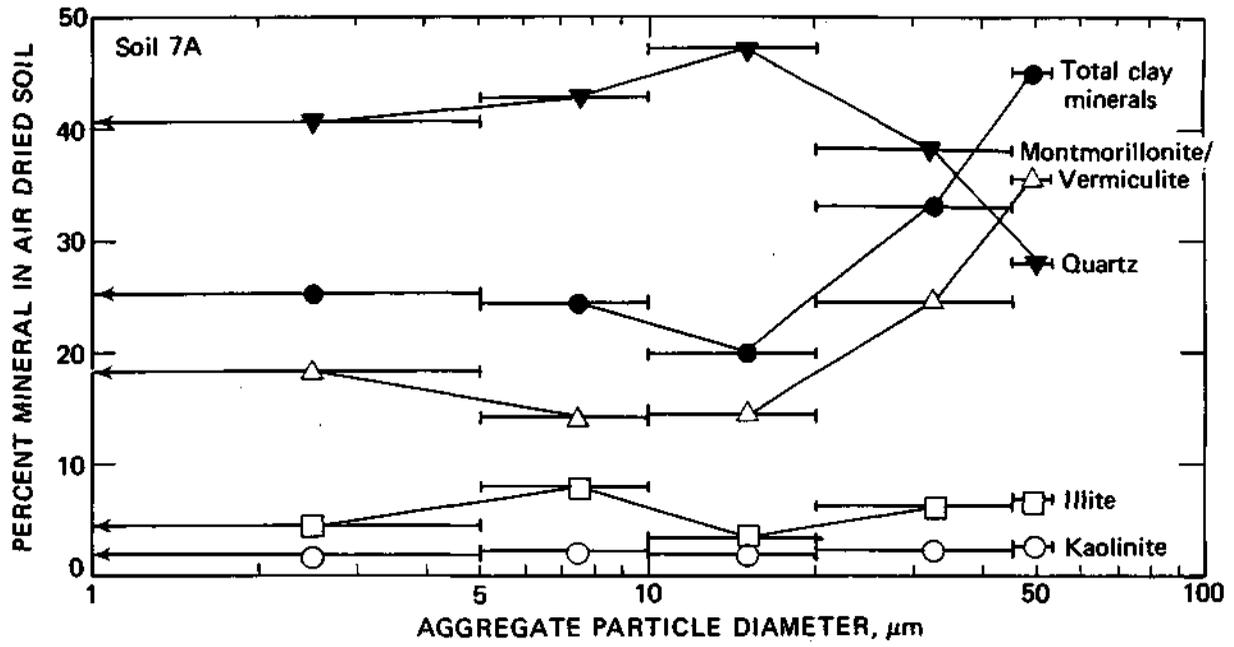


Figure 10. Variation of mineral abundances with aggregate size in soil sample 7A.

4 RESULTS: MEASUREMENTS OF THE COMPOSITION OF SOURCE MATERIALS, AEROSOLS, AND PRECIPITATION

4.1 Source Composition

4.1.1 Unpaved Road Materials

Generally two types of materials are used on unpaved roads on Champaign County and the counties surrounding it. the two types are 1) crushed limestone rock and 2) crushed or natural washed gravel derived from glacial deposits. Champaign County uses approximately 85% crushed limestone, county-wide. Some adjacent counties use one or the other of the two materials exclusively, while others use a combination. This section presents results on measured elemental compositions of both types of unpaved road surface source materials, but most samples analyzed were crushed limestone.

Several kinds of results are presented in the following paragraphs. First we present data on the mean values and the spatial variability of total element contents of road materials, and then examine how differences between limestone and washed gravel road materials contribute to the observed variability. This is followed by data on extractable element contents of the same samples. Data on the variation of extractable element concentrations with particle size come next. Finally, we review the pertinent mineralogy results on road materials from the discussion of the mineralogy measurements in Section 3.5.

4.1.1.1 Total element means and variability

Table 11 gives the maximum and minimum measured total element concentrations, as well as the mean, standard deviation (S.D.), and coefficient of variation (C.V.) for nine elements. For each element, data are presented separately for crushed limestone (CL) and washed gravel (WG) samples, as well as for "all" samples. the "all" category includes one sample (later designated L/S) from the aerosol sampling site access road, consisting of limestone dust mixed with soil from beneath the roadbed.

Table 11 summarizes data given earlier, in the section on comparison of analytical methods. We present here only data for the most preferred analytical method available for each element. As discussed earlier, the preferred methods were 1) LiBO_2 fusion followed by AAS, 2) XRF, and 3) INAA.

Mean values of nine elements are plotted in Figure 11 for comparison of element abundances in washed gravel and crushed limestone road materials. It is clear that Ca and Si were the most abundant of the elements measured in crushed limestone. Ca was also the most abundant element measured in washed gravel; however Si was not measured in the washed gravel samples.

Table 11. Mean values and variability of total element concentrations in Bondville area unpaved road materials.

Element	Road material*	Analysis method**	N	Percent total element in air dried road materials					C.V.*** %
				Max	Min	Mean	S.D.	S.E.M.	
Na	CL	F/AAS	5	0.36	0.21	0.27	0.07	0.03	24
	WG	F/AAS	1	0.58	0.58	0.58			
	all	F/AAS	7	0.58	0.21	0.36	0.15	0.06	43
Mg	CL	F/AAS	5	3.70	0.41	1.72	1.20	0.54	70
	WG	F/AAS	1	3.76	3.76	3.76			
	all	F/AAS	7	3.76	0.41	1.82	1.39	0.52	76
Al	CL	F/AAS	5	1.72	1.12	1.40	0.24	0.10	42
	WG	F/AAS	1	2.90	2.90	2.90			
	all	F/AAS	7	3.12	1.12	1.86	0.81	0.31	44
Si	CL	XRF	3	17.42	7.07	13.13	5.40	3.12	41
	all	XRF	4	23.83	7.07	15.80	6.93	3.46	44
K	CL	F/AAS	5	0.72	0.38	0.56	0.12	0.05	22
	WG	F/AAS	1	1.34	1.34	1.34			
	all	F/AAS	7	1.34	0.38	0.76	0.37	0.14	48
Ca	CL	F/AAS	5	28.90	19.79	24.15	3.50	1.56	14
	WG	F/AAS	1	10.25	10.25	10.25			
	all	F/AAS	7	28.90	10.25	20.42	7.01	2.65	34
Ti	CL	XRF	3	0.10	0.05	0.08	0.03	0.02	33
	all	XRF	4	0.26	0.05	0.12	0.09	0.04	74
Mn	CL	F/AAS	5	0.126	0.091	0.110	0.013	0.006	12
	WG	F/AAS	1	0.086	0.086	0.086			
	all	F/AAS	7	0.126	0.081	0.102	0.016	0.006	16
Fe	CL	F/AAS	5	1.56	0.94	1.16	0.25	0.11	21
	WG	F/AAS	1	2.08	2.08	2.08			
	all	F/AAS	7	2.08	0.94	1.34	0.40	0.15	30
Zn	CL	F/AAS	5			<0.009			
	WG	F/AAS	1			<0.009			
	all	F/AAS	7			<0.009			
Pb	CL	F/AAS	5			<0.08			
	WG	F/AAS	1			<0.08			
	all	F/AAS	7			<0.08			

* CL = crushed limestone; WG = washed gravel; "all" includes CL, WG, and a sample from the aerosol site access road consisting of limestone dust mixed with soil which had mixed upward into the roadbed from below.

** F/AAS = LiBO₂ fusion, followed by atomic absorption spectrophotometry; XRF = x-ray fluorescence; INAA = instrumental neutron activation analysis.

*** C.V. = coefficient of variation = 100(S.D./Mean).

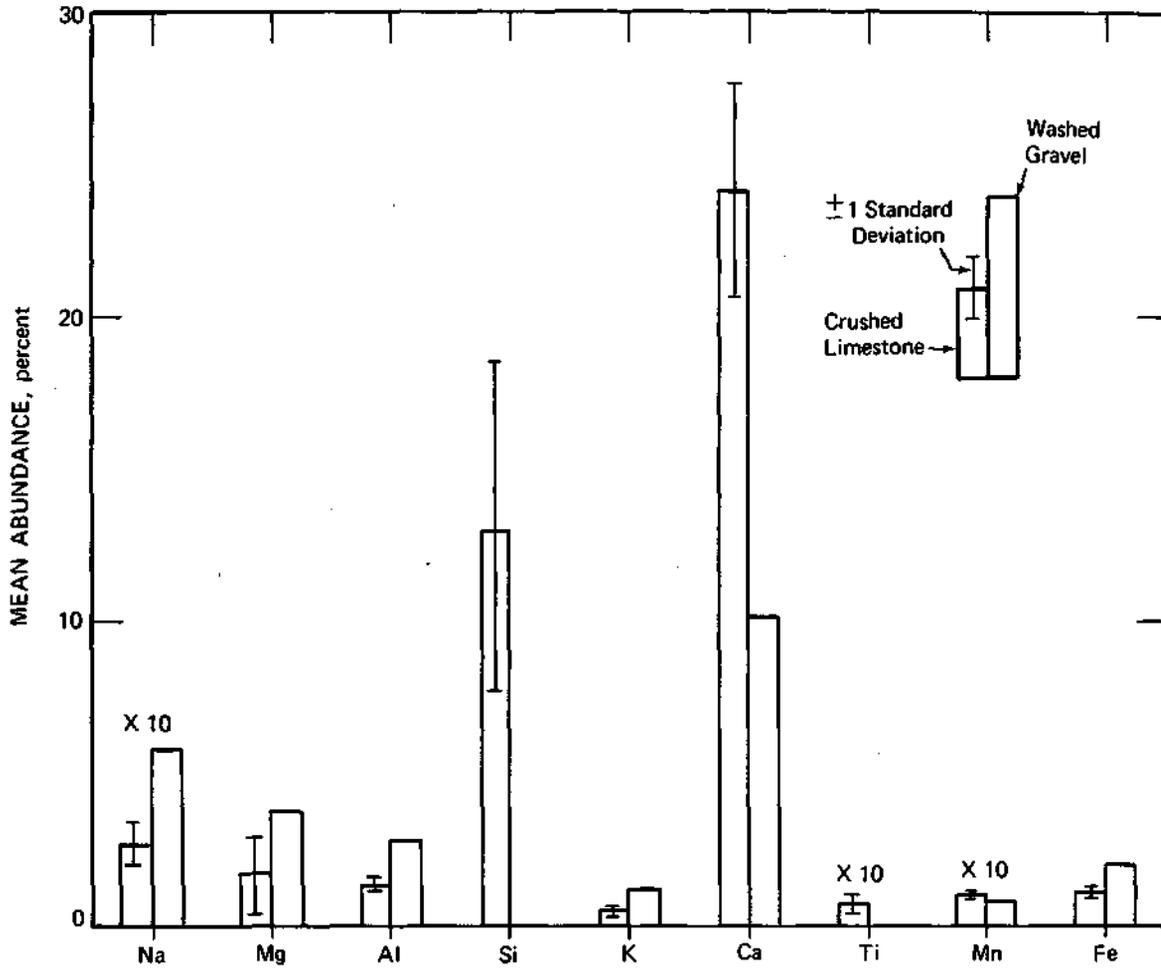


Figure 11. Comparison of element abundances in crushed limestone and washed gravel road materials. The crushed limestone values are the mean of 5 samples, except for Si and Ti (3 samples each). The washed gravel result is for a single sample. The elements marked X10 are shown 10 times larger than their true values (see Table 11).

The variability of the total element contents (Table 11), as expressed by the coefficient of variation, $C.V. = 100(S.D./Mean)$, ranges from 16 to 76%, in the "all" category, with five of the nine elements grouped between 30 and 50%. The observed variability is due in part to systematic differences in composition between the two types of materials used on unpaved roads--crushed limestone and washed gravel. This is clearly seen by comparing the single WG sample to the means and ranges of the crushed limestone samples for Na, Mg, K, and Ca. In each case, the element concentration for the single WG sample was outside the range of the CL samples; Na, Mg, and K were more abundant in the washed gravel, but Ca was less abundant.

Table 11 also shows that the access road, with its mixed soil and limestone surface, was also a source of variability in the "all" category. This may be seen in the consistently smaller coefficients of variation of the CL category (as compared to the "all" category) for Na, Al, K, Ca, and Ti.

Despite the rather limited numbers of samples of the various kinds of road materials, the mean elemental concentrations in the "all" category are the best estimate available of the composition of area road materials. They represent approximately the relative frequency of limestone, washed gravel, and limestone/soil roads in the vicinity of the aerosol sampling site on Bondville Rd.

4.1.1.2 Extractable element means and variability

The variability of extraction results with changes in experimental conditions was of much discussed earlier in this report. Our purpose in examining the extractability of several elements from soil and road dust samples was 1) to measure an "extractable" source composition to apply to rain water impurity source reconciliation calculations, and 2) to gain understanding of the process of dissolution of these materials in rain. Thus, the conditions selected for the extractions reported here were chosen to approximate those that might be experienced by soil or road dust particles entrained into a rain system. We chose a pH 3 simulated rain (i.e., dilute nitric acid) solution as an extractant and shook 25 mg of the dust samples in 25 mL of the extractant for 20 min on a wrist shaker to approximate the conditions a particle in a droplet would experience in the turbulent environment of a typical summer convective rain shower.

Results are given in Table 12. Results are limited to two CL samples and two L/S samples. With so few samples the information given on variability of results (i.e., S.D. and C.V.) within individual sample type are of somewhat limited value. Nevertheless, they are included here for completeness and because they appear to show that for some elements the variability of the "all" category arises from differences in mean element concentrations between sample types. These differences appear to be clear for K, somewhat less clear for Ca, and not present for Mg, based on Table 12, but firm conclusions must await additional sample analyses.

Table 12. Variability of extractable Mg, K, and Ca concentrations in sieved air dried unpaved road materials.

Element	Road material*	N	Percent extractable** element in road materials				C.V.,*** %
			Max	Min	Mean	S.D.	
Mg	CL	2	0.0440	0.0332	0.0386	0.0076	20
	L/S	2	0.0438	0.0422	0.0430	0.0011	3
	All	4	0.0440	0.0332	0.0408	0.0051	13
K	CL	2	0.0096	0.0061	0.0078	0.0025	32
	L/S	2	0.0204	0.0176	0.0190	0.0020	10
	All	4	0.0204	0.0061	0.0134	0.0067	50
Ca	CL	2	3.67	3.51	3.59	0.11	3
	L/S	2	3.30	3.11	3.20	0.13	4
	All	4	3.67	3.11	3.40	0.24	7

* CL = crushed limestone; L/S = limestone and soil mixture; "all" includes both CL and L/S.

** Approximately 25 mg of sample extracted by shaking for 20 min in 25 mL of pH 3 simulated rain water.

*** Coefficient of variation, C.V. = $100(S.D./Mean)$.

Comparisons of results for Mg, K, and Ca in Tables 11 and 12 show that relatively small amounts of these elements were extracted under the conditions used. For example, comparison of the respective mean values for all samples analyzed (which were not the same samples in both cases) indicates that 2.2% of the total Mg, 1.8% of the total K, and 16.6% of the total Ca were extracted from road dust samples.

The concentrations of extractable elements in road materials that we have discussed in this subsection are of interest because a bulk sample is the easiest one to collect. Thus, extractable compositions measured in surface material subsamples that may be more difficult to collect, or generate, but that are presumably more representative of what the wind might blow off the surface, should all be compared to that of the bulk source materials. If no differences were found, then it would be prudent to use the simplest sampling method. The following subsection describes the results of measuring extractable element concentrations on subsamples consisting of a series of size fractions of road dust samples. These subsamples were generated in the University of Wisconsin Water Chemistry Laboratory soil aerosol chamber.

4.1.1.3 Composition variation of extractable elements with particle size

To compare results from separate size fractions with those of bulk materials, the size fraction results must be in the same units as those of the bulk materials. Unfortunately, it was not possible to measure the total mass collected on each impactor stage; thus it was not possible to report results in terms of mass fractions in each particle size category, as is required for a direct comparison of results.

This difficulty arose because static charge buildup on the Nuclepore filters used as impaction substrates in our first test runs at the University of Wisconsin interfered with proper collection of the aerosols. The Whatman-41 filters used as replacements for the Nuclepore filters could not be weighed accurately before and after sample collection because of moisture sorption effects. Thus total mass of the aerosol collected on each impaction stage is not known, and it is impossible to calculate the mass fraction of the extractable elements.

We can, however, examine the relative distribution of extractable element within the limited portion of the size spectrum analyzed (i.e., 0.1 to 16 μm , aerodynamic diameter). (Recall that particles larger than 16 μm were discarded.) This is done by plotting $\frac{M}{M}$ In D versus D on a logarithmic scale, where M is the mass increment in a particular size interval represented by one impactor stage, and M is the sum of the M 's. Thus, $\frac{M}{M}$ is the fraction of the total mass in a given size interval. This quantity is divided by $\ln D$, or the difference in the natural logs of the upper and lower size cutoffs of the given impactor stage, to obtain an ordinate value such that the area under the "curve" is proportional to the fraction of the total extractable element accounted for by a given size interval.

It should also be pointed out that the extraction method used on the impactor samples was different from that used on the bulk samples, so that direct comparison of the results would not have been possible in any case. The bulk samples were extracted by shaking 25 mg of material in 25 mL of pH 3 simulated rain on a wrist shaker for 20 min. The impactor samples were shaken in the same volume of the same extractant, but they were shaken for 4 days instead of 20 min, and the sample mass was neither 25 mg nor constant. Variations in sample mass cause differences in dilution ratio, which has important consequences for the comparability of results. This phenomenon was discussed earlier in this report. This phenomenon causes smaller samples to give anomalously high extracted element concentrations, relative to larger samples. If the sample masses were to decrease with increasing particle size, the dilution ratio effect could cause anomalously high concentrations for the larger particle size classes.

The solid lines plotted in Figure 12 represent mean values of 4 crushed limestone road samples, with vertical bars showing plus and minus one standard error. Results for samples of other kinds of surfaces (Rd-1a, an L/S sample, and Rd-9, a WG sample) are indicated by open circle and open triangle symbols, respectively.

For each element determined, we will discuss the CL results first, and then compare the results from the individual samples of other types to them. If results for the WG or L/S samples differ by more than one standard error, they will be referred to as deviating high or low from the CL results.

Figure 12 shows that the size distributions of extractable Na, Mg, K, and Ca are quite similar to each other. They all have maximum M/M In D values in the 8-16 μ m size class. However, there are some minor differences between elements. Na has a secondary maximum in the smallest size class, and the slope of the "curve" is more uniform in the middle of the spectrum for K than the other elements.

The deviations of the WG and L/S samples from the means of the CL samples are summarized in Table 13. Over the four elements, there were only four deviations greater than one standard error for the WG sample, and none of these was greater than 2 standard errors. For the L/S sample, there were more deviations greater than one standard error, but again none of these appears to be greater than two standard errors. Furthermore, no pattern of consistently high or low deviations appears in the table, either by size class or by element. In summary, therefore, single WG and L/S samples have not shown significant deviations from the size distributions of the CL samples. Nevertheless, in the absence of measured masses for the several size fractions, the observed factor-of-2 (maximum) differences in M/M In D between size classes could be entirely attributable to differences in dilution ratio. Thus, these results should be considered tentative until the experiment can be repeated under conditions where the mass of each size class can be measured.

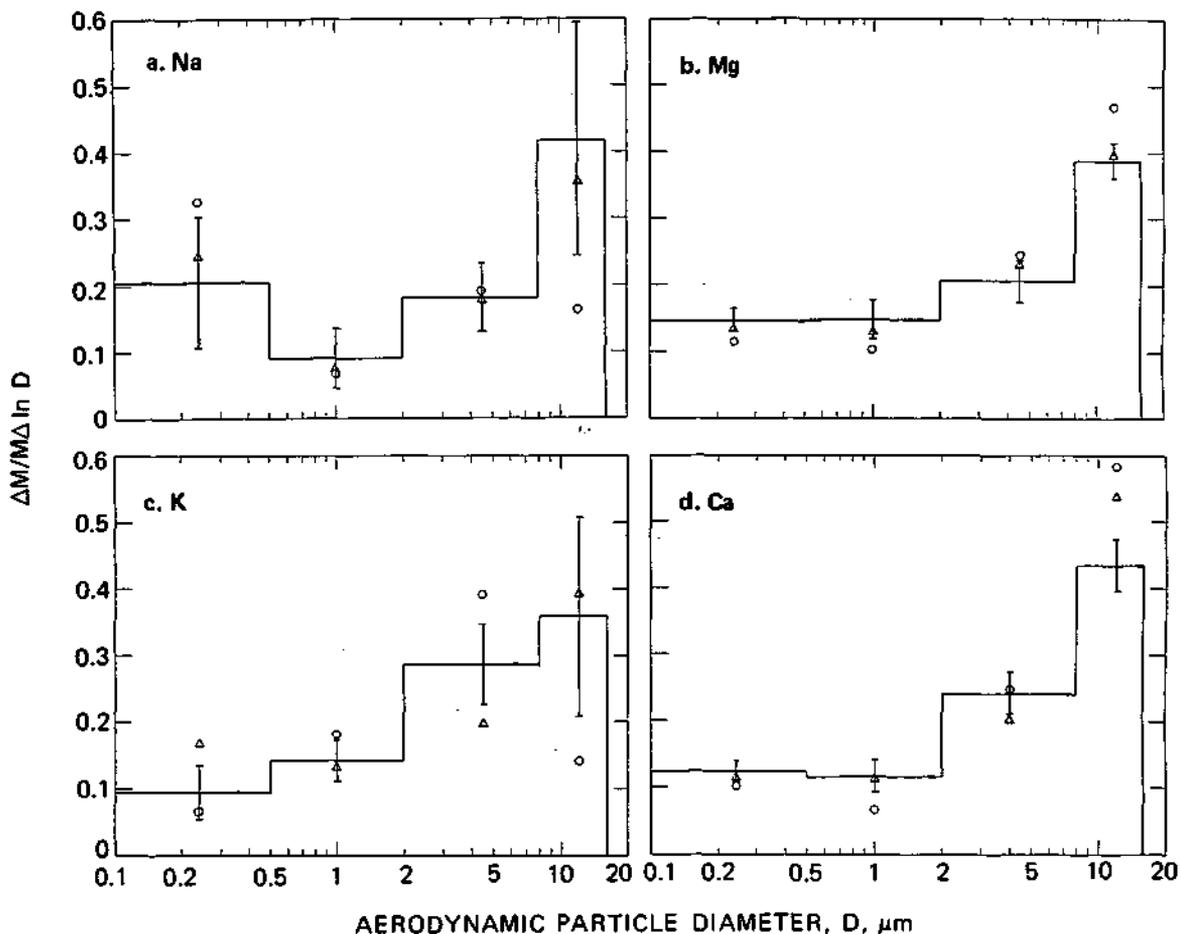


Figure 12. Size distributions of extractable Na, Mg, K, and Ca in road dust samples. Samples generated in University of Wisconsin Water Chemistry Laboratory Chamber. The horizontal lines and vertical bars are the mean and ± 1 standard error, respectively, for samples Rd-3, Rd-6, Rd-7, and Rd-8. The circle is the mixed limestone and soil sample Rd-1A and the triangle is the washed gravel sample Rd-9.

Table 13. Deviations of single WG and L/S samples from mean CL results.

Sample type	Element	Size class, μm			
		0.1-0.5	0.5-2	2-8	8-16
WG	Na	--*	--	--	--
	Mg	--	--	--	--
	K	high	--	low	--
	Ca	--	--	low	high
L/S	Na	high	--	--	low
	Mg	low	low	--	high
	K	--	high	high	low
	Ca	low	low	--	high

* Indicates a deviation <1 standard error.

4.1.1.4 Review of pertinent mineralogy

Results of our exploratory investigations comparing the mineralogical composition of soils, unpaved road materials and aerosols were presented earlier, but it is useful to review here the results obtained on the road materials samples. It is important to reemphasize that these results are based on very few samples. In this case, we have results for only a single sample each of crushed limestone and washed gravel road materials. Nevertheless, the results suggest relationships that are sufficiently interesting to report now as preliminary results. The current results are also useful in pointing to the need for further research to confirm or refute the present findings, and to answer questions they raise.

The main purposes for identifying the minerals in road and soil source materials are to see whether mineral composition can be used to distinguish 1) between soil and road dust, and 2) between crushed limestone and washed gravel roads.

On both questions, the preliminary indications are that it should be possible to distinguish between the respective materials based on mineral content. Comparing the two road samples (Rd-7 and Rd-9) with the group of bulk soil samples (5B,7A, and M-50) in Table 9, we found that the road materials had about the same abundances as illite/muscovite and kaolinite, 2) had lower abundances for montmorillonite/vermiculite, quartz, orthoclase/microcline, and oligoclase/andesine, and 3) had greater abundances for calcite and dolomite. In the cases of the calcite and dolomite, none was detected in any of the soil samples, so that these minerals look especially attractive as indicators for road materials.

Comparisons between crushed limestone and washed gravel road materials are based on only a single sample of each; yet the differences are large enough to suggest strongly that it would be possible to distinguish the two types based on mineral content. Comparing the abundances given in Table 9, we found that the crushed limestone had smaller abundances, relative to the washed gravel, for the three clays (illite/muscovite, kaolinite, and montmorillonite/montmorillonite/vermiculite), as well as for quartz, orthoclase/microcline, and oligoclase/andesine. The crushed limestone, as expected, had much larger abundances of calcite and dolomite.

Previous experience with source reconciliation calculations (Gatz, 1975) indicates that the observed differences in mineral content, even allowing for the uncertainties introduced by the small numbers of samples, should make it possible to distinguish soil and road sources in aerosol samples. It also seems likely that mineral content could be used to apportion the relative contributions of limestone and washed gravel roads in aerosol samples, although this must be confirmed by additional sample analyses.

4.1.2 Soil Material

The soil material of interest in this research was that likely to be blown into the air by the wind. Thus, we sampled the top 5 cm of the plowed layer (which is about 20 cm deep) in fields used almost exclusively for growing corn and soybeans. The results given in this section are mostly for samples collected in the 1 square km area surrounding the Bondville Rd. sampling site. Soils of three different series are found in this location. They are the Drummer, Elburn, and Flanagan series. A map showing the distribution of soil series over the sampling grid is shown in Figure 13. According to Fehrenbacher et al. (1967), the Drummer series is a member of Soil Associations B, I, and W, the Elburn series is a member of Association W, and the Flanagan series is a member of Association B. Despite the diversity of soil series and associations represented in our sampling grid, it was not clear at the outset whether there would be measurable differences in chemical composition, since the surface materials from the various soil series were expected to have very similar histories. Typically, Flanagan soils are found on the highest ground, Drummer in the depressions, and Elburn on the slopes in between. These differences could possibly be reflected in different abundances for some elements. However, the area sampled is extremely flat, with maximum differences in elevation of less than 5 meters over the sampling grid (Figure 2), so such possible differences should be minimal.

No matter what differences in elemental abundances might be found between soil series, it is very unlikely that such differences would ever be apparent as differences in composition between aerosol samples. As Figure 13 shows, the pattern of the various soils in the sampling area is sufficiently interwoven and interlaced that, even if all the soil aerosol were to come from as short a distance as 1 km, the soil surface over a 1 km path would "look" much the same to the wind; i.e., extremely heterogeneous, no matter what its path to the sampler. Nevertheless, we now explore the variability of chemical composition in the local soils around our Bondville Road aerosol sampling site.

In considering the chemical composition of a soil, it is important to state the purposes for which, and the methods by which, the samples were analyzed. For example, agronomists are mainly concerned with the amounts of soil elements that are available to plants, and they analyze soils by methods that give concentrations of, for example, available Ca or available N. Similarly, for the purposes of atmospheric chemistry, we are interested in analyzing soils in specific ways to obtain specific kinds of information.

For atmospheric chemistry, there are at least two different kinds of information about the chemical composition of soil that are important. The first of these is the total element content. (Of course, information on the chemical compounds or minerals in soils is also of great interest in atmospheric chemistry, but since these materials are difficult to measure in atmospheric samples due to the limited sample mass generally available, most of the information on aerosol composition available for comparison is limited to elemental concentrations.) The

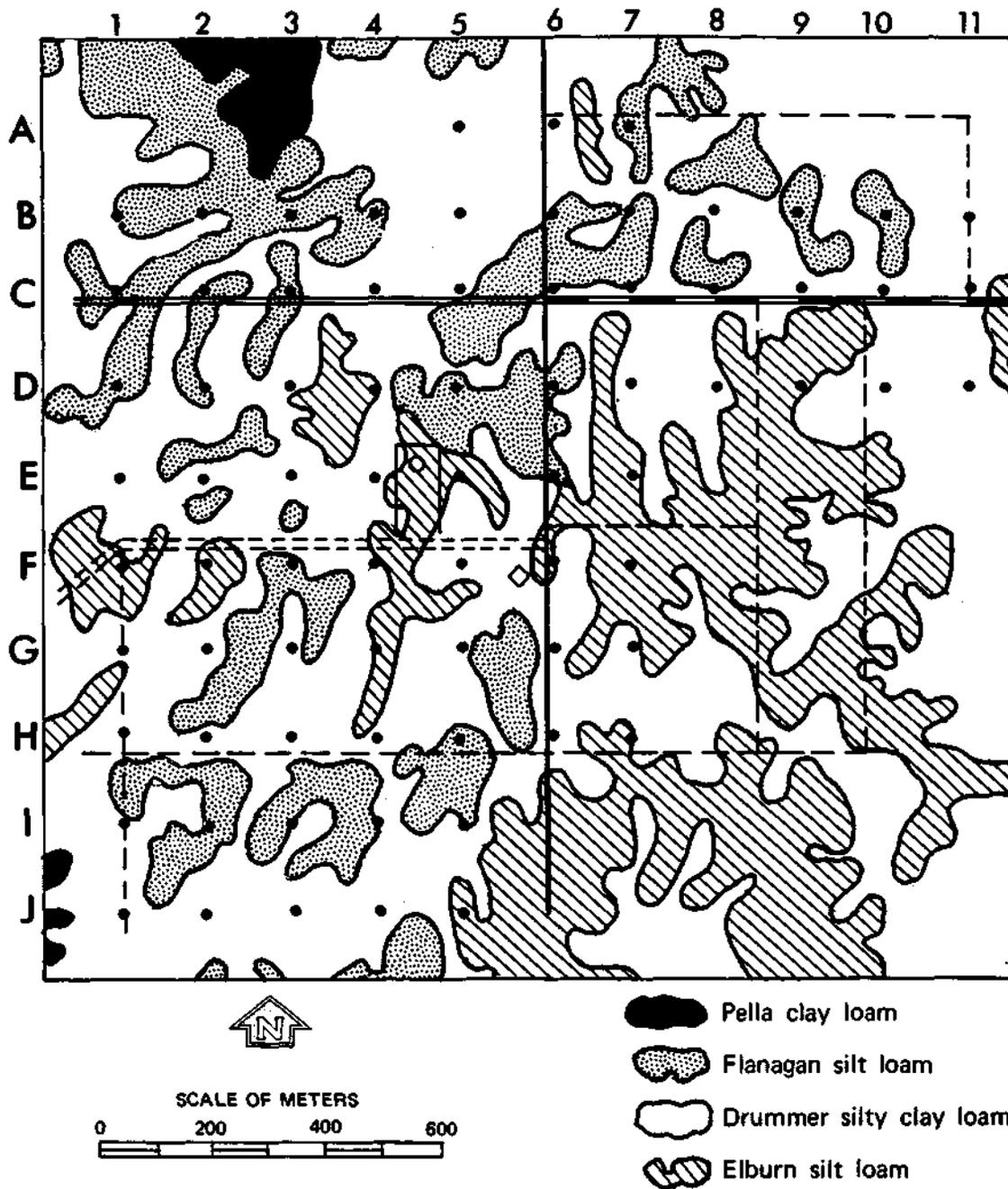


Figure 13. Soils map in the vicinity of the Bondville Road sampling site (H. Mount, personal communication, 1980).

total element content of soils is of interest mostly for characterizing the composition of soils for use in aerosol source apportionment calculations. This is the case simply because the aerosol samples used in such calculations are commonly analyzed for their total elemental composition, and to be compatible the source emissions must be analyzed the same way.

The other kind of information about soil composition that is of interest to atmospheric chemists is the amount of a given element in soil that is "available" or susceptible to "extraction" by rain when airborne soil particles are collected by cloud droplets or rain drops. Such "rain soluble" source compositions would appear to be the proper ones to use for source apportionment calculations on impurities in precipitation, just as total element source compositions are needed for source apportionment calculations on aerosols.

In any determination of source composition, whether total or extractable, one finds that the results are not constant, but variable, from one sample to another. It is very important to characterize the degree of variability in the composition of any source, because the variability is a measure of the uncertainty in the source composition statistic (probably the mean) used in source apportionment calculations, and this uncertainty leads to a corresponding uncertainty in the source apportionment results.

Any statement about soil source composition variability must specify the area over which the samples were collected. However, it is not entirely clear what sized source area (and what distance away) is important to determining the composition of aerosol or precipitation at a given site. Thus, it is also not clear what size area should be sampled to provide the appropriate source compositions. Perhaps the following general concept is useful in this regard. The size of the area whose composition is averaged should increase with distance from the receptor, because atmospheric mixing will make it impossible to distinguish between areas less than some critical size, even if their respective compositions are demonstrably different when compared against each other. Thus, for example, it should be sufficient for us to know the average composition of the Sahara desert aerosol if our receptor is in Illinois, but we might have to know whether the square mile immediately north of our sampler has the same composition as the square mile immediately to the south.

With this general concept in mind, and uncertain what fraction of our aerosol was coming from different distances, say, 1 km, 10 km, or 100 km, we decided to measure the variability of soil composition in the nearest square km as a first step, and out to 100 km as a second step. In the square km surrounding the aerosol sampling site, we collected 74 samples from a square grid network (Figure 2). All of the samples were measured for pH, about half for "rain-soluble" Mg and Ca, and about 6 for about 10 total elements.

In the following paragraphs we consider, in turn, the mean values and spatial variability of, first total, and then extractable, elements in soil. We then consider the variation with particle size of the extractable elements. This is followed by a brief summary of the important mineralogical results on soil samples. Finally in this section we show results for the variability of soil pH and its relationships with the extractable elements.

4.1.2.1 Total element means and variability

Table 14 gives the maximum and minimum total element concentrations, as well as the mean, standard deviation (S.D.), standard error of the mean (S.E.M.), and coefficient of variation (C.V.) for 10 elements. This table summarizes data given earlier in the comparison of analytical methods, but includes only results for the most preferred analytical method. As discussed earlier, the preferred methods were 1) F/AAS, 2) XRF, and 3) INAA. The results in Table 14 summarize analyses of 4 or 6 individual samples from the Bondville site area. Of the 10 elements determined, 7 were measured by F/AAS and 3 by XRF; none of the 10 elements reported in Table 14 was measured by INAA.

The variability of the total element concentrations, as expressed by the C.V., ranges from 3 to 33%. These values are considerably less than those for the unpaved road materials in Table 11. An element by element comparison shows that the variability in soils is larger than that in road materials "all" category for only one element--Mn. Otherwise, the road materials C.V. exceeds the soil C.V. by a factor ranging from about 1.6 to 8.

Using the mean element abundances in soil from Table 14, we note that Si was the most abundant element, followed in order by Al, Fe, K, Na, Ca, Mg, Ti, S, and Mn. In road materials (Table 11) Ca was the most abundant element, followed by Si, Al, Mg, Fe, K, Na, Ti, and Mn. A clear difference in composition is apparent between soil and the road materials presented earlier.

These differences appear in both the rank of the various elements by abundance and the abundances themselves. A comparison of mean element abundances (from Tables 11 and 14) of soil and unpaved road material is given in Figure 14 where it is clear that Si and Al are the most abundant soil elements, while Ca and Si are the most abundant road dust elements. Figure 14 also shows ratios of element abundances in soil and road materials--the larger abundance divided by the smaller. On this basis, Ca, with a ratio of 29.1, shows the greatest difference between materials. The ratio for Mg is next largest, at 3.8, but all the elements except Fe have larger/smaller ratios of 2.0 or more.

The relatively greater abundances of Ca, Mg, and Mn in road materials may well provide the difference in composition needed to distinguish between soils and road materials in the ambient aerosol. On the other hand, for differences which may make it possible to distinguish between these two sources in precipitation, we may need the relative compositions of extractable elements.

Table 14. Variability of total element concentrations in Bondville area surface soils.

Element	Analysis method*	N	Percent total element in air dried soil					C.V.,** %
			Max	Min	Mean	S.D.	S.E.M.	
Na	F/AAS	6	0.78	0.72	0.76	0.02	0.01	3
Mg	F/AAS	6	0.63	0.34	0.48	0.12	0.05	25
Al	F/AAS	4	5.63	4.46	5.04	0.51	.25	10
Si	XRF	6	37.25	31.40	34.68	2.52	1.02	7
S	XRF	3	0.06	0.03	0.047	0.015	0.009	33
K	F/AAS	6	1.84	1.67	1.75	0.07	0.03	4
Ca	F/AAS	6	0.92	0.52	0.70	0.15	0.06	21
Ti	XRF	6	0.45	0.39	0.42	0.02	0.01	6
Mn	F/AAS	4	0.034	0.022	0.028	0.005	0.002	18
Fe	F/AAS	4	2.25	1.56	1.98	0.33	0.17	17
Zn	F/AAS	4			<0.009			
Pb	F/AAS	4			<0.08			

* F/AAS = LiBO₂ fusion, followed by atomic absorption spectrophotometry;

XRF = X-ray fluorescence; INAA = instrumental neutron activation analysis.

** Coefficient of variation, C.V. = 100(S.D./Mean).

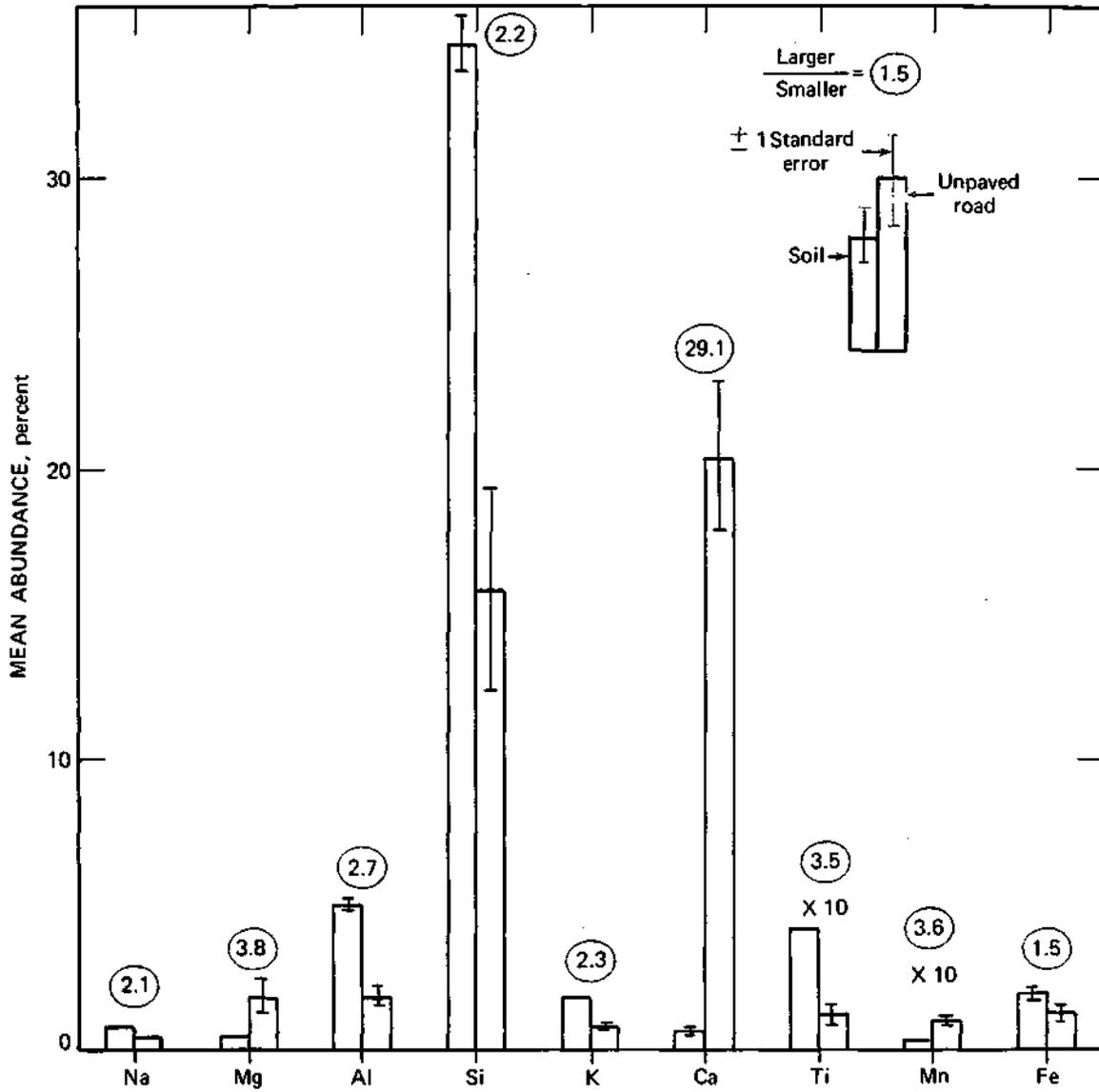


Figure 14. A comparison of mean element abundances in soil and unpaved road materials. Where no error bars appear, the error was too small to distinguish from the line at the top of the bar. Elements labeled by "X10" are shown at ten times their true abundance, for clarity.

4.1.2.2 Extractable elements

4.1.2.2.1 Means and variability

As discussed earlier in this report, results of extracting materials from samples of soil, road dust, or aerosols vary markedly with experimental conditions. Thus it is important to state clearly the conditions of the extraction. The extraction results given here were obtained by shaking 0.10 g samples in 100 mL of pH 3.3 simulated rainwater for 20 min. Both "bulk" samples (i.e., material that passed through a sieve with a 2.0 mm openings) and "sieved" samples (i.e., material that passed through a 53 μ m sieve) were analyzed for Ca, Mg, and pH. Results are summarized in Table 15.

The table gives means and various distribution statistics for each of the three soil series sampled. Differences between soil series are discussed later in this section. Examination of the table shows that for both elements the means of the sieved samples are usually slightly less than those of the bulk samples; however, none of the differences was found to be significant using the paired t-test.

The spatial distributions of bulk and sieved Ca and Mg are shown in Figure 15. The four patterns are broadly similar. High values occurred immediately northwest of the road intersection in the north-central portions of the sampling grid and at two points along the western border of the grid. Low values occurred near the instrument site and south from there, although some high Mg values occurred toward the southern border of the grid.

The observed similarities in the spatial patterns prompted an examination of the relationship between extractable Ca and Mg in the sieved samples. A plot of the relationship is shown in Figure 16, and it is clear that there is a positive correlation. A table of correlation coefficients, R , between all combinations of the measured parameters is given in Table 16, where the hydrogen ion concentrations used in the correlations were derived from soil pH measurements. The table shows slightly higher correlations between elements within the same sample type than between types for the same element. For example, an R of 0.884 was observed between sieved Ca and Mg, while the R for bulk and sieved Ca was 0.801 and for bulk and sieved Mg was 0.617. Correlations between element concentrations and hydrogen ion concentrations were negative and mostly less than 0.5.

Analyses of variance were performed to test for differences in extractable element concentrations between 1) sieved and bulk samples, 2) soil series, and 3) different farmers' fields in the sampling grid. The results confirmed the earlier findings obtained using the t-test that differences between bulk and sieved samples were not significant at the 0.05 significance level. Results of the test for differences between soil series are shown in Table 17. Results are shown for both the Welch and the Brown-Forsythe tests. These both have the advantage that equality of variances in each group is not assumed. Both tests agree that differences between soil series are not significant at the

Table 15. Summary of Ca and Mg concentrations in soil extracted in pH3 simulated rain water.

Element	Soil series	N	Percent extractable* element in air dried soil					C.V.** %
			Max	Min	Mean	S.D.	S.E.M.	
Bulk Ca	Drummer	18	0.539	0.172	0.302	0.088	0.021	29
	Elburn	6	0.271	0.162	0.213	0.047	0.019	22
	Flanagan	10	0.531	0.180	0.288	0.110	0.035	38
	all data	34	0.539	0.162	0.282	0.093	0.016	33
Sieved Ca	Drummer	18	0.492	0.188	0.290	0.073	0.017	25
	Elburn	6	0.285	0.159	0.219	0.049	0.020	22
	Flanagan	11	0.528	0.146	0.255	0.106	0.032	42
	all data	35	0.528	0.146	0.267	0.084	0.014	31
Bulk Mg	Drummer	18	0.230	0.041	0.086	0.049	0.012	56
	Elburn	6	0.068	0.032	0.052	0.014	0.006	27
	Flanagan	11	0.201	0.028	0.077	0.056	0.017	72
	all data	35	0.230	0.028	0.078	0.048	0.008	62
Sieved Mg	Drummer	18	0.138	0.042	0.077	0.029	0.007	37
	Elburn	6	0.059	0.034	0.047	0.010	0.004	22
	Flanagan	11	0.154	0.027	0.060	0.036	0.011	60
	all data	35	0.154	0.027	0.067	0.031	0.005	46
pH	Drummer	18	6.78	4.83	5.65	0.56	0.13	10
	Elburn	6	5.80	4.66	5.20	0.42	0.17	8
	Flanagan	11	7.32	4.73	5.58	0.72	0.22	13
	all data	35	7.32	4.66	5.55	0.60	0.10	11

* 0.10 g of soil extracted by shaking for 20 min in 100 mL of pH 3.3 simulated rain water.

** Coefficient of variation, C.V. = 100 (S.D./Mean).

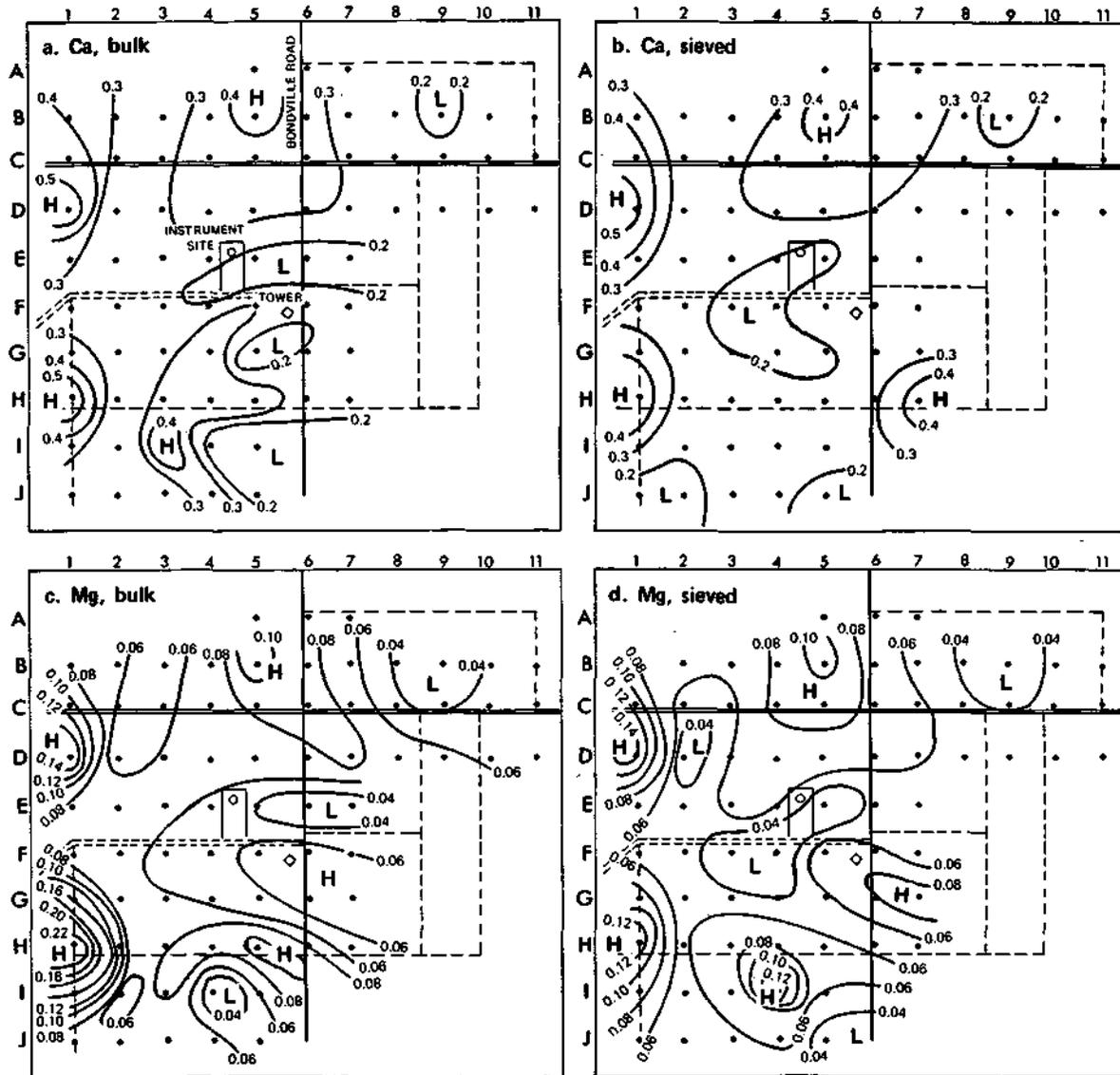


Figure 15. Spatial distribution of extractable % Ca and Mg in bulk and sieved air dried soil. Samples of 0.1 g were extracted by shaking in 100 mL of pH 3.3 simulated rainwater for 20 minutes.

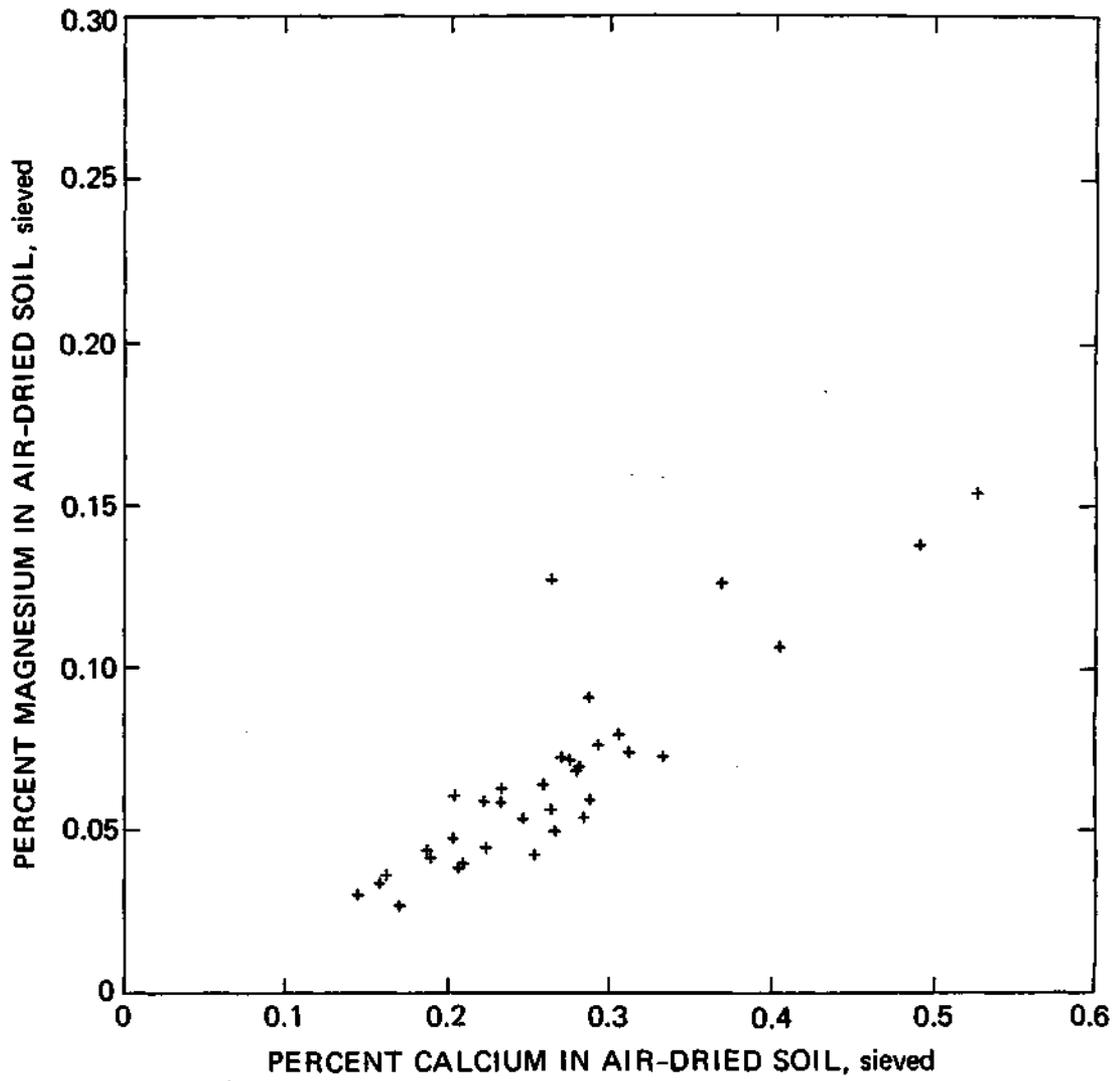


Figure 16. Scatter plot of pH 3.3-extractable sieved Ca vs sieved Mg concentrations.

Table 16. Correlation table for extracted soil constituents.

	<u>Sieved</u>		<u>Bulk</u>	
	<u>Ca</u>	<u>Mg</u>	<u>Ca</u>	<u>Mg</u>
Sieved Ca	1.0			
Sieved Mg	0.884	1.0		
Bulk Ca	0.801	0.678	1.0	
Bulk Mg	0.667	0.617	0.842	1.0
H ⁺	-0.445	-0.357	-0.534	-0.304
pH	0.630	0.480	0.648	0.411

Table 17. Summary of analyses of variance to test for significance of differences between means of soil series.

<u>Soil chemistry</u> <u>parameter</u>	<u>Differences between soil</u> <u>series significant at 5% level?</u>	
	<u>Welch*</u>	<u>Brown-Forsythe*</u>
Bulk Ca	yes	no
Bulk Mg	yes	no
Sieved Ca	no	no
Sieved Mg	yes	yes
pH	no	no

* For a description of these methods, which have the advantage of not assuming equality of variances in each group, see Brown, M. B., and A. B. Forsythe, 1974: The small sample behavior of some statistics which test the equality of several means, Technometrics, 16, 129-132,

0.05 level for sieved Ca and pH, but that differences are significant between series for sieved Mg. However, the tests do not agree for either Ca or Mg on the bulk samples. In both of these cases, the Welch test found significance, but the Brown-Forsythe test did not.

The spatial distributions of extractable Ca and Mg in Figure 15, together with the observation that local farmers vary in the timing of "lime" (CaCO_3) applications (i.e., liming in the fall, but not every field every year), suggested that there might be significant differences in these elements between farmers' fields. (See Figure 2 for locations of fields.) In the test for differences between fields, the analysis of variance detected significant (0.05) differences between fields for pH, but not for either sieved or bulk Ca or Mg. Plotted values of mean values (\pm S.E.M.) for all of these parameters are shown in Figure 17.

4.1.2.2.2 Variation with particle size

Variation of soil composition with particle size was measured in two different ways. The two methods measured different aspects of the situation. The first method consisted of generating a soil aerosol by directing two jets of air onto a sieved ($<53 \mu\text{m}$) sample placed into a chamber at the University of Wisconsin Water Chemistry Laboratory, and collecting the particles on several stages of a cascade impactor (the UW method). In this method the mass of each element was measured on each of four impactor stages. These individual-stage masses can be summed to get a total mass over the size range represented by the impactor stages analyzed. Thus, the masses on the individual stages, M_i , can be divided by the total mass, M to obtain the fractional mass on each stage. This shows the relative distribution of element mass over a given size interval.

The other method consisted of separating particles by size on a sonic sifter. The percent abundances of extractable elements, but not total particle masses, were measured in each size class. Thus, the UW method gives data which allow us to see how the total extractable mass of an element is proportioned among the various size classes, whereas the sonic sifter data have been plotted to show variation in percent abundance of extractable elements with size.

The extractable element size distributions for Na, Mg, K, and Ca, as measured in the impactor samples generated at the University of Wisconsin, are shown in Figure 18. The distributions are plotted as

M/M In D VS. aerodynamic diameter, D , on a log scale, so the area of a bar representing a given size class is proportional to the fraction of the sum of the measured element masses represented by that particular size interval. The height of each bar represents the mean, and the vertical line the S.E.M. for each size class, based on four samples: 5D, 5B, 7A, and 7F. (See Figure 2 for locations.) It is instructive to compare the results to corresponding ones for road materials, which were presented in Figure 12.

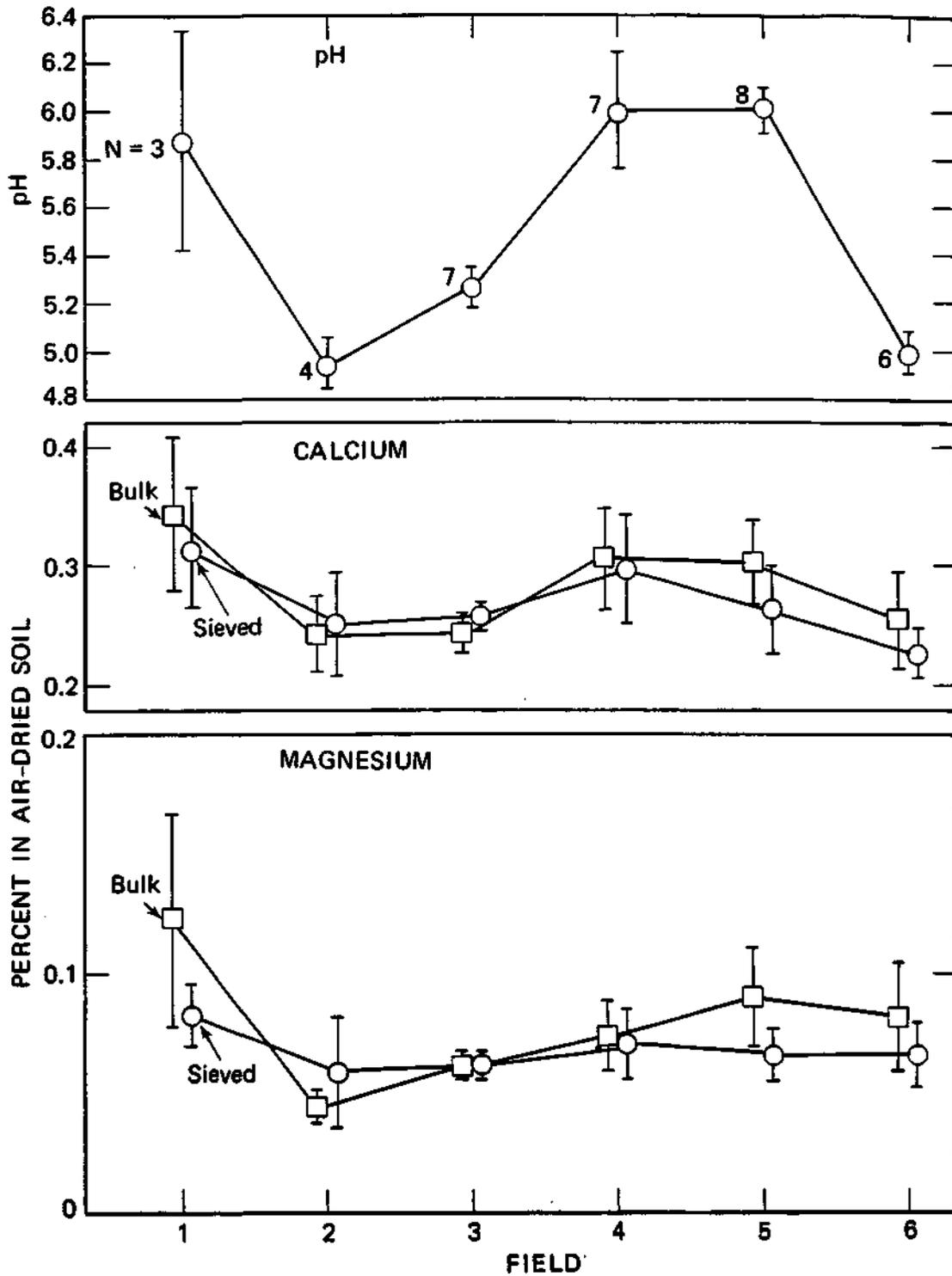


Figure 17. Variation of soil pH and Ca and Mg abundances between fields. Field locations are shown in Figure 2. The uncertainties shown are + 1 S.E.M.

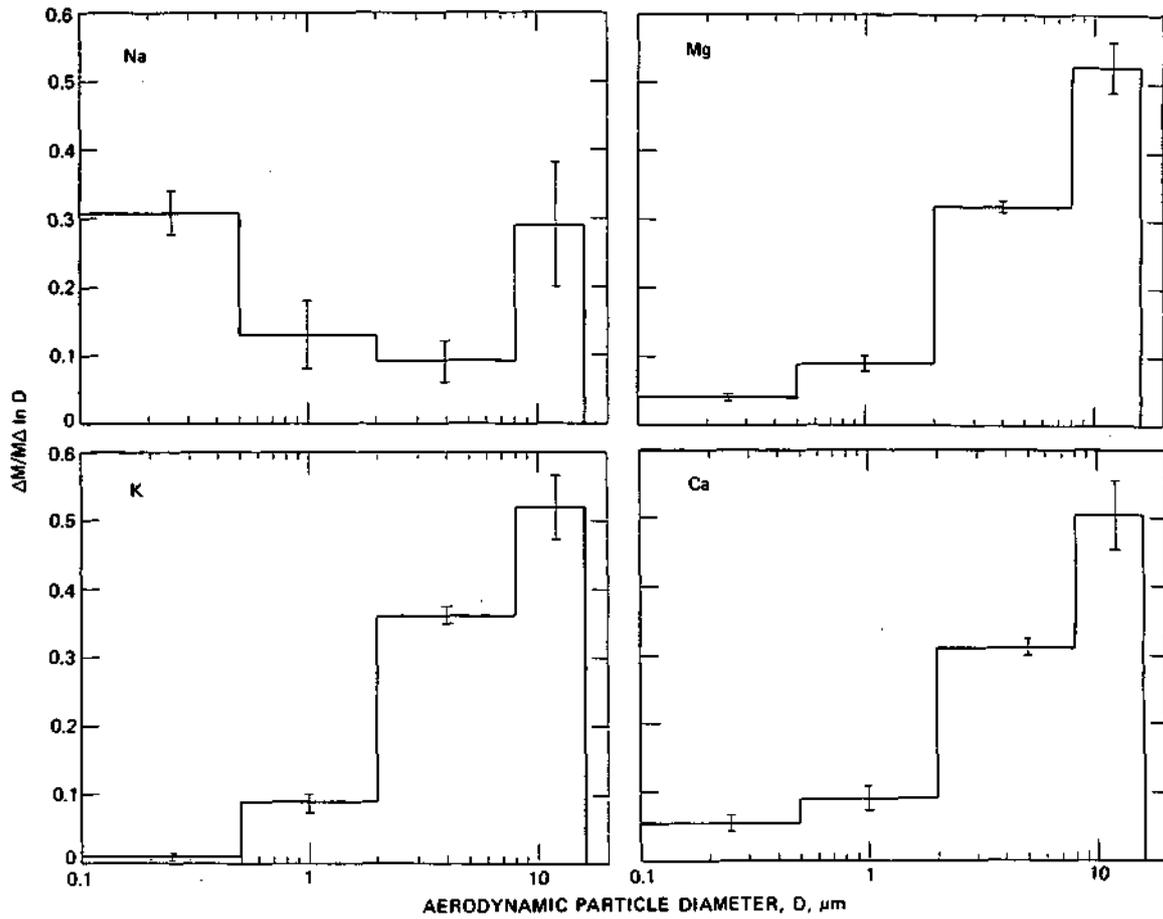


Figure 18. Size distributions of extractable Na, Mg, K, and Ca in soil samples. Samples were generated in the University of Wisconsin Water Chemistry Laboratory chamber.

For extractable Na, the size distributions in soils and road materials were similar in that a small-particle peak was present. The small-particle peak was more prominent in the soil samples. None of the other elements measured showed a similar small-particle peak in either type of source material. Variability, as judged from the height of the S.E.M. bars, was somewhat less for soils than road materials.

For extractable Mg, the M/M In D peak occurred in the largest size class for both soils and road materials, but the peak was higher and the change with size was more uniform for soils. Again, the soil samples exhibited less sample-to-sample variability.

The results for extractable K and Ca were very similar to those for Mg, except that K had a greater difference in variability between the two different source materials.

The variations of extractable Na, Mg, K, and Ca abundances with particle size are shown in Figure 19. The figure shows results for duplicate analyses carried out on each of two different soil samples - 7A and 5B. The duplicate results show excellent agreement, except for the K results on one pair of samples.

For a given element, the abundance vs. particle size curves of the two soil samples generally had the same shape. Because of the discrepancy in duplicate K analyses of the smallest particles, however, K may be an exception of the "same-shape" behavior.

Close examination of Figure 19 shows that all four elements had relatively constant abundances over the various size categories analyzed. There were no samples for which abundances varied over size by more than a factor of two for any of the four elements measured. However, because of the good agreement between duplicates and between samples, there appear to be some systematic differences between elements that are worth pointing out. For Na, the abundances were lowest in the smallest particle size range (less than 5 μm), then increased to a peak in the 20-45 μm class, and decreased somewhat in the 45-53 μm class.

The Mg abundances displayed opposite tendencies to those of Na. The abundances were highest in the smallest particles, then dropped to a minimum in the 20-45 μm range, and then rose again. The variation of K abundances with size is difficult to describe with great certainty because of the discrepancy in one pair of duplicates, but the possibility of a uniform K abundance with size is present. The variation of Ca abundance with size is very similar to that of Mg, except that the minimum occurred in the 10-20 μm range.

4.1.2.3 Mineralogy

Mineralogically, the bulk compositions of the three soil samples analyzed were relative uniform - about 40% quartz, 30% clay minerals (illite/muscovite, kaolinite, and montmorillonite/vermiculite), and about 15% each of orthoclase/microcline and oligoclase/andesine. The calcite and dolomite characteristic of road samples were absent, as were the sulfate compounds that were so abundant in the aerosol samples.

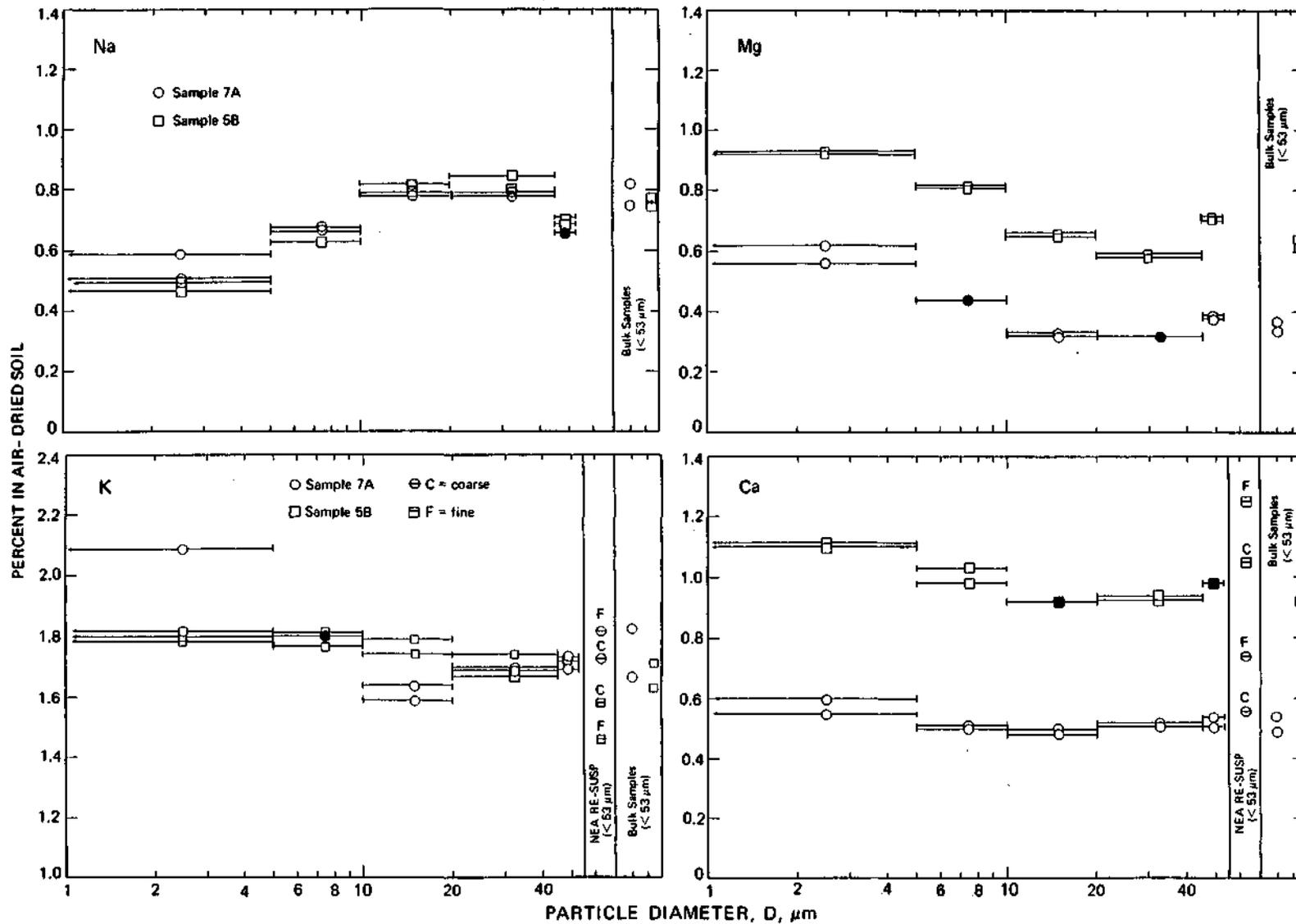


Figure 19. Size distributions of total elements in aggregates divided according to size by the ATM Sonic Sifter. Solid symbols designate identical duplicate analyses.

Two unexpected results were obtained from the mineralogical examination of sonic sifter size fractions. The clay abundance increased with size, although "clay-sized" particles are generally defined as less than 2 μm diameter. The quartz abundance decreased with size, although quartz is a major component of "sand-sized" particles, which are larger than 50 μm diameter. The abundances of the remaining minerals varied little with size.

4.1.2.4 Soil pH

4.1.2.4.1. Reproducibility

A subset of 15 soil samples was analyzed for soil pH twice—first in 1978 and again in 1981—to assess the reproducibility of the analyses. On both occasions samples were analyzed using the techniques described in Chapter 2, although different analysts made the two sets of measurements. Results appear in Table 18. The overall pooled standard deviation, obtained by taking the square root of the mean of the individual variances computed for each pair of measurements, was less than 0.1 pH unit. Moreover, most of the summed variance was contributed by two pairs of measurements where the measured pH values differed by 0.30 and 0.36 pH units, respectively. Thus, the distribution of errors is skewed, having a long tail toward a few large values. A typical pair of measurements would differ only by a few hundredths of a pH unit, so the measurements may be considered very precise.

4.1.2.4.2 Local results

The distribution of surface soil pH surrounding the Bondville Road sampling site is shown in Figure 20. The pH at individual sites varied from 4.66 at site 5J to 7.78 at site 5C. Values greater than 6 occurred in bands running from west to north of the instrument site and west to east south of the site. A band of pH 5.5 or less stretched across the site and extended eastward. Other areas of pH 5.5 or less were found in the northeast corner of the sampling grid and along its southern border.

To test the validity of the contour analysis of the soil pH based on 160 m grid intervals, additional samples were collected for pH analysis at 45 m intervals along two transects within the original sampling grid. The locations of the two transects, one oriented north-south and the other east-west, are shown in Figure 13. This set of samples was collected in October, 1979; thus, this sampling was separated from the first by one, or possibly two, fall periods, during which field liming for soil pH control normally occurs in central Illinois. Field 6 (Figure 2) is known to have been limed in fall, 1978, and other fields may have been limed then or in fall, 1979. Thus a comparison of results from the two sampling periods may show the effects of lime (CaCO_3) additions during the interval between sample collections.

Sample collection and pH analysis techniques were the same for both groups of samples.

Table 18. Reproducibility data for soil pH measurements.

<u>Sample No.</u>	<u>pH Measurement</u>		<u>Variance</u>
	<u>1</u>	<u>2</u>	
5B	6.88	6.78	0.002500
4J	5.20	5.17	0.000225
3B	5.61	5.60	0.000025
4I	4.98	5.12	0.004900
9B	4.91	4.82	0.002025
7A	4.61	4.73	0.003600
2A	5.20	5.16	0.000400
7E	4.91	5.10	0.009025
3I	4.94	5.02	0.001600
7G	5.39	5.40	0.000025
10B	5.17	5.15	0.000100
5G	5.35	5.65	0.022500
3D	6.13	6.10	0.000225
1E	6.26	5.90	0.030625
1F	5.98	5.80	0.008100
			<u>0.085875</u>
		TOTAL	

Pooled standard deviation = $\sqrt{\text{variance}} = \sqrt{0.085875/15} = 0.0757$

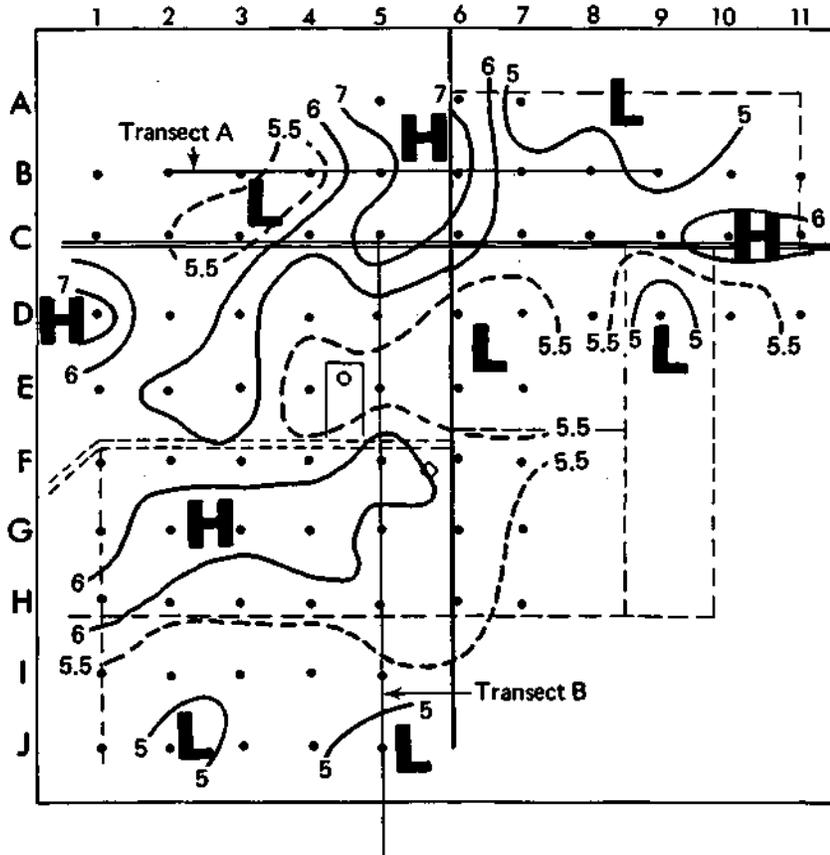


Figure 20. Distribution of soil pH around Bondville Road sampling site.

Comparative results are shown in Figure 21. First of all, it is clear that the results from the coarse grid interval reproduced the major trends found in the fine interval results, in both transects. For example, in Transect A, the major peak that occurred at 640 m in the 1979 samples was also present in the 1978 results, and both sets of samples yielded high pH values at the north end of Transect B and low values at the south end.

Although the overall trends of the two data sets agree, close inspection reveals some differences. The major difference occurred at about 400 m on transect A, where the 1979 sample was more than 2 pH units more alkaline than the 1978 sample. Laboratory notes revealed some confusion over the validity of the number assigned to this sample in the field, and it is likely that the 1979 measurement was not valid. At other points along the transects, for example, between 160 and 400 m and 500 and 800 m along Transect B, the 1979 samples appear to be consistently higher in pH than the 1978 set, although the general trends of the respective data sets are similar. These consistent differences may have resulted from lime applications between the two sampling periods, as mentioned earlier.

Additional evidence for a systematically higher pH of the 1979 data set is seen in a numerical comparison between years on the two transects. For Transect A, the mean deviation, comparing each 1979 sample to the nearest 1978 sample, was 0.35 pH units. The root mean square (RMS) deviation, by the same method, was 0.43 pH units. For Transect B, the corresponding values were 0.40 (mean deviation) and 0.48 (RMS deviation). Since the deviations for the two transects were substantially in agreement, and exceeded the expected analytical uncertainty (0.1 pH units, as shown earlier) by a factor of about 3, there is a good likelihood that many of the sampled fields were limed either in fall, 1978, or fall, 1979. Nevertheless, the overall agreement in general trends confirms that the major features of the spatial analysis of surface soil pH in Figure 20 are valid, and the positions of relative high and low values are apparently not substantially altered by applications of lime.

The main point in making a detailed examination of spatial variations in soil pH surrounding our sampling site was to get an indication, with minimal analysis effort, of the variation in soil element concentrations on a finer scale than that reported earlier. If variations in soil pH are to be valid indications of soil element variations, it is necessary to show correlation between soil pH and the concentration of soil elements such as Ca and Mg. Visual comparison of the spatial variations of soil pH in Figure 20 with those of Ca and Mg concentrations in Figure 12 suggests that higher element concentrations occurred with higher soil pH values. To examine this possibility, we performed regression analyses using the element concentrations as dependent variables and soil pH as the independent variables. Regression lines for the individual soil series are shown in Figure 19 and their slopes (m) and intercepts (b) are given in Table 19. The table also gives the slopes and intercepts for the combined three-series data set, although the corresponding lines are not shown in Figure 19 to avoid cluttering.

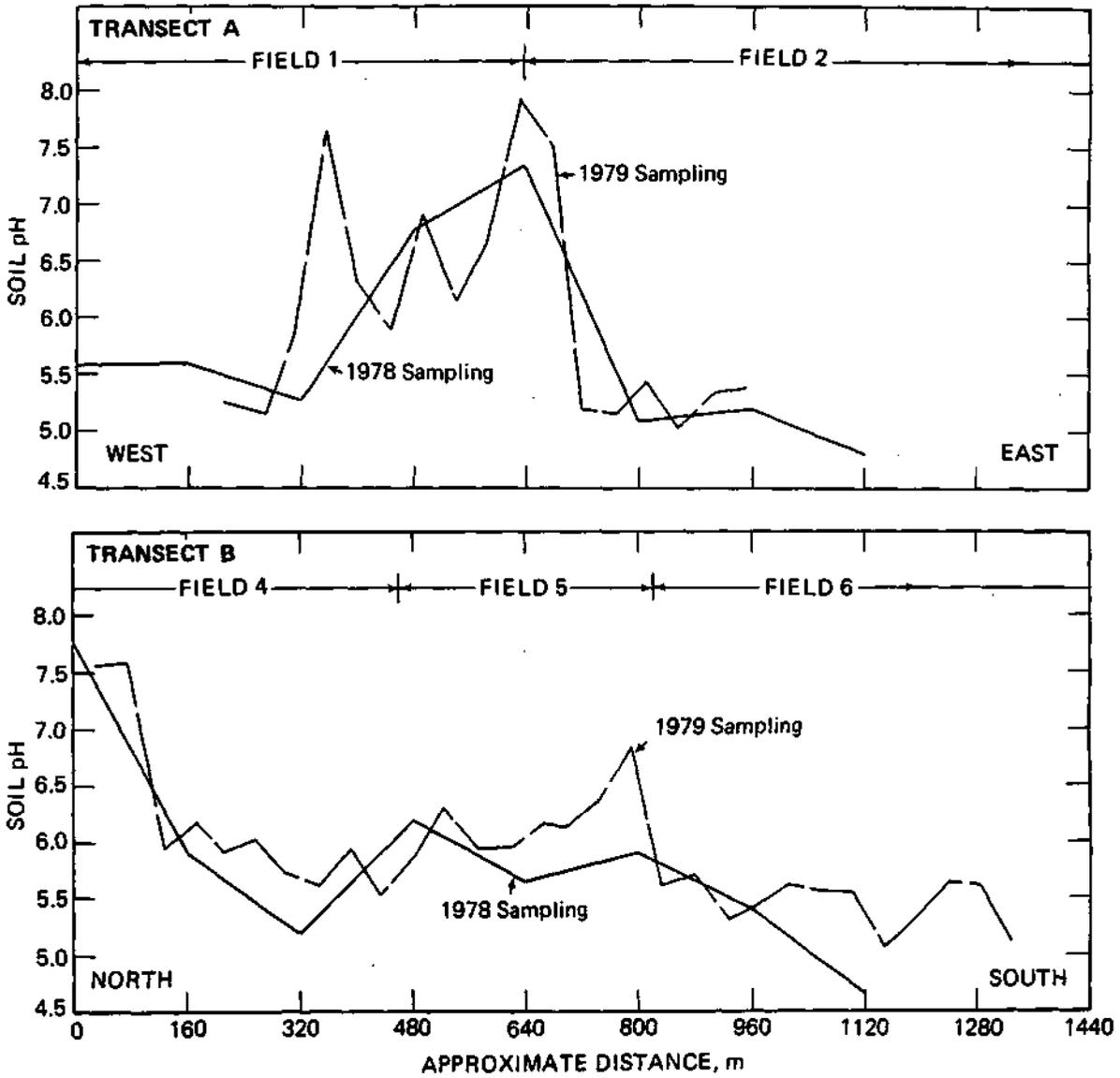


Figure 21. Comparison of soil pH along two transects at sampling intervals of 160 m (1978) and 45 m (1979).

Table 19. Summary of regression analyses for pH 3.3 extractable soil elements versus soil pH. Bulk samples passed 2 mm sieve; sieved samples passed 53 mm sieve.

<u>Parameter</u>	<u>Soil series</u>	<u>No. of samples</u>	<u>R²</u>	<u>Regression equation:</u>		<u>Significant m?</u>	
				<u>% Element = b + (m)(pH)</u>	<u>b</u>	<u>m</u>	<u>95%</u>
Bulk Ca	All data	34	0.39	-0.2652	0.0982	Y	Y
	Drummer	18	0.16	-0.0535	0.0629	N	N
	Elburn	6	0.15	-0.0127	0.0434	N	N
	Flanagan	10	0.70	-0.4655	0.1330	Y	Y
Sieved Ca	All data	35	0.40	-0.2201	0.0877	Y	Y
	Drummer	18	0.20	-0.0379	0.0580	N	N
	Elburn	6	0.26	-0.0974	0.0608	N	N
	Flanagan	11	0.58	-0.3723	0.1123	Y	Y
Bulk Mg	All data	35	0.17	-0.1036	0.0326	Y	N
	Drummer	18	0.03	0.0019	0.0149	N	N
	Elburn	6	0.16	-0.0177	0.0134	N	N
	Flanagan	11	0.37	-0.1851	0.0470	Y	N
Sieved Mg	All data	35	0.23	-0.0697	0.0245	Y	Y
	Drummer	18	0.01	0.0567	0.0037	N	N
	Elburn	6	0.40	-0.0327	0.0153	N	N
	Flanagan	11	0.69	-0.1699	0.0411	Y	Y

Figure 22 shows considerable scatter in the data points. This is reflected numerically in the generally small values for the explained variance (R^2) in Table 19. Nevertheless, there is considerable consistency in the results from one element/size group to the next. In all four cases, the slopes of the regression lines for all samples and for the Flanagan series are significant at the 0.05 level. The same is also true at the 0.01 level, except for bulk Mg. Conversely, although the slopes for Drummer and Elburn soils show increasing element concentrations with increasing pH, none of the slopes was significantly different from zero. Slopes for both sets of Ca data were greater than for Mg. There appears to be little difference in the results between bulk and sieved soils.

In summary, it appears that a significant relationship between soil pH and soil Ca and Mg concentrations occurred for the Flanagan series, but not for Elburn or Drummer. This relationship is strong enough to also give a significant relationship when all data are considered together. Nevertheless, it is clear from the scatter in the data that other influences beside pH-3.3 extractable Ca and Mg concentrations affect soil pH, and the spatial variability of soil pH, even with double the number of samples, cannot be viewed as providing more information on soil element concentration variability than was gained from the measured element concentrations themselves.

4.1.2.4.3 Regional results

As a first step in assessing the possibility that soil aerosols arriving from different directions could have different elemental composition, we measured the pH of the soil and unpaved road samples collected regionally. The road samples were air dried and sieved (2 mm). The fraction passing the sieve was subsampled in the same manner as the soil materials. The pH of both soil and road materials was measured using the method described earlier. As might be expected from the local variability of soil pH exhibited in Figure 20, and confirmed by examination of the data, neither an isopleth analysis, nor even a map of the measurements, is even informative. Analysis of variance showed that there were some significant differences between soil associations, for which data are plotted in Figure 23, but it is also clear that any given pH value would not be diagnostic of any particular soil association or any particular locality. A value near pH 8 is diagnostic of road materials, but would, of course, still not identify a source locality, since unpaved roads are distributed more or less uniformly throughout the state.

Our intent in analyzing these results is to look at the variability of surface composition in terms of what would be "seen" by the wind as it moves across the surface over a period of several hours. It is clear from the spatial distribution of the pH of both soil and road materials that winds from any direction would pass over a very heterogeneous surface within 100 km of our sampling site, and thus aerosol pH (if it could be measured so as to be equivalent to the pH measurements made on soil or road materials) could not be used to identify source locations, unless the source were very local and contributed heavily to the total

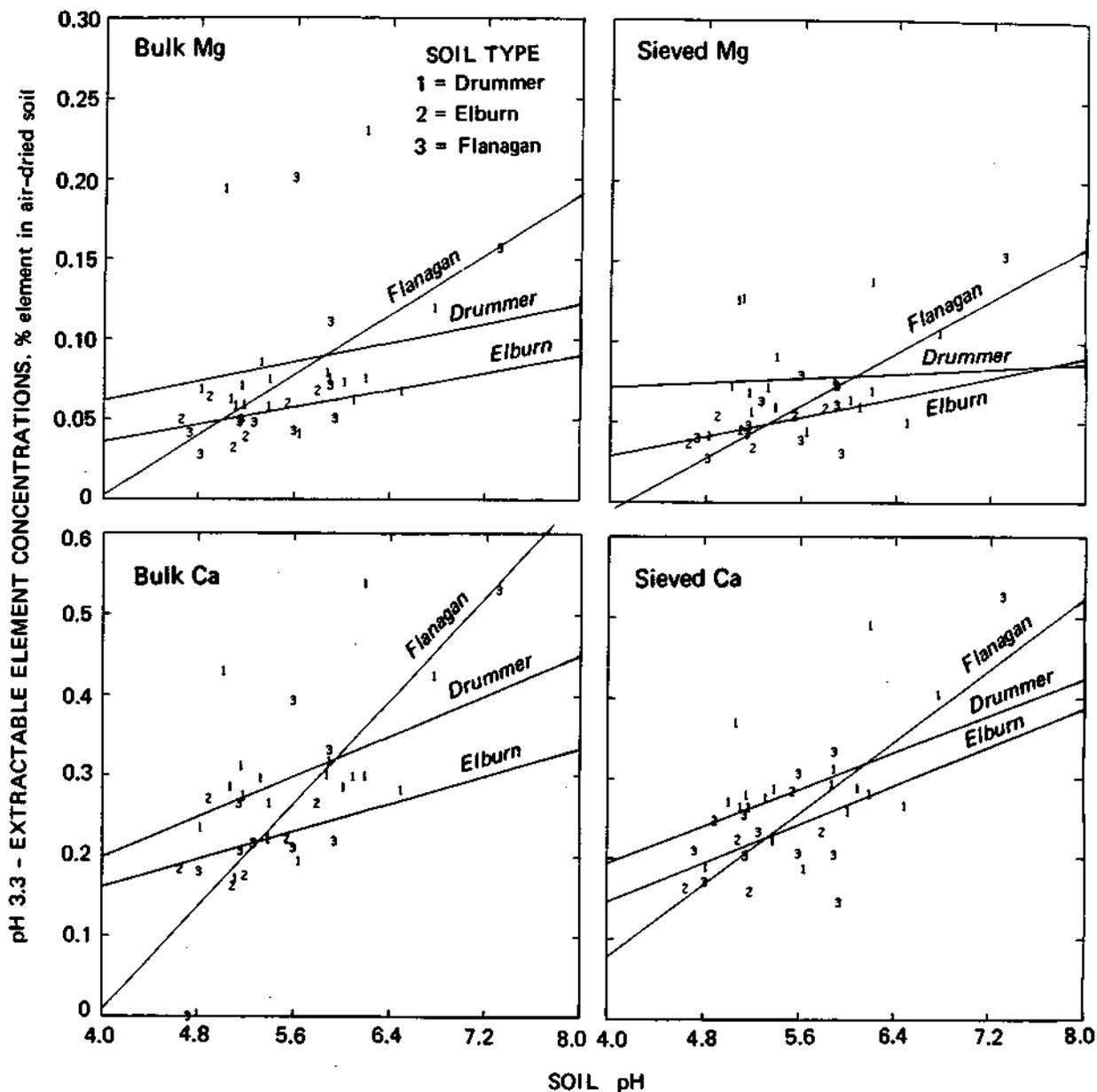


Figure 22. Regression lines showing relationships between pH 3.3-extractable soil element concentrations and soil pH soil series symbols. Samples of 0.1 g were extracted in 100 mL of pH 3.3 simulated rain water shaken 20 minutes on a wrist shaker.

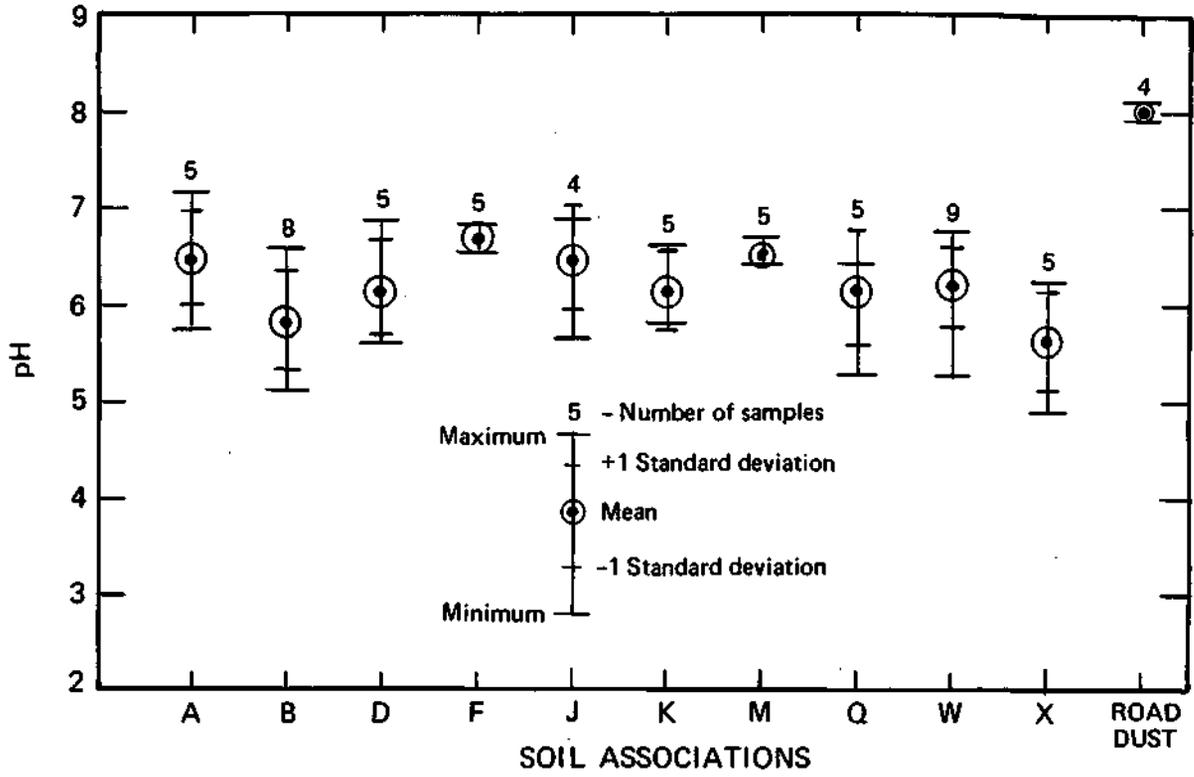


Figure 23. Results of pH measurements on regional surface materials, grouped by soil association and road materials.

aerosol mass. The same conclusion is likely in terms of elemental composition of road and soil materials within 100 km of our sampling site, although we have not made the measurements to prove it.

4.2 Aerosol Composition and Sampler Comparison

4.2.1 Introduction

In this section, we present results of an extensive set of aerosol chemistry measurements made at the Bondville Road field site in October and November, 1978. Six different types of samplers were used. They were: 1) a Nuclepore filter exposed face down under an inverted funnel rain shield (referred to as the "funnel" sampler), 2) the Water Survey vane sampler (the "vane" sampler), 3) the NCAR vane sampler (the "NCAR" sampler), 4) the Casella impactor sampler (the "Casella" sampler), 5) the Florida State University streaker sampler (the "streaker" sampler), and 6) the Beckman dichotomous virtual impactor (the "dichotomous" sampler).

All six types were operated near ground level, and four of the six were operated on a nearby 35 m tower. Details of the experimental procedures were given in Section 2.1.1.

Results are presented in the form of:

- 1) Summary tables of ambient concentrations for 10-13 elements measured by the ground and tower dichotomous and streaker samplers,
- 2) Tables of daily concentrations and summary statistics for Ca, Mg, K, and S measured by the six samplers on the ground and the four on the tower, and
- 3) Comparisons between samplers, including:
 - . tower vs. ground measurements by the NCAR, Casella, streaker, and dichotomous samplers,
 - . differences between the six samplers on the ground, and
 - . differences between the four samplers on the tower.

4.2.2 Summary Tables

Table 20 summarizes observed element concentrations in fine and coarse particle size ranges from the dichotomous sampler on the ground. Note that the fractions of the filters for which element measurements were below detection limits are given as an indicator of data quality. Note also that concentrations were reported as 0 if the filter blank was greater than the measured element mass on the filter. The table shows that the distributions of most elements were skewed toward high concentrations, since mean values exceed medians.

Based on either medians or means, the table shows that S, Cl, K, Mn, Cu, Zn, Br, Pb, and total mass occurred in higher concentrations in the fine mode, while Al, Si, Ca, and Fe occurred in higher concentrations in the coarse mode. (Ti was not classified, since it was above its detection limit on less than half the filters in both size classes.) The element

Table 20. Summary of ambient elemental concentrations measured on 41 sampling days, October-November, 1978, Bondville ground dichotomous sampler.

A. Fine particles.

Element	% of filters <D.L.	Concentration*, ng/m ³				
		Maximum	Median	Minimum	Mean	S.E.M.
Al	61	190	8.5	0.0	49.0	9.56
Si	0	904	105	15.0	156	27
S	0	5394	1080	315	1418	179
Cl	0	45	23	10	24.0	1.44
K	0	314	57	17	83.5	10.6
Ca	0	499	40	7	85.5	15.3
Ti	90	35	0	0	2.72	1.01
Mn	22	17	7	1	7.01	0.64
Fe	0	395	91	19	109	13.3
Cu	12	8	4	0	4.10	0.34
Zn	0	79	21	6	25.9	2.61
Br	0	58	16	4	17.7	1.70
Pb	0	289	92	27	103	8.7
Total mass	27	36200	4900	1050	8933	1468

B. Coarse particles.

Element	% of filters <D.L.	Concentration*, ng/m ³				
		Maximum	Median	Minimum	Mean	S.E.M.
Al	12	574	93	0	128	19.4
Si	5	5214	277	0	542	152
S	0	1142	56	0	117	30.8
Cl	17	43	12	0	12.4	1.56
K	10	551	35	0	65.1	17.5
Ca	0	9640	188	0	516	236
Ti	66	171	2	0	14.6	5.30
Mn	29	63	4	0	6.79	1.71
Fe	0	1099	96	0	164	36.0
Cu	73	5	0.5	0	0.74	0.17
Zn	12	35	6	0	7.68	1.19
Br	17	11	2	0	2.80	0.45
Pb	0	43	12	0	14.3	1.91
Total mass	66	36100	1350	1050	4066	1062

*

Measurements less than detection limits were taken as one-half detection limits.

with by far the highest concentration in the fine mode was S, while Si and Ca had the highest concentrations in the coarse mode.

Table 21 summarizes the measurements by the dichotomous sampler on the tower. Again, means exceed medians, showing distributions skewed toward high concentrations. The lists of elements having higher concentrations in the fine or coarse modes are the same as for the dichotomous sampler on the ground, except that Cl and Mn (both means and medians) and K (mean only) had higher concentrations in the coarse mode on the tower. Also, both mean and median Ti were higher in the coarse mode on the tower. Cu concentrations were less than detectable on more than half of the filters in both size classes.

As at the ground sampler, S had the highest concentrations (both mean and median) in the fine mode, and Si and Ca had the highest concentrations in the coarse mode.

Tables 22 and 23 summarize the FSU streaker measurements on the ground and tower, respectively. Note that there were 167 individual 2-hr measurements by the ground sampler and 332 by the tower sampler. Thus, the two data sets are not strictly comparable. Mean concentrations exceed medians for all elements at both heights, indicating the usual distribution, skewed toward high concentrations. S, Si, and Ca had the highest concentrations (both mean and median) at both heights, although not always in that order.

4.2.3 Daily Concentrations and Summary Statistics

This section presents daily concentrations and summary statistics of Ca, Mg, K, and S measurements made in six samplers on the ground and four on the tower at the Bondville Road field site. Ca and K were measured by all samplers, but Mg and S by only some.

Results for Ca are given in Table 24. Means exceed their respective medians for all samplers, both on the tower and the ground. There appear to be rather large differences between mean (or median) concentrations measured by the various samplers, both on the ground and on the tower. The range of medians among the six samplers on the ground was 0.30 to 1.31 $\mu\text{g}/\text{m}^3$, while the corresponding range for the means was 0.91 to 2.10 $\mu\text{g}/\text{m}^3$. The corresponding ranges for the four samplers on the tower (medians first) were 0.56 - 1.64 and 0.74 - 1.86 $\mu\text{g}/\text{m}^3$. The highest concentrations on the ground and the tower were obtained by the two streaker samplers.

Results for Mg are given in Table 25. Mg was not measured by the streaker samplers or the dichotomous samplers, so there are only four samplers to compare on the ground, and two on the tower. Again, means exceeded medians for all samplers at both heights. For Mg also, the ranges of mean and median values obtained appears large. For the four ground samplers, the range of medians was 0.05 to 0.14 $\mu\text{g}/\text{m}^3$, and that of the means was 0.06 - 0.16 $\mu\text{g}/\text{m}^3$. The ranges obtained on the tower were narrower, however: 0.08 - 0.09, and 0.09 - 0.11 $\mu\text{g}/\text{m}^3$, respectively.

Table 21. Summary of ambient elemental concentrations measured on 24 sampling days, October-November, 1978, Bondville tower dichotomous sampler.

A. Fine particles.

Element	% of filters <D.L.	Concentration*, ng/m ³				
		Maximum	Median	Minimum	Mean	S.E.M.
Al	100	—	—	—	—	—
Si	0	262	82.0	29.0	103	14.7
S	0	7172	1897	481	2402	357
Cl	75	15.0	0.5	0	2.88	0.92
K	0	281	112	44.0	132	14.5
Ca	0	96.0	32.0	16.0	43.8	5.07
Ti	100	—	—	—	—	—
Mn	4	24	7	0	8.71	1.19
Fe	0	298	81.5	29	90.9	13.1
Cu	83	7	0	0	0.81	0.33
Zn	0	112	31.5	12	37.6	5.03
Br	0	75	24.5	9	24.6	2.84
Pb	0	384	146	52	151	14.8
Total mass	—	47400	12250	<1000	15600	2424

B. Coarse particles.

Element	% of filters <D.L.	Concentration*, ng/m ³				
		Maximum	Median	Minimum	Mean	S.E.M.
Al	38	635	51.0	0	115	32.1
Si	0	3692	835	196	1178	207
S	0	1566	166	51.0	263	67.3
Cl	17	31	11.5	0	13.4	1.95
K	0	477	110	30.0	156	24.7
Ca	0	1741	430	176	639	102
Ti	17	115	15.5	1.0	28.9	5.73
Mn	4	25	8	0.5	9.69	1.46
Fe	0	857	226	84	306	43.2
Cu	62	4	0.5	0	1.10	0.24
Zn	0	37	11	3	13.7	2.10
Br	0	14	5	0	5.04	0.66
Pb	0	62	21.5	7	24.9	2.77
Total mass	—	26200	5050	<1000	6933	1482

Measurements less than detection limits were taken as one-half detection limits.

Table 22. Summary of ambient element concentrations measured by FSU streaker sampler on the ground, Bondville, IL, 13-27 October, 1978, based on 167 individual 2-hr measurements.

Concentration*, ng/m³

<u>Element</u>	<u>Maximum</u>	<u>Median</u>	<u>Minimum</u>	<u>Mean</u>	<u>S.E.M.</u>
Al	2727	452	125	633	38.0
Si	15739	1339	123	2370	193
S	4907	1626	236	1940	74.3
K	3072	555	124	724	40.6
Ca	34885	1606	1.0	2536	264
Ti	539	104	58.4	136	6.80
Fe	2643	515	57.7	676	38.1
Zn	335	42.4	17.3	52.1	3.30
Br	63.6	17.1	7.5	19.6	0.81
Pb	514	147	40.8	165	7.67

* Measurements less than detection limits were taken as one-half detection limits.

Table 23. Summary of ambient element concentrations measured by FSU streaker sampler on the tower, Bondville, IL, 13 October - 3 November and 10-17 November, 1978, based on 332 individual 2-hr measurements.

Concentration*, ng/m³

<u>Element</u>	<u>Maximum</u>	<u>Median</u>	<u>Minimum</u>	<u>Mean</u>	<u>S.E.M.</u>
Al	1735	411	123	490	15.6
Si	5562	1111	70.2	1418	57.8
S	10321	1947	64.5	2431	100
K	2056	525	158	607	17.6
Ca	8653	1298	0	1799	84.1
Ti	359	87.8	57.1	101	2.60
Fe	2727	445	46.0	555	22.0
Zn	376	54.2	18.4	68.3	2.76
Br	56.5	15.0	0	17.7	0.56
Pb	483	162	42.7	174	4.79

* Measurements less than detection limits were taken as one-half detection limits.

Table 24. Daily Ca concentrations (ug/m³) for various samplers operated at the Bondville Road field site, October - November, 1978.

Julian date	Month	Day	Ground samplers						Tower samplers			
			Funnel	Vane	NCAR	Casella*	Streaker	Dichot	NCAR	Casella*	Streaker	Dichot
290	10	17	1.10	1.37	---	0.31	2.03	---	---	0.33	1.77	---
291	10	18	1.43	1.93	---	---	1.93	---	---	---	1.66	---
292	10	19	2.88	3.03	0.84	1.42	3.32	---	---	0.99	3.34	---
293	10	20	2.82	2.94	2.16	---	5.95	---	---	---	4.48	---
294	10	21	1.55	2.13	1.26	---	3.86	---	1.55	---	2.92	---
295	10	22	4.44	6.04	3.70	4.77	7.66	---	1.86	2.95	3.25	---
296	10	23	0.85	0.91	0.44	---	1.28	---	0.39	---	1.26	---
297	10	24	0.93	1.21	0.42	1.18	2.07	---	0.58	0.54	0.86	---
298	10	25	0.28	0.33	---	---	0.66	0.15	---	---	1.15	0.29
299	10	26	0.53	0.68	0.32	0.09	0.77	0.90	0.17	0.25	1.30	0.52
300	10	27	1.03	1.24	0.64	---	---	---	1.01	---	1.97	1.05
301	10	28	---	---	0.47	0.32	---	---	0.49	0.98	1.25	---
302	10	29	1.02	1.16	---	0.32	---	---	0.51	---	3.05	---
303	10	30	2.69	3.00	2.31	---	---	---	1.11	---	2.76	1.64
304	10	31	1.68	1.87	1.95	0.39	---	---	1.53	1.57	2.77	1.46
305	11	1	2.93	3.62	2.38	0.39	---	---	1.53	1.57	2.71	1.88
306	11	2	3.08	0.07	3.56	---	---	2.32	2.23	---	1.70	1.61
307	11	3	13.88	17.31	7.91	1.67	---	9.98	2.11	0.70	---	0.93
308	11	4	2.17	2.34	0.03	1.67	---	1.34	1.60	0.70	---	1.21
309	11	5	0.95	1.00	0.52	---	---	0.49	---	---	---	0.71
310	11	6	---	0.26	0.15	0.14	---	0.22	0.20	1.12	---	0.20
311	11	7	0.40	0.35	0.35	0.14	---	0.35	---	1.12	---	0.28
312	11	8	0.44	0.48	0.39	---	---	0.42	0.58	---	---	0.34
313	11	9	0.92	1.19	1.02	0.37	---	---	1.67	0.15	---	0.84
314	11	10	---	---	0.98	0.37	1.72	1.34	0.60	0.15	1.29	0.72
315	11	11	---	---	0.82	---	1.13	0.53	0.31	---	1.01	0.56
316	11	12	0.54	0.32	0.20	---	0.59	0.26	0.06	---	0.54	0.21
317	11	13	0.20	0.17	0.35	---	0.40	0.13	0.59	---	0.93	0.21
318	11	14	0.51	0.44	0.35	0.14	1.31	0.25	0.42	0.18	1.62	0.40
319	11	15	0.32	0.35	0.29	0.14	0.68	---	0.35	0.18	0.76	0.30
320	11	16	0.19	0.12	1.03	---	0.36	0.10	0.25	---	0.32	---
321	11	17	0.09	0.08	0.05	0.08	---	0.05	0.09	0.10	---	---
322	11	18	0.27	0.31	0.24	0.08	---	0.20	0.32	0.10	---	---
323	11	19	0.39	0.41	0.11	---	---	0.22	0.19	---	---	0.24
N			30	31	30	12	17	18	27	12	24	21
Maximum			13.88	17.31	7.91	4.77	7.66	9.98	2.23	2.95	4.48	1.88
Median			0.94	1.00	0.50	0.34	1.31	0.30	0.58	0.62	1.64	0.56
Minimum			0.09	0.07	0.03	0.08	0.36	0.05	0.06	0.10	0.32	0.20
Mean			1.68	1.83	1.17	0.91	2.10	1.07	0.83	0.82	1.86	0.74
S.E.M.			0.47	0.57	0.29	0.39	0.50	0.54	0.13	0.23	0.22	0.12

* Casella samples were 2 days long as of day 301 (ground) and day 304 (tower).

Table 25. Daily Mg concentrations ($\mu\text{g}/\text{m}^3$) for various samplers operated at the Bondville Road field site, October - November, 1978.

Julian date	Month	Day	Ground samplers				Tower samplers				
			Funnel	Vane	NCAR	Casella*	Streaker	Dichot	NCAR	Casella*	Streaker
290	10	17	0.16	0.20	---	0.03	---	---	---	0.02	---
291	10	18	0.15	0.22	---	---	---	---	---	---	---
292	10	19	0.29	0.32	0.10	0.13	---	---	---	0.08	---
293	10	20	0.28	0.29	0.23	---	---	---	---	---	---
294	10	21	0.15	0.22	0.13	---	---	---	0.15	---	---
295	10	22	0.21	0.25	0.13	0.13	---	---	0.11	0.16	---
296	10	23	0.14	0.15	0.07	---	---	---	0.12	---	---
297	10	24	0.11	0.14	0.08	0.12	---	---	0.07	0.08	---
298	10	25	0.06	0.07	---	---	---	---	---	---	---
299	10	26	0.09	0.11	0.06	0.02	---	---	0.02	0.04	---
300	10	27	0.16	0.19	0.10	---	---	---	0.15	---	---
301	10	28	---	0.02	0.10	0.06	---	---	0.11	0.16	---
302	10	29	0.12	0.14	---	0.06	---	---	0.06	---	---
303	10	30	0.36	0.40	0.26	---	---	---	0.23	---	---
304	10	31	0.33	0.38	0.42	0.06	---	---	0.34	0.24	---
305	11	1	0.35	0.46	0.28	0.06	---	---	0.23	0.24	---
306	11	2	0.31	0.01	0.41	---	---	---	0.22	---	---
307	11	3	0.32	0.37	0.33	0.08	---	---	0.24	0.05	---
308	11	4	0.15	0.22	0.01	0.08	---	---	0.14	0.05	---
309	11	5	0.13	0.14	0.08	---	---	---	---	---	---
310	11	6	---	0.07	0.04	0.02	---	---	0.06	0.16	---
311	11	7	0.06	0.05	0.05	0.02	---	---	---	0.16	---
312	11	8	0.06	0.05	0.04	---	---	---	---	---	---
313	11	9	0.10	0.12	---	0.04	---	---	0.19	0.02	---
314	11	10	---	---	0.10	0.04	---	---	0.07	0.02	---
315	11	11	---	---	0.12	---	---	---	0.05	---	---
316	11	12	0.05	0.04	0.02	---	---	---	0.01	---	---
317	11	13	0.04	0.04	0.05	---	---	---	0.09	---	---
318	11	14	0.08	0.08	0.23	0.03	---	---	0.07	0.04	---
319	11	15	0.08	0.10	0.07	0.03	---	---	0.09	0.04	---
320	11	16	0.03	0.04	0.27	---	---	---	0.02	---	---
321	11	17	0.01	0.01	0.01	0.02	---	---	0.02	0.01	---
322	11	18	0.03	0.04	0.02	0.02	---	---	0.03	0.01	---
323	11	19	0.08	0.08	0.01	---	---	---	0.04	---	---
N			30	31	29	12			26	12	
Maximum			0.36	0.46	0.42	0.13			0.34	0.24	
Median			0.12	0.14	0.10	0.05			0.09	0.08	
Minimum			0.01	0.01	0.01	0.02			0.01	0.01	
Mean			0.15	0.16	0.13	0.06			0.11	0.09	
S.E.M.			0.02	0.02	0.02	0.01			0.02	0.02	

* Casella samples were 2 days long as of day 301 (ground) and day 304 (tower).

Results for K are given in Table 26. Again, all means exceeded their respective medians, and seemingly large differences between samplers were observed. Among the six samplers on the ground, the ranges of medians and means were, respectively, 0.09 - 0.49 $\mu\text{g}/\text{m}^3$ and 0.10 - 0.62 $\mu\text{g}/\text{m}^3$. Among the four samplers on the tower, the corresponding ranges were 0.06 - 0.58 and 0.10 - 0.63 $\mu\text{g}/\text{m}^3$.

Results for S are given in Table 27. S was not measured by the vane, NCAR, or Casella samplers; thus there were only three samplers on the ground and two on the tower that yielded S measurements. As usual, all means exceeded medians. For S, however, the ranges of the medians and means were somewhat less than for the other elements. The ranges of medians and means for the three samplers on the ground were 1.50 - 1.94 and 1.99 - 2.25 $\mu\text{g}/\text{m}^3$, respectively, while those of the two tower samplers were 2.22 - 2.23 and 2.54 - 2.72 $\mu\text{g}/\text{m}^3$.

4.2.4 Comparisons between Samplers

Results of all paired t-tests are given in Table 28. Time series plots comparing measurements of the same element by two or more different samplers are shown in Figures 24-29.

4.2.4.1 Identical samplers at two different heights

Results of the comparison of the NCAR samplers on the ground and tower are given in Table 28 and Figure 24. The table shows that the mean concentrations of Ca, Mg, and K were higher on the ground than on the tower, but none of the differences was significant at the 5% level. The figure shows that the largest differences in concentrations between the two heights occurred when peak concentrations were observed on the ground, but not on the tower, as would be the case for very local sources of dust raised from the surface. Comparison of the tower-ground differences between the three elements reveals some important similarities and some important differences, which future work should attempt to explain.

Results of the comparison of the Casella samplers on the ground and tower are given in Table 28 and Figure 25. The mean concentration of Ca was higher on the ground, but those of Mg and K were higher on the tower. None of the differences was significant at the 5% level, however.

Results for the comparison of streaker data at the two heights are given in Table 28 and Figure 26. The mean concentrations of Ca, K, and S were all higher on the ground, but again, none of the differences was significant at the 5% level. The figure shows that the time variations of the respective elements were similar at the two heights, and that the higher mean values of Ca and K at the ground were caused by higher ground-level concentrations during peaks that occurred simultaneously at both heights.

Comparisons of the dichotomous sampler measurements at the two heights are given in Table 28 and Figure 27. Means concentrations of Ca and K at the ground were higher than those on the tower, but not

Table 26. Daily K concentrations (ug/nr) for various samplers operated at the Bondville Road field site, October - November, 1978.

Julian date	Month	Day	Ground samplers						Tower samplers			
			Funnel	Vane	NCAR	Casella*	Streaker	Dichot	NCAR	Casella*	Streaker	Dichot
290	10	17	0.16	0.21	---	0.23	0.69	---	---	---	0.53	---
291	10	18	0.17	0.22	---	---	0.87	---	---	---	0.57	---
292	10	19	0.22	0.24	0.14	0.06	0.92	---	---	0.05	0.68	---
293	10	20	0.31	0.33	0.28	---	1.21	---	---	---	1.08	---
294	10	21	0.33	0.38	0.38	---	1.38	---	0.33	---	1.16	---
295	10	22	0.38	0.37	0.35	0.15	1.19	---	0.29	0.29	1.12	---
296	10	23	0.12	0.11	0.15	---	0.27	---	0.10	---	0.52	---
297	10	24	0.18	0.20	---	0.15	0.60	---	0.21	0.18	0.34	---
298	10	25	0.16	0.15	---	---	0.49	0.16	---	---	0.58	0.22
299	10	26	0.09	0.08	0.14	0.03	0.24	0.26	0.04	0.04	0.42	0.16
300	10	27	0.12	0.16	0.15	---	---	---	0.16	---	0.50	0.24
301	10	28	---	---	0.16	0.07	---	---	0.11	0.19	0.60	---
302	10	29	0.15	0.14	---	0.07	---	---	0.10	---	0.70	---
303	10	30	0.29	0.31	0.36	---	---	---	0.23	---	0.99	0.64
304	10	31	0.31	0.31	0.50	0.08	---	---	0.30	0.18	0.85	0.47
305	11	1	0.23	0.29	0.22	0.08	---	---	0.27	0.18	0.89	0.53
306	11	2	0.40	---	0.98	---	---	0.81	0.39	---	0.86	0.65
307	11	3	0.28	0.34	0.37	0.11	---	0.69	0.35	0.03	---	0.45
308	11	4	0.27	0.14	---	0.11	---	0.44	0.32	0.03	---	0.55
309	11	5	0.20	0.18	0.13	---	---	0.24	---	---	---	0.38
310	11	6	---	0.07	0.07	0.11	---	0.12	0.09	0.05	---	0.12
311	11	7	0.06	0.05	0.06	0.11	---	0.07	---	0.05	---	0.11
312	11	8	0.13	0.11	0.11	---	---	0.20	0.12	---	---	0.20
313	11	9	0.18	0.20	---	0.10	---	---	0.40	0.01	---	0.37
314	11	10	---	---	0.19	0.10	0.48	0.36	0.19	0.01	0.59	0.34
315	11	11	---	---	0.29	---	0.64	0.33	0.12	---	0.56	0.38
316	11	12	0.14	0.10	0.14	---	0.35	0.18	0.05	---	0.30	0.18
317	11	13	0.08	0.07	0.03	---	0.34	0.08	0.11	---	0.36	0.12
318	11	14	0.07	0.04	0.22	0.03	0.31	0.07	0.07	0.06	0.29	0.10
319	11	15	0.10	0.10	0.11	0.03	0.33	---	0.11	0.06	0.31	0.15
320	11	16	0.08	0.09	0.06	---	0.33	0.10	---	---	0.40	---
321	11	17	0.03	0.02	0.01	0.02	---	0.03	0.02	0.03	---	---
322	11	18	0.04	0.03	0.01	0.02	---	0.06	0.05	0.03	---	---
323	11	19	0.16	0.12	0.04	---	---	0.13	0.11	---	---	0.16
N			30	30	27	12	17	18	26	11	24	21
Maximum			0.40	0.38	0.98	0.23	1.38	0.81	0.40	0.29	1.16	0.65
Median			0.16	0.14	0.15	0.09	0.49	0.17	0.12	0.06	0.58	0.24
Minimum			0.03	0.02	0.01	0.02	0.24	0.03	0.02	0.01	0.29	0.10
Mean			0.18	0.17	0.21	0.10	0.62	0.24	0.18	0.10	0.63	0.31
S.E.M.			0.02	0.02	0.04	0.02	0.09	0.05	0.02	0.03	0.05	0.04

* Casella samples were 2 days long as of day 301 (ground) and day 304 (tower).

Table 27. Daily S concentrations (ug/m3) for various samplers operated at the Bondville Road field site, October - November, 1978.

Julian date	Month	Day	Ground samplers				Tower samplers				
			Funnel	Vane	NCAR	Casella	Streaker	Dichot	NCAR	Casella	Streaker
290	10	17	2.50				2.96	---		3.00	---
291	10	18	2.13				3.21	---		3.22	---
292	10	19	0.26				0.95	---		1.17	---
293	10	20	1.06				1.72	---		1.92	---
294	10	21	2.25				3.11	---		3.33	---
295	10	22	1.66				2.91	---		3.14	---
296	10	23	0.70				1.31	---		1.62	---
297	10	24	0.87				1.55	---		0.66	---
298	10	25	1.80				2.57	1.67		2.46	1.96
299	10	26	0.57				1.32	1.13		1.46	0.78
300	10	27	0.73				---	---		1.48	0.95
301	10	28	---				---	---		1.58	---
302	10	29	0.96				---	---		1.61	---
303	10	30	4.11				---	---		5.52	5.00
304	10	31	2.32				---	---		3.50	2.34
305	11	1	1.65				---	---		3.06	2.33
306	11	2	6.32				---	5.57		8.07	7.37
307	11	3	5.37				---	4.61		---	5.94
308	11	4	3.28				---	4.11		---	5.32
309	11	5	1.91				---	1.09		---	1.80
310	11	6	---				---	0.59		---	0.70
311	11	7	0.22				---	0.35		---	0.53
312	11	8	1.10				---	1.02		---	1.32
313	11	9	1.82				---	---		---	2.23
314	11	10	---				2.89	3.13		2.38	3.60
315	11	11	---				3.39	3.24		3.06	3.76
316	11	12	4.70				3.66	4.35		2.30	4.89
317	11	13	1.79				2.87	1.42		2.09	1.72
318	11	14	0.91				1.30	0.64		0.94	0.89
319	11	15	1.24				1.47	---		1.37	1.38
320	11	16	1.26				1.94	1.24		2.14	---
321	11	17	1.15				---	0.98		---	---
322	11	18	2.03				---	1.59		---	---
323	11	19	2.97				---	2.11		---	2.48
N			30				20	18		24	21
Maximum			6.32				3.66	5.57		8.07	7.37
Median			1.72				1.94	1.50		2.22	2.23
Minimum			0.22				0.95	0.35		0.66	0.53
Mean			1.99				2.25	2.16		2.54	2.72
S.E.M.			0.27				0.18	0.38		0.32	0.43

* Casella samples were 2 days long as of day 301 (ground) and day 304 (tower).

Table 28. Results of paired t-test comparison of aerosol element concentrations measured by several different samplers at two different sampling heights, Bondville Road field site, October - November, 1978. N - number of data pairs for the comparison.

Sampler	Calcium			Magnesium			Potassium			Sulfur		
	N	Higher mean	Probab. of equal means	N	Higher mean	Probab. of equal means	N	Higher mean	Probab. of equal means	N	Higher mean	Probab. of equal means
Ground vs. tower												
NCAR	26	Ground	0.159	24	Ground	0.130	22	Ground	0.051	-----	-----	-----
Casella	12	Ground	0.730	12	Tower	0.239	11	Tower	0.456	-----	-----	-----
Streaker	17	Ground	0.154	-----	-----	-----	17	Ground	0.222	17	Ground	0.164**
Dichot	15	Ground	0.265	-----	-----	-----	15	Ground	0.959	15	Tower	0.002**
Samplers on the ground												
Vane, NCAR	27	Vane	0.087	26	Vane	0.267	23	NCAR	0.702	-----	-----	-----
Vane, Streaker	15	Streaker	0.004**	-----	-----	-----	15	Streaker	0.000**	-----	-----	-----
Vane, Dichot	16	Vane	0.364	-----	-----	-----	15	Dichot	0.011*	-----	-----	-----
NCAR, Streaker	14	Streaker	0.005**	-----	-----	-----	13	Streaker	0.001**	-----	-----	-----
NCAR, Dichot	17	Dichot	0.578	-----	-----	-----	16	Dichot	0.069	-----	-----	-----
Streaker, Dichot	8	Streaker	0.011*	-----	-----	-----	8	Streaker	0.001**	11	Streaker	0.065
Vane, Casella	17	Vane	0.081	17	Vane	0.000**	17	Vane	0.005**	-----	-----	-----
NCAR, Casella	17	NCAR	0.270	16	NCAR	0.037*	14	NCAR	0.065	-----	-----	-----
Streaker, Casella	8	Streaker	0.001**	-----	-----	-----	8	Streaker	0.002**	-----	-----	-----
Dichot, Casella	9	Dichot	0.244	-----	-----	-----	9	Dichot	0.044*	-----	-----	-----
Funnel, Vane	30	Vane	0.242	32	Vane	0.232	29	Vane	0.810	-----	-----	-----
Funnel, NCAR	26	Funnel	0.043*	25	Funnel	0.332	23	NCAR	0.258	-----	-----	-----
Funnel, Casella	16	Funnel	0.102	16	Funnel	0.001**	16	Funnel	0.002**	-----	-----	-----
Funnel, Streaker	15	Streaker	0.004**	-----	-----	-----	15	Streaker	0.000**	18	Streaker	0.004**
Funnel, Dichot	15	Funnel	0.103	-----	-----	-----	15	Dichot	0.031*	15	Funnel	0.085
Samplers on the tower												
NCAR, Streaker	19	Streaker	0.000**	-----	-----	-----	18	Streaker	0.000**	-----	-----	-----
NCAR, Dichot	18	NCAR	0.310	-----	-----	-----	18	Dichot	0.000**	-----	-----	-----
NCAR, Casella	15	NCAR	0.431	15	NCAR	0.153	15	NCAR	0.017*	-----	-----	-----
Casella, Streaker	11	Streaker	0.000**	-----	-----	-----	10	Streaker	0.000**	-----	-----	-----
Casella, Dichot	11	Dichot	0.564	-----	-----	-----	11	Dichot	0.001**	-----	-----	-----
Streaker, Dichot	13	Streaker	0.000**	-----	-----	-----	13	Streaker	0.000**	13	Streaker	0.848

* Differences significant at the 5% level.

** Differences significant at the 1% level.

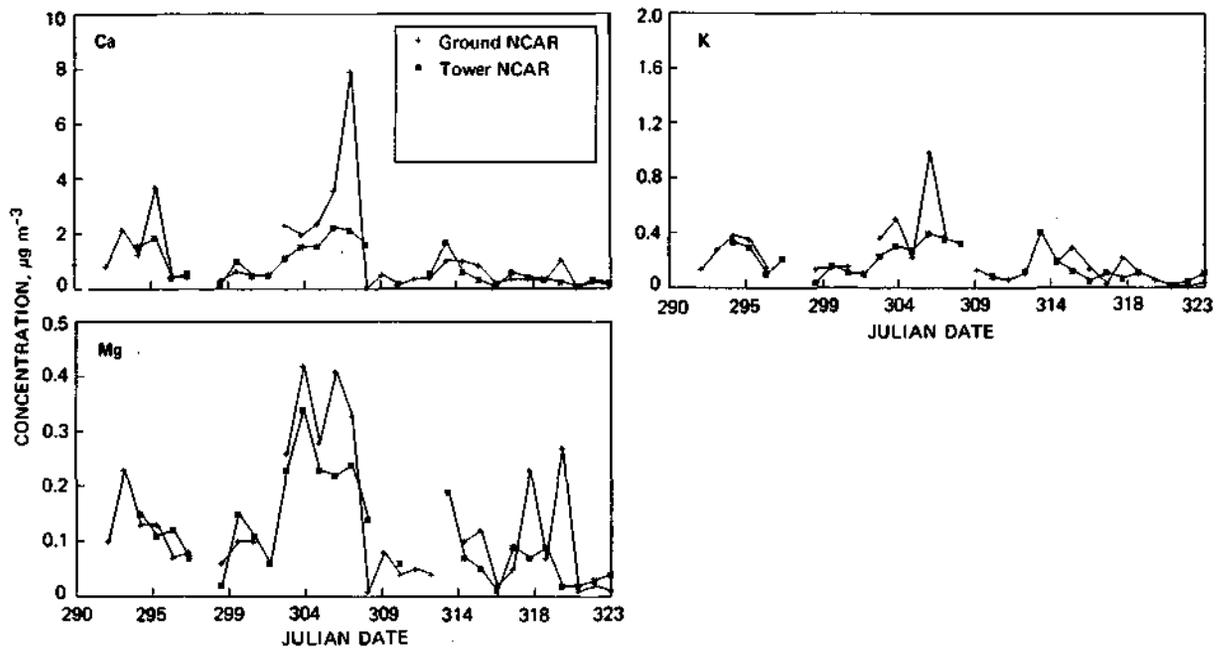


Figure 24. Comparison of airborne element concentrations measured by NCAR samplers at two heights at the Bondville Road sampling site.

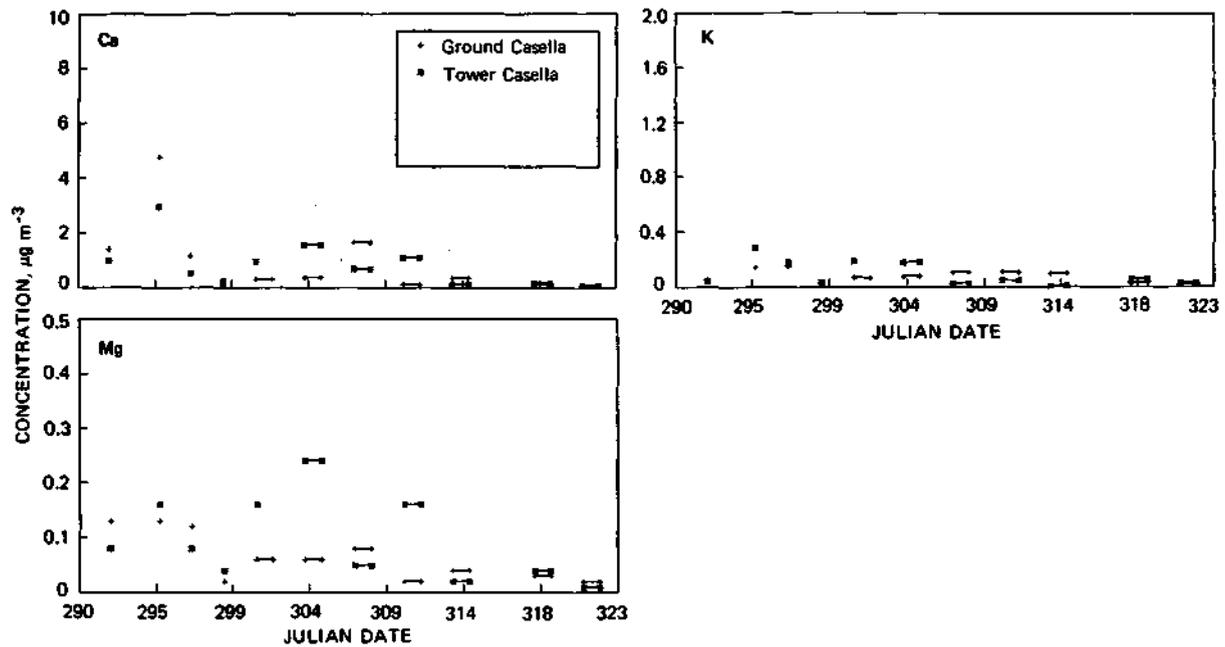


Figure 25. Comparison of airborne element concentrations measured by Casella impactors summed over particle size at two heights at the Bondville Road sampling site.

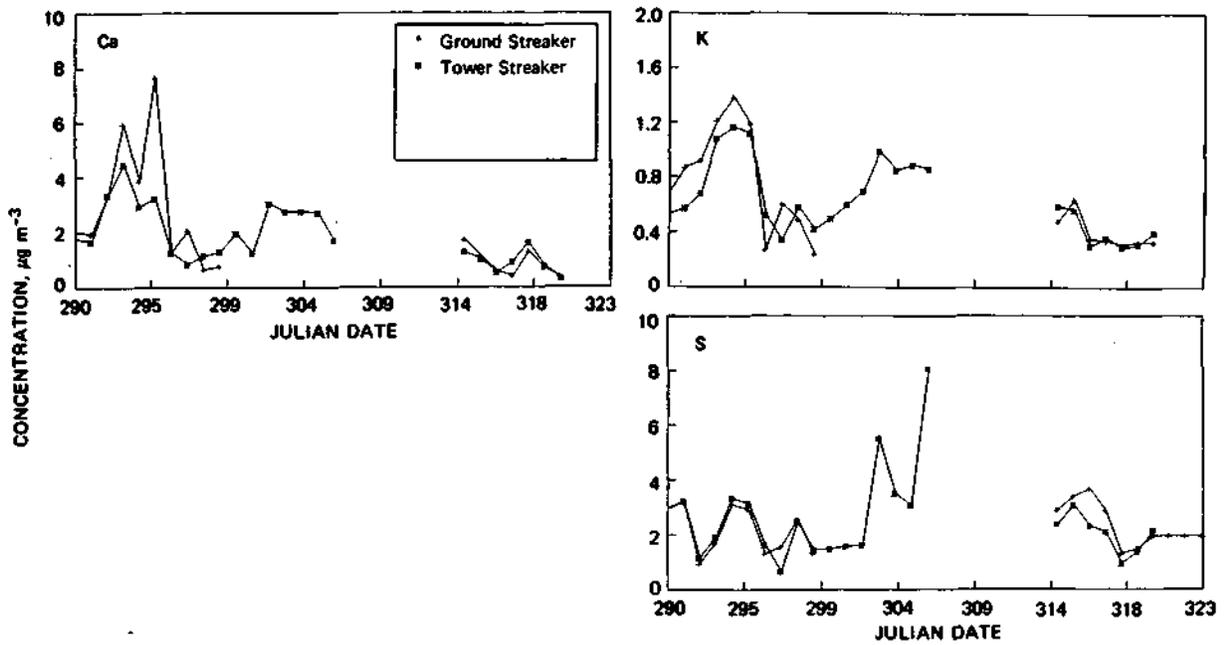


Figure 26. Comparison of airborne element concentrations measured by Streaker samplers at two heights at the Bondville Road sampling site.

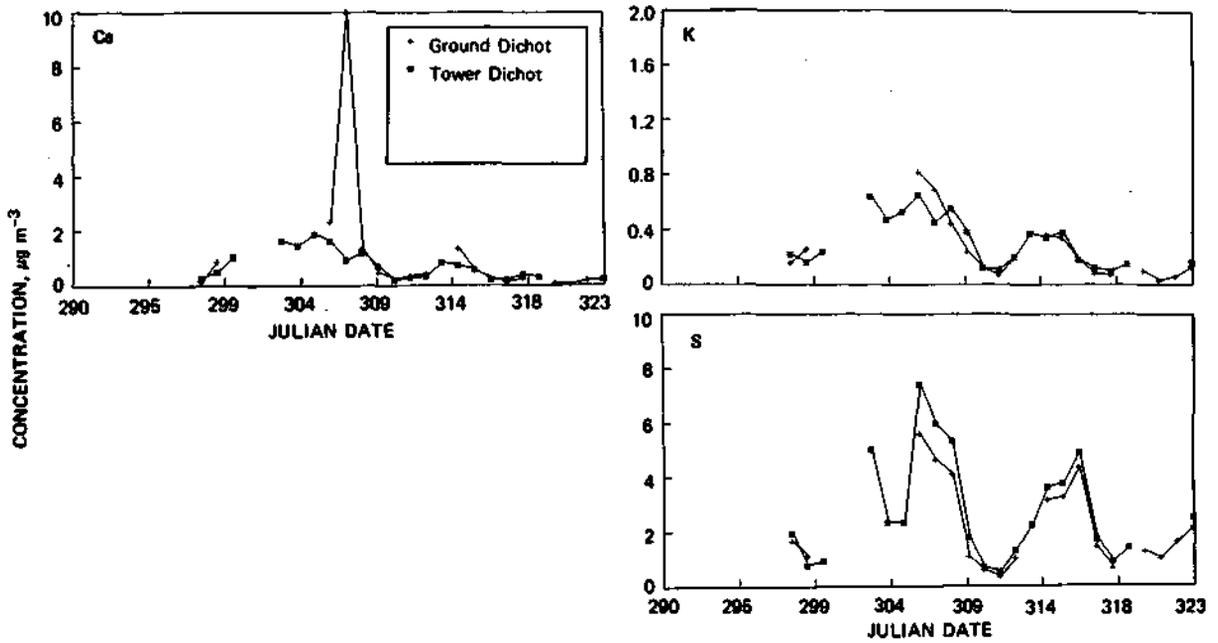


Figure 27. Comparison of airborne element concentrations measured by dichotomous virtual impactors at two heights at the Bondville Road sampling site.

significantly (5%). Concentrations of S were significantly (1%) higher on the tower than the ground, contrary to the streaker measurements, for which no significant differences were found between heights. The figure shows very similar time variations on the tower and ground for each individual element. For Ca and K, the differences in means appear to have been caused mostly by one high concentration at ground level. For S, there were small, but consistent differences in concentration over many points.

4.2.4.2 Comparisons of Six Samplers on the Ground

In a case of multiple comparisons such as this, it must be recognized that a certain number of "significant" differences will occur simply by chance. Statistical rigor requires that special methods be used to compensate for such occurrences in the assignment of significance. (See, e.g., Gatz, 1979.) We have not taken these extra steps at this point. However, the validity of the results is strengthened by their consistency across elements, and the number of significant differences found appears to be far larger than expected simply due to chance.

Results of paired t-tests are given in Table 28, and simultaneous time series plots of five of the six samplers appear in Figure 28. The funnel sampler data are not shown, but are quite similar to those of the vane sampler, as may be seen by comparing daily measurements in Tables 24-27.

Ca was measured by all six samplers on the ground, enabling 15 separate pairwise comparisons. The streaker sampler measurements were significantly higher than those of the dichotomous sampler at the 5% level, and higher than those of all other samplers at the 1% level. The only other significant difference between samplers on the ground was that the funnel sampler measured higher concentrations than the NCAR sampler (5% level).

Mg was measured by four samplers on the ground, enabling 6 separate pairwise comparisons. The Casella impactor measured Mg concentrations significantly smaller than the other three samplers—smaller than the vane and funnel samplers at the 1% level and smaller than the NCAR sampler at the 5% level.

K was measured by all six samplers on the ground, again enabling 15 separate pairwise comparisons. Here again the streaker measurements were significantly (1%) higher than those of the other five samplers. The Casella impactor, in addition to giving lower values than the streaker, also gave significantly lower values than the vane and funnel (at 1%) and the dichotomous sampler (at 5%). The dichotomous sampler also measured concentrations significantly higher (at 5%) than the vane and the funnel.

S was measured by three samplers on the ground, enabling three separate pairwise comparisons. Only one significant difference was found. The streaker measurements were significantly higher than those of the funnel (at the 1% level).

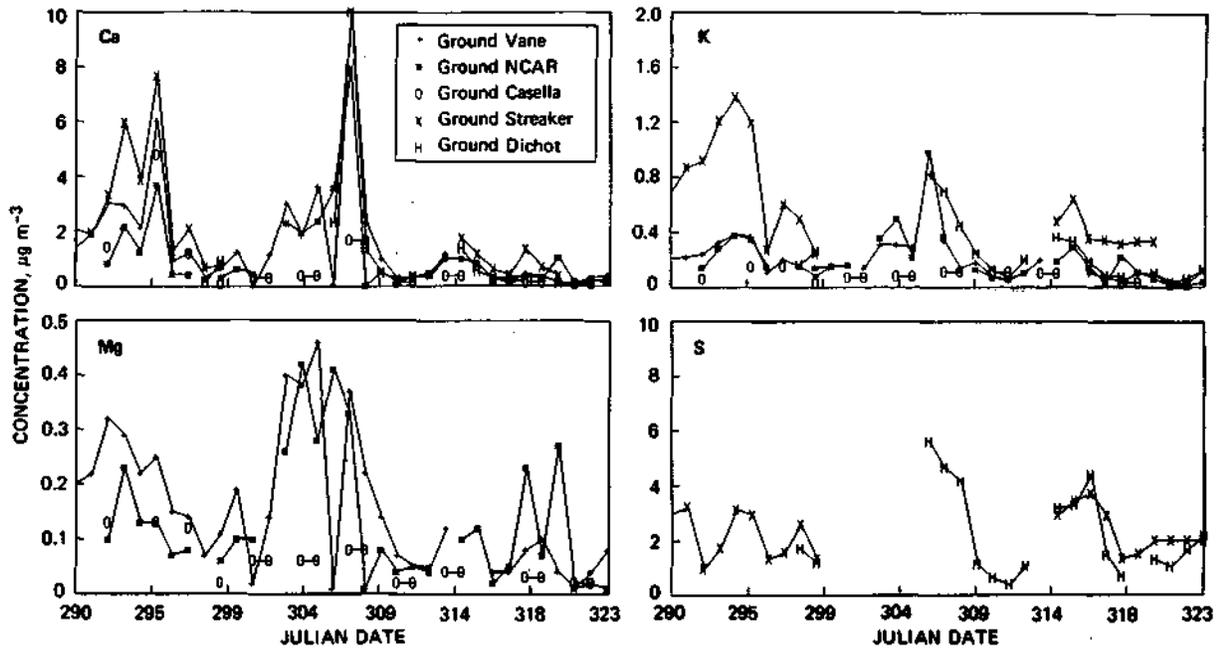


Figure 28. Comparison of airborne element concentrations measured by five samplers at ground level at the Bondville Road sampling site.

4.2.4.3 Comparisons of Four Samplers on the Tower

Results of the pairwise t-tests are given in Table 28, and comparative time series plots appear in Figure 29.

Ca was measured by all four samplers, enabling six separate pairwise comparisons. The concentrations measured by the streaker sampler were significantly higher than those of the other three samplers at the 1% level. No other significant differences were found.

Mg was measured by two samplers, allowing one comparison. No significant differences were found.

K was measured by four samplers, allowing six pairwise comparisons. The streaker results were significantly higher than those of the other three samplers at the 1% level. The dichotomous sampler gave significantly higher concentrations (1%) than the NCAR and Casella samplers, and the NCAR sampler gave higher concentrations (5%) than the Casella. Thus, the Casella sampler gave significantly lower values than all the other samplers.

S was measured by two samplers, allowing just one comparison. The observed difference was not significant.

In summary, two samplers were found to have major differences from the others, based on their measurements of Ca, Mg, K, and S. The differences between samplers are diagrammed in Figure 30.

The streaker gave significantly higher Ca and K concentrations (at the 1% level in all except one case) than all other samplers, both on the ground and tower. The streaker also gave significantly (1%) higher S concentrations than the funnel on the ground, but it was not significantly different from the dichotomous sampler for S, either on the ground or on the tower. Comparison of the streaker results for the other elements in Tables 22 and 23 with those for the same elements measured by the dichotomous sampler (Tables 20 and 21) show similar differences between samplers. The streaker-measured median or mean concentrations were typically higher than the sum of the corresponding fine and coarse dichotomous concentrations by factors of two or more. Recall, however, that the results reported for the two kinds of samplers were not measured over the same time periods.

The Casella impactor yielded concentrations that were frequently lower than those from the other samplers. For Ca, the Casella was significantly lower than the streaker (only), on both the ground and the tower, whereas for K it was significantly lower than all the other samplers at both heights (except the NCAR on the ground). It was also significantly lower than the samplers that measured Mg on the ground, but not significantly different from the NCAR, the only other sampler to measure Mg on the tower.

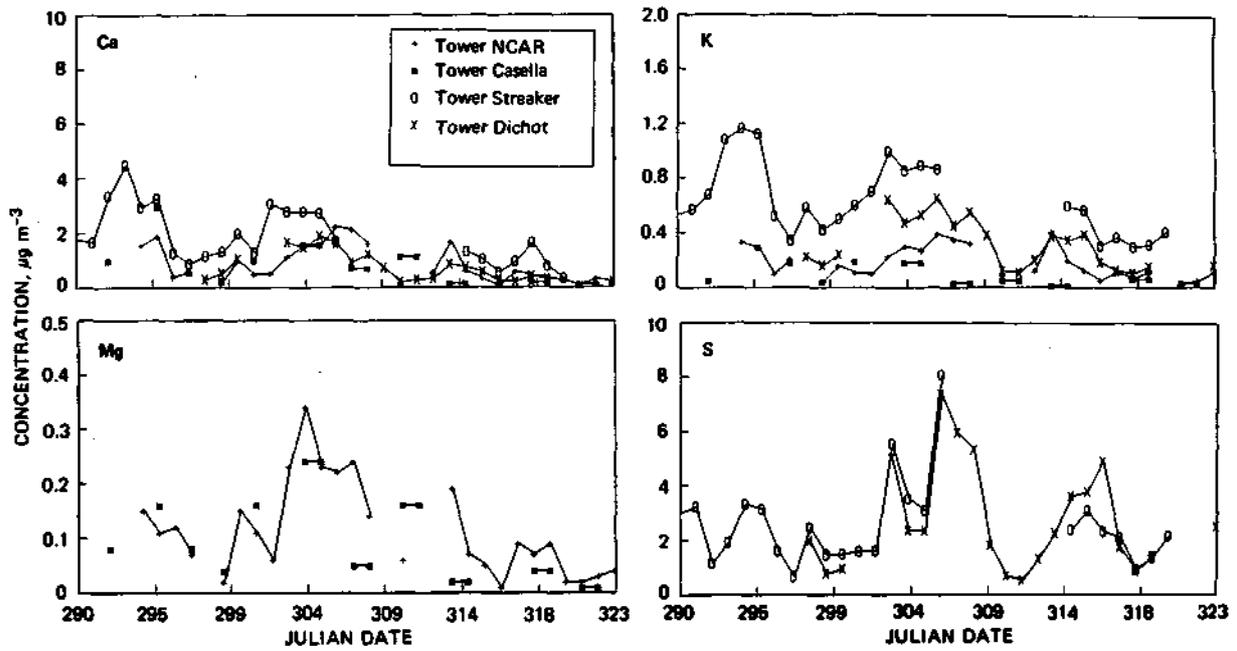
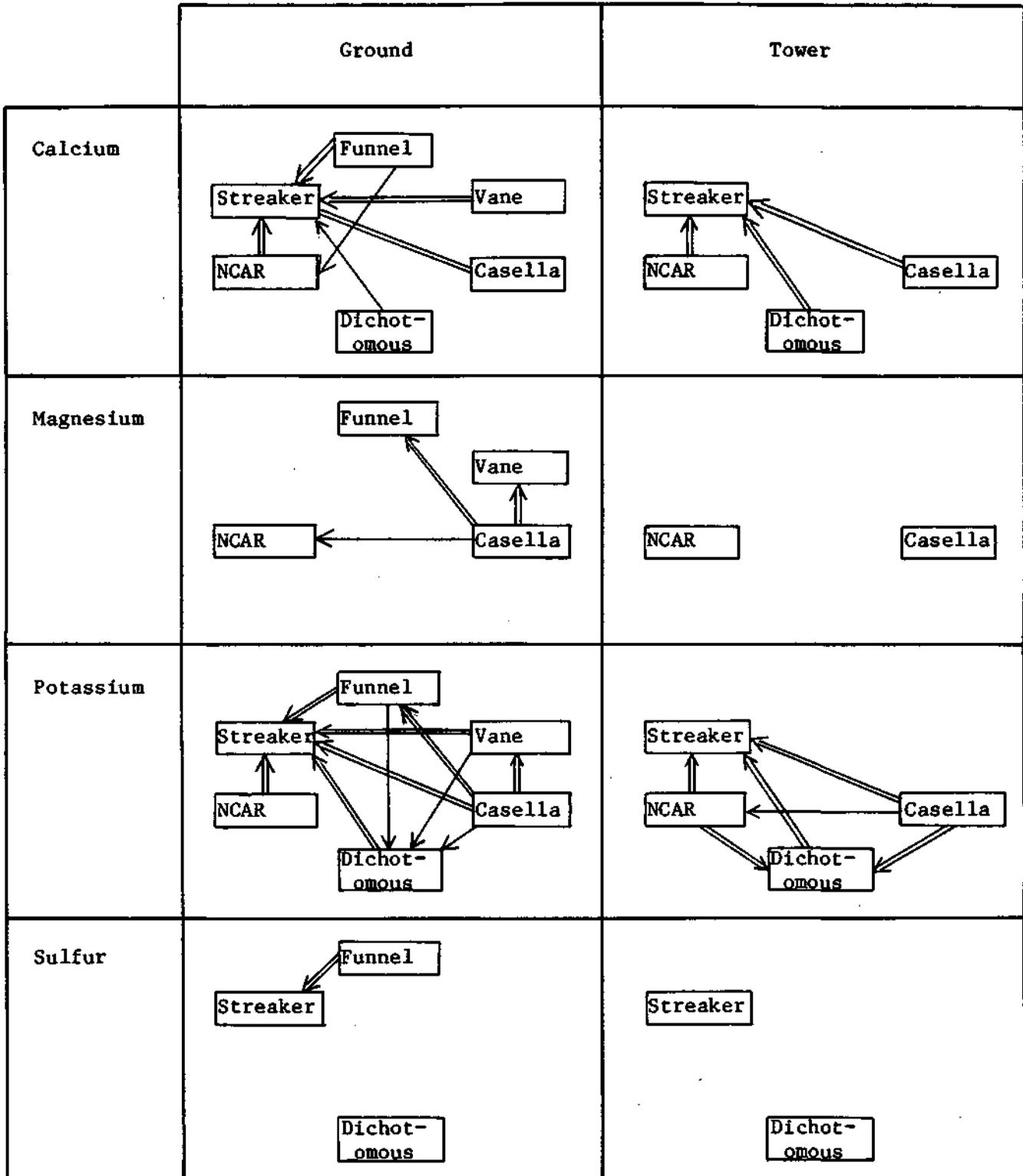


Figure 29. Comparison of airborne element concentrations measured by four samplers on the tower at the Bondville Road sampling site.

Figure 30. Diagram of significant differences between element concentrations measured by different samplers on the ground and on the tower. A single arrow indicates 5% significance, a double arrow 1%. The sampler toward which the arrow points had the higher mean concentration.



Only a few significant differences were found that did not involve either the streaker samplers or the Casella samplers. The dichotomous samplers gave significantly higher concentrations for K (but not for Ca) than the funnel and vane on the ground, and for K (but not Ca) than the NCAR on the tower.

4.3 PRECIPITATION COMPOSITION

A summary of the concentrations of elements, ions, and insoluble matter in event precipitation samples collected at the Bondville Road field site between 30 September 1979 and 3 August 1981 is presented in Table 29. Medians and volume-weighted means of the mass concentrations are shown, along with maximum and minimum values. The volume-weighted mean concentrations in units of ueq/L are also shown, and summed to show the anion/cation balance. The table indicates that, by mass, SO_4 and NO_3 were the major anions and Ca and NH_4 the major cations. By equivalents, the same two anions dominated, but SO_4 was somewhat more important, exceeding NO_3 by a factor of 2.3, while H was by far the dominant cation. Approximately 40% of the total impurities (by mass) was insoluble (i.e., retained on the filter), judging from either the median or the volume-weighted mean total and insoluble residue values.

Table 29. Precipitation impurity abundances for 191 event samples collected at Bondville, Illinois, between 30 September 1979 and 3 August 1981.

	N	mg/L			Volume weighted mean	ueq/L Volume weighted mean
		Minimum	Median	Maximum		
Cations						
H	191	0.000	0.055	1.318	0.066	66
Na	191	0.002	0.070	0.501	0.079	3.43
Mg	191	0.001	0.022	0.493	0.031	2.55
K	191	0.001	0.017	0.228	0.025	0.64
Ca	191	0.004	0.169	3.31	0.244	12.2
NH ₄	191	0.010	0.260	2.21	0.340	18.8
					Sum	103.6
Anions						
Cl	191	0.000	0.170	0.650	0.166	4.68
NO ₃	191	0.010	1.50	6.88	1.74	28.1
SO ₄	191	0.050	2.43	12.4	3.12	65.0
					Sum	97.8
Total insol residue	139	0.00	4.16	93.6	3.93	
Total residue	139	2.06	10.6	103.1	9.71	
pH	191	2.88	4.26	7.05	4.18	

5 DISCUSSION

5.1 QUESTIONS THAT MOTIVATED THIS WORK

We first address three major questions that were posed when this work began. They are:

1. What elements from the earth's crust are present in the air and in precipitation?
2. What fraction of atmospheric aerosols or precipitation impurities came from crustal sources, and what are the frequency distributions of these contributions?
3. What are the chemical mechanisms linking crustal materials in aerosols and precipitation? Specifically, what fractions of alkaline aerosols dissolve in water as a function of time, dilution ratio, and pH?

5.1.1 Crustal Elements in Air and Precipitation

Figure 31 compares our local measurements of alkaline elements in air and precipitation with the most abundant elements in global average rock, shale, limestone, and soil. The element abundances in the various media are normalized to K to provide a first indication of possible sources. K was chosen for the normalization because measurements of it were available for both the global averages and for the local aerosols and precipitation, and also because it has a relatively constant abundance in all the materials compared. In the figure, 12 elements are listed (left to right) in order of their abundance (mass fraction) in global average rock (Mason, 1966), which is represented by the first (leftmost) bar for each element. Two of these elements were not able to be measured by XRF in the aerosols, and several others were not measured in precipitation. It should be noted that the measurements in precipitation were for soluble portions only, while those of the other materials were of the total element content.

Figure 31 shows that the Si/K ratio in coarse aerosol was greater than in the fine aerosol, but somewhat less than those of all the global averages. One may expect some fractionation losses of Si during crustal aerosol formation, since large quartz (SiO_2) grains would either not become airborne, or would soon deposit gravitationally.

For Al, the ratio in coarse aerosol was greater than in fine aerosol by a factor of more than 10, about equal to the ratio in limestone, and somewhat less than that in the other crustal materials.

The Fe/K ratio was also greater in coarse than in fine aerosols; the coarse aerosol ratio was very close to that of soils, and exceeded that of the other crustal materials.

The coarse aerosol Ca/K ratio again exceeded that of the fine, and was intermediate between that for limestone and those of the other crustal materials, including soil. The ratio in precipitation (soluble portions only) was also intermediate between soil and limestone, and was somewhat larger than that of the coarse aerosols.

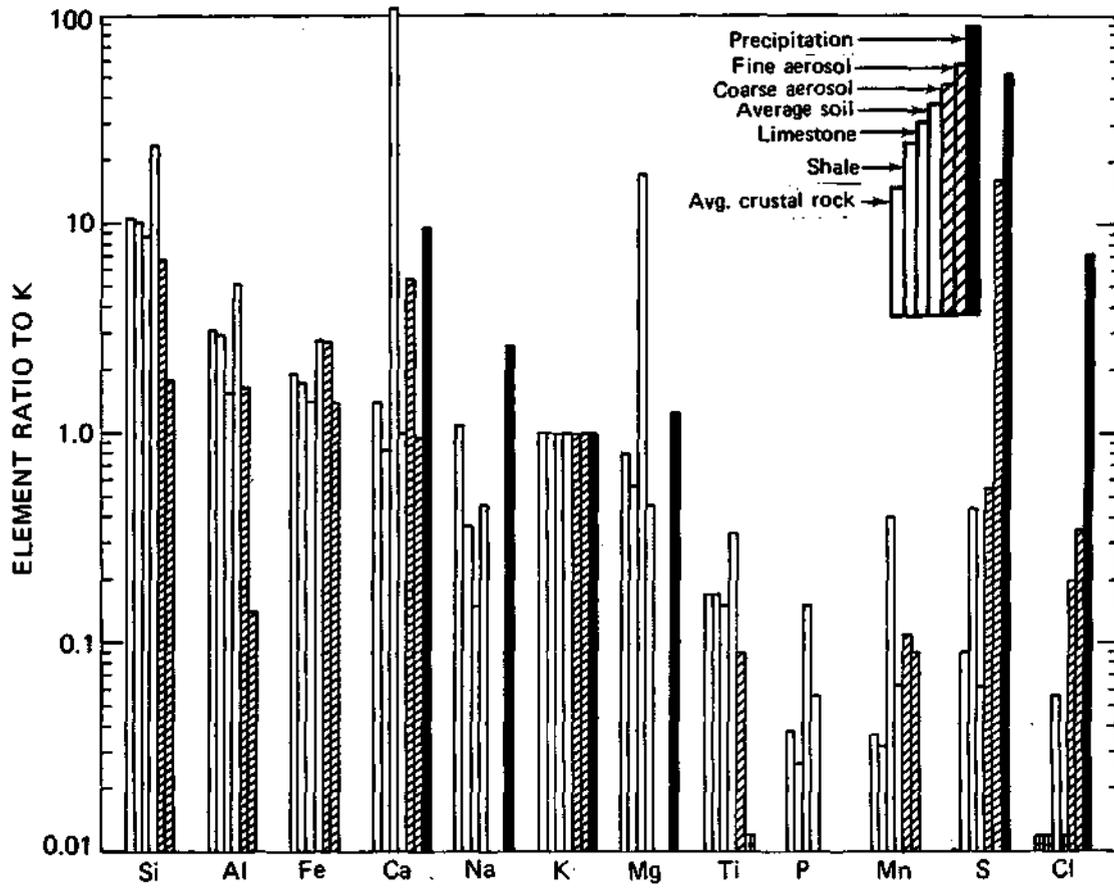


Figure 31. Average crustal rock, shale, and limestone data from Mason (1966); average soil data from Vinogradov (1959). Aerosol and precipitation data were measured in this study.

Na was not measured in aerosols, but its ratio to K in precipitation was greater than that of all of the crustal materials, probably reflecting sea salt or road deicing salt as a major source of Na in precipitation.

Mg was also not measured in the aerosol, but its ratio to K was, like that of Ca, intermediate between limestone and the other crustal materials.

Aerosol Ti was much like Si, having a ratio to K in coarse aerosol that was greater than that of the fine aerosol, but somewhat less than those of the average crustal materials.

P was not measured in precipitation, and is not shown for aerosols, since its concentrations in aerosols were usually below detection limits.

Mn/K ratios in fine and coarse aerosols were similar, and both were intermediate between those of soil and limestone.

S and Cl were similar to each other, but different from all the other elements in Figure 31 in that their ratios to K were greater in aerosol than in the crustal materials, greater in fine than in coarse aerosol, and even greater in precipitation. These differences undoubtedly are related to the fact that there are appreciable atmospheric concentrations of these elements in gaseous form, and to possible differences in mechanisms of precipitation scavenging, but the details are not at all clear.

A clear indication of the crustal elements in aerosols and precipitation can be obtained from factor analysis of elemental concentrations in the two kinds of samples. Table 30 shows loadings tables from factor analyses of fine and coarse aerosols collected on the ground at the Bondville Road field site. For the fine aerosol, factor 1 shows high loadings for Ca, Si, K, and total mass, strongly suggesting a crustal source. Fe and Mn were, notably, not on this factor, but on factor 3 with Zn, suggesting an anthropogenic source of fine metals. For the coarse aerosol, factor 1 had high loadings of Mn, Ca, total mass, K, Fe, Si, and Al, and is clearly a crustal source.

Table 31 is a loadings table from the factor analysis of the event precipitation data described earlier. Again, factor 1 had high loadings for Ca, Mg, K, and total insoluble mass, and must be considered to indicate a crustal source. Na was not among these elements, but on factor 3 with Cl, indicating a sea salt or road salt source.

In summary, of the 12 most abundant elements in average crustal rock, all but P were detected in aerosols and/or precipitation. Ratios to K and factor analyses strongly suggest crustal sources for Si, Al, Fe, Ca, K, Mg, Ti, and Mn in aerosols (at least in coarse aerosols), and for Ca, Mg, and K in precipitation. Other studies (e.g., Gatz et al, 1984) indicate that Al and Fe in precipitation are also likely to have a crustal source.

Table 30. Loadings table from factor analysis on airborne element concentrations measured at ground level, Bondville, fall, 1978, based on correlations of concentrations about the mean.

A. Fine particles (< 2.5 μm).

	Factor			
	1	2	3	4
Ca	0.95			
Si	0.94			
Total mass	0.78	(0.43)		
K	0.76			
Pb		0.95		
Br		0.94		
Zn		0.68	0.67	
Fe			0.84	
Mn			0.80	
Cl				0.95
S	0.56	0.53		-0.56
<hr/>				
Variance explained (%)	33	27	19	13
<hr/>				
Cumulative variance (%)	33	60	79	93

B. Coarse particles (2.5 - 15 μm).

	factor		
	1	2	3
Mn	0.97		
Ca	0.93		
Total mass	0.91		
K	0.91		
Fe	0.87		
Si	0.87		
Al	0.84		
Br		0.88	
Pb		0.85	
Zn		0.79	
S		0.78	
Cl			0.92
<hr/>			
Variance explained (%)	54	28	12
<hr/>			
Cumulative variance (%)	54	82	94

Table 31. Loadings table from factor analysis on event precipitation samples.

Correlation of concentrations about the mean				
	Factor			
	1	2	3	4
Ca	0.87			
Mg	0.85			
K	0.78			
Total insol	0.73			
NH ₄		0.84		
NO ₃		0.80		
SO ₄		0.71		0.50
Na			0.90	
Cl			0.83	
H				0.95
<hr/>				
Variance expl'd (%)	29	25	19	13
Cumulative variance (%)	29	54	73	86

5.1.2 Source Apportionment

5.1.2.1 Aerosols

An approximate calculation of source contributions for soil and road dust to summer aerosols at the Bondville Road site has already been published (Gatz et al., 1981). Figure 32 shows the frequency distribution of contributions for these two sources. These results are based on mass balance calculations carried out separately on all 36 filters in the data set.

The equation by which the observed elemental abundance, P_{el} , of any element is related to the compositions and contributions of its sources is

$$P_{el} = \sum P_{el,source} C_{source}$$

where the p's are the elemental mass fractions (in percent) of the elements in the source emissions, and the C's are the fractional contributions of the sources to the total aerosol concentrations. For K, where we assume that soil and road dust are the only sources, the equation is

$$P_K = P_{K,soil} C_{soil} + P_{K,roads} C_{roads}$$

The contribution of soil to airborne K in percent is then $100(p_{K,soil} C_{soil}/P_K)$, and in concentration units (ng/m^3) is the same expression (without the factor of 100, so that it is a fraction, rather than a percent) multiplied by the total mass concentration in ng/m^3 .

Such estimates of contributions to specific element concentrations may be obtained for each sample, and frequency distributions may be plotted, as in Figure 32, and mean or median values obtained. Alternatively, the mean source contributions to total mass (12% for roads, 39% for soils, from Figure 32) may be used for the C's, and measured source compositions for the p's, together with the mean observed total mass concentration, to get approximate values. The calculated contributions to Al, Si, Ti, and Fe at the Bondville Road site in summer, 1978, from soils and road dust (Table 32) were obtained in this way. Estimates are also given in Table 32 for Ca and K, the two elements used in the calculation of source contributions. For these two elements, the calculated and observed total concentrations are, of course, equal. Table 32 indicates that soil contributed 85% of the mass of all these elements except Ca, for which roads contributed 92%.

In Table 32, the agreement between calculated and observed total concentrations for the other elements is reasonable, except for Si, for which the calculated concentration is higher than the observed by a factor of 2.26. This discrepancy was probably caused by the use of source compositions measured on bulk soil and road dust, rather than compositions based on the composition of aerosols derived from the respective source materials. There appears to be a tendency for fractionation of Si during soil aerosol mobilization, such that Si abundances in aerosol material are smaller than those of the bulk material. This would explain the overcalculation of Si concentrations.

VANE SAMPLER - SUMMER 1978

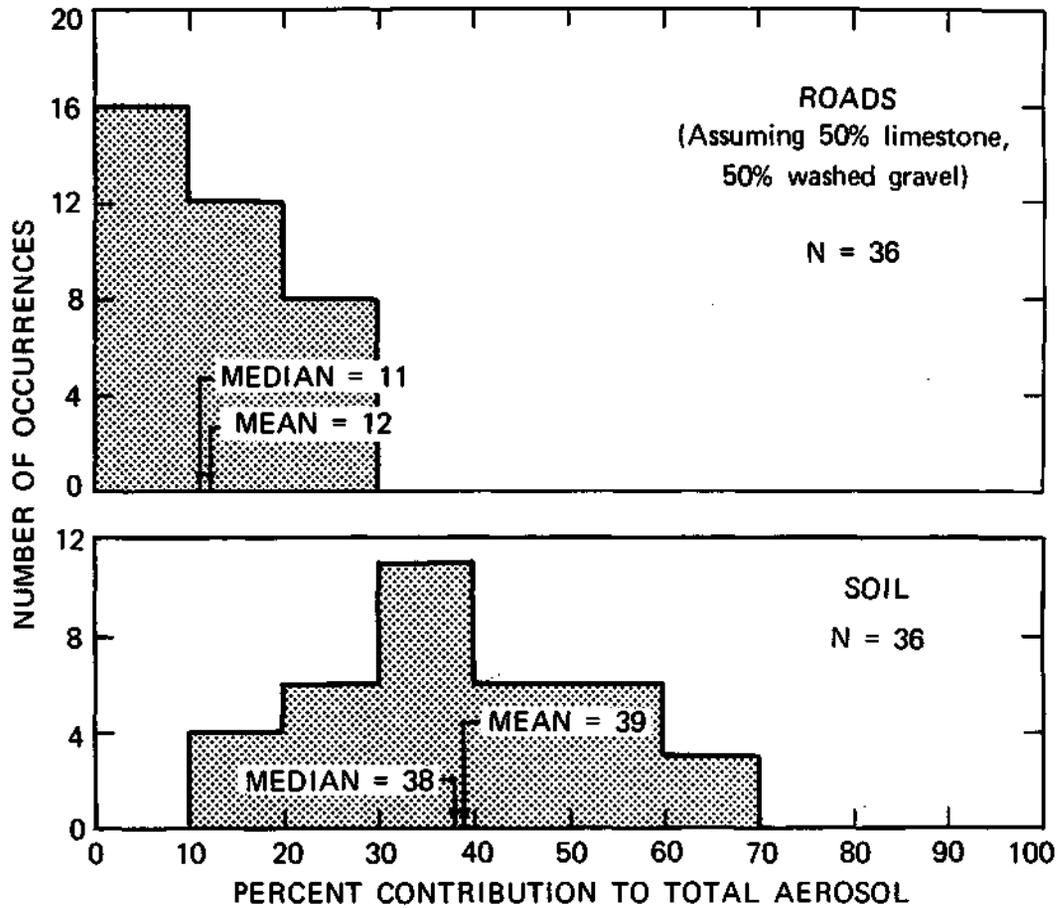


Figure 32. Frequency distributions of percent contributions to total aerosol from unpaved roads and soils, based on data from ISWS vane sampler, summer 1978.

Table 32. Apportionment results for contributions to individual element concentrations from soil and road dust (based on data of Gatz, 1984).

Element	Soils		Roads		Total concentration ng/m ³	
	Concentration, ng/cu m	Percent of calc'd total	Concentration, ng/cu m	Percent of calc'd total	Calculated	Observed
Al	782	92	68	8	850	729
Si	5292	86	861	14	6153	2712
K*	290	92	26	8	316	316
Ca*	71	8	819	92	890	890
Ti	65	94	4	6	69	97
Fe	344	85	61	15	405	526

* The calculation was based on observed K and Ca, for which only two sources were assumed. Thus, the calculated concentrations equal those observed.

Parallel to our laboratory work of generating and analyzing aerosols from source materials has been an effort to measure the composition of crustal aerosols under ambient conditions. Whichever laboratory methods appear to be the most promising for generating aerosol samples from crustal sources, it will be important to compare the composition of the laboratory-generated aerosols against those made on naturally-formed crustal aerosols, if it is possible to identify such natural aerosols.

Consideration of the relative abundances of certain elements in some major crustal source materials suggests that the Ca/Al ratio might be useful in identifying and distinguishing between naturally-formed crustal aerosols. For example, Table 33 shows the Ca/Al ratios that might be expected in aerosols from Champaign, Illinois, area soils and unpaved road materials. These values are based on elemental analyses of resuspended samples of sieved soils and road dust.

A sequence of short (1-4 hr) discrete samples, such as provided by the Florida State University "Streaker" sampler (Nelson, 1977) is useful for such investigations. An additional clue to the nature of ambient aerosols can be found in the timing of crustal element peak concentrations at samplers separated by distance of 10 km or more. Simultaneous peaks (allowing for the timing capabilities of the samplers) suggest a wide-spread phenomenon such as wind erosion, while non-simultaneous peaks would be caused by more localized sources, such as traffic on nearby unpaved roads or soil tilling activities.

Figure 33 is an example of a suspected wind erosion episode. It shows sequences of 2-hr Al concentrations and Ca/Al ratios from streaker sampler measurements at two sites (Weldon and Bondville, Illinois) separated by about 34 km. The simultaneous and relatively persistent (about 24 hr) occurrence of high Al concentrations at two separated sites suggests a wind erosion aerosol. The meteorological situation (cold front accompanied by strong gusty winds) is consistent with this interpretation. Also consistent is the occurrence of Ca/Al ratios of about 0.3 at both sites during the period of high Al concentrations. This value is not quite as small as that suggested for soil aerosols in Table 33, but it is smaller than any of the road dust values, and also occurred simultaneously at separated locations. Further, the mean Si/Al ratios observed on the streaker filters during the same period was 1.91 at Bondville and 1.85 at Weldon. These values are in the range of a number of clay minerals (Rahn, 1976), i.e., between 1 and 2, that is consistent with a soil aerosol strongly influenced by clay minerals released upon impact of saltating (bouncing) soil aggregates with the surface during wind erosion (Bagnold, 1965).

Once an episode of ambient crustal aerosol has been identified, the remaining task is to characterize that aerosol in terms of its elemental abundances (mass fractions). This is not possible for the streaker data because total aerosol mass is not measured. The episode shown in Figure 33 occurred during a field project in which aerosols were also sampled using a dichotomous virtual impactor. This sampler yields both total and individual element masses. Unfortunately, the sampler malfunctioned during the period of interest, and no sample data are available.

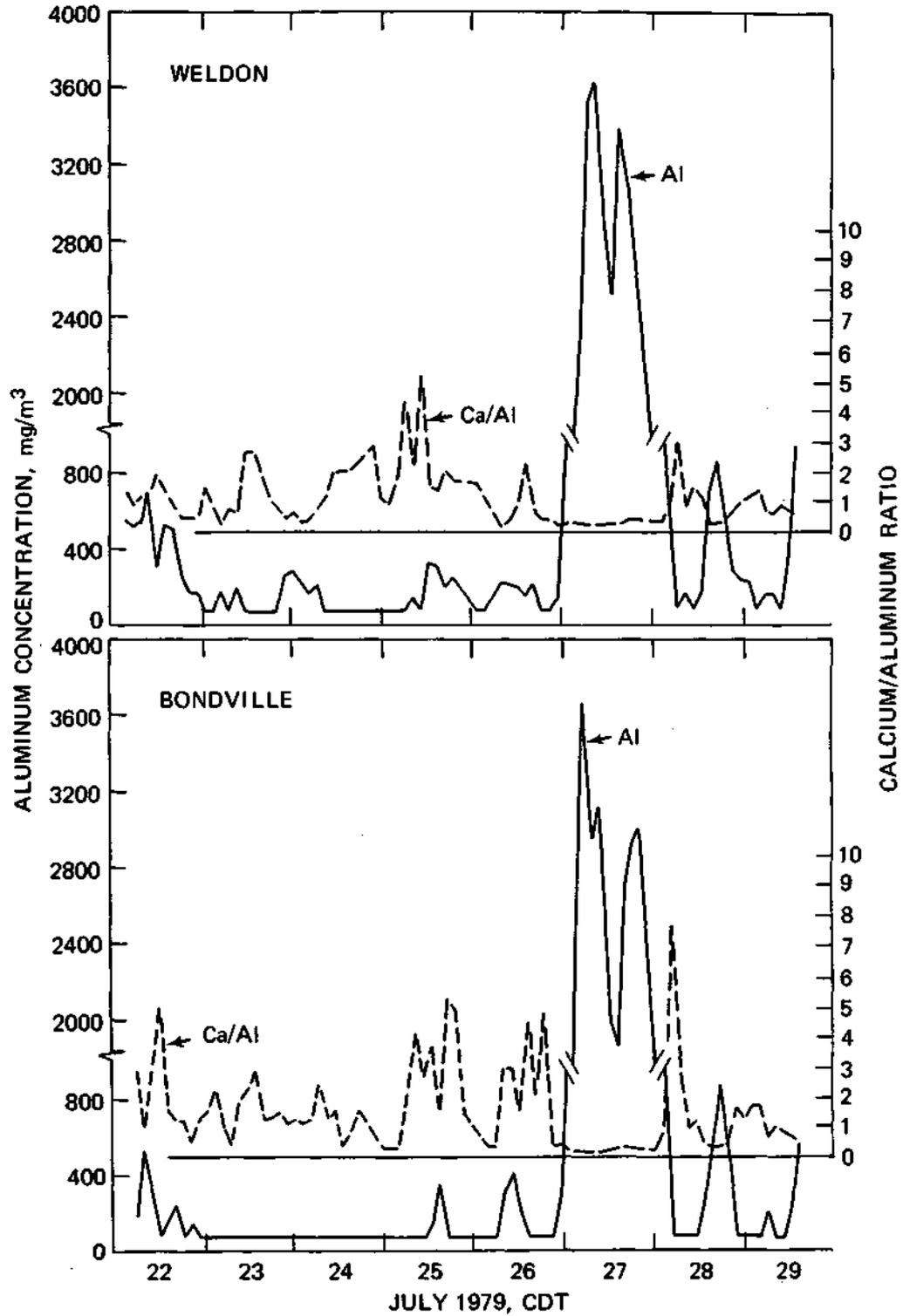


Figure 33. Time variations of Al and the Ca/Al ratio at the Weldon and Bondville, Illinois, sites, showing the simultaneous occurrence of high Al concentrations and low Ca/Al ratios, indicative of a wind erosion episode.

Table 33. Summary of criteria for identifying episodes of ambient aerosols from individual kinds of sources, based on resuspended samples of sieved (53 μ m) source materials.

Source	Aerosol generation mechanism	Occurrence of crustal element peaks at separated sites	Ca/Al (approx)	
			< 2.5 μ m	2.5-15 μ m
Soil	Wind erosion	Simultaneous	< 0.1	< 0.1
Soil	Tilling	Non-simultaneous	< 0.1	< 0.1
Limestone road dust	Vehicle/wind raised	Non-simultaneous	5	11
Washed gravel road dust	Vehicle/wind raised	Non-simultaneous	1 (?) [*]	2 (?) [*]

* Based on a single resuspended sample.

We are currently searching streaquer data on hand for other episodes characteristic of soil wind erosion, as well as soil tilling and road dust from both limestone- and washed gravel-covered unpaved roads. Initial results suggest that a number of such episodes can be identified. It is likely that dichotomous sampler data will be available from some of the these, and will allow estimates of elemental abundances in ambient crustal aerosols.

5.1.2.2 Precipitation

A paper on source contributions, especially from soil and road dust, to precipitation at the Bondville Road site has been submitted for publication (Gatz, 1984). Figure 34 (not shown in the submitted paper) shows the frequency distributions of contributions obtained from separate CEB calculations on 137 event precipitation samples, based on the source compositions in Table 34. These compositions were obtained from known molecular composition (ammonium sulfate, sulfuric acid, nitric acid), the literature (sea salt-Junge, 1963), and our mean measurements of the fine fraction of unsuspended source material (unpaved road dust, soil), and assuming that the Ca and K in precipitation were completely soluble.

In the paper, results were presented where the composition of the soil and unpaved road materials and the soluble fractions of Ca and K in precipitation were varied to test the sensitivity of the results to variability of input values. Resulting variations in results are presented in Table 35. The table shows that apportionment of plausible sources yielded estimates of a 2% contribution of sea salt to the total mass of precipitation impurities, a 32% contribution by ammonium and sulfate (including H_2SO_4), and a 16% contribution from nitrates. Varying the assumed source contributions of source composition (at 100% element solubility in precipitation) suggested that means (and reasonable limits) on the contributions of the two crustal materials might be 11.6% (9-24%) for road dust and 6.6% (3-7%) for soil. Varying the assumptions about the soluble fraction of Ca and K in precipitation showed that for Ca and K solubilities between 50 and 100%, the range of contributions increased (relative to the assumption of complete solubility of both elements) to 11-24% for road dust, and 0-22% for soils. Using Muhlbaier's (1978) mean measured solubilities for Ca and K, the mean road dust contribution increased slightly to 12.0%, relative to the assumption of complete solubility of both elements, and the soil contribution increased by a factor or more than 2, to 15%.

An effort to use extracted soil and road dust sample composition as input to the CEB calculation was unsuccessful. Apparently the extraction technique removed considerably less Ca and K from the source materials than precipitation does, with the result that the sum of the calculated road and soil source contributions exceeded 100% of the measured impurities in the precipitation. Some possible reasons for the limited extractability of these samples are apparent from the experiments discussed next.

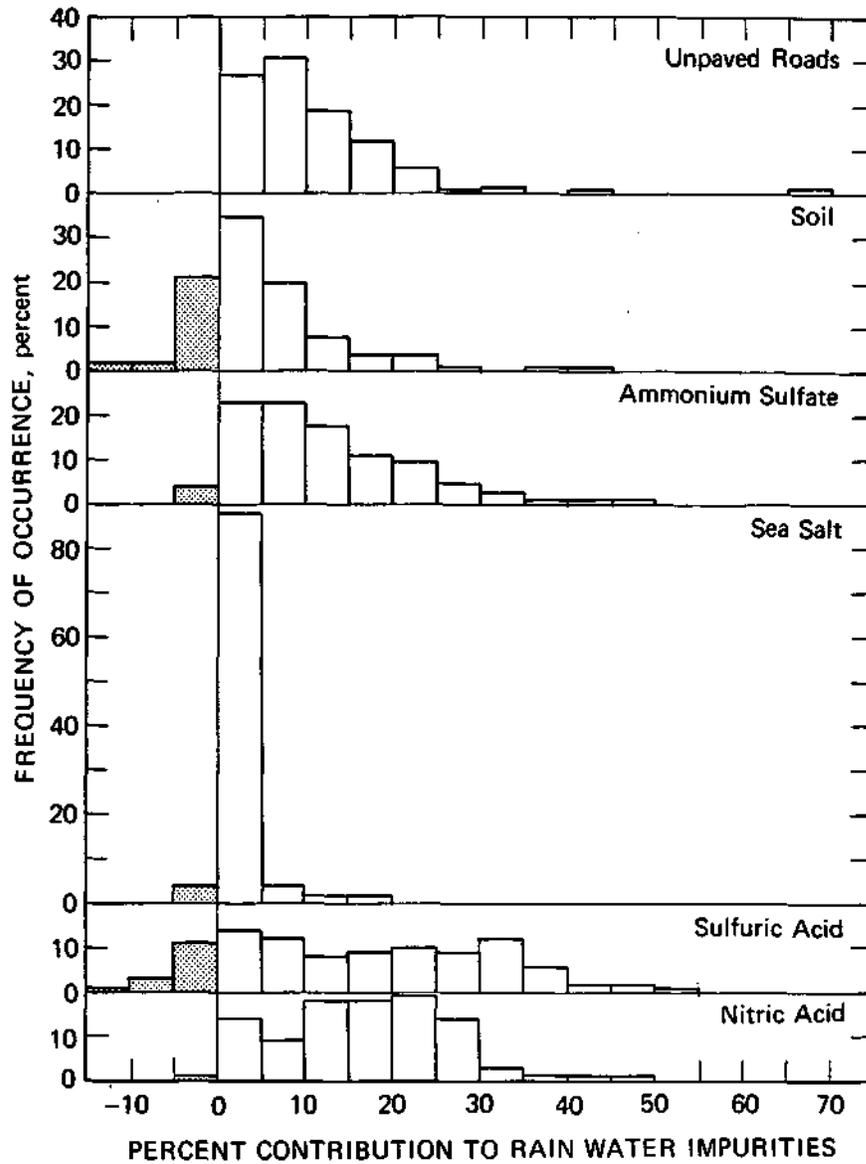


Figure 34. Frequency distributions of percent contributions to rain water impurities for six "sources," based on individual event precipitation samples from the Bondville, Illinois, site.

Table 34. Source (fractional) compositions for CEB analyses.

	Sources assumed					
	Unpaved roads	Soil	Ammonium sulfate	Sea salt*	Sulfuric acid	Nitric acid
Ca	0.1933	0.0095		0.011		
Mg				0.036		
K	0.0094	0.0169		0.011		
NH ₄			0.273			
SO ₄			0.727	0.075	0.979	
NO ₃						0.984
Na				0.298		
Cl				0.536		
H					0.021	0.016

* From Junge (1963), p 165.

Table 35. Summary of results of source apportionment calculations on event precipitation samples collected at the Bondville Road field site, 30 September 1979 - 3 August 1981.

Source	Contribution to total mass, percent			
	Results for		Results for plausible	
	mean source composition		range of source compositions	
	Complete solubility	Incomplete solubility*	Complete solubility	Incomplete solubility**
Unpaved roads	11.6	12.0	9.3 - 24.1	10.8 - 23.5
Soil	6.6	14.7	3.3 - 6.6	0 - 21.5
Ammonium sulfate	12.1	12.1	12.1	11.8 - 12.1
Sea salt	2.4	2.4	2.4	2.4
Sulfuric acid	19.4	19.4	19.4	18.9 - 19.4
Nitric acid	16.0	16.0	16.0	15.6 - 16.0
Total	68.1	76.6	64.6 - 77.3	68.1 - 85.7

* Ca: 94%, K: 64% soluble (Muhlbaier, 1978). (See Table 5, Gatz, 1984.)

** Ca: 50% or 100%, K: 50% or 100% soluble. (See Table 5, Gatz, 1984.)

5.1.3 Assessment of Chemical Mechanisms Involving Alkaline Aerosols in Precipitation Chemistry: Effects of Dilution Ratio, pH, and Time on the Extractability of Elements from Soils.

Figures 5 and 6 show that extracted Ca and Mg (as a fraction of soil mass) generally increase as the dilution ratio increases and as pH decreases.

However, even the most effective extractions were unable to extract all of the respective elements present in the soil samples. For example, the maximum mass fractions of Ca and Mg extracted from soil 7A were 0.35% (pH 4.1, Figure 5) and 0.17% (pH 2.1, Figure 6), whereas the total abundances of Ca and Mg in this sample, as determined by F/AAS (Table 4), were 0.52% and 0.36%, respectively. Thus, the maximum fractions of Ca and Mg extracted during 20 min of shaking were 69% and 46%, respectively, of the total masses of those elements present in the sample.

In contrast to the limited amounts of Ca and Mg that we were able to extract from soil samples, the same elements have usually been observed to be much more soluble in precipitation samples, although the available data on element solubility in precipitation are somewhat limited. Table 36 is a compilation of available data from the literature and some unpublished data of our own on solubilities of Na, Mg, K, and Ca in precipitation. This compilation of alkaline element solubility data deserves more discussion than will be devoted to it here, and we plan to devote a forthcoming paper to such a discussion. For now, we simply would point out that mean solubility percentages for Ca were typically >90% in precipitation, at least in rural areas of the U.S. Mean values for Mg were often >80%, but there was more variability in this case.

Thus, Ca and Mg solubility in precipitation is typically considerably greater than the best we were able to achieve by extraction of soil samples. Of the several variables that are known to, or likely to, affect element extractability, pH cannot account entirely for the observed differences, since the pH values used in the extractions spanned those that occur in precipitation at the sampling site. Other possible causes include dilution ratio, contact time between soil particles and water, and the size distribution of the soil particles. We will consider each of these in the following paragraphs.

Dilution ratio The trends of Figures 5 and 6 were for increasing element extractability with increasing dilution ratio. If the trend continues into the region of typical water:total residue ratios in precipitation, perhaps 100,000 to 200,000 (Figure 4), the fractions of Ca and Mg that could be extracted from soils would be approaching those typical of precipitation.

Contact time Another possible reason for the discrepancy between the >80% solubilities for Ca and Mg typical of precipitation samples and the smaller fractions extracted in our experiments has to do with the contact time between the soil samples and the extractant. The results in Figures 5 and 6 indicated maximum extracted fractions of 69% of the Ca present and 46% of the Mg. In these experiments the samples

Table 36. Available data on solubility of alkaline elements in precipitation.

A. Monthly samples from the United Kingdom.

<u>Location, UK</u>	<u>Year*</u>	<u>Mean percent soluble</u>				<u>Reference</u>
		<u>Na</u>	<u>Mg</u>	<u>K</u>	<u>Ca</u>	
Chilton, Berkshire	1972	99	na	na	76	1
	1973	99	98	na	97	1
	1976	99	>94	91	93	2
Leiston, Suffolk	1972	99	na	na	<49	1
	1973	87	99	na	94	1
	1976	99	91	>88	75	2
Lerwick, Shetland Isles	1972	100	na	na	99	1
	1973	100	100	na	99	1
Collafirth, Shetland Isles	1976	100	98	95**	81	2
Plynlimon, Montgomeryshire	1972	99	na	na	62	1
	1973	100	99	na	91	1
	1976	100	87	76	44	2
Styrrup, Nottinghamshire	1972	95	na	na	100	1
	1973	98	97	na	100	1
	1976	97	84	76	83	2
Trebanos, Glamorganshire	1972	100	na	na	<53	1
	1973	99	98	na	98	1
	1976	100	88	93	81	2
Wraymires, Lancashire	1972	99	na	na	<68	1
	1973	100	99	na	94	1
	1976	100	na	93	87	2
	1977	100	>89	94	80	3

* All samples were collected monthly. Monthly samples were analyzed separately in 1972-1973, and composited by quarters for analysis in 1976 and 1977. At Leiston in 1972 samples were collected from February - December only.

** Based on composites from two quarters.

References: 1) Cawse, 1974. 2) Cawse, 1977. 3) Cawse, 1978.

Table 36 (continued)

B. Event wet-only samples from the St. Louis, Missouri, area (Gatz, 1975, unpublished data).

Site No.	Year	Mean percent soluble					
		n*	Mg	n	K	n	Ca
0	1973	10	56	8	53	10	95
	1974	10	89	10	78	10	90
	1975	11	89	8	78	11	95
22	1973	9	67	9	55	9	96
	1975	13	92	12	79	13	98
33	1974	8	85	8	67	8	96
	1975	9	95	9	74	9	99
44	1975	10	88	8	64	10	97
49	1975	11	89	10	78	11	97
79	1974	10	95	10	76	10	96
81	1973	14	80	12	70	14	97
113	1973	11	67	10	50	11	94
	1974	9	84	9	56	9	96
151	1973	13	36	11	60	13	89
	1974	6	87	6	51	6	95
159	1973	7	56	13	55	12	81
300	1973	7	76	7	54	6	94
301	1974	10	87	7	85	10	95
302	1974	5	74	4	54	5	93
303	1975	11	86	10	65	11	96
304	1975	12	87	8	75	12	94

* n = Number of cases.

Table 36 (continued)

C. Event samples (bulk collectors) from the St. Louis area. Soluble fractions computed from network mean soluble and insoluble deposition values reported by Gatz (1980).

Date	No. of sampling sites	Mean percent soluble			
		Na	Mg	K	Ca
11 Aug 1972	24	49	81	90	99
9 Aug 1974	56	61	80	61	98
13 Jul 1975	78	—	—	84	—
18 Jul 1975	74	—	—	90	—
19 Jul 1975	66	—	65	92	94
31 Jul 1975	61	—	—	91	—
1 Aug 1975	78	—	—	98	—
13 Aug 1975	71	—	—	99	—
14 Aug 1975	65	—	68	85	93
	Mean	55	74	88	96

D. Weekly wet-only and bulk samples from Glen Ellyn, Illinois (Gatz, 1982, unpublished data).

Sample type*	Site number	No. of samples	Median percent soluble			
			Na	Mg	K	Ca
Wet-only	1	44	96	84	46	98
Dry-only	1	24	88	38	20	55
Bulk	1	40	89	75	28	92
Bulk	2	28	92	65	22	84

* Seasonal distribution of cases varies between sample types. Other data suggest that solubility varies with season.

Table 36 (continued)

E. Two event samples from Chalk Point, Maryland (six sites).

Year*	Mean percent soluble							
	n	Na	n	Mg	n	K	n	Ca
1976	10	94	9	>72	10	60	9	93

* Sample dates: 1 April and 29 July, 1976.

F. Summary of Parts A - E.

Location	Year	No. of sites	Mean percent soluble**			
			Na	Mg	K	Ca
United Kingdom (monthly bulk samples, year around)	1972	7	99	na	na	<72
	1973	7	98	99	na	96
	1976	7	99	>90*	>87	78
	1977	1	100	>89	94	80
St. Louis, Missouri (event wet-only samples, summer)	1973	7	na	63	57	92
	1974	7	na	86	67	94
	1975	7	na	89	73	97
St. Louis, Missouri (event bulk samples, summer)	1972-	24-78	55	74	88	96
	1975					
Chalk Point, Maryland (two bulk events)	1976	6	94	>72	60	93
Glen Ellyn, Illinois (weekly wet-only samples, year around)	1979-	1	96	84	46	98
	1981					
Glen Ellyn, Illinois (weekly bulk samples, year around)	1979-	2	91	70	25	88
	1981					

* Six sites only.

** Values for Glen Ellyn are medians.

were shaken for 20 min to simulate the likely contact time between particles and water in a typical convective storm.

Contact times would be longer in stratiform precipitation situations, and in a typical sampling situation, the particles would be in contact with water for an additional period of time after deposition in the collector until the collector was retrieved from the field and the sample arrived in the laboratory and was filtered. This additional contact time would usually range from a minimum of about 1 day to perhaps 10 days for weekly sampling and shipping to a central analytical laboratory.

The results shown in Figures 7, 8, and 9 show that Ca and Mg extractability increased with time, at least for about 4 days. Comparison of the 4-day extractions with the shortest (20-min) extractions in Figures 7 and 8 indicates that 4-day extractions increased the amount of Ca extracted by about 40% at pH 3 and by about 70% in deionized water, compared to the 20-min extraction. The corresponding figures for Mg were 50% at pH 3 and 83% in deionized water. The relative increases at 4 days appear to be inversely related to the acidity of the extractant—the more acidic the extractant (in the range 3.0-5.8) the smaller the relative increase at 4 days. These results cannot be related directly to the results in Figures 5 and 6, since the pH of the respective extractants in the two experiments differed, but they still clearly indicate that extractant yields increase with contact times, at least during the first 4 days and for pH values in the range of 3-6.

Particle size distribution The extracted soil samples were previously screened to remove aggregates larger than 53 μm , thus leaving aggregates up to that diameter in the samples. The size distributions of typical atmospheric aerosols are known to be quite different, however, having one mode (the accumulation mode) between 0.1 and 1.0 μm , and another between 1.0 and 10 μm (the coarse mode). Thus, the particles that are likely to enter precipitation are considerably smaller than those used in our extractions. Smaller spherical particles, smaller particles would have larger surface/volume ratios than larger particles, and thus would be susceptible to more rapid dissolution in liquids. Further, smaller particles would be more likely to be completely dissolved during a given period of contact with water than the same mass of larger particles. Thus the size of the particles used in the extractions could account for at least some portion of the observed differences in solubility.

5.2 OTHER ISSUES RAISED DURING THE WORK

Beside the issues surrounding the original objectives of this work, there were several other issues that arose during the course of the work that deserve at least brief comment. Several of these additional issues occurred in connection with the mineralogical measurements made by Dr. Briant Davis. Another is the difficulty of properly sampling large atmospheric particles.

5.2.1 Mineralogical Measurements

The issues related to the mineralogical measurements include: 1) the possibility of using mineral tracers in CEB calculations, 2) observations of high gypsum concentrations on local filter samples, 3) indications of long-distance transport of soil dust, and 4) the anomalous lack of a very abundant local soil mineral in local aerosols.

Comparison of the mineral composition of soils and unpaved road materials (Table 9) show differences sufficient to suggest that apportionment of these two sources in aerosol samples may be possible. Calcite and dolomite would be tracer minerals for unpaved roads, and montmorillonite/vermiculite would be a tracer for soil in such calculations.

The observed mineral composition of the aerosol samples makes it clear, however, that local crustal sources are not the only contributors to the local aerosol. It is well known, of course, that sulfate compounds, formed by atmospheric oxidation of SO_2 during transport, make up a sizable portion of the aerosol mass. Our results show that this fraction was near 50% in four of our seven aerosol samples. In two of these cases, gypsum (CaSO_4) alone accounted for nearly 50% of the aerosol mass. It is possible, of course (Davis *et al.*, 1981) that some sulfate detected may have been an artifact, formed by reactions that took place on the filter substrate or the collected particles.

A bit of evidence that the gypsum formed by reaction of SO_2 or H_2SO_4 with airborne or collected calcite particles (perhaps wet with fog or haze droplets) is shown in Figure 35, plotted from the mineralogical data in Table 9. Although the data points are few, high gypsum abundances never occurred simultaneously with high calcite abundances, suggesting that calcite was consumed in the formation of the gypsum.

Another possible sulfate source is wind blown western soil, which often contains appreciable quantities of gypsum. Such materials would have to have been carried long distances by wind to be sampled in Illinois.

Other evidence that some of the soil materials on the filter came from some distance away is shown by the occurrence, on a few filters, of illite/muscovite or quartz in greater abundance than in any of the local soil samples analyzed. Moreover, the high abundances of these minerals

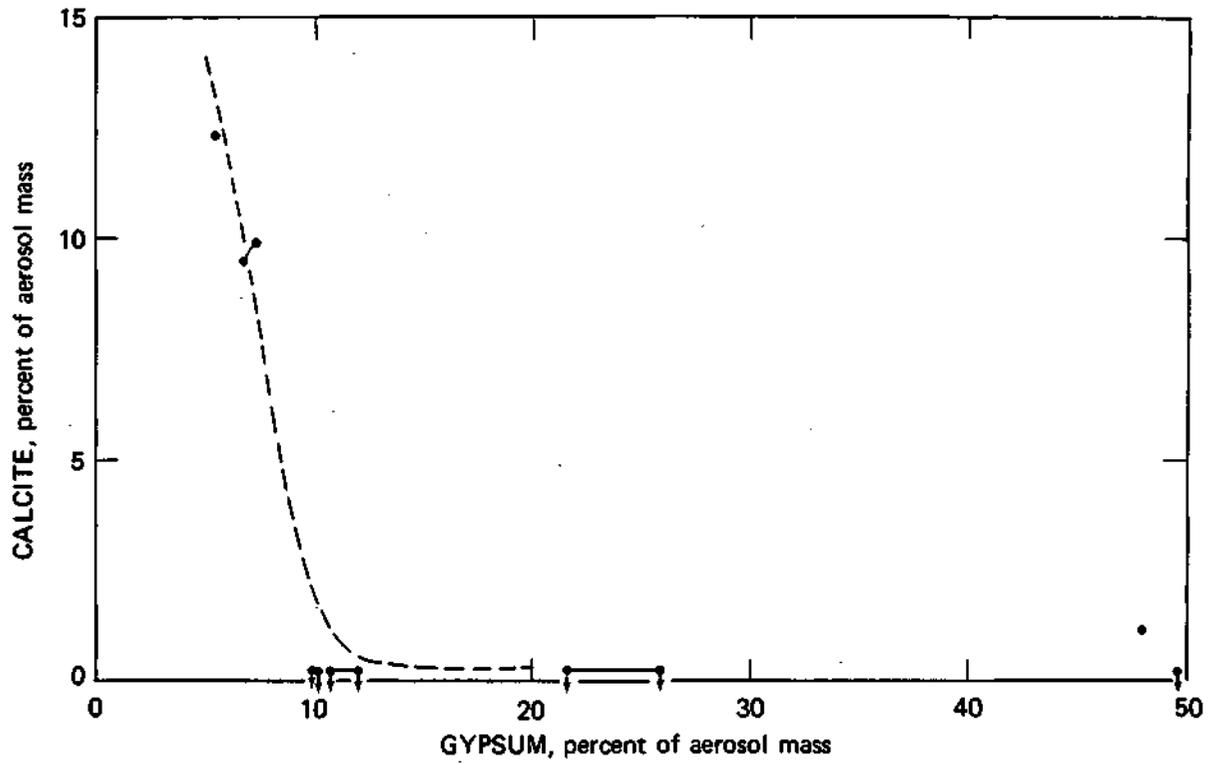


Figure 35. Variation of calcite abundance with gypsum abundance in aerosol samplers from the Bondville, Illinois, site.

on filters also exceeded those of all the separate soil size fractions, so it cannot be argued that the high abundances were created by size fractionation during mobilization of particles from the soil surface. In other words, even if the particles on the filter were 100% soil with the highest observed abundance of, say, illite/muscovite (6.9% in sample 7A5, the 45-53 μm fraction of sample 7A), we could not account for an abundance of, say, 20% illite/muscovite, such as was found on filter Q21.

Additional evidence for a distant source of some of the minerals is found in the fact that illite/muscovite occurs in high concentrations in soils of the southern U.S., and winds were southerly during collection of duplicate samples Q1 and Q2, which had high abundances of illite/muscovite (Table 9). Clearly, soil dust transport on such a scale is feasible. Soil dust from the Sahara has been observed in the West Indies (Prospero et al., 1979; Prospero and Carlson, 1972; Carlson and Prospero, 1972) and dust from Asian deserts has been observed over Alaska (Rahn et al., 1979) and Hawaii (Shaw, 1980).

The picture is complicated by the absence of expandable (i.e., montmorillonite/vermiculite) clay minerals in any of the aerosol samples, while local soils contain these minerals in abundances as high as 32% (Table 9).

We believe the data suggest that aggregation of the expandable clays into larger particles and the electrostatic clinging of the clay mineral particles to larger silt- and sand-sized particles selectively keeps these minerals out of the aerosol. The phenomenon of an expandable-clay-poor aerosol over a soil rich in montmorillonite/vermiculite was also noted by Davis in South Dakota (Davis, personal communication, 1980). The sonic sifter data support this suggestion in that the clay minerals have their highest abundances in the 20-45 μm fraction, sample 7A4, and the 45-53 μm fraction, sample 7A5. Furthermore, these percentages are higher than those in either of the bulk soil duplicates 7A(S1, S2) or 5B(S1, S2). Since this concentrating phenomenon does not occur to the same degree with the other clay minerals, we believe it reflects the fact that expanding clay minerals have more surface charge and are more likely to aggregate than the others.

The data as a whole suggest that the ambient aerosol characteristics are very different from the local source materials. These sources should make important contributions to the ambient aerosol, so either:

1. The local sources have not been sampled in a way that correctly characterizes their aerosol, or
2. Important local source(s) exist that we have not considered, or
3. Long range transport of a significantly different surface material makes a greater contribution to the local aerosol than previously expected.

Resolution of this question requires additional studies, currently underway, to determine the composition of aerosols generated from a local source, as distinct from that of the bulk surface material.

5.2.2 Large Airborne Particle Measurements

Because of their tendency to cross air streamlines, particles larger than about 10 μm diameter are known to be difficult to sample isokinetically. This difficulty was apparent in the results of our sampler comparisons, given in Sections 4.2.3 and 4.2.4. A measure of the maximum differences between samplers in measuring airborne element concentrations is the ratio of the maximum to minimum concentrations. These ratios could be calculated from either the median or mean concentrations of a given element measured by a given sampler, but we have arbitrarily chosen to work with medians. Results in Table 29 show ratios of maximum to minimum median concentrations of four elements measured by the several different samplers at the ground or on the tower during our field observations. The data set is not ideal, since some elements were not measured in all samplers.

Table 37. Ratios of maximum to minimum median element concentrations measured by several different samplers at ground and tower locations at the Bondville, Illinois field site.

	<u>Ground</u>		<u>Tower</u>	
	<u>No. of samplers</u>	<u>Max/min</u>	<u>No. of samplers</u>	<u>Max/min</u>
Ca	6	4.4	4	2.9
Mg	4	2.8	2	1.1
K	6	5.4	4	9.7
S	3	1.3	2	1.0

At our rural site, Ca, Mg, and K were expected to occur on large particles, while S was expected to occur on small particles, as it generally does in the eastern U.S. Figure 18 shows the dominant large-particle character of Ca, Mg, and K in soil particles resuspended in a laboratory chamber; size distributions in local aerosols measured by the Casella impactor (not shown) were similar for Ca and Mg, but K distributions often had a prominent small-particle peak.

The table shows max/min ratios mostly larger than 2.5 for Ca, Mg, and K, and less than 1.4 for S. Some of the difference between elements could have been caused by fewer samplers measuring S, but this aside, concentrations of large particles were not consistently measured.

Part of the difficulty may have to do with the fact that different samplers are expected to collect particles efficiently in different size ranges. The dichotomous sampler has a 50% cutoff of 15 μm for its coarse particle range. Collection efficiency-size relationships are not known for the streaker, but its geometry would suggest that particles larger than 5-10 μm diameter would be inefficiently collected. The Casella impactor has previously been reported best among a large group of samplers compared for large particle measurements (May et al., 1976).

Filters suspended under inverted funnels may be expected to sample large particles inefficiently, but filters in vane samplers should experience lessened effects from particle inertia. Results, however, did not parallel expectations.

Figure 30 shows that for Ca, Mg, and K, the streaker almost always measured significantly higher concentrations than all the other samplers, and the Casella impactor almost always measured significantly lower concentrations than all the other samplers. One can only speculate that the true concentrations perhaps lie somewhere in the middle ground, near the values measured by the greatest number of samplers. It seems likely that errors of some kind affect the absolute concentrations measured by the streakers and the Casella impactors. Nevertheless, the relative concentrations can be useful—in the case of the streakers, the relative time variations, and in the case of the Casellas, the relative size distributions.

5.3 UNRESOLVED ISSUES FOR FUTURE RESEARCH

Several issues explored in the work up to now have not been satisfactorily resolved, but are clearly important to future progress in understanding the sources and chemistry of precipitation constituents.

One of these issues concerns the chemical or elemental composition of alkaline source materials, including both soils and dust from unpaved roads. Information on composition is needed as input to source apportionment calculations. Some information on total element concentrations in bulk soils is available (Boerngen and Schacklette, 1981), but little information is available for unpaved road materials. However, even the data available for bulk soil are not entirely relevant, since element fractionation is likely to occur during the processes of particle mobilization. The best compositions to use in source apportionment calculations would be those of aerosols derived from alkaline surface materials. A current research effort in this organization has as its goal the development of optimal methods of generating proper crustal "aerosol" samples for analysis. A soil-blowing wind tunnel, intended to simulate natural saltation processes during wind erosion of soils, is being used as a standard of comparison for the evaluation of several alternative methods of sample generation.

Another important issue concerns the processes by which alkaline particles neutralize acids in precipitation. These processes include dissolution of alkaline particles and ion exchange of base cations. We now know that availability of base cations through the processes of dissolution and ion exchange is influenced by pH, dilution ratio, and contact time, but additional details of these relationships remain to be worked out. For example, it would be useful to know what fractions of each of the major base cations (Ca, Mg, K) are derived from readily soluble salts, from ion exchange, and from dissolution of mineral matter.

Some additional effort may be justified to determine the nature of the matrix effect that causes errors in Ca determination by air/acetylene flames in highly-concentrated samples.

There are indications that measurements of the mineral composition of aerosols and source materials would permit improved source apportionment calculations. However, some problems remain to be worked out by future research.

Finally, regional assessments of source strengths of alkaline materials from roads and soils should be carried out, and compared with those of other sources, with concentrations of base cations in precipitation, and with regional deposition, in mass budget calculations. A preliminary effort in this direction is the subject of current work at the Illinois State Water Survey.

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