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SOLUBILIZATION RATE OF ATMOSPHERIC PARTICULATE MATTER AND IMPACT ON WATER QUALITY

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I. INTRODUCTION

Considerable effort has been concentrated on the study of acid precipitation and its effects on aquatic and terrestrial systems. For example, some studies have examined the effects of dry deposition and the interrelationship between wet and dry inputs of atmospheric components. Although the total atmospheric concentrations of a variety of major and minor components have been determined and total mass loadings have been estimated, the ultimate fate and impact of atmospherically-derived components depends on their post-deposition interactions. For dry fallout, both the extent and rate of solubilization of the particles after entering aqueous systems must be considered.

Inputs from atmospheric sources can constitute a significant percentage of the total chemical budget of an aquatic system (Eisenreich, 1981), particularly in systems with large surface area to volume ratios. Aerosols can enter through raindrops by rainout and washout or by dry fallout (Adewvyi and Carmichael, 1982; Slinn and Slinn, 1981; Eisenreich _et_ _al_., 1981; Sehmel, 1980). Physiological effects of aerosols in the respiratory system will also depend on the rate and extent of release of the various components (Miglio, _et_ _al_., 1977). For example, if the time scale for the removal of particles from the respiratory system is longer than the time scale for the solubilization of harmful components, then a physiological effect from the chemical components of these particles is more likely than if the expulsion time scale is much shorter than the time scale for solubilization. Retention of particles and moisture, resulting in dissolved reactive species in cracks and on the surfaces of construction material, may also be implicated in corrosion and structural weakening of construction materials (Fassina, 1978). Observations of high acidity levels in fogs, or "acid fog" (Waldman et al., 1982) may also be partially a result of rapid solubilization of aerosols. Due to the importance of pH to many aqueous processes, the release of acidity from atmospheric particles deposited in aqueous systems is of particular interest.

Information available in the literature is useful for a preliminary understanding of the principles and problems in considering the solubility of ambient aerosols. Important points to consider are the general composition of aerosols, the soluble fraction, introduction of error during sampling and other inadequacies of investigative techniques, and post-deposition interactions and impacts.

Chemical Composition of Atmospheric Particles

The dominant components of atmospheric aerosols are sulfate, nitrate, ammonia, and hydrogen (Stelson and Seinfeld, 1981; Stevens et al., 1980; Tu and Kanapilly, 1978). Other major components may include calcium, magnesium, water, carbonaceous material, sodium, chloride, potassium, silica, and bromine. The relative contributions depend on geographical location, influence from local sources, and local meteorological conditions (Stelson and Seinfeld, 1981). Some of the common minor components observed in aerosols are Ti, Mn, Fe, Cu, Al, and Pb. In addition, numerous other elements have been detected, as shown in Table I. Although beyond the scope of this discussion, considerable information on other characteristics of the chemical composition of aerosols, for example variation in composition of particles of different sizes, is available (e.g.--Gordon, 1980; Lewis and Macias, 1980).

Enrichment of some elements relative to others due to anthropogenic emissions has also been documented (Gordon, 1980; Adams et al., 1980; Duce et al., 1975). For example, Adams et al. (1980) found in remote areas of South America S, Cl, Br, Se, Zn, As, Mo, Cd, Ag, In, Sb, I, Hg, W, Au, and Pb were enriched in atmospheric particles over what would be expected from normal crustal weathering processes.

Metals present in aerosols are sometimes assumed to exist as oxides such as Al_3O_2, CaO, Fe_2O_3, and PbO (e.g.--Lewis and Macias, 1980), but some specific compounds have been identified. Cunningham et al. (1983), for example, have investigated compounds of ammonia and sulfate in aerosols. Lead compounds have received considerable attention due to automotive inputs of this potentially toxic metal. Combustion of tetraethyl lead in automobile engines has been shown to result in particles containing lead halides, lead oxyhalides, and lesser amounts of lead phosphates, sulfates, and ammonium halides. Upon aging in the atmosphere, these form less soluble lead carbonates, oxycarbonates, oxides, and sulfides (Ter Haar and Bayard, 1971; Biggins and Harrison, 1979; Robbins and Snitz, 1972). Biggins and Harrison (1979) used X-ray diffraction to identify compounds in street dust, which includes an atmospherically-derived fraction. They found mostly $PbSO_4$ and some Pb^0, $PbSO_4*(NH_4)_2SO_4$, $PbO*PbSO_4$, and $2PbCO_3*Pb(OH)_3$. Although the overwhelming number of possible natural and man-induced organic compounds in aerosols precludes discussion here, atmospheric input of organics to aquatic systems has received considerable attention (Eisenreich, et al., 1981; Doskey and Andren, 1981; Andren and Strand, 1981; Ketseridis et al., 1976).

Table I. Examples of Relative Concentrations of Various Elements Reported in the Literature

Element	ref(1)		ref(2)		ref(3)	
	fine	coarse	fine	coarse	insol.	sol.
	ng/m^3		ng/m^3		ng/m^3	
Ca	100	100	800	8110	-	-
Na	200	30	-	-	-	-
K	100	300	140	520	-	-
Cl	40	80	190	340	-	-
Fe	150	590	200	1290	2100	4
Mn	10	10	-	-	50	20
Ti	10	80	-	-	-	-
Cr	-	-	-	-	4	0.4
Pb	660	120	300	42	150	20
Cd	-	-	-	-	0.16	0.2
S	3300	300	9900	480	-	-
N	3300	500	-	-	-	-
Zn	30	10	64	30	18	4
Co	-	-	-	-	0.5	0.1
C	5200	3200	-	-	-	-
Al	70	1100	120	1800	3400	3
Si	410	2800	530	4650	-	-
Cu	20	4	2	2	20	3
As	30	-	-	-	-	-
Se	10	-	-	-	-	-
Br	150	40	41	14	-	-
Sr	4	4	-	-	-	-
Ni	-	-	-	-	3	0.8
V	-	-	-	-	11	2
Total	33400	27100	-	-	-	-

(1) Lewis and Macias (1981).
(2) O'Conner and Jaklevik (1979) (remote site).
(3) Hodge *et al*. (1978) (data from Ensenada, B.C., Mex.).

Identification of all of the compounds typically found in aerosols remains a monumental task. Of course, for many purposes, identification of all compounds is also unnecessary. Knowledge of the major components or of specific compounds of interest due to their potential role as nutrients or toxic agents is frequently sufficient.

Compounds of nitrate, sulfate, and ammonia are very significant in the solubilization of aerosols. Not only are they frequently major components of aerosols, as mentioned above, but they are related to problems associated with acid rain and tend to be soluble. Appel et al. (1978) calculated that nitrate and sulfate may comprise about fifteen percent of the total aerosol mass and found that nitrate and sulfate exist primarily as ammonium salts in California aerosols. This demonstrates the role that ammonia plays in neutralizing acidic particles and vapors (Stelson and Seinfeld, 1981). Sulfuric and nitric acids are highly soluble in water and probably contribute appreciable acidity to raindrops by scavenging of particles and gaseous diffusion combined with oxidation (Adewvyi and Carmichael, 1982).

In another study, continental aerosol samples were found to contain $(NH_4)_2SO_4$ as the dominant component while NH_4HSO_4 was found to dominate in marine aerosols (Tu and Kanapilly, 1978). Sulfate, hydrogen ion, and ammonium in a ratio equivalent to NH_4HSO_4 was also found in aerosols collected in the Smoky Mountains (Stevens et al., 1980). Tanner et al. (1979) found that ammonium showed a high correlation with sulfate in all respirable particle size fractions. Other compounds that have been identified which contain sulfate, nitrate, and/or ammonia, and which may constitute a significant part of the soluble fraction of aerosols (see below) include $(NH_4)_3H(SO_4)_2$ and NH_4NO_3 (Brosset, 1978; Keyser et al., 1978; Doyle et al., 1979).

Solubility of Aerosols

The composition of the soluble fraction of aerosols may vary in proportions from the composition of the total mass due to differences in solubility products of solids in the aerosol (O'Conner and Jaklevik, 1981) and differences in exposure of surfaces to the solution resulting from morphological characteristics. Other factors which may influence solubility are the presence of ionic species in the leaching solution, insoluble organic and inorganic coatings on ordinarily soluble solids, the rate and extent of release of hydrogen ion for species which have solubilities dependent on pH, and kinetic factors (Stumm and Morgan, 1981; Elzerman, 1981). Long term solubilities may also be affected by readsorption of previously solubilized minor constituents and by complex heterogeneous processes (Talbot *et al*., 1978).

As discussed above, evidence indicates that sulfate, nitrate, and ammonium salts are among the major components of aerosols. These compounds also tend to be soluble and therefore are important in solubilization of aerosols. For example, Walker and Weschler (1980) found the total soluble fraction of aerosols to increase with decreasing particle size, primarily as a result of solubilization of sulfate and ammonium. The solubility of some other components has also been investigated. For example, Hodge *et al*. (1978) determined Pb, Cd, Ag, Zn, Cu, Ni, Co, Fe, Mn, Cr, V, and Al are trace components of the fraction of aerosols soluble in sea water (see Table I). Elzerman *et al*. (1980) investigated the solubility of Pb from aerosols, and Ochs and Gatz (1980) determined approximately 30 percent of the total mass of particles greater than 4.6 um diameter in their samples was soluble. Tanaka *et al*. (1981) and Gatz (1982) have also reported results on soluble and insoluble trace metal fractions of aerosols. Cautreels and Van Cauwenberghe (1976) present some of the few available data on solubilization of organic carbon from aerosols.

It appears that most investigators have focused on particle size fractionation and on the determination of the total soluble component within these fractions (e.g.--Kadowaki, 1976; McDonald and Duncan, 1979; Lewis and Macias, 1980). Such studies increase knowledge of particle size and collection and chemical characteristics, but are of minimal value in determining the rate of solubilization.

Very little information is available concerning the rate of aerosol solubilization. Perhaps the lack of information on the rate of solubilization of aerosols stems from difficulties in obtaining valid information. Isolating sufficient aerosol material and measuring the rate of release of soluble components without introducing artifacts or contamination and while maintaining physical and chemical conditions representative of environmental systems of interest require considerable effort and interpretation. Several approaches have been used, as discussed below, but no one technique seems to satisfy all requirements. Generally, conclusions must, therefore, be based on interpretation of results from several sources.

Walsh and Duce (1976) devised a method to determine the rate of release of soluble vanadium in sea water. In their method, sections of Whatman No. 41 filters were aged (submerged) in 25 ml of sea water for periods of time ranging from 30 sec to 60 min. After aging, the filter sections were dried and placed on a 47 mm Nuclepore filter (0.4 um pore size) in an in-line filter holder. The sea water extracts were then re-filtered through this system to collect any particles which may have fallen off during the aging process. After drying, the process was repeated for another aging period. The results obtained for vanadium were consistent over several replications, but problems are apparent in this method. For example, passing the extract over the filter results in additional contact time with the particles. Second, by repeated wetting and drying of the particles on the filter, some compounds could undergo transformation to a more or less soluble form.

A different method to study the solubility of plutonium isotopes under various conditions was used by Miglio et al. (1977). The radioactive aerosols were collected on cellulose membrane or glass fiber filters. Segments of these filters were cut out and sandwiched between two membrane filters an then placed in a polyethylene filter holder and immersed in solvent. The filters were allowed to remain in the solvent for two hours and aliquots of the solvent withdrawn for analysis at predetermined intervals. Additionally, the effects of solvent temperature, stirring, solvent volume, container, and filter position were observed. Variation of these parameters affected both the extent and rate of release of plutonium. Aerosol size and shape also seemed related to the dissolution rate for plutonium. Irregular particles and small particles were observed to dissolve faster than large, smooth particles.

Keyser et al. (1978) mentioned the need for solubilization studies and suggested the use of a continuous flow apparatus in which constant volumes of extractant could be analyzed over a time interval. Elzerman et al. (1980) tested the utility of such a method by determining the rate of release of soluble lead from ambient aerosols in a pumped flow apparatus and concluded that the method showed promise.

Leaching studies, including both extent and rate of solubilization, have also been conducted on materials other than aerosols. For example, Talbot _et al_. (1978), Fisher _et al_. (1979), and Theis and Richter (1979) investigated leaching from fly ash samples. Sung _et al_. (1982) conducted leaching experiments with Mt. St. Helen's ash samples for metals and nonmetals. Numerous leaching studies of hazardous wastes (e.g.--Weant and Overcash, 1977) have resulted from current interest in their disposal (EPA, 1978). Most of these investigations, however, are not directly relevant to consideration of the rate of solubilization of ambient aerosols in natural aqueous systems either due to the source of the sample, or the conditions, for example, high ionic strength or acidity, used in the leaching experiment.

In a more applicable experiment, Lindburg and Harriss (1980) examined samples taken from a power plant plume. These samples were leached to determine the solubility of several components such as Pb, Zn, and sulfate. The samples were agitated for two hours in distilled water, followed by agitation in 0.08 N HNO_3 for two hours. The fly ash samples were then leached for seven days in 0.1 N HNO_3. The extended extraction in 0.1 N HNO_3 released small additional amounts of trace constituents and no further sulfates compared to the distilled water leaching.

Sampling Errors

Many problems exist in the collection and interpretation of data for aerosols and aerosol deposition. For example, ambient particulate matter is commonly collected with a high-volume air sampler. Generally, the air is filtered through a glass fiber filter for twenty-four hours at a known flow rate. Although the collection efficiency of high-volume air samples is a function of particle size and wind and turbulence factors (Liu and Pui, 1981), the aerosol sample collected is termed "total suspended particulate" (TSP) matter (CPCT, 1980; Jutze and Foster, 1967). Prediction of the mass flux of particles into a system from this data, however, might be incorrect, for example, due to a bias against large particles.

Artificial or surrogate collection surfaces designed to catch dry fallout may not be well suited for deposition studies either. Biases in the resultant data have been observed (Kerr, 1980; Slinn and Slinn, 1981; Galloway, 1975; Hicks *et al.*, 1980). Several micrometeorological methods have been suggested to obtain more realistic and reproducible particle flux data (Williams, 1981), and certainly, further research into such methods is necessary if valid data are to be compiled. Surrogate collection surfaces have some utility, however, and are convenient to use. Large particles (greater than 10-20 um) can be collected on dry surfaces. Commonly used materials include glass, polyethylene, and stainless steel (Stern, 1976; Butler, 1979). Containers of water may be useful in simulating lake surfaces (Caiazza *et al.*, 1978), but may be susceptible to local meteorological conditions and not applicable to long-term flux estimations (Hicks *et al.*, 1980).

Studies conducted on particle size distributions have shown that sulfate and ammonium are predominantly associated with submicrometer size particles (Kadowaki, 1976; Lawson and Winchester, 1978; Tanner *et al.*, 1979; Cunningham *et al.*, 1983). Such observations reveal a possible source of error in aerosol sampling with many filter media. For example, when using 0.8 um pore size Nuclepore filters, as described later, error might result from high penetration of small particles in the early periods of sampling.

Another possible source of error is adsorption of gases such as SO_2. Appel et al. (1979) found that a variety of filter media collected and held gaseous nitric acid, although Nuclepore polycarbonate filters were not tested. High ambient concentrations of SO_2 may lead to adsorption onto collected particles or absorption into associated water followed by oxidation (Pierson et al., 1976; Adewvyi and Carmichael, 1982), causing significant increases in observed amounts of sulfate. In addition, oxidized forms of lead and calcium, which can comprise a significant fraction of the collected aerosol mass, may adsorb gaseous sulfur dioxide (Lynch et al., 1978). Other observations show that NH_4NO_3 in aerosol samples may volatilize more slowly into ammonia and nitric acid free air than pure NH_4NO_3 on a filter (Doyle et al, 1979), suggesting the possible importance of matrix effects.

Errors in the determination of sample mass have been observed due to effects of relative humidity (Stelson and Seinfeld, 1981) and sampler motor brush wear (Patterson, 1980). Sample contamination is also a frequent cause of sampling error (Appel et al., 1980; Lodge, 1976; Hoffman et al., 1976).

Post-Depositional Interactions and Impact

The immediate interactions that occur upon deposition of aerosols to a water system have received little attention (Elzerman, 1981). Longer time periods allow progressively more interaction, unless equilibrium is attained, but the initial interactions may be very significant in determining the fate and effects of atmospheric inputs. Processes within raindrops, respiratory systems, and other moist or aqueous systems following the introduction of aerosols are also relatively unstudied. Release to solution will be a function of the actual solid phases present and the leaching solution. Heterogeneous reactions involving ambient aerosols, which generally have diverse composition, might be expected to be complex and not easily predicted. Of course, the possible importance of slowly solubilized components (sometimes considered insoluble) should not be overlooked in modeling applications (Gatz, 1982).

For example, the impact of acid deposition depends on the concentration or amount of acid received by the lake and the sensitivity of the lake to acid inputs (Galloway, 1979). The acidification of a lake can have numerous gross adverse effects, such as depletion of the buffering system, increased mobility of toxic metals, loss of fish populations, decreased productivity, changes in nutrient cycling, and disruption of the community structure (Schofield, 1979; Stumm and Morgan, 1981; Ruttner, 1975). Specific interactions that occur on smaller scales, for example, the effect of direct acid inputs to a lake surface on particle solubilization, have not been investigated. Even in lakes that are well-buffered, the addition of nitrate, ammonium, and phosphate from soluble atmospheric aerosols can lead to nutrient overloading (Caiazza et al., 1978; Eisenreich et al., 1977). Similarly, toxic materials, such as lead or cadmium, may enter a water system on particles and subsequently be solubilized.

Since aerosol fallout from the atmosphere can impact directly on a lake surface, characterization of the surface microlayer, the top few millimeters or less, is of particular importance (Elzerman, 1981). Elzerman et al. (1980) found that about fifty percent of the soluble lead from atmospheric particles is released in less than one minute. Additional preliminary results also indicate relatively rapid solubilization may occur for all of the major soluble components (Perry and Elzerman, 1982). This rapid release implies that most of the soluble component of deposited particles will be released in the surface microlayer. In the case of wet deposition, significant solubilization will occur in the raindrop before deposition. Also, significant solubilization of aerosols may occur during even brief contacts with water in, for example, lungs of animals or humans, small crevices of construction materials, and fogs.

Elzerman _et_ _al_. (1979) and Lion _et_ _al_. (1979) found that particle concentrations in the surface microlayer are greater than those in the bulk water over the entire particle size range, but surface enrichment in the large size (4-20 um) category may be particularly evident. Enrichment of particles in the surface microlayer probably occurs due to atmospheric deposition and bubble flotation mechanisms (Elzerman, 1981). Elzerman _et_ _al_. (1979), for example, indicated the importance of the atmosphere as a possible source of enrichment of trace metals in the surface microlayer. The existence of surface accumulated organic material which can form a slick or film across the water surface has also been noted (Elzerman and Armstrong, 1981). Potentially, this film could coat the surface of particles as they enter the water and prevent immediate solubilization or alter sinking behavior (Elzerman, 1981). Subsequent transport of the intact particle to the bulk water or even to the sediments where the soluble components could be released at a later time might then occur. Additional studies of the characteristics of the surface microlayer are needed to confirm this hypothesis. Although a net downward flux of atmospherically-derived dissolved and particulate components is probable since many eventually appear in the sediments, considerable cycling in both directions probably occurs between the bulk water and the surface microlayer (Elzerman, 1981).

By identifying the major soluble components of aerosols, the rate at which release of the soluble fraction occurs, and the flux of aerosols into a receiving body of water, a better understanding of the significance of atmospheric inputs can be gained. In addition, fundamental knowledge of the interactions of atmospheric aerosols in aqueous systems of various characteristics will allow insight into the fate of these components once they enter a watershed system, fog, raindrop, respiratory system, or moist area of a sampling device, geological material, or construction material.

II. STUDY OBJECTIVES

The overall objective of the investigation was to determine the composition and rate and extent of solubilization of the fraction of ambient aerosols released to solution within the first hour of contact with various aqueous solutions. Specific objectives were as follows:

1. review and integrate available information on aerosol solubility,
2. investigate and develop sample collection and laboratory procedures to determine the rate, extent, and components of aerosol solubilization,
3. study the rate of release to solution of sulfate, nitrate, ammonium, phosphate, chloride, acidity, lead, cadmium, iron, calcium, magnesium, manganese, alkaline and alkaline earth metals, and organic carbon from ambient aerosols representative of the semi-rural Clemson, S.C., area,
4. evaluate the significance of the rate and extent of solubilization of soluble components of aerosols in aquatic systems.

III. EXPERIMENTAL METHODS

Cleaning Procedures

To avoid or minimize contamination, all Nalgene containers and plastic filter holders used in the study were soaked for a minimum of 3 days in 15% nitric acid and rinsed in doubly distilled deionized (DDD) water. Containers were then filled with 0.5% nitric acid and allowed to stand for at least 3 more days before DDD water rinsing. Finally, the containers were filled with DDD water and allowed to stand until needed. Glass containers for the phosphate analysis were cleaned using 1:1 nitric acid and those for the TOC analyses were cleaned using chromic acid following the procedures described in Standard Methods (1980). Pipette tips (>100 ul) were cleaned for use following the acid soaking procedure described above. Metal-free pipette tips (≦100 ul) were purchased from the Bio-Rad Corporation and used as received. Sample filters were handled by either stainless steel or plastic forceps.

Aerosol Sample Collection

Aerosol samples were collected on the roof of Rhodes Research Center on the campus of Clemson University in Clemson, South Carolina, which is located in the semi-rural Piedmont section of South Carolina. The permanent population of Clemson is 8,120, the student population is approximately 11,000, and the population of Pickens County, in which Clemson is located, is 79,300 (U.S. Department of Commerce, 1981).

Approximately 20 samples were collected during the course of the experiment during the years 1979 to 1982. Various amounts of sample were collected during different weather sequences, as detailed in the Master of Science theses of Owens (1980), Perry (1982), and Norton

(1983). However, the same collection procedure was used in each case, as described below. Although investigation of sample to sample variance was not emphasized in this study, no significant variation in results considered correlating with season or previous weather was noticed. Consequently, this report treats the samples as one group and acknowledges the above mentioned theses as a source of more detail. As discussed later in RESULTS AND DISCUSSION, the major conclusions for all samples were very similar.

Except as noted otherwise, polycarbonate Nuclepore filters (20 cm x 25 cm and 0.8 um pore size) were used as the collection media for the study. The choice of the Nuclepore filter was dictated by its low trace metal background levels and its lack of significant adsorption of trace constituents such as lead from the extraction solutions (Owens, 1980). Glass fiber, paper, cellulose membrane, and teflon filters all proved unacceptable. The 0.8 um diameter pore size was chosen as a compromise between small particle sampling efficiency and a reasonable flow rate through the filter during the sampling and extraction.

Aerosols were collected for 12 to 24 hours using a high-volume air sampler. Flow rates during sampling were not monitored. Filters were weighed before and after sample collection to determine the mass of aerosol collected (typically 15 to 50 mg per 30 cm x 25 cm sheet). Excess moisture was removed from the filters by desiccation for 12 hours before and after aerosol collection and prior to mass determination.

Extreme care was taken to avoid contamination of the filters from outside sources. Filters were handled with forceps or plastic gloves and were kept and handled in a clean room outfitted with class 100 HEPA filters. After collection, samples were stored in Zip-Loc plastic bags between two of the divider sheets that accompanied the filters from the manufacturer.

Artifact sulfate, nitrate, and ammonia, which could result from conversion of gaseous forms to ionic forms on the filter, were evaluated using a method modified from that suggested by Appel et al. (1980). An 0.1 um pore size teflon filter was used in a 47 mm filter holder to prefilter particles from the air. A Nuclepore 0.8 um pore size filter followed this prefilter to test whether it would adsorb any atmospheric gases leading to erroneously high levels of sulfate, nitrate, or ammonia. Adsorption of gases onto Nuclepore polycarbonate filters was found to be insignificant. Accumulation of artifact sulfate and nitrate by interactions of the gases with aerosols collected on the filter was not evaluated.

Extraction Solutions

Four extraction solutions were used to solubilize the aerosols. See Appendix A for solution compositions. The four solutions were as follows:

1. Natural lake water collected at the outfall of Lake Issaqueena: The water was filtered through a cleaned 0.4 um Nuclepore filter before use. The pH of the water was 6.5. Filters were cleaned following the soaking procedures described at the beginning of this chapter.

2. Synthetic rain water prepared to resemble precipitation that occurs in the Clemson area: Data gathered at the National Atmospheric Deposition Program (NADP, 1978) site on campus was used to determine the desired composition of the solution. The pH of the solution was adjusted to 3.6 by the addition of a dilute mixture of nitric and sulfuric acids (1:1).

3. Synthetic lake water prepared to an alkalinity of 200 mg-calcium carbonate/l. The pH of the solution was adjusted to 7.8 by bubbling carbon dioxide through the solution.

4. Double distilled deionized (DDD) water.

The synthetic rain and lake waters were prepared using double distilled deionized (DDD) water, analytical grade chemicals, and Baker Ultrapure acids to provide solutions with low metal backgrounds.

Extraction Procedures

Three extraction procedures were investigated, as follows:

(1) A pumped flow extraction method involving the use of a Nuclepore in-line filter holder connected to a peristaltic pump was used for most work. This method was used by Elzerman *et al*. (1980) except that here smaller aliquot volumes were taken to increase time resolution. Aliquot containers were changed every six seconds for investigation of major soluble components producing a 2 ml aliquot with a flow rate of 20 ml per minute; for minor soluble components, the aliquots were 10 ml (30 sec.). Elzerman *et al*. (1980) had shown the observed rate of solubilization of lead was independent of flow rate in this system over the range 5 to 20 ml per minute.

The 20 cm x 25 cm filters were cut into 47 mm diameter discs using a Plexiglas die and placed in 47 mm Nuclepore plastic filter holders. The actual surface area of the filters exposed to the extraction solutions was 42 mm. The holders were clamped to a ring stand and connected downstream from a peristaltic pump which drew the extraction solutions from polyethylene storage reservoirs. See Figure 1 for the experimental setup. Time zero was defined at the first emergence of effluent from the filter holder, which was 10 to 15 seconds after pumping was started. After collection, 50 ul of Ultrapure nitric acid was added to each aliquot on which trace metal determinations were to be made.

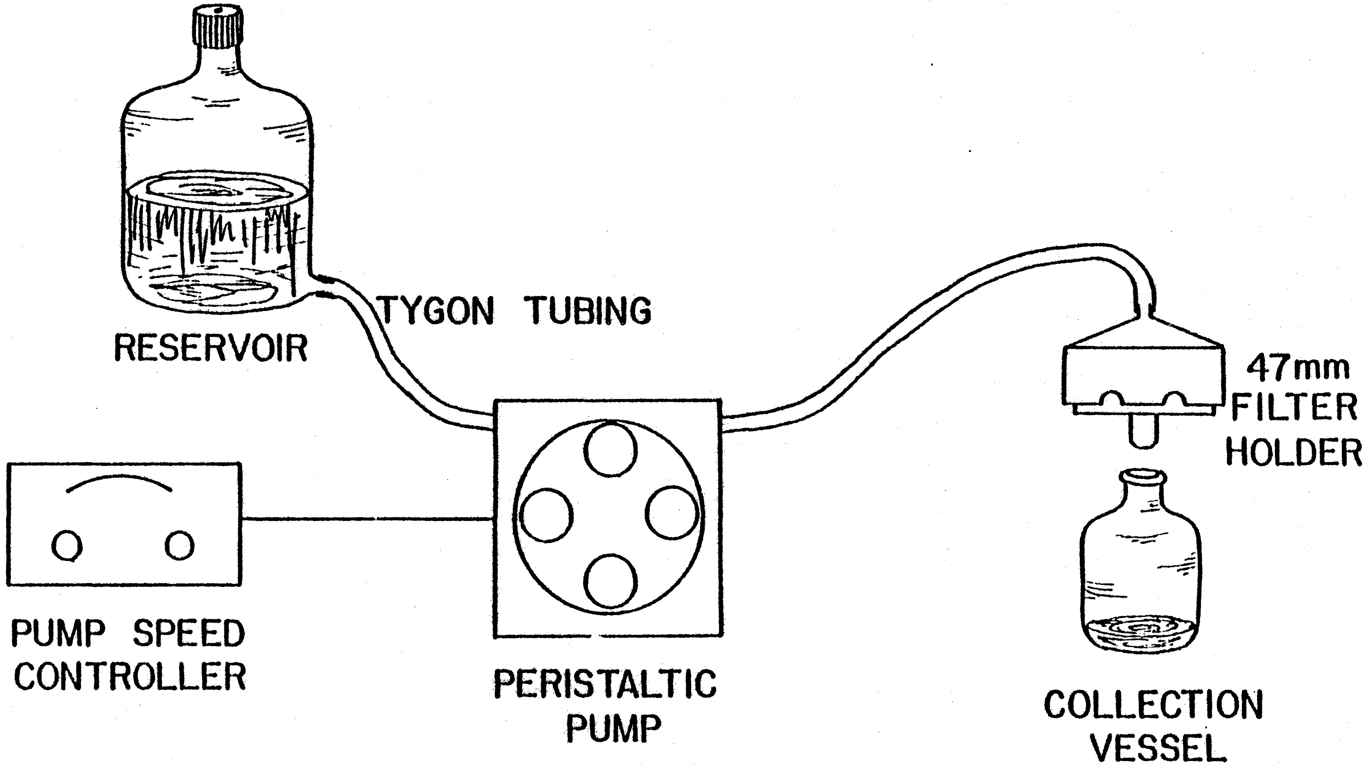


Figure 1. Pumped-flow extraction with in-line filter holder

Glass fiber filters were used for the total organic carbon(TOC) studies. The filters were combusted in a muffle furnace at 400°C for 4 hours before use (OIC, 1978).

2) A sequential filter and aliquot system modified from the method developed by Walsh and Duce (1976) was also investigated. A filter disc was placed in a Millipore open-ended filtration unit and a 10 ml aliquot of extractant was then injected onto the exposed surface of the filter. This first aliquot was immediately pulled through the filter by vacuum. A second 10 ml aliquot of extractant was injected onto the surface of a fresh filter disc (cut from the same 20 cm x 25 cm filter), however, the contact time was increased to one second before the extractant was pulled through the filter. This procedure was repeated with thirteen other fresh filter sections and aliquots, with the contact times increasing with each succeeding aliquot.

(3) A sequential filtration system using a single filter, as designed by Walsh and Duce (1976), was tested to compare with the other methods. A Millipore open-ended filtration unit was connected to a vacuum pump, and a 10 ml aliquot of extractant was injected onto the exposed surface of the filter and allowed to sit for five seconds. The aliquot was then pulled through the filter, the filter was removed and carefully dried and the process repeated again.

All three of the above techniques gave similar results (See Perry, 1982). The pumped flow method (1), however, was the most convenient and yielded the least variable and most internally consistent data. Therefore, results presented below are derived primarily from this technique. Each system had some usefulness in studying the release of major components of ambient aerosols, however, each presented certain problems, especially the possibility of contamination for trace metal investigation. The pump-flow system, with an in-line filter holder, allowed for minimal handling of the filter discs after aerosol collection thus reducing the possibility of contamination, and permitted the best control of contact time between the extraction solution and the aerosols on the filter.

The pump-flow system is not without limitation, however. Mixing in the upper end of the chamber could result from the flow of the extraction solutions over the surface of the filter as the upper chamber filled. However, Owens (1980) determined from a study of lead release from aerosols and sodium chloride put on filters, that the effective delay caused by the mixing is on the order of a few seconds. By collecting effluent from the filter holder in 30 second increments, the effect of mixing is made relatively insignificant. Another potentially undesirable characteristic of the pumped-flow technique is the time necessary to fill the air space above the filter, approximately 10 to 15 seconds. This period of time allows for some solubilization to occur before the extraction solution begins exiting the filter, which might contribute to the large concentration observed in the first fraction collected (see RESULTS AND DISCUSSION). Finally, particles smaller than the filter pores may wash through the filter without being solubilized, but this effect is probably insignificant (See RESULTS AND DISCUSSION).

Distribution of aerosols over the filter surface could also affect comparative results. Several filters were cut from the various regions of a 20 cm x 25 cm filter and extracted as described above. The results indicated that the components were distributed uniformly over the filter surface since concentrations obtained from different discs from the same sheet agreed within experimental error.

In addition to the filtration techniques, a stirred batch contact system was used to continuously monitor the release of hydrogen ion. This approach offered the advantage of a continuous data output and could be used with other continuous monitoring techniques. Of course, it must be recognized that batch and column methods may yield different results due to physical and concentration effects. Investigations indicated, however, that for the low concentrations present in the samples tested, all techniques gave similar results.

Analytical Procedures

All metal analyses were performed on a Perkin-Elmer Model 403 atomic absorption spectrophotometer with an HGA-2100 graphite furnace attachment. See Appendix B for furnace operating conditions. Concentrations were determined by employing the standard addition method on each sample. Triplicate analyses for the trace metals indicated a repeatability of approximately 10%. Chloride concentrations were determined using an Orion Model 94-16 Ag^{+1}/S^{-2} specific ion electrode and the Gran's plot method described by Orion Research for low-level chloride measurements (Orion Research, 1977). The electrode was used in conjunction with a Model 901 Orion Research Ionalyzer. The degree of precision for the chloride analysis is estimated to be approximately ± 10%. Total organic carbon was determined using an Oceanographic International Corporation (OIC) PAR-2000 instrument following the ampoule technique described in the OIC manual (OIC, 1978). Triplicate analyses for the TOC's indicated a repeatability of approximately 10%. Phosphates were determined using a Beckman ACTA UV-VIS Spectrophotometer and the method described by Eisenreich *et al*. (1975).

Sulfate was analyzed using the barium chloride turbidimetric technique (EPA, 1979). Hydrogen ion (calculated from pH), nitrate, and ammonia were determined using specific ion electrodes (EPA, 1979; A.P.H.A., 1980). Calcium and magnesium were determined with an atomic absorption spectrophotometer using direct aspiration into an air-acetylene flame (EPA, 1979). Specific conductance was measured using an AC powered Wheatstone bridge device and conductivity cell standardized with potassium chloride at 25°C (A.P.H.A., 1980).

Blanks were carried through all procedures. Required corrections were generally insignificant after allowing for the original (pre-extraction) composition of the extraction solutions.

Total Releaseable Fraction and Experimental Extraction Times

An operational definition for the total amount of a constituent releaseable to solution, the total releaseable fraction (TRF), was necessary to allow for comparisons between the various extraction solutions and for determination of whether the amount of material released to solution was significant. Owens (1980) used a two hour extraction in a stirred reactor containing 0.1N nitric acid as the method for determining the TRF for lead. This method was also adopted for further investigation of lead, cadmium, manganese, iron and chloride. Adjustment was made to account for the exposure of only 42 mm of the 47 mm disc in a filter holder. This method of determining the quantity of material releaseable provided an estimation of the maximum amount of soluble material that could be released to a water system under extreme acidic conditions.

This method was also initially adopted for determining the TRF for total organic carbon, but several problems arose. First, the glass fiber filters used for the TOC collection disintegrated during the 2.5 hour stirring procedure. This made decanting the solution for analysis very difficult, even after centrifuging. Filtering the solution could have resulted in contamination or loss of carbon to the filter by adsorption. Second, the method may not have been providing an accurate measure of the TOC releaseable since the sum of TOC released in five minutes during pumped-flow extractions was often greater than the TRF. As an alternate approach, filter discs were cut into strips and placed in TOC combustion ampoules with a minimum volume of water. The ampoules were then purged of CO_2 and digested following the OIC (1978) suggested procedures.

The TRF for phosphate was determined by placing sample discs in 10 ml of DDD water and digesting in the same manner as the sample aliquots from the extraction procedures following the method of Eisenreich (1975). The TRF for sulfate, nitrate, ammonium and hydrogen ion were determined by stirring in DDD water for one hour. Stirring in DDD water for two weeks released no more sulfate, nitrate, hydrogen ion, or ammonium than released in one hour (Perry, 1982).

Five minutes was chosen as the time interval over which extractions for rate of release investigations were performed. This time was operationally defined as that time in which the 'initial reactions' would occur and provided information on the early stages of aerosol solubilization using the pump-flow system. Also, in almost all cases, concentrations in the effluent from the pumped flow apparatus decreased below detection limits or to the level of the influent concentration within five minutes.

Samples of Known Lead Compounds

Samples for the investigation of release of lead from pure lead compounds were prepared by placing approximately 4 ug of Pb as PbO or $Pb(NO_3)_2$ on a metal-free 0.4 um Nuclepore filter as a liquid concentrate. Concentrates were prepared so as to allow for <300 ul to be placed on the filters. The concentrate was distributed as evenly as possible over the filter surface using an Eppendorf microliter pipette. The filters were then dried on a clean plastic platform under a 125 watt light bulb in a cleanroom. Extractions were performed as described earlier.

IV. RESULTS AND DISCUSSION

Initial Observations

Solubilization of solid phases of ambient aerosols began almost immediately upon contact with the extraction solutions. Constituents of aerosols were released to solution as compounds dissolved, as particles lost adsorbed materials from their surfaces, and as particles fell apart exposing more surface to the solution. Preliminary work involved the screening of several samples to determine the major and minor (or trace) components of the soluble fraction. Extracts were analyzed for various components. It was determined that the anions sulfate and nitrate and the cations hydrogen, ammonium, calcium, and magnesium comprised the major components of the soluble fraction of atmospheric aerosols (see Table II) as would be expected from information in the literature discussed above in the INTRODUCTION. Summation of anions and cations generally balanced, within the precision of the experiments. Ion balances were generally less consistent in later aliquots collected than in earlier ones (See Perry, 1982).

Rate and Extent of Solubilization of Major Components

Previous work had shown that the trace metal components lead and vanadium can be released to solution on a time scale of minutes or less (Walsh and Duce, 1976; Elzerman *et al.*, 1980). Therefore, an arbitrary time frame of one hour was chosen over which extractions were monitored for this study. As mentioned previously, no significant additional dissolution of the major components occurred after a one hour contact time with distilled water at 4°C. Nitrate concentrations actually decreased, due possibly to microbial activity. Of course, for some

Table II. MAJOR COMPONENTS OF THE SOLUBLE FRACTION OF CLEMSON AEROSOLS

Component	Typical Percent of Total Soluble Mass
Sulfate	65.6
Nitrate	5.8
Ammonium	17.7
Hydrogen	0.3
Calcium	0.5
Magnesium	0.1
Other	10.0

species, such as siliceous compounds, slow dissolution may continue to occur for longer periods.

For the major components of the soluble fraction of aerosols, such as sulfate, nitrate, hydrogen ion, ammonium and calcium, all evidence collected indicates most solubilization in DDD water actually occurs in minutes or less. Perry (1982), using the pump-flow system to study the rate and extent of release of the major soluble components of Clemson aerosols to DDD water, reported that more than half of the soluble mass was released within 20 seconds after contact with the extraction solutions. The release was observed as a large initial pulse in a first stage followed by a decreasing rate of release in a second stage. The initial stage may be described as the release of the 'immediately soluble' material in the aerosols during the first few seconds of the procedure, which results in a high concentration of solubilized constituents in the first aliquot.

Figure 2 shows release of the total soluble fraction (sum of ion concentrations) as a percent of the total released in five minutes versus time for three representative samples in DDD water. In the samples tested, 30 to 60 percent of the total mass was soluble. In general, release of the major soluble components appeared to occur in a matter of seconds. Release in the first effluent fraction collected (first six seconds after effluent first appeared for major components) was as high as 50 percent or more of the total release (see Table III). This first fraction also contained any material solubilized during the time required to fill the filter holder (see below). Over 80 percent of the total release generally occurred within 20 seconds. No significant release of sulfate, nitrate, ammonium, or hydrogen was observed after 60 seconds.

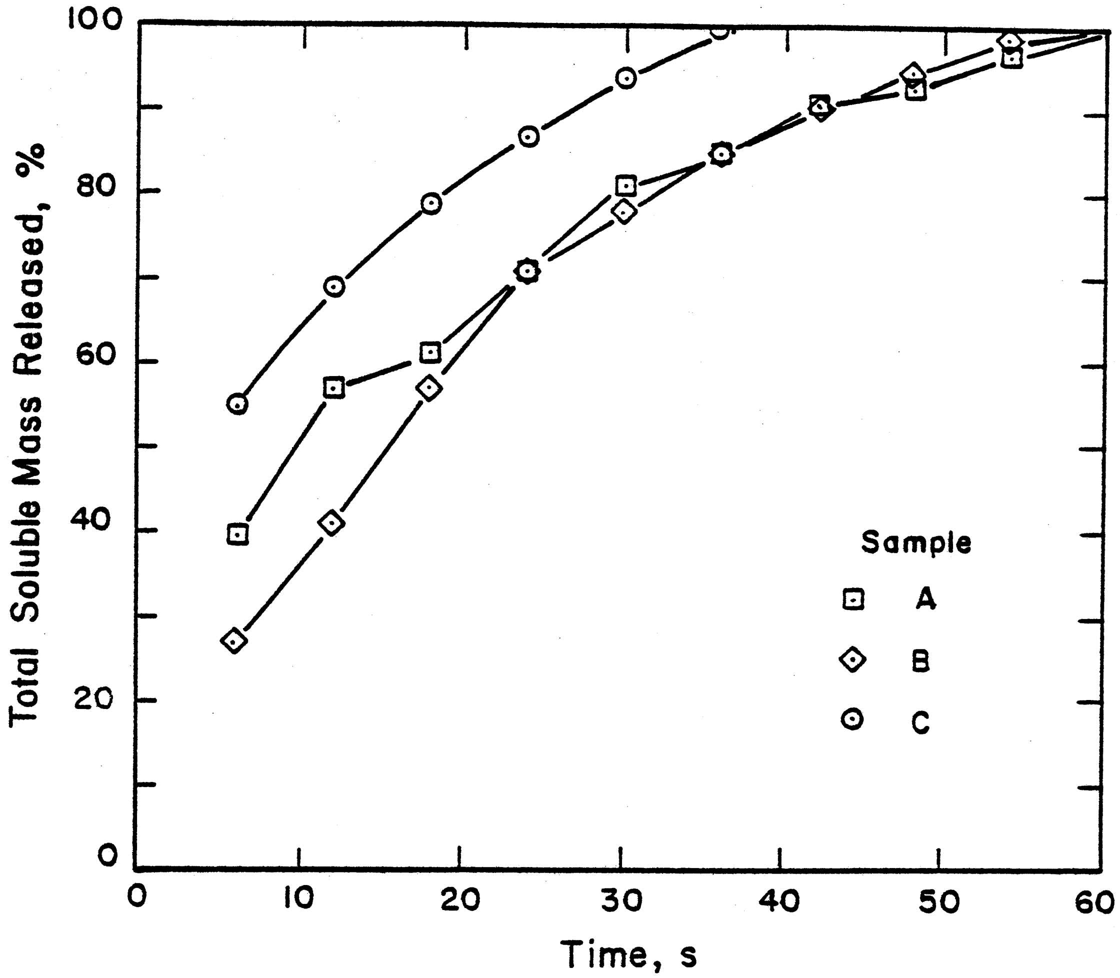


Figure 2. Sum of Percent Soluble Mass Releases vs. Time

The results of the pumped-flow technique are influenced by the flow characteristics of the filter holder. At the start of an experiment, much of the water entering is initially held above the filter to fill the top half of the filter holder. This results in a longer (approximately 10 to 15 seconds) effective contact time for the first aliquot then for later ones and may affect the concentrations of the soluble material observed in the first fraction. In addition, rapid release of hydrogen ion may mobilize some components into these early fractions, especially trace metals. Finally, mixing effects in the filter holder may delay expulsion of solubilized material and affect the relationship between actual and observed release. However, further investigation of the possible delay by mixing indicated the effects were important only over time scales of less than 5 seconds. In any case, the available data indicate that the potential artifacts from the pumped-flow technique do not significantly influence the major conclusion that the release of the majority of the soluble materials occurs on the order of seconds to minutes.

Plots of effluent concentration (concentrations in the fractions collected) versus time always showed logarithmic decay. Delayed release from some solid phases, which caused concentration peaks in later fractions, were occasionally observed, and may have indicated the presence of less quickly soluble phases or surfaces that were not immediately exposed to solution. With the exception of the first data point in the effluent concentration versus time plots (the concentration in the first fraction), the data could be described using a first-order decay model (see below). The concentration in the first effluent fraction was always too high to be consistent with the first-order description of the remaining points, due partially to the longer exposure time for the first fraction described above. Compensation for this longer exposure time in the first fraction by calculation was hampered by incomplete knowledge of the filling and mixing characteristics of the filter holder, as mentioned above, but calculations using estimations still did not always account for the high concentrations in the first aliquot.

Potentially, some material in the first effluent fraction (an "immediately soluble fraction") may actually be solubilized more quickly than the material which is observed to follow a first-order decay of concentration in the later effluent fractions, which could be described in a more complicated two-phase descriptive model. As an alternate approach, Elzerman et al. (1980) suggested the use of a two-stage model to describe the release of lead solubilized from ambient aerosol samples using the pumped-flow extraction technique. Lead in the first fraction (30 seconds in their method) was considered an essentially "immediate soluble" fraction and this fraction was then compared to lead released on a longer time scale. In general, the rate of release in the second stage, after the initial fraction, could then be described by a first-order relationship,

$$C_t = C_0 \exp(-kt)$$

The constant (k) was estimated by plotting ln (C_t/C_0) versus time. Since the first fraction was considered separately, the second fraction was taken as C_0.

Application of the above approach of Elzerman et al. (1980) to solubilization of the major components of aerosols also proved useful. The value of the rate constant for release of total dissolved solids

(k_T) was determined by fitting a regression line through the points. The percent of the total soluble material in the first fraction, the rate constants (k_T), and the correlation coefficients from the linearized ln (C_t/C_o) versus time plots for representative samples in DDD water are presented in Table III. The data in Table III are for summed measured masses, but similar results were obtained using specific conductivity as an estimate of dissolved solids. Scatter in the data resulted primarily from increasing noise in the data as concentration measurements approached the detection limits at longer times.

The average k_T value calculated for total dissolved solids (also typical of the values obtained for sulfate, nitrate, ammonium, and hydrogen ion - see Table VI) was about 1.5 min^{-1} in DDD water, compared to typical k value of 0.5 min^{-1} for lead in lake water (Elzerman et al., 1980 and see below). Caution in interpreting these results is necessary since the absolute value of the constant k can be dependent on the actual experimental apparatus and conditions. The k values for lead and major soluble components given above were obtained with the same technique, however, and thus it would appear that the release of acidity and the major soluble components to solution are similar and may be more rapid than the release of lead. The significance of this difference, if real, is probably slight in most aqueous systems of interest since all of these soluble components are apparently released to solution in minutes or less.

Probably a more significant difference in the solubilization of the aerosol components is the extent of solubilization. For the major soluble components, approximately 40 percent of the total release (TRF) occurred in six seconds (see Table III), and in 30 seconds, an average

Table III. Percent of Total Soluble Material in First Fraction and First-Order Rate Constants for Second Stage

Sample	Percent of TRF in in First Fraction	Second Stage Release Rate Constant (k_T)* min^{-1}	
A	39	1.56	(0.76)
B	37	1.44	(0.97)
C	55	1.98	(0.98)

*correlation coefficients for linear regression of plots given in parentheses (see Text) of 80 percent had been released. Also, essentially all of the ammonia, nitrate, sulfate, and acidity was solubilized from the aerosols in a few minutes, whereas Elzerman _et_ _al_. (1980) found not all of the lead in the aerosols they tested was soluble (also see below). Release of the major components appears independent of pH in ranges likely to be encountered, whereas release of some minor components, such as lead, appears very dependent on pH (see below).

Continuous monitoring of pH in a stirred batch extraction produced results consistent with the pumped-flow results. The pH change with time was monitored with a chart recorder. Figure 3 is a transcribed plot of this output. Unfortunately, the applicability of this approach is limited. Electrodes are best suited for continuous monitoring, but response times may prevent attainment of useful results. For example, nitrate and ammonia electrodes respond slowly at low concentrations and are therefore unsuitable for continuous monitoring purposes. Spectrophotometric methods using flow-through cells can be used but may be complicated by the requirement of some in-line mixing of color producing reagents. Atomic absorption flow-through methods may also be useful for metals if concentrations allow for the use of flame aspiration.

Rate and Extent of Solubilization of Minor Components

As discussed above, major soluble components in ambient aerosols seem to be released to solution within minutes of contact with water. The figures on the following pages, Figures 4 through 9, show a similar pattern for the minor constituents. The figures show specific, but representative, examples of the release of Cd, Fe, Mn, Pb, PO_4, and

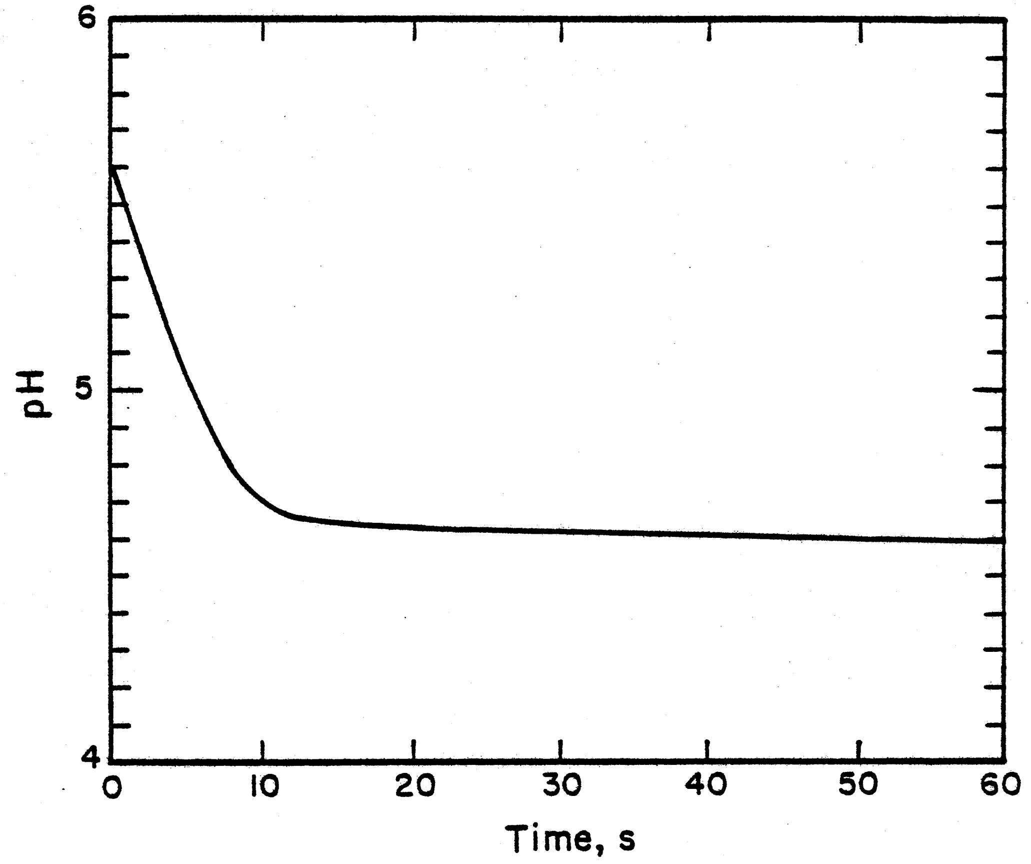


Figure 3. Continuous Monitoring of pH Changeover Time in Stirred Batch Extraction

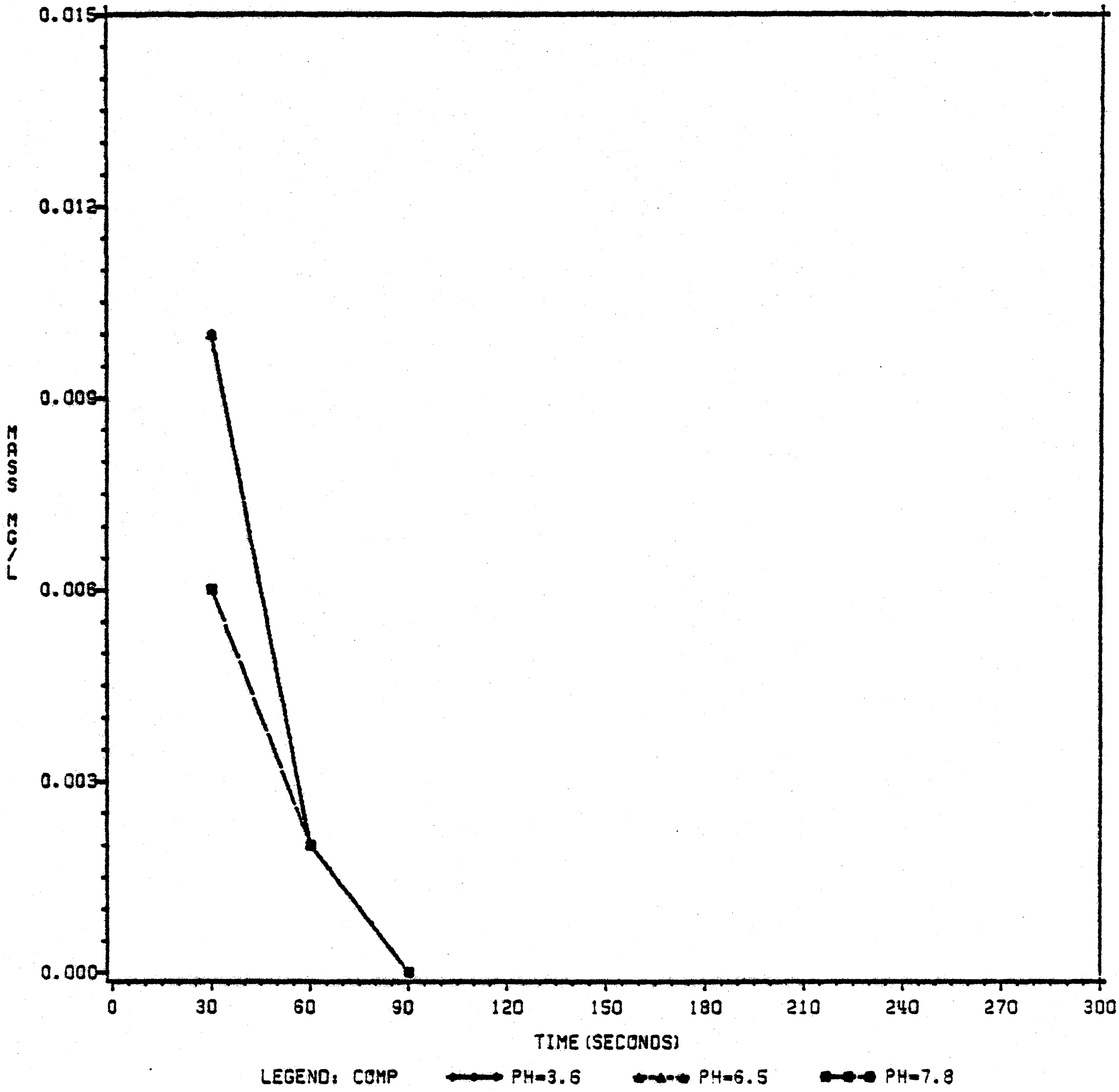


Figure 4. Cd Release from Sample 0606: Concentration vs Time

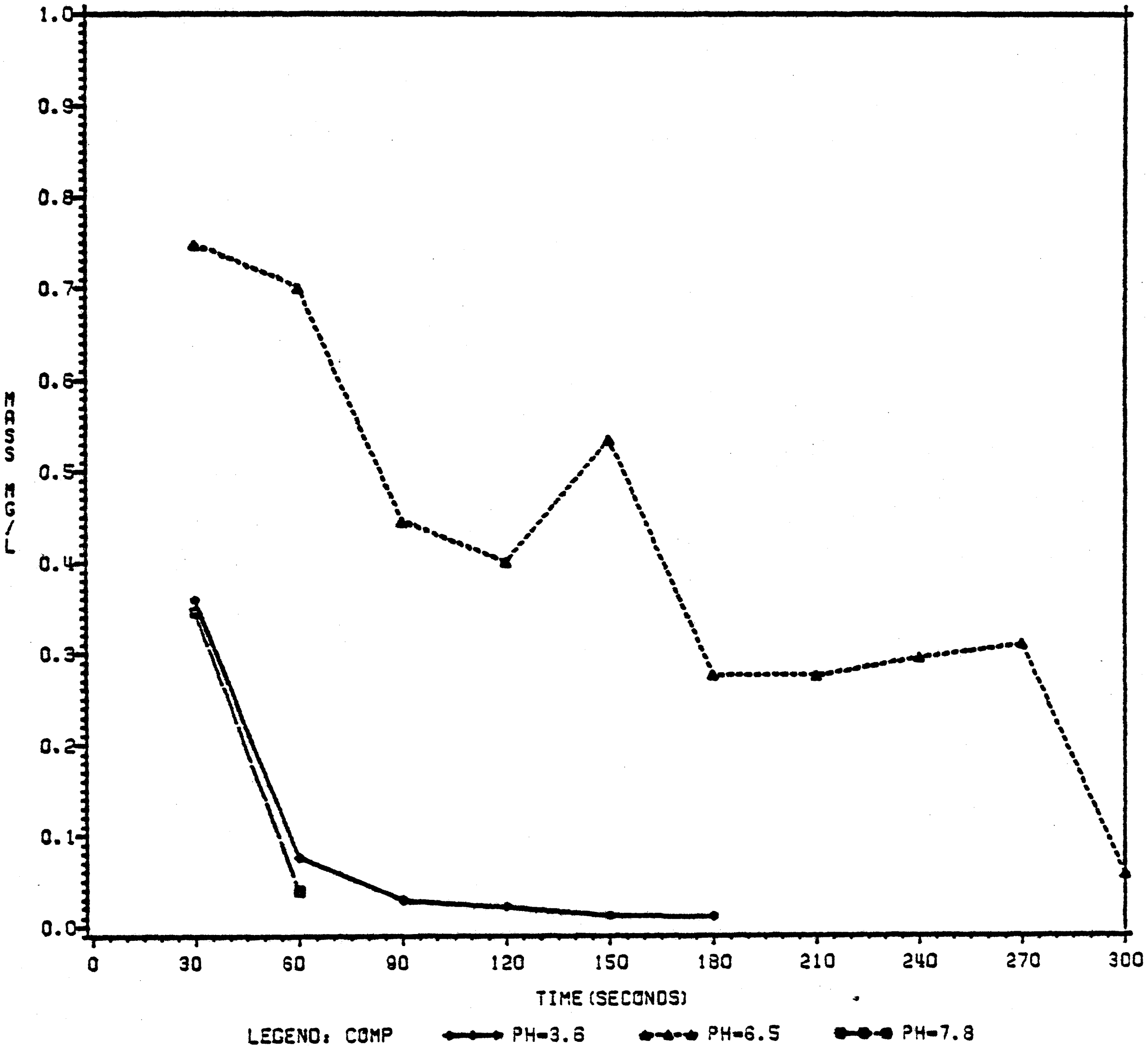


Figure 5. Fe Release from Sample 0401: Concentration vs Time

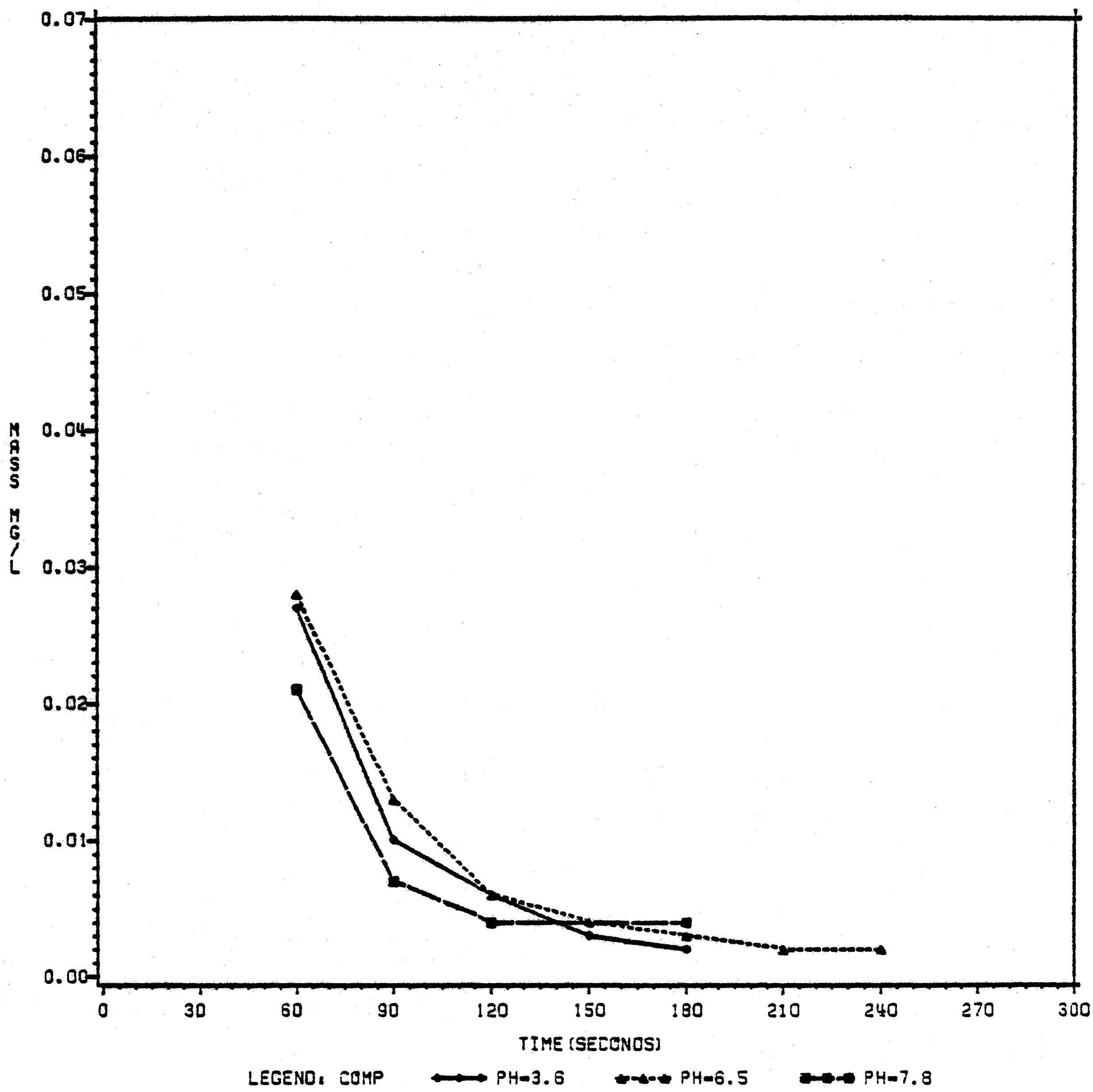


Figure 6. Mn Release from Sample 0401: Concentration vs Time

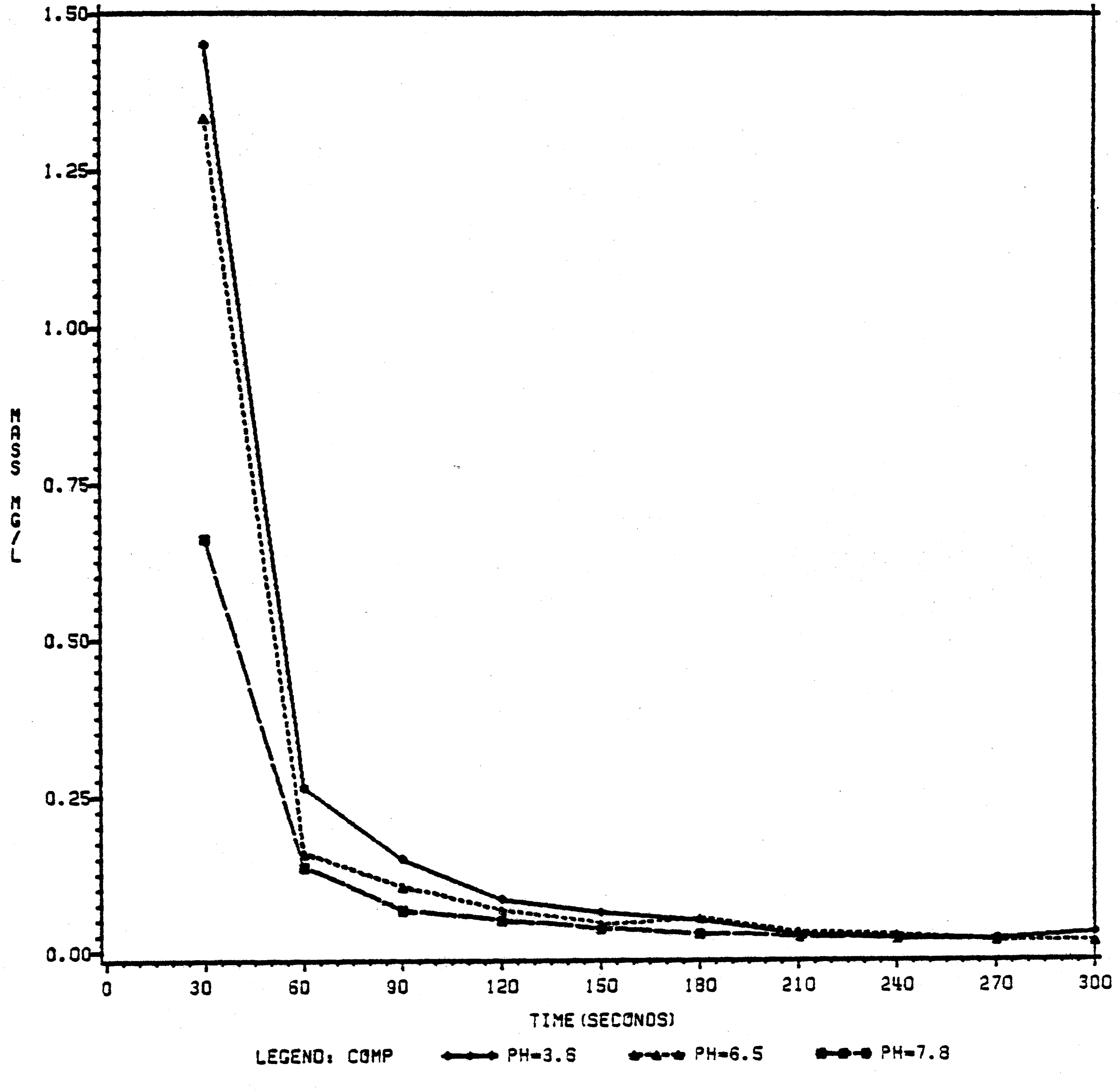


Figure 7. Pb Release from Sample 0423: Concentration vs Time

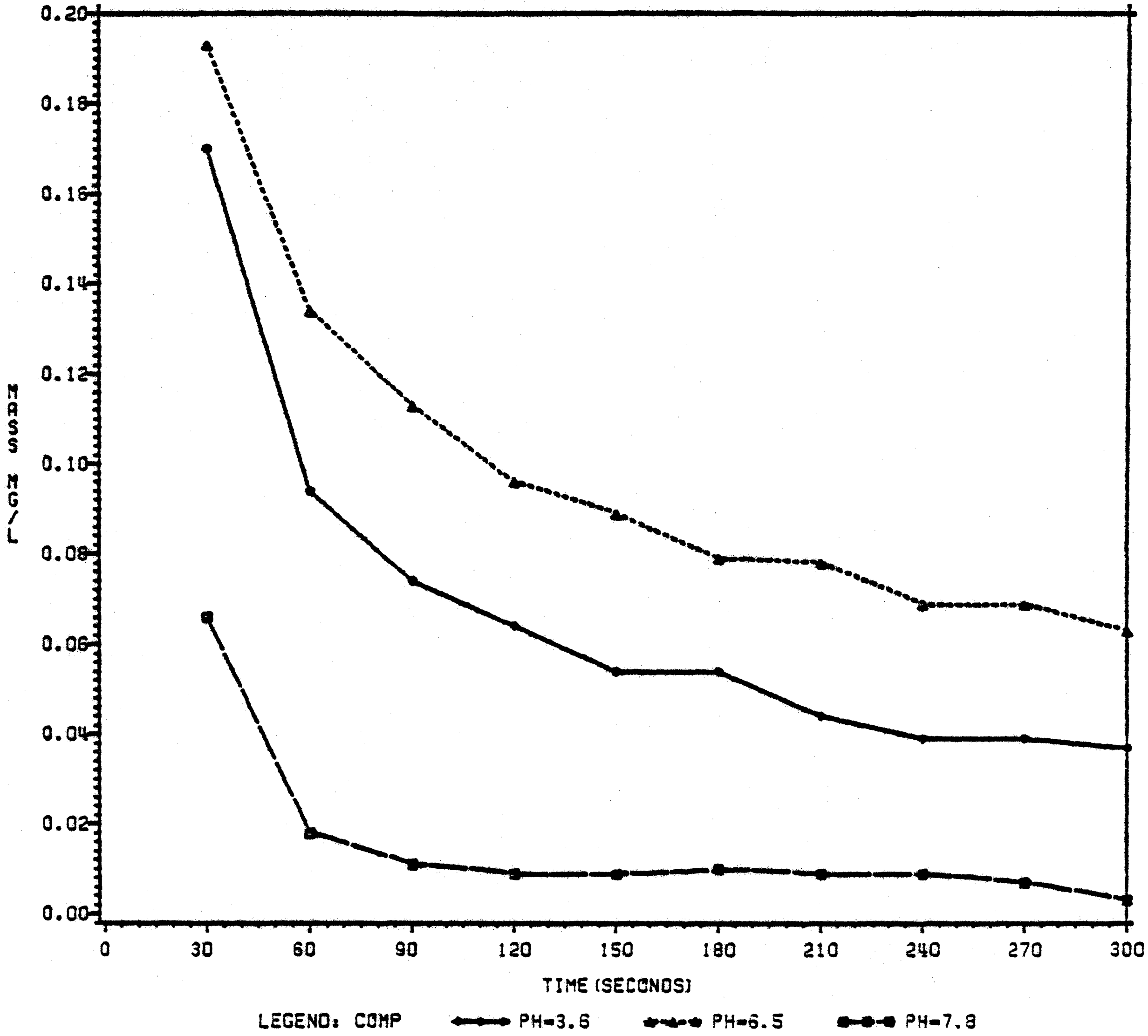


Figure 8, TOC Release from Sample 1105: Concentration vs Time

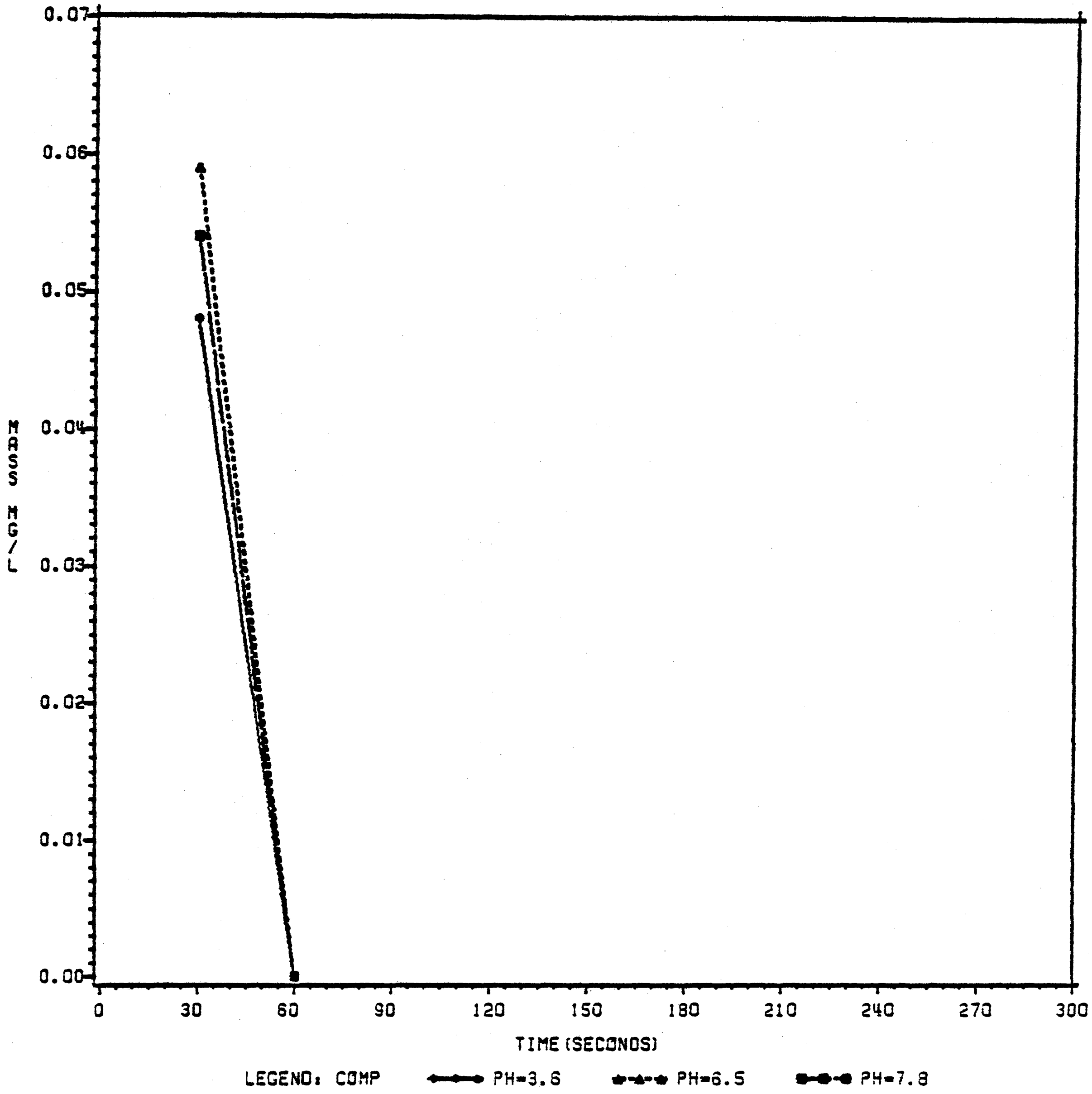


Figure 9. PO_4 Release from Sample 0423: Concentration vs Time

TOC using the pump-flow apparatus. The aliquots were collected at 30 second intervals (10 ml of sample) for a period of 300 seconds. Analysis of the 10 samples from each run was performed individually, and the data plotted as the mass of the constituent per 10 ml of sample versus time in seconds. Note that typically a significant amount of each constituent was released in the first 30 second period followed by decreasing amounts in each successive fraction, similar to results for the major soluble components of Clemson aerosols.

The chloride studies failed to show release of chloride ions to solution during the extraction procedures, although there were detectable levels of chloride in the collected aerosols. The technique used for the chloride analysis did not have sufficient sensitivity and precision to allow observation of changes in the extraction solutions. Complicating the chloride measurement further was the amount of chloride added to the synthetic solutions in their preparation. In particular, the calcium chloride used to prepare the synthetic lake water could easily mask any chloride released during the extractions.

In general, initial observations confirmed that the soluble fraction of minor components of ambient aerosols are apparently released to solution soon after contact with water at a rate that decreases with time. Of course, the rate constants and percentage release values obtained for the minor constituents of ambient aerosols are specific to the particular system and flow rates used in this research, and the rate constants and other parameters of other researchers may differ from those obtained here. Care must be taken when comparing values from various sources, and differences in experimental parameters and the experimental design considered. However, the pump-flow system proved useful in that it allowed for the comparison of relative effects of various experimental conditions using the same technique. Ideally, concrete quantitative observations would be more desirable, but they may not be practically obtained nor add materially to our understanding.

Similarly, the data obtained may be described in different ways with different degrees of complexity. A model matching the goals of the research was desired; and again the two-stage model proposed by Elzerman et al. (1980) to describe the release of soluble components from aerosols using the pump-flow system was useful. As seen in Figures 4 through 9, the concentrations of Fe, Cd, Mn, Pb, PO_4, and TOC in the first aliquot collected from the extraction of the aerosols were the highest for each of the extraction solutions. Generally, the majority of the total soluble fraction was released in the first fraction, as shown in Table IV. In all cases, except the TOC release from the synthetic rain water, the release was >50%, indicating the first thirty seconds was a period of rapid solubilization.

The second stage, (<30 to 300 seconds), was described by Elzerman et al. (1980) by first order decay of the concentration in the eluant of the pumped-flow apparatus. Another look at Figures 4 through 9 indicates a similar trend, as also seen above for the major components. The release of materials in the second phase can thus be reasonable well described using the first order equation described above. C(0) was again chosen as the concentration value of the second aliquot collected, the beginning of the second-stage release. Estimations of the rate constant were simplified by plotting ln C(t)/C(0) versus time and calculating the slope. Figures 10, 11, 12, and 13 show representative plots for ln C(t)/C(0) versus time for Fe, Mn, Pb, and TOC. Plots for

Table IV. PERCENT OF TOTAL FIVE MINUTE RELEASE SOLUBILIZED IN FIRST FRACTION FOR Cd, Pb, Mn, Fe, TOC, AND PHOSPHATE

Extraction Solution	pH	% of Total Five Minute Release in First Fraction					
		Cd	Pb	Mn	Fe	TOC	PO_4
Artificial Rain	3.6	89	67	79	58	44	100
Lake Issaqueena	6.5	92	74	80	--	--	100
Artificial Lake	7.8	81	64	78	62	74	100

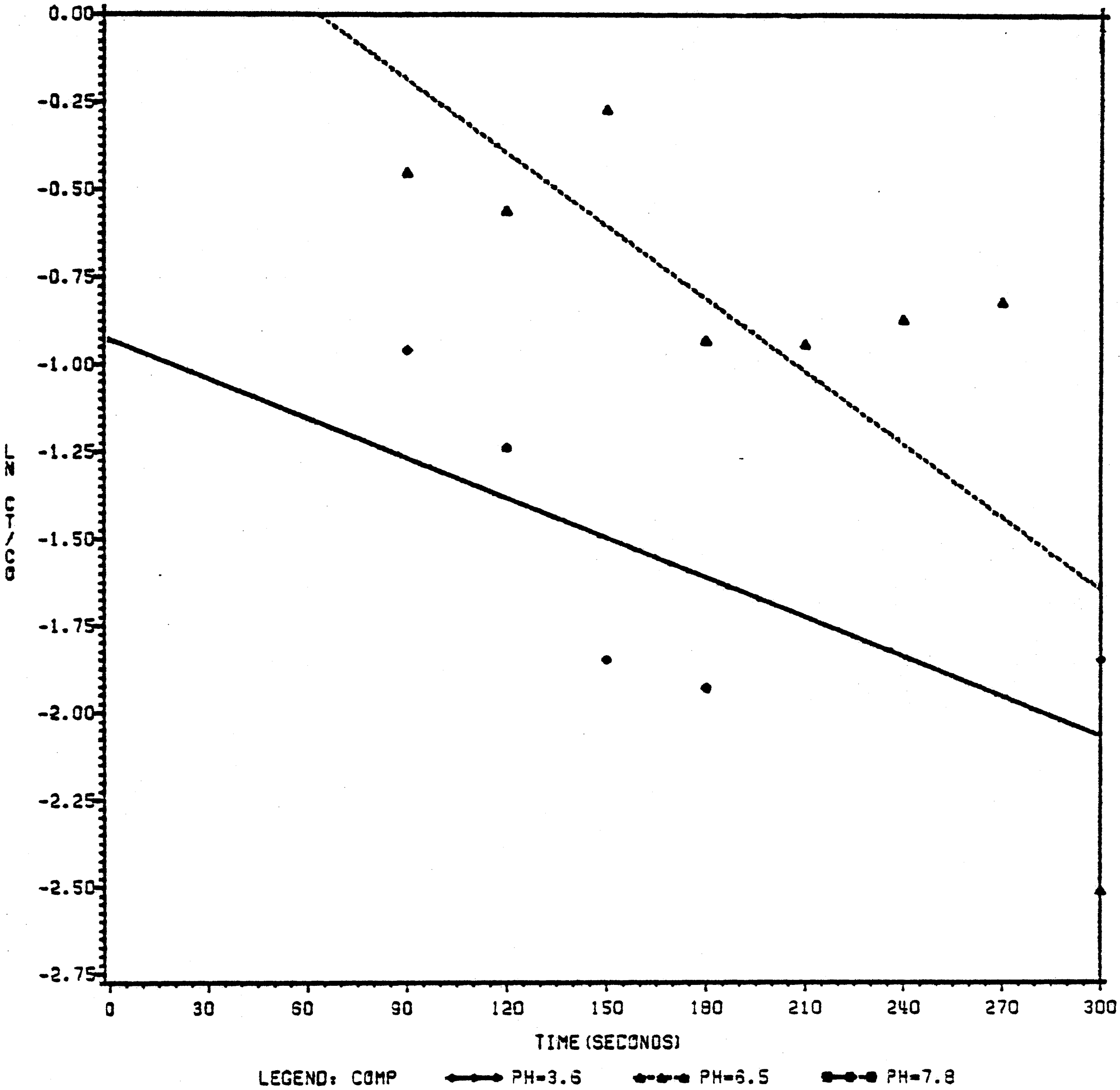


Figure 10. ℓn C(t)/C(0) vs Time for Fe Sample 0401

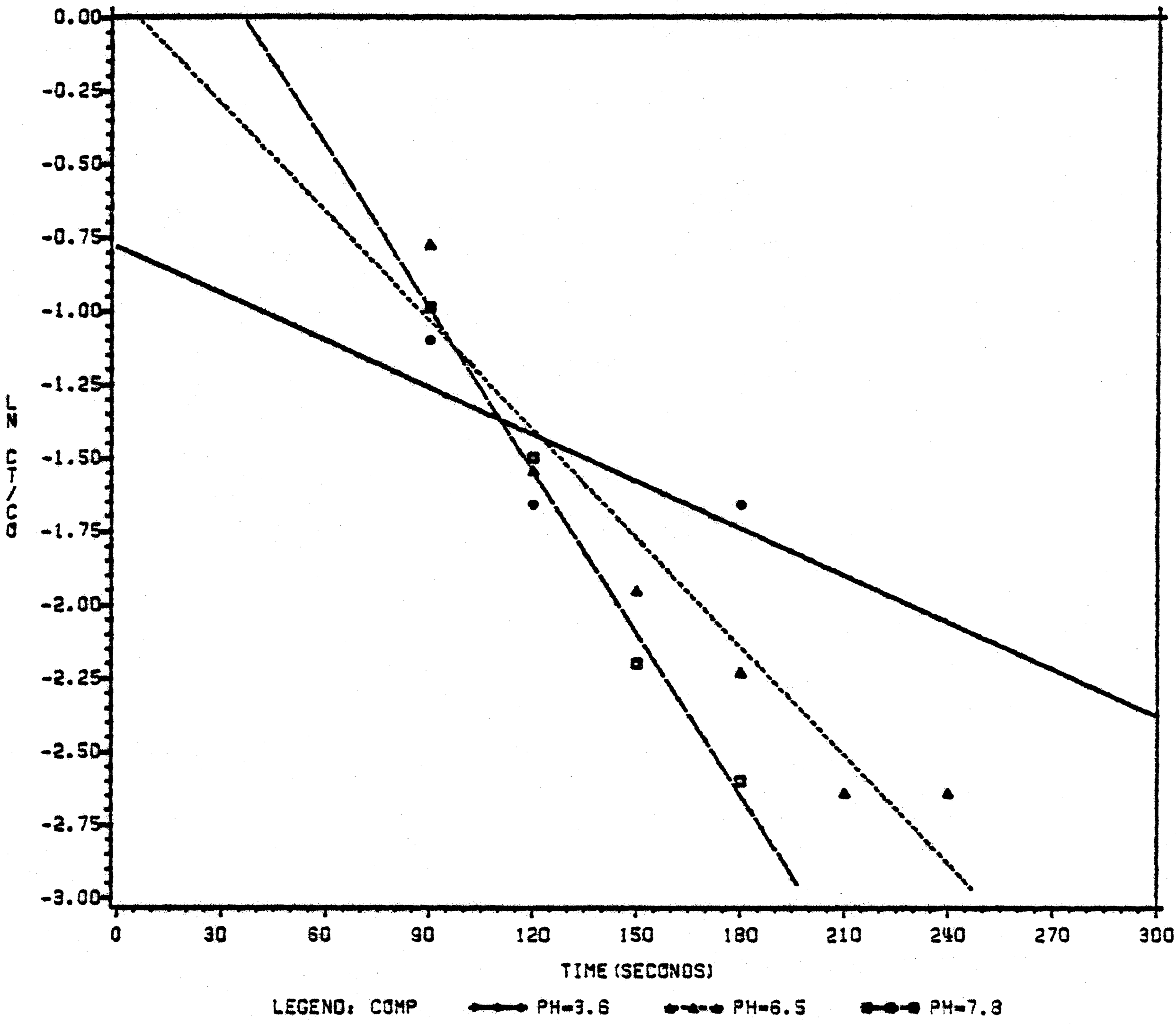


Figure 11. ℓn C(t)/C(0) vs Time for Mn Sample 0401

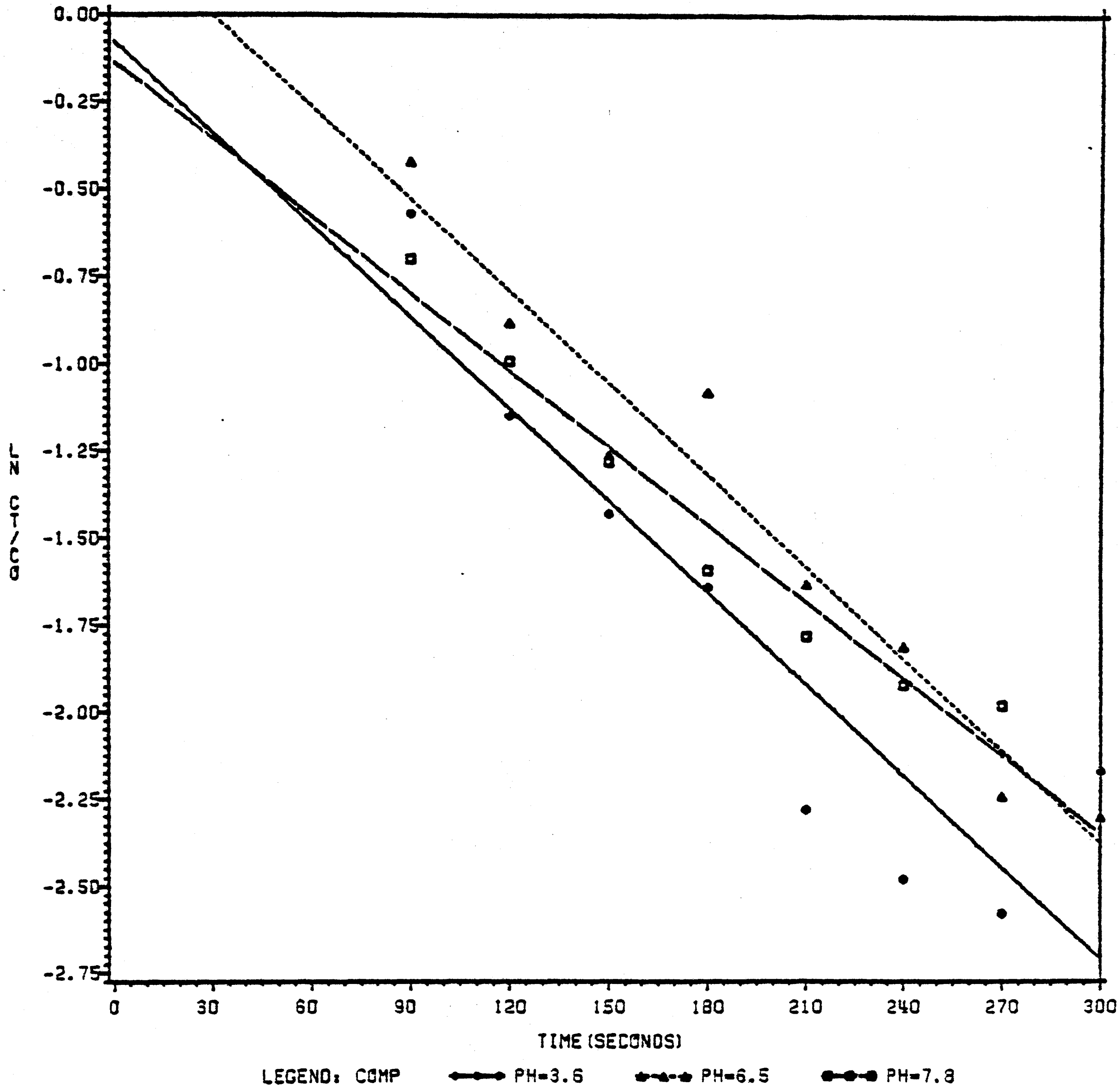


Figure 12. ℓn C(t)/C(0) vs Time for Pb Sample 0423

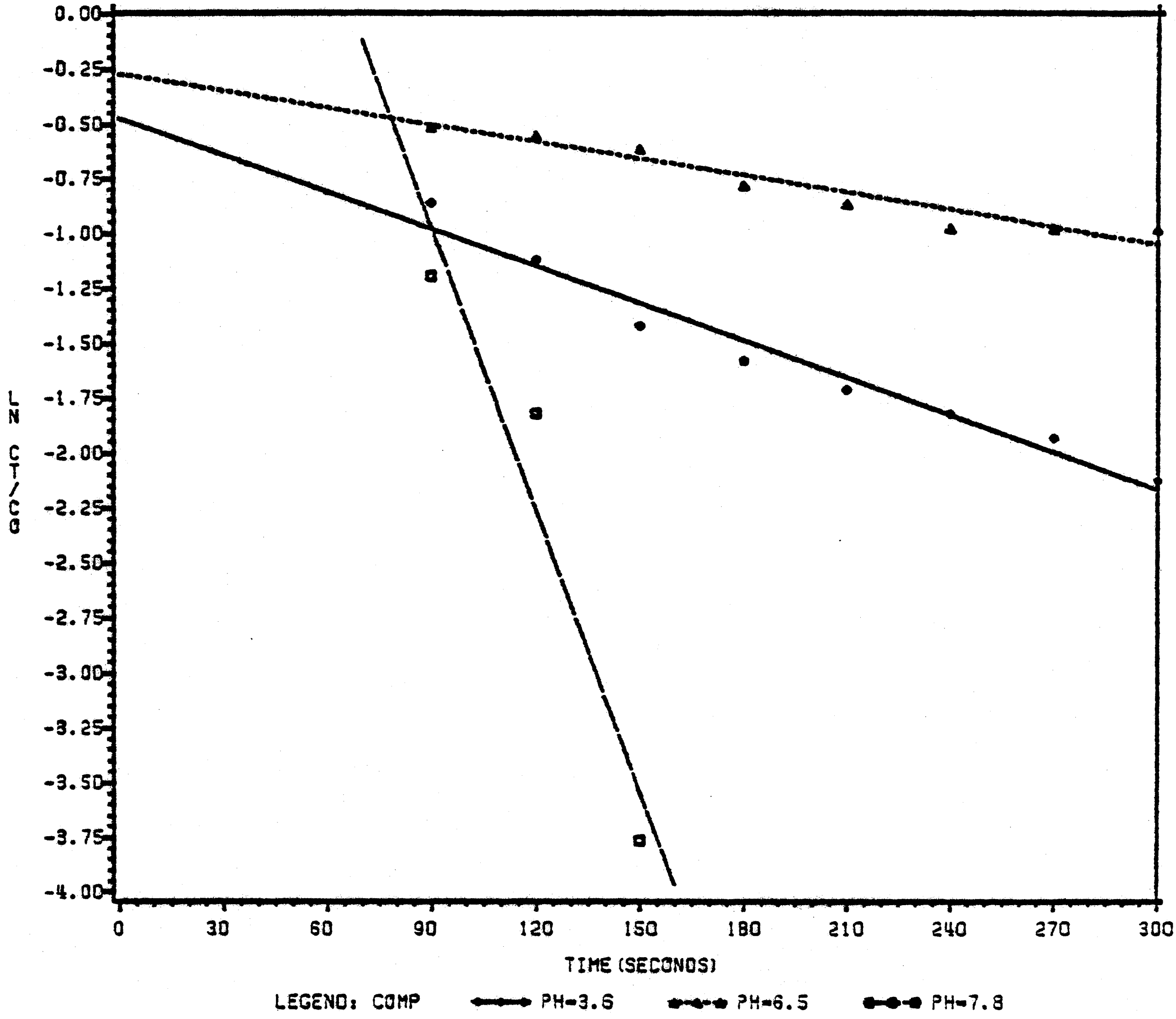


Figure 13. *ℓn* C(t)/C(0) vs Time for TOC Sample 1105

Cd and PO_4 could not be produced as concentrations after 90 seconds were below detection limits. The Clemson University Computer System was used with SAS/GRAPH to determine the linear regressions.

Table V presents the first-order constants for the second stage release of the minor components. As noted above, comparisons of these rate constants must be done with caution, but nevertheless can be instructive. Rate constants for any particular constituent with different extraction solutions varied, but not always significantly, or in a consistent trend. In some cases, rate constants for metals were greater at pH 3.6 than at either of the higher pH levels. This indicates that, following the initial release of the immediately soluble fraction, the rates of release for the different extraction solutions were similar. Comparing rate constants for different elements indicates the metals Fe, Mn, and Pb had similar second-stage release rates, which tended to be greater than TOC.

Measured rate constants for the major components were slightly higher in most cases than those for the minor components (see Tables III and VI). However, for the major components, aliquots were collected in six second rather than 30 second intervals, and an appropriate conclusion from the current level of analysis is that both the major and minor soluble components were released to solution in minutes or less. Differences in the rate constants for the major and minor components are not as important to actual releases that will occur as they may seem initially. If >80% of the total soluble acidity, sulfate, nitrate and ammonia is released in less than 30 seconds, and >50% of the total soluble fraction of minor components is released in the first 30 seconds, the net effect is similar in both cases.

TABLE V

SECOND STAGE RELEASE RATE CONSTANTS AND CORRELATION COEFFICIENTS FOR Mn, Cd, Pb, Fe, AND TOC

Element	pH	Sample Date Rate Constant (min^{-1}) (Correlation Coefficient)					
		0220	0401	0423	0606	0718	1105
Mn	3.6	*	1.12(1.0)	.68(.97	1.68(1.0)	***	***
	6.5	*	.74(.96)	*	.23(.87)	***	***
	7.8	*	1.11(1.0)	.51(.87)	.19(.89)	***	***
Pb	3.6	.98(.98)	.45(.94)	.68(.98)	***	***	***
	6.5	.80(.93)	.50(.89)	.53(.98)	***	***	***
	7.8	.54(.98)	.39(.95)	.44(.98)	***	***	***
Fe	3.6	**	.71(.96)	***	.47(.93)	***	***
	6.5	**	.42(.74)	***	*	***	***
	7.8	**	*	***	.61(.97)	***	***
TOC	3.6	.38(.98)	***	.20(.97)	***	.64(.97)	.45(.93)
	6.5	.07(.92)	***	.16(.97)	***	.14(.94)	.16(.97)
	7.8	.23(.97)	***	.25(.82)	***	1.00(.98)	2.50(.98)

*Concentrations after 90 seconds below LLD
**Data not applicable due to contamination
***Not analyzed for element

Table VI. SECOND STAGE RELEASE RATE CONSTANTS FOR SULFATE, NITRATE, AMMONIUM AND HYDROGEN IONS*

Ion	Sample A	Sample B	Sample C
	(Rate Constant (min^{-1})		
SO_4	2.33	1.07	1.00
NO_3	1.39	1.33	--
H	1.08	1.80	--
NH_3	0.74	3.77	3.62

For example, estimates of the residence time of airborne particles in the surface microlayer (SM) of the Atlantic Ocean and the Great Lakes range from a few seconds to tens of minutes (Elzerman, 1981). The SM is the interface between the atmosphere and the bulk waters of a water body and is generally considered to be 0.01 mm to 1 mm thick (Elzerman, 1981). Consequently, the data from the pump-flow system suggests that a large amount of the soluble material can be released to th SM before the particles pass through to the bulk waters. Therefore, the material released in what has been designated the first stage or initial fraction will be important since it will result in the greatest amount of material being released to the relatively small volume of the SM and less to the larger volume of the bulk waters as the particle sinks. This rapid rate of release of the trace metals from deposited aerosols may be a factor in the observed enrichment of trace metals in the SM (Elzerman and Armstrong, 1979; Lion et al., 1979).

Raindrops are another important case. Particles that serve as nucleation sites for raindrops have a finite period of time in which soluble components can be released. Likewise, particles scavenged by falling drops have only a short time (minutes) for the release of their soluble components. The soluble components in the initial stage would be important in this scenario. The data gathered using the pump-flow system suggests that an internal of even less than a minute may be sufficient to allow for the release of many soluble components to the raindrop.

As discussed in EXPERIMENTAL METHODS, four fractions of soluble components in ambient aerosols have been defined: 1) that released in the first-stage (aliquot), 2) that released in the second-stage (second aliquot to five minutes), 3) the amount released in five minutes (sum of 1 and 2), and 4) the total releaseable fraction (TRF, determined by long-term leaching or digestion). Significant conclusions can be drawn by comparing the data on the different fractions. The first fraction (30 seconds) data for minor components appear in Tables VII and VIII. As discussed earlier, the greatest quantity of soluble components was released during this interval. Another look at Table IV shows that in most cases >50% of the amount of material solubilized in five minutes was actually released in the first thirty seconds. This suggests that the first seconds of a particle's exposure to water will be important in influencing the initial fate of soluble components. Tables IX and X show that the trace metals released in five minutes are in most cases >50% of the TRF, whereas phosphate is only about 20%. The value for the TRF will give an indication of releases under extreme conditions, or perhaps over longer periods of time. Continuous pumping of solution in the pumped-flow technique means it is a non-equilibrium technique. Any compound exposed to the solution and having a finite solubility should eventually all be removed from the filter.

pH Effects on Release

There was no clear relationship between pH and the rate of release in the second stage. Elzerman *et al*. (1980) reported a possible inverse relationship between pH and the rate of release, but this trend did not always occur. However, hydrogen ion concentration can have an effect on the amount of a material released to solution. As stated earlier, four extraction solutions of varying pH's were used in this study. The first, a natural lake water, had an initial pH of 6.5. The second solution was a synthetic solution with a prepared pH of 3.6 at the

Table VII. Mn, Cd, Pb, AND Fe SOLUBILIZED BY EXTRACTION SOLUTIONS IN FIRST STAGE AS PERCENT OF TOTAL RELEASEABLE FRACTION

Extraction Solution	pH	% of TRF in First Fraction			
		Mn	Cd	Pb	Fe
Artificial Rain	3.6	49	49	56	11
Lake Issaqueena	6.5	43	45	48	12
Artificial Lake	7.8	45	34	30	8

Table VIII. PHOSPHATE, Cl, AND TOC SOLUBILIZED BY EXTRACTION SOLUTIONS IN FIRST STAGE AS PERCENT OF TOTAL RELEASEABLE FRACTION

Extraction Solution	pH	% of TRF in First Fraction	
		PO_4	TOC
Artificial Rain	3.6	21	24
Lake Issaqueena	6.5	23	30
Artificial Lake	7.8	23	20

Table IX. Mn, Cd, Pb, AND Fe SOLUBILIZED BY EXTRACTION SOLUTIONS AFTER FIVE MINUTES AS PERCENT OF TOTAL RELEASEABLE FRACTION

Extraction Solution	pH	% of TRF Released in 5 Minutes			
		Mn	Cd	Pb	Fe
Artificial Rain	3.6	62	55	84	19
Lake Issaqueena	6.5	54[1]	49	65	
Artificial Lake	7.8	58	42	47	13

Table X. PHOSPHATE, Cl AND TOC SOLUBILIZED BY EXTRACTION SOLUTIONS AFTER FIVE MINUTES AS PERCENT OF TOTAL RELEASEABLE FRACTION

Extraction Solution	pH	% of TRF Released in 5 Minutes	
		PO_4	TOC
Artificial Rain	3.6	21	54
Lake Issaqueena	6.5	23	114[1]
Artificial Lake	7.8	23	27

[1] Contaminated value

beginning of the study. The final extraction solutions were a synthetic lake water with an adjusted pH of 7.8 and DDD water.

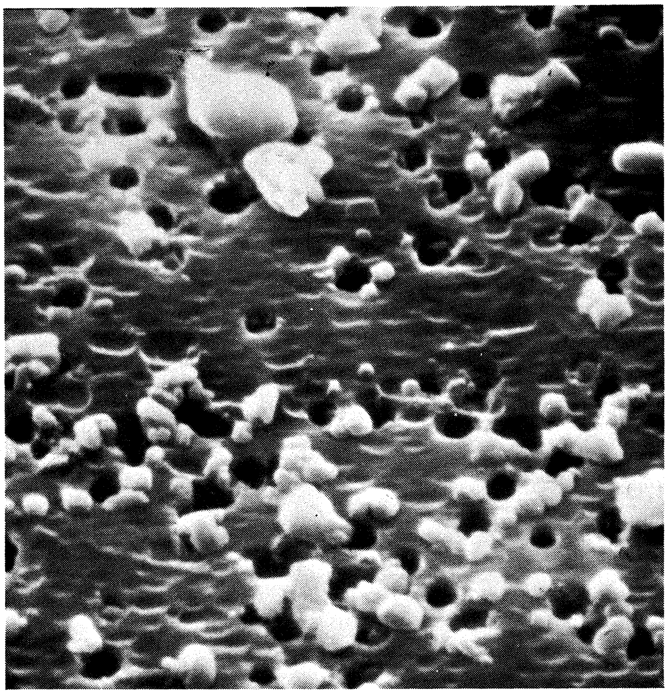
For major soluble components, the amount of release was not significantly affected by pH. pH effects were most apparent for lead in both the initial stage an the total five minute release. The effect is clear in Tables VII and IX. As expected, the lowest pH solution, 3.6, released the greatest quantity of lead in the 30 second fraction (65% of the TRF) and the five minute fraction (84% of the TRF). The basic solution, pH 7.8, showed the least amount of lead released with 30% of the TRF during the first 30 seconds and 47% of the TRF over 5 minutes. Cadmium release showed a lesser degree of pH dependence. The cadmium released in the first fraction was 49% and 45% for the 3.6 and 6.5 pH solutions, respectively, while the 7.8 pH solution extracted 34% of the TRF in the first fraction. The pH effect is even less apparent for Cd in the data for release in five minutes. Iron and manganese did not show any significant pH dependence on the extent of release (Tables VII and IX). The phosphate release studies also failed to show a significant effect of pH on release (Tables VIII and X). The release of phosphate was <23% of the TRF over the five minute period for all three solutions. The TOC data showed little pH effect on the percentage release for the first fraction (Tables VIII and X). However, the five minute release dated showed significant effects of pH on release, with 54% and 27% of the TRF for pH's 3.6 and 7.8, respectively.

SEM and XRF Results

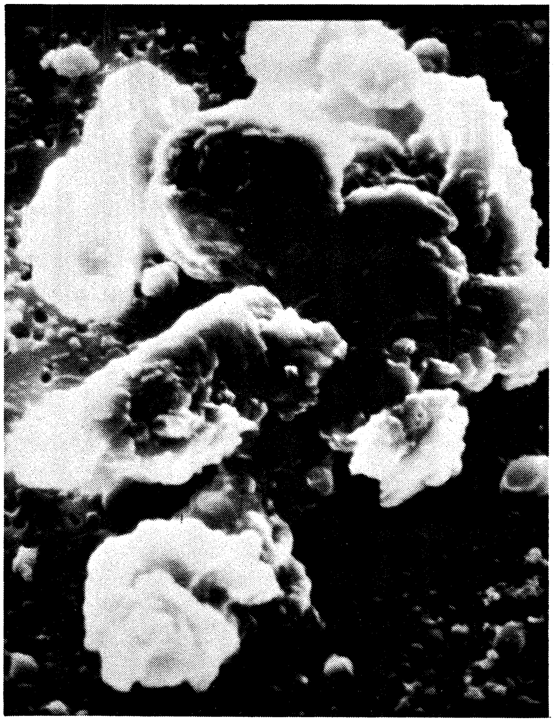
A scanning electron microscope (SEM) was used to study the surface of the aerosol-laden filters. On the following pages are electron micrographs of filters subjected to the extraction procedures described earlier with DDD water for various amounts of time. Figures 14 A and B show SEM micrographs representing particles prior to extraction. Note the pores in the filter surface, which are approximately 0.8 um in diameter, according to the manufacturer. Figure 14 A shows a large number of particles that are <0.8 um in diameter, which theoretically could pass through the filter pores (see discussion below). Other particles visible in the micrographs range upwards to >10 um. Figure 14 B shows a typical large agglomerate representative of those found scattered over the surface of the filter. The agglomerates were likely ammonium sulfate that may have formed in the atmosphere and been collected by the samplers or formed on the filter during collection. As discussed in the INTRODUCTION, ammonium sulfate has been reported as a common major constituent of ambient aerosols (O'Conner and Jaklevik, 1981; Lewis and Macias, 1980).

Figures 15 A and B are micrographs of particles after contact with water for a short period of time (1 minute). Figure 15 A shows the large agglomerate has begun to fall apart, revealing particles that were contained within. These small particles may have served an nucleation sites for the agglomerate. Also note a general decrease in the number of small particles, compared to figure 14, suggesting solubilization or loss by wash-through of the small particles, leaving on the filter larger, more insoluble particles. Figures 16 A and B show the filter surface after one hour of contact with DDD water. Again, note further reduction in the number of small particles and the absence of the large agglomerates.

SEM-XRF (combined scanning electron microscopy and X-ray fluorescence spectroscopy) was used to analyze individual particles remaining



A



B

Figure 14. Filter Surface Prior to Extraction

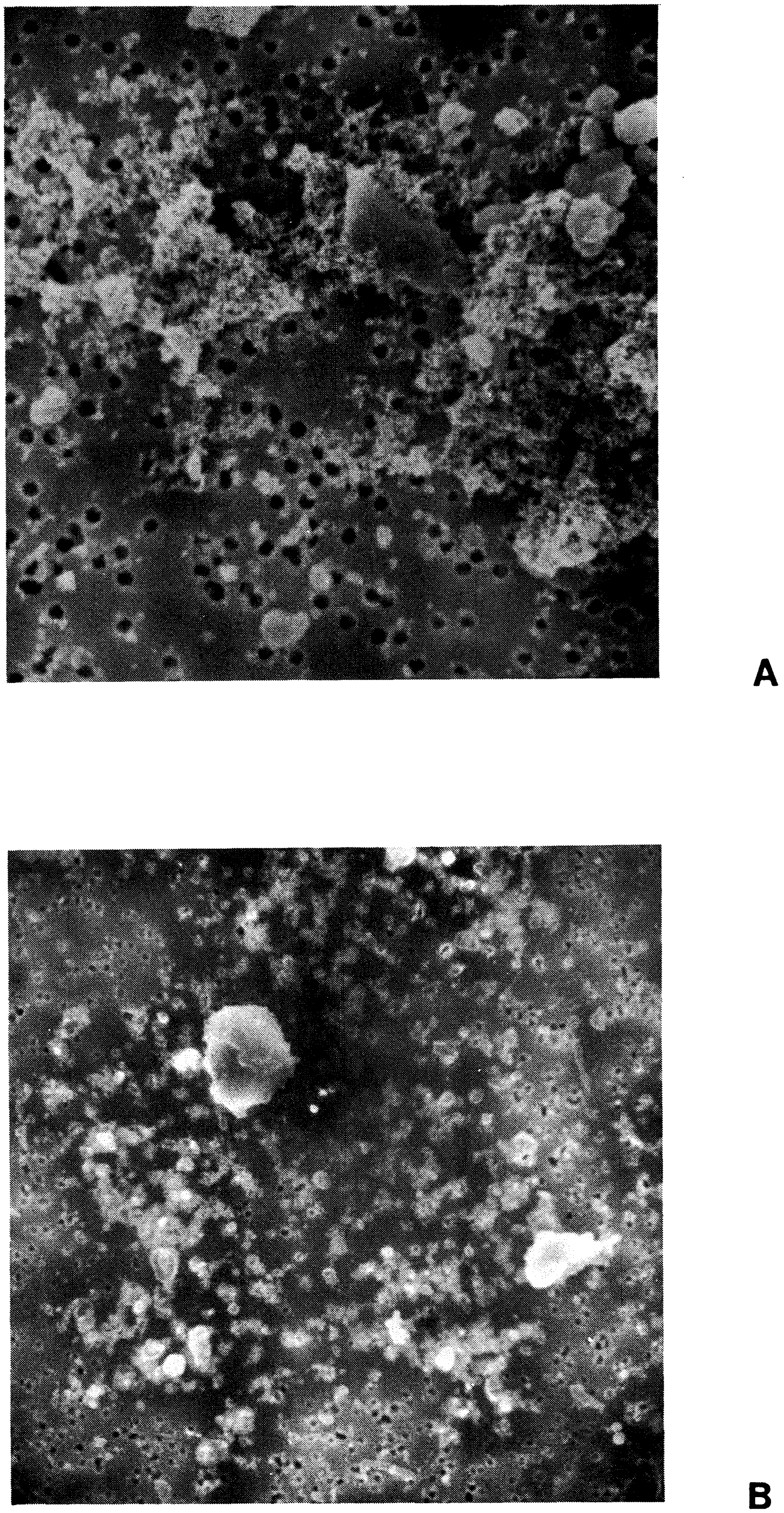


Figure 15. Filter Surface after Short Extraction Interval

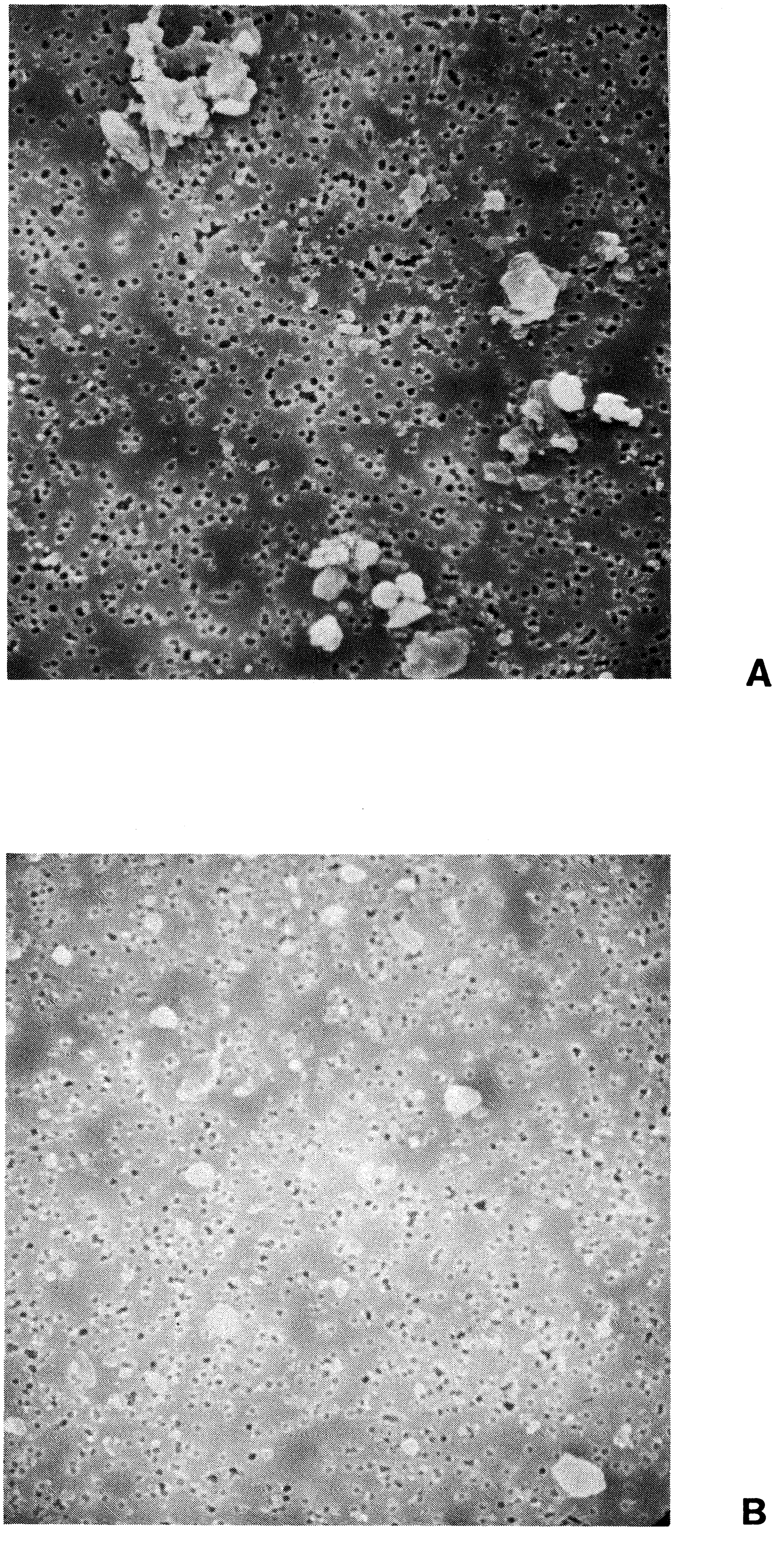


Figure 16. Filter Surface after Long Extraction Interval

on a filter disc following one hour exposure to DDD water at a flow rate of 20 ml/minute in the previously described pump-flow device. Various particles were observed and some typical results are presented in Table XI.

The major elemental components of the undissolved fraction were Al, Si, and Fe, with smaller amounts of Ca and K present, suggesting that the particles that remained after solubilization were likely derived from soil or fly ash. The abundance of iron in the SEM-XRF spectra is not surprising as Clemson is in the Piedmont region of South Carolina where clays high in iron content are common. The presence of iron in the insoluble fraction is also consistent with the release data, discussed above, which showed only a small amount of the iron was solubilized. The silica was likely in the form of fly ash, clays, or a-quartz(SiO_2), as seen by O'Connor and Jaklevic (1981) in St. Louis aerosols. The Al was probably also associated with clays. The apparent absence of carbon in the samples, which can be a major component of aerosols (Lewis and Macias, 1980), is easily explained since elements below Na were not detected by the XRF technique used.

Investigation of Particle Wash-Through

The significance of possible 'wash-through' of small particles through the 0.8 um pores of the aerosol collection filter during the extraction procedures and the possible contribution of these 'undissolved' particles to the concentrations seen in the first aliquots were investigated. The SEM micrographs shown in Figures 14 A and B of an unextracted filter indicate a number of particles <0.8 um in diameter were present on the Nuclepore filter surfaces. These particles could

Table XI. SEM-XRF OF THE INSOLUBLE FRACTION OF CLEMSON AEROSOLS

Sample	Approximate Size	Description of Particle Shape	Major Elements (in Approximate Order of Decreasing Abundance)
1	5 µm	irregular plate	Al, Si, Fe
2	10 µm	irregular plate	Si, Al, K, Ca, Fe
3	3 µm	irregular plate	Al, Si, Fe
4	1 µm	rod	Si, Al, K, Fe
5	10 µm	irregular plate	Al, Si, Fe
6	5 µm	agglomerate	Si, Al
7	1 µm	crystal	Si

theoretically wash-through the filter pores 'undissolved' and contribute to the constituent concentrations in the aliquot.

A simple three chamber filter devise was used to investigate wash-through, consisting of three plastic filter holders in series separated by a small void space above each stage. The 0.8 um pore filter with collected aerosol was placed on the upper of the three tiers followed by an 0.4 um pore Nuclepore filter on the middle tier, and finally on the lower tier an 0.2 um Nuclepore filter. A Tygon tube was connected to the outlet port of the lower chamber to allow a vacuum to be placed on the system to obtain flow through the small pore sizes of the two lower filters. The extraction solution for this investigation was DDD water. Extractions were performed for 30 seconds and 180 seconds. These two intervals were chosen to show the possible effects of particle wash-through to the initial stage from small 'free' particles scattered over the surface of the filter and the possible delayed contribution of small particles coming from the breakup of the previously mentioned ammonium sulfate agglomerates. Following the extraction procedures the filters were dried before preparation for the SEM analysis.

Figures 17 A, B, and C show the filter surfaces after the 30 second extraction interval. Note the similarity between the micrographs in Figure 17 A and those for the short extraction interval in Figures 15 A and B. Figures 17 B and C show representative areas of the 0.4 um and 0.2 um filters as seen under the SEM. Note the absence of particles on their surfaces, which indicates that little significant particle wash-through had occurred of particles <0.8 um but >0.2 um in diameter. Figures 18 A, B, and C are micrographs from the 180 second wash-through

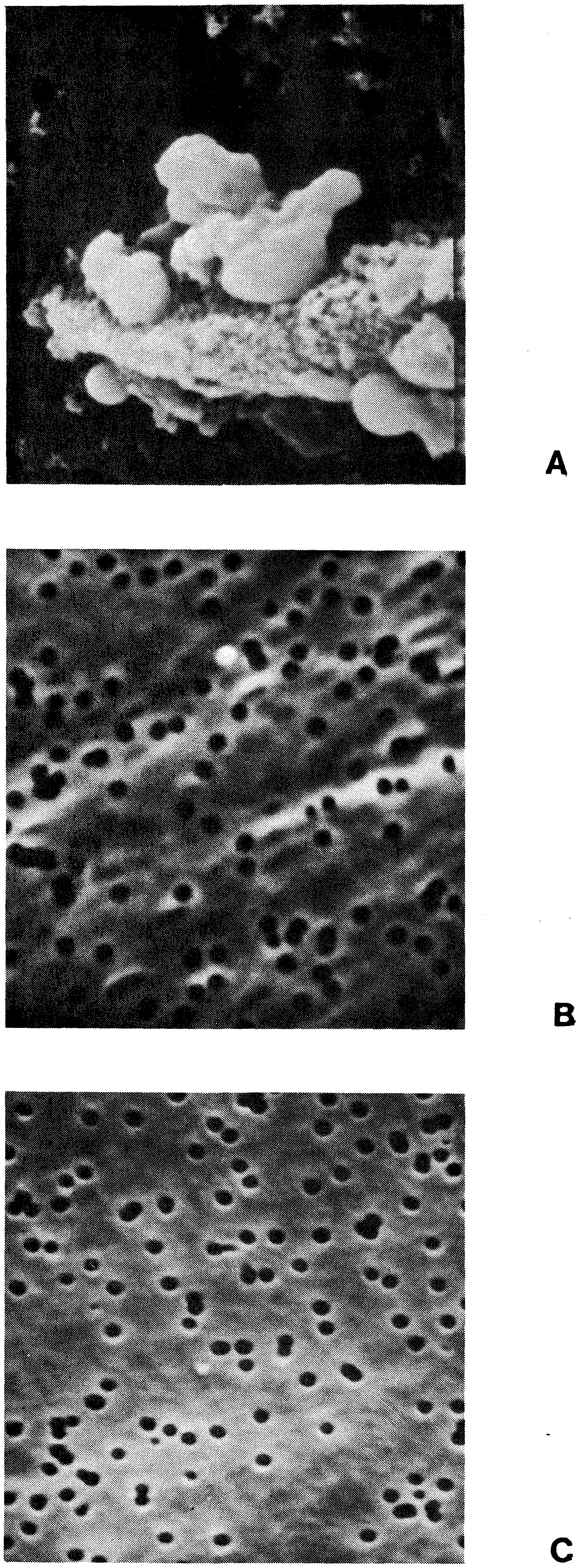


Figure 17. SEM Photographs of the 30 Second Wash-Through Study: A(0.8 μm), B(0.4 μm) and C(0.2 μm)

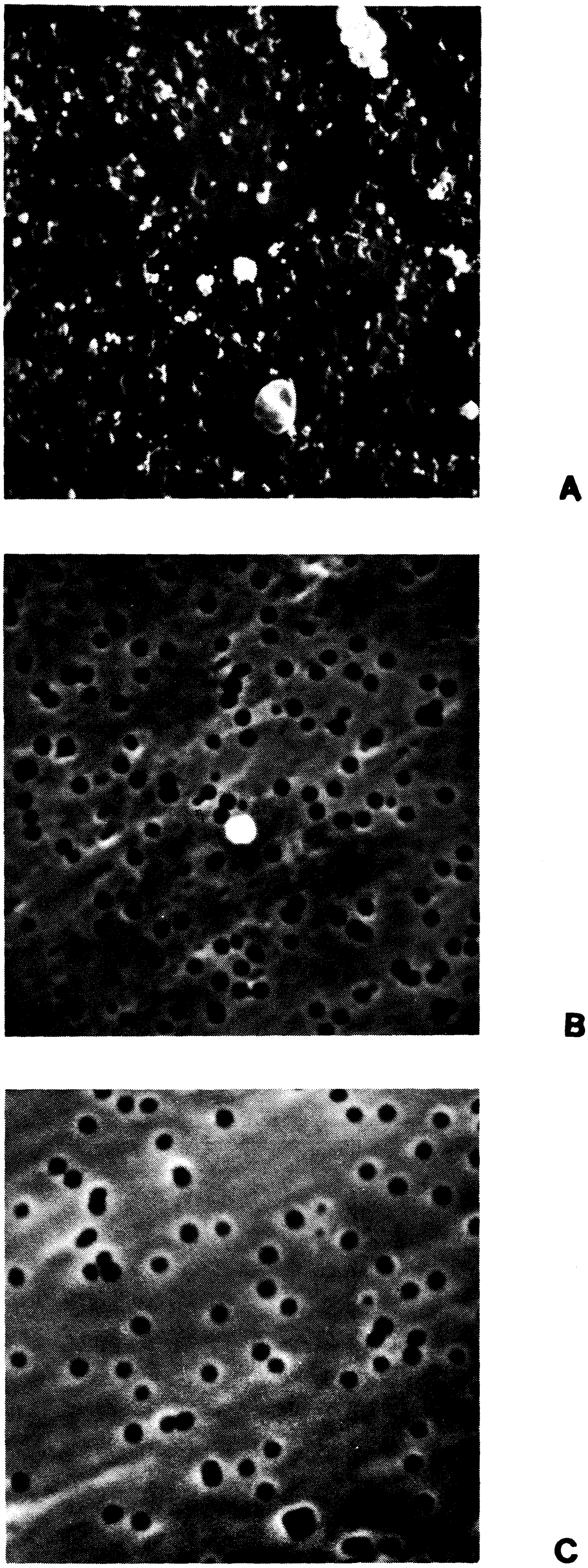


Figure 18. SEM Photographs of the 180 Second Wash-Through Study: A(0.8 μm), B(0.4 μm) and C(0.2 μm)

study. Note the presence of the less soluble material remaining on the 0.8 um filter in Figure 18 A and the presence of particles <0.8 um in diameter which have remained on the filter. As seen before in the 30 second extraction, the 0.4 um and 0.2 um filters show an absence of particles on their surfaces.

The SEM micrographs do not give absolute evidence that particle wash-through did not occur. What they suggest is that the effect was not significant enough to change the observed rate and extent of release. Several possible explanations can be given for the apparent lack of particles on the lower two filters in each of the two cases. The first is that those particles that do pass through the 0.8 um pores undissolved quickly dissolve and pass through the lower filters. The second possibility is that some of the particles that wash through are <0.2 um in diameter and pass through all three filters. An observation to make at this point is that not all of the particles <0.2 um passed through the 0.8 um filter, therefore it is unlikely that all of these small particles would wash-through the lower smaller pore-sized filters. From the above observations and discussion it seems likely that the large concentrations seen in the first extraction aliquot are not a result of particle wash-through.

Known Lead Compound Release Study

Two lead compounds were used to study the release of lead to solution from pure substances. Compounds with different solubilities were chosen to observe the effect of solubility on the extent and rate of release. The lead compounds chosen were lead nitrate, $Pb(NO_3)_2$, and lead oxide, PbO, which have solubilities of 276.5 g/l and 0.017 g/l, respectively (CRC, 1980). Approximately 4 ug of Pb as Pb in the individual compound were placed on each filter, as described in EXPERIMENTAL METHODS. Both compounds are crystalline as a solid. When the compounds were dissolved in water, placed on a filter and dried under a light, the structure of the dried compound was possibly different from the original substance. This type of study allowed for the observation of the release of lead without interferences from other compounds. It also allowed for the study of a compound whose form on the filter was known to be the same over the entire filter surface. The TRF for the lead compound study was approximately 4 ug.

Data for the release of lead from the pure compounds (Tables XII and XIII) were similar in trend to those for the collected aerosol lead (See Figures 19 and 20). A large initial concentration occurred in the first eluant aliquot (30 seconds) followed by exponentially diminishing concentrations thereafter. The 3.6 and 6.5 pH solutions released essentially all of the lead from lead nitrate in the first thirty seconds. For the lead oxide, >70% of the total mass released in five minutes was released in the first thirty seconds for all three solutions. The first fraction release percentages also show the effect of pH on lead release for both compounds (Table XII). The lead nitrate data showed the 3.6 and 6.5 pH solutions released 101.4% and 94.5% of the TRF respectively, while the artificial lake solution released only 61.8% of the TRF in the first fraction. The lead oxide study showed the same trend of pH effect with first stage releases of 48.6%, 42.5% and 21.7% of the TRF for the increasing pH values, respectively. The data for release in five minutes for both compounds also showed the same pH trend. As expected, the lead nitrate, the more soluble of the two compounds, released a greater amount of lead to solution than did the less soluble lead oxide.

Table XII. LEAD COMPOUNDS SOLUBILIZED BY EXTRACTION SOLUTIONS IN FIRST FRACTION AS PERCENT OF TOTAL LEAD RELEASEABLE

Extraction Solution	pH	% of TRF in First Fraction	
		Lead Nitrate	Lead Oxide
Artificial Rain	3.6	101.4	48.6
Lake Issaqueena	6.5	94.5	42.5
Artificial Lake	7.8	61.8	21.7

Table XIII. LEAD COMPOUNDS SOLUBILIZED BY EXTRACTION SOLUTIONS IN FIVE MINUTES AS PERCENT OF TOTAL LEAD RELEASEABLE

Extraction Solution	pH	% of TRF Released in Five Minutes	
		Lead Nitrate	Lead Oxide
Artificial Rain	3.6	107.9	59.0
Lake Issaqueena	6.5	100.7	48.3
Artificial Lake	7.8	69.3	29.8

Total lead per filter = 4 μg

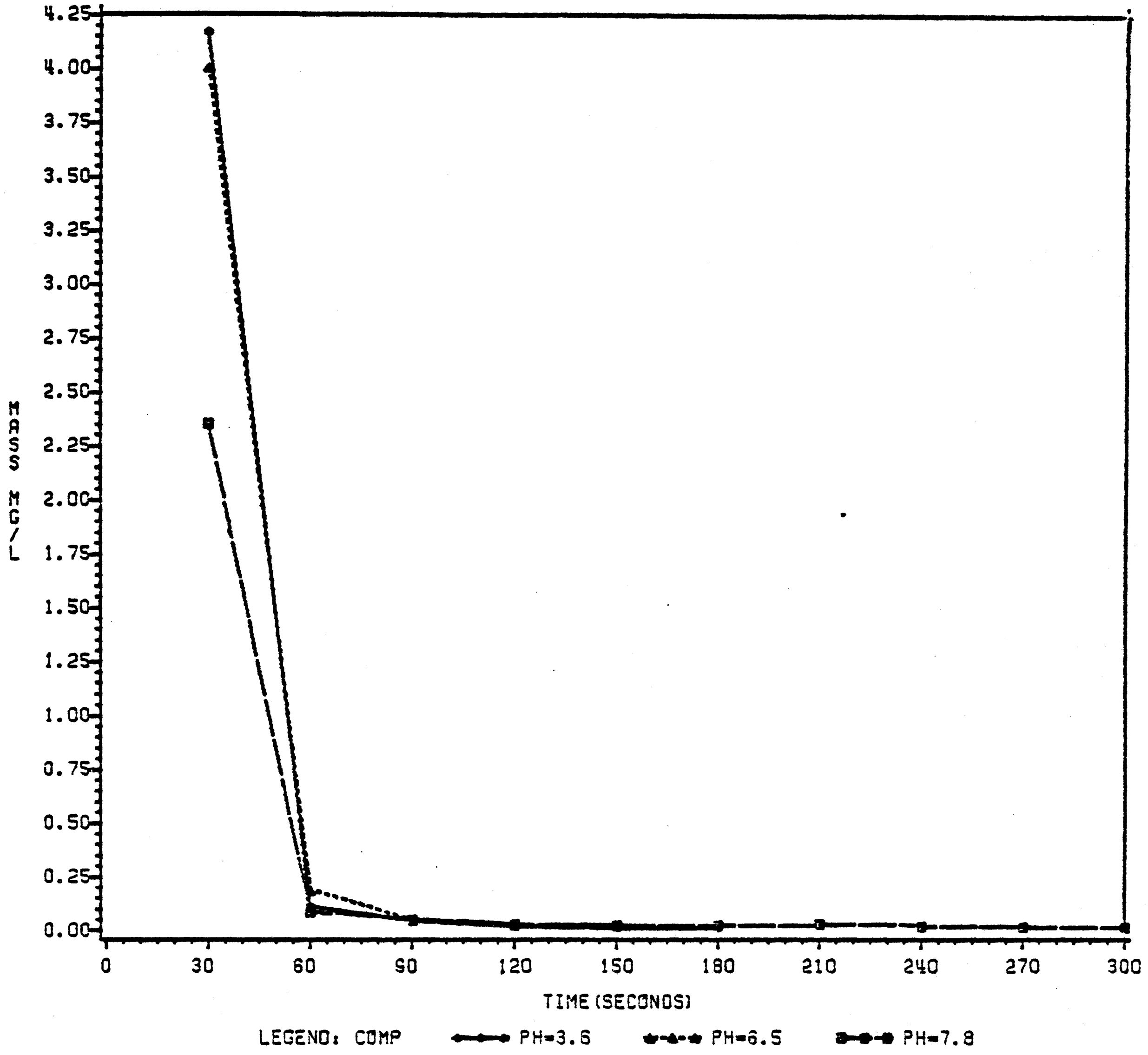


Figure 19. Lead Nitrate Release from Prepared Filter

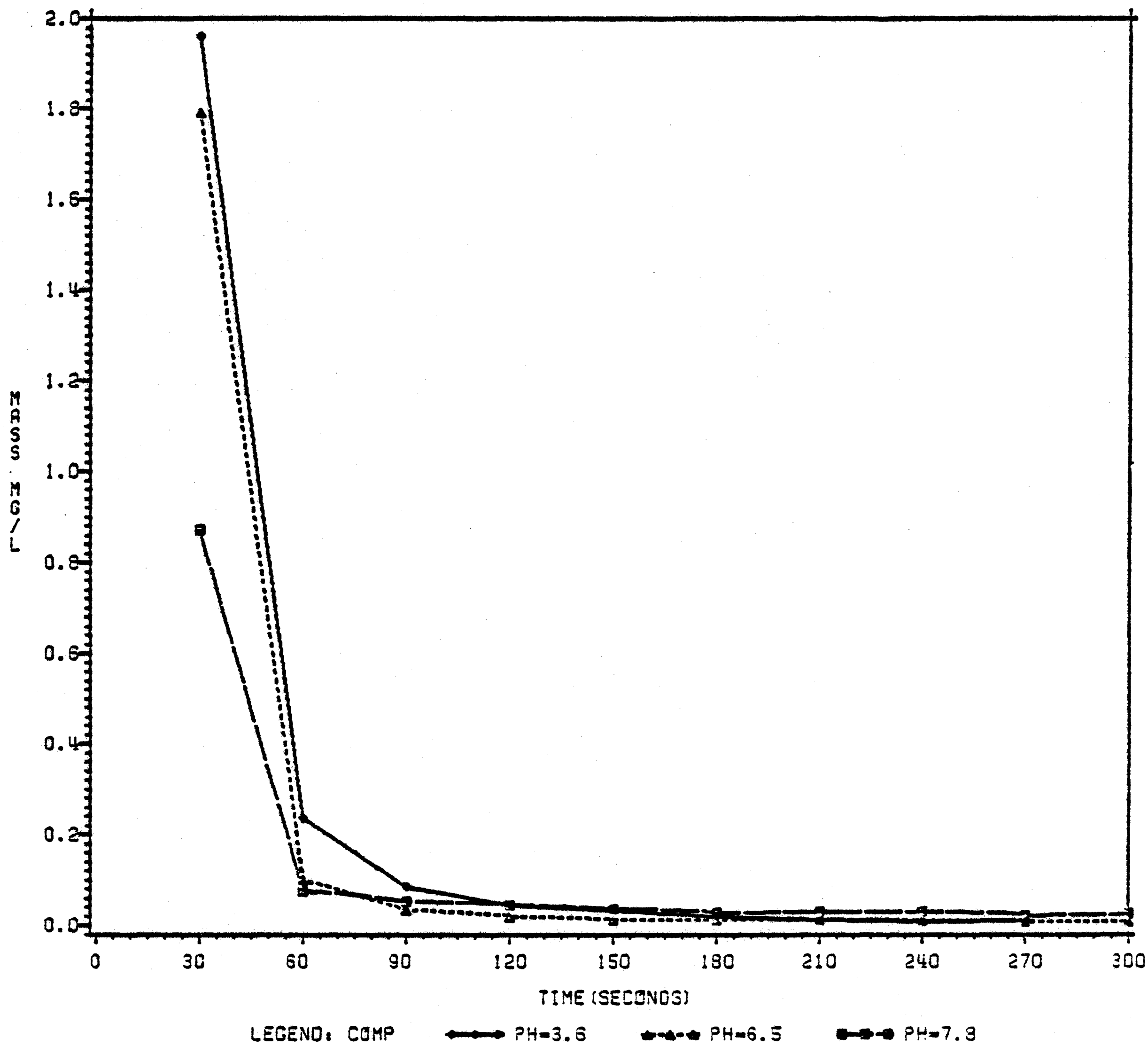


Figure 20. Lead Oxide Release from Prepared Filter

If the release of lead from the pure compounds is treated as above for the ambient aerosols, rate constants can be derived for the second-stage of release. See Figures 21 and 22 for representative ln C(t)/C(0) versus time plots. Again, the value of the second fraction (60 seconds) served as C(0), Tables XIV and XV give the rate constants for the lead nitrate and lead oxide release studies. The more soluble compound, lead nitrate, was apparently released more quickly. The rate constants for the release of lead from aerosols (Table V) are similar to those for the two pure compounds. Although there is no direct relationship between the rate constants, the 3.6 and 7.8 pH extraction solutions showed second-stage rate constants more consistent with those of lead oxide than lead nitrate.

Several interesting points can be made regarding the release from the pure lead compounds. As with the extent and rate of release for the minor components of aerosols, the general trend and time scale of the release of lead from the pure compounds is more significant than the actual measured rate constants. The more soluble lead nitrate appeared to be released at a faster rate than did the less soluble lead oxide, however, both compounds and ambient aerosols showed similar release trends, which might indicate mechanisms for release are similar. The effect of pH on the extent of release of lead from ambient aerosols and the pure compounds was also similar, especially for the lead oxide and the ambient aerosols.

Note that not all consequences of the mechanism and technique have been investigated. Lead oxide has a smaller equilibrium solubility than lead nitrate, but continuous pumping of solution through the filter should eventually remove all of the lead oxide. As discussed above,

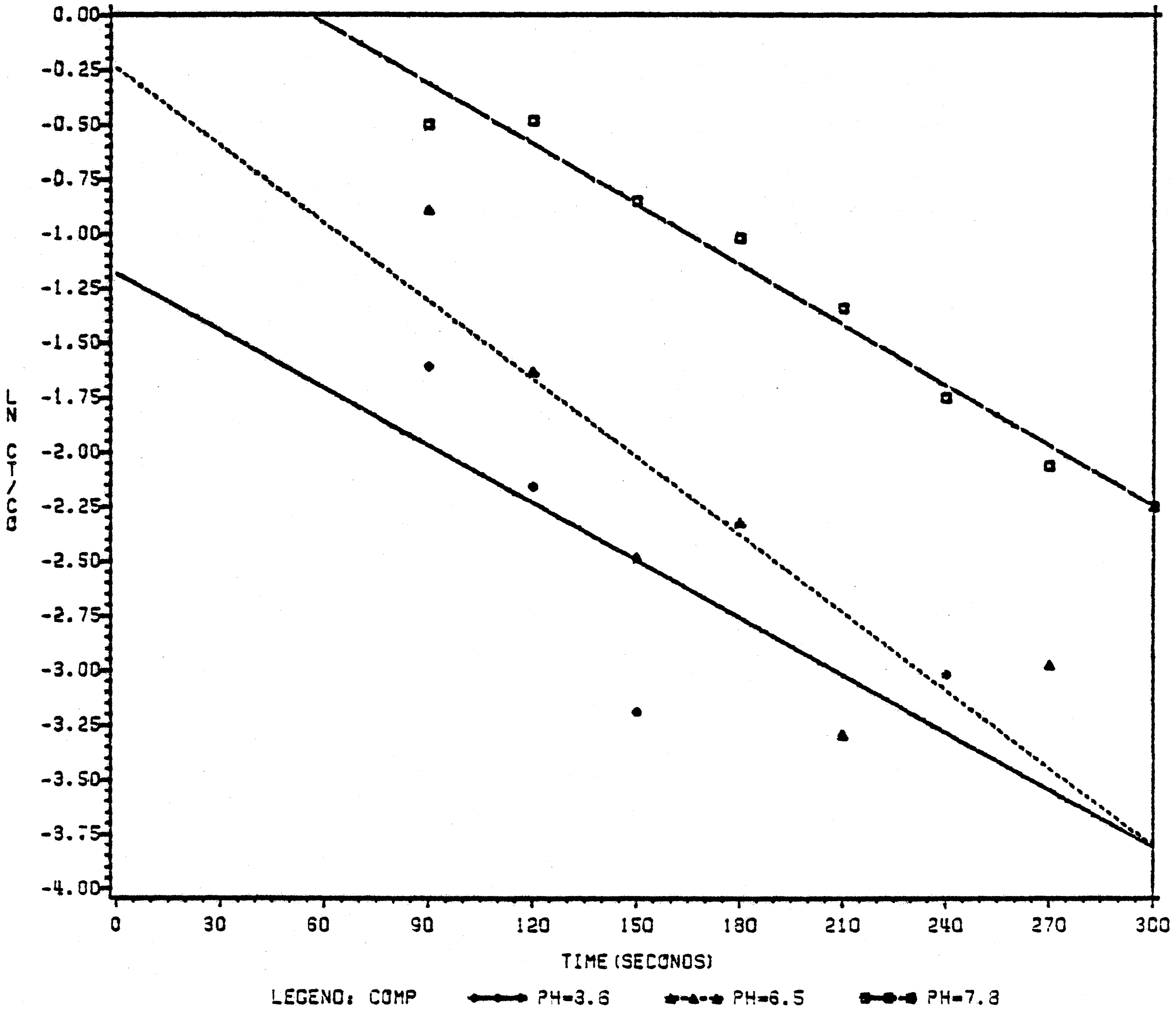


Figure 21. ℓn C(t)/C(0) vs Time for $Pb(NO_3)_2$

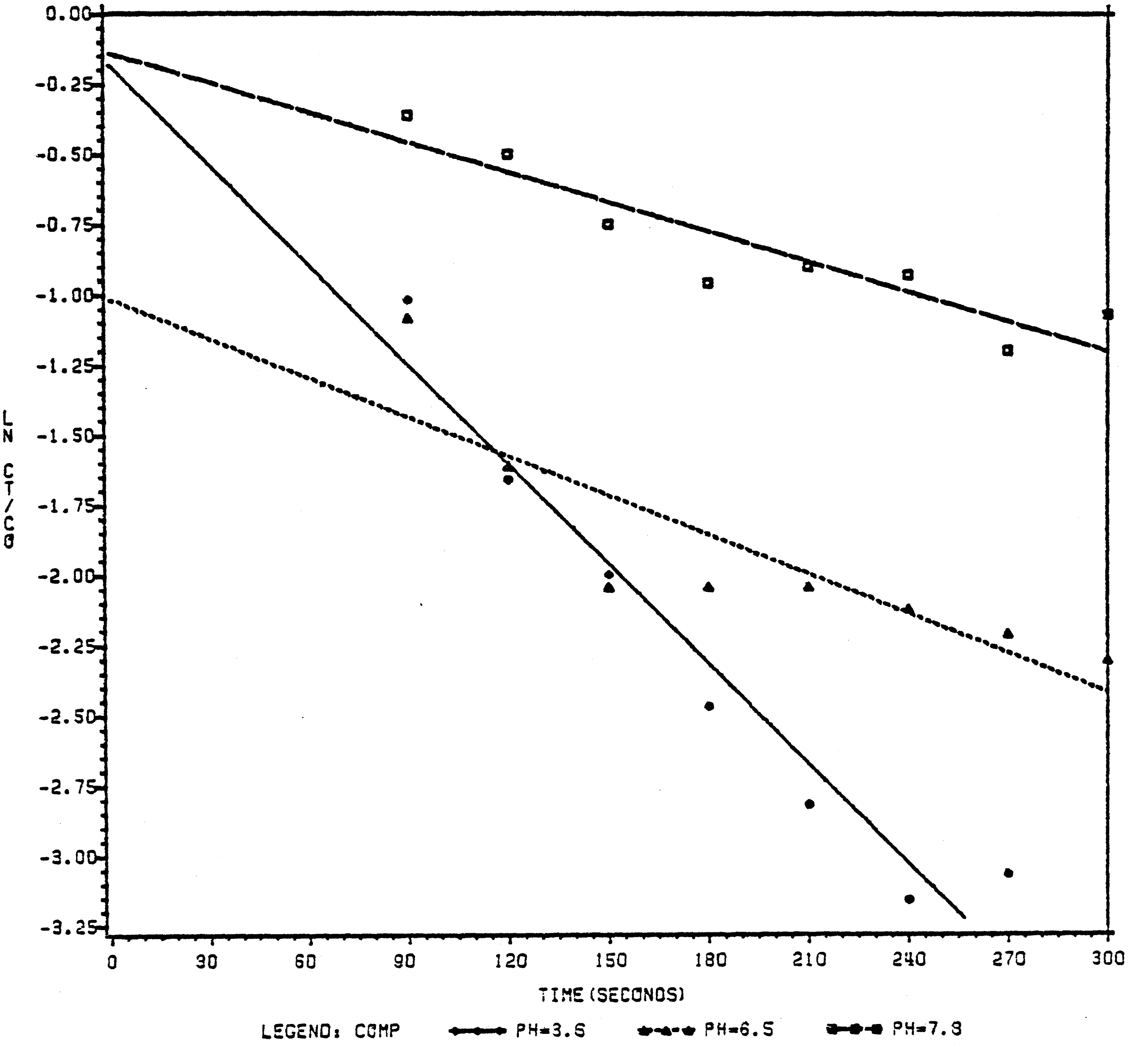


Figure 22. ℓn C(t)/C(0) vs Time for PbO

Table XIV. SECOND STAGE RATE CONSTANTS AND CORRELATION COEFFICIENTS FOR LEAD NITRATE

pH	Rate Constant (min^{-1}) (Correlation Coefficient)		
	Experiment		
	1	2	3
Lead Nitrate			
3.6	1.56(.98)	1.01(.97)	2.06(1.0)
6.5	.77(.97)	.88(.99)	1.16(1.0)
7.8	.55(.99)	.26(.89)	.39(.89)

Table XV. SECOND STAGE RATE CONSTANTS AND CORRELATION COEFFICIENTS FOR LEAD OXIDE

pH	Rate Constant (min^{-1}) (Correlation Coefficient)	
	Experiment	
	1	2
Lead Oxide		
3.6	.71(.97)	.63(.95)
6.5	.28(.86)	.35(.88)
7.8	.21(.93)	.24(.96)

however, the data indicate some lead is quickly solubilized from lead oxide, followed by a much slower release. The fraction of lead initially released from lead oxide may result from the smaller particles, from an adsorbed form of lead, or from contaminants.

Application of Data

The data generated from the pump-flow system cannot be directly applied to conditions other than those set forth in this research. The rate constants and percent releases cannot be used to estimate exactly what will happen under natural conditions in the environment. They are, however, useful in comparing the relative effects of various parameters on releases and the general time scale of release. For example, the three different pH solutions caused a different rate and amount of release of lead from ambient aerosols and pure lead compounds. The rate constants and release percentages from the pump-flow system may not be useful in determining actual quantitative releases of lead to water systems, but the system does allow the study of the relative effects that the different pH solutions would have on the release. The lead data in Table X is a good example. The three solutions with pH's 3.6, 6.5, and 7.8 resulted in the release of 85%, 65%, and 47% of the TRF from aerosols, respectively. These percentages do not indicate that these quantities of lead will necessarily be released to some water system, but that a water system with a low pH could release more lead to solution than would a higher pH solution in a short time interval.

Furthermore, investigation of different techniques for estimating the rate of release of soluble components from ambient aerosols determined that the pump-flow system yields data consistent with other techniques and capable of indicating the approximate time scale of release to solution (see above and Perry, 1982). The important time interval for contact between ambient aerosols and aqueous systems of interest, for example rain, is on the order of tens of seconds to minutes or longer. The pump-flow technique suggests that in this time interval considerable or even total release to solution of the soluble components of ambient aerosols can occur and the release rate tends to decay exponentially.

V. SUMMARY AND CONCLUSIONS

The pump-flow method of Elzerman *et al*. (1980) with an in-line filter holder was found to be useful for studying the release of the soluble components of aerosols to solution. One of the primary advantages of the technique was that it minimized outside contamination.

Further investigation is recommended regarding the release of minor components from aerosols to solution as affected bu and particle size. The use of various-sized collection filters would aid in this work. Shorter collection intervals for the study of the release of minor as well as major aerosol components might also be useful. Also, the influence of meteorological and wind trajectory factors should be more fully considered.

The two-stage model used by Elzerman *et al*. (1980) for the release of lead from aerosols to solution was found applicable to the release of major and minor trace components from aerosols. The model is adequate for many purposes to demonstrate what may occur in the early stages after particle contact with a moist surface. Solubilization generally occurs quickly in the first few seconds followed by an exponential decrease in the mass rate of release.

The major conclusion of this research is that the release of major and minor soluble components from ambient aerosols to water systems begins immediately and is significant within seconds after impaction or impingement to a water system. The pH of the solution will have some effect on the rate and extent of release of several trace constituents, for example Pb, but not on others like Mn, Fe, and PO_4 or on the major soluble components. Regardless of the pH of the solution, release of soluble components essentially begins immediately upon contact with water. A majority of the soluble fraction is usually released in less than 30 seconds and essentially all of the soluble fraction is released in less than 5 minutes. Therefore, the fate of soluble components of aerosols, many which are environmentally significant, will initially be controlled by the dissolved phase process.

Many of the soluble components of aerosols are associated with smaller-sized particles, which allows for their possible transportation to sites far removed from their sources (Wiener, 1979). This increased time that a particle remains 'airborne' will increase the probability that a particle will come in contact with water, allowing for the release of soluble materials to solution that might otherwise fall as dry fallout. As suggested by this research, the pH of precipitation may control the amount and rate of release of components in rain drops.

Particles may also be deposited directly on the surfaces of lakes, oceans, or rivers as dry fallout. Once in contact with the surface microlayer (SM) of a body of water, the soluble components will be released on short time scales. Estimates of the residence time of particles in the SM range from a few seconds to tens of minutes (Elzerman, 1981), a period of time sufficient to allow for many of the major and minor components to be released. Once released to the SM, a number of processes, chemical, biological, and physical, can affect the soluble components and may control the concentration of chemical species in this thin layer. The SM has been shown to contain enriched levels of trace metals, microorganisms, particles, and dissolved and particulate organic matter (Elzerman _et_ _al_., 1979, Lion _et_ _al_., 1979). The presence of organic acids, humic acids for example, and proteins may provide sites for complexation of heavy metals which may result in their enrichment in the SM (Piotrowicz et al., 1972). The possibility of trace constituents becoming associated with particulate matter present in the SM is another possible fate (Elzerman, 1981).

The deposition of aerosols in the respiratory tract has been shown to have an effect on human health (Nat. Academy of Science, 1979). The most sensitive region of the lungs is the alveoli, where gas exchange occurs. The epithelial tissues in this region are very thin, thus allowing for access of soluble aerosol material to the pulmonary blood within minutes (Nat. Academy of Science, 1979). Studies with the pump-flow system suggest that release of soluble components of aerosols to surrounding fluids is very rapid. Therefore, the rate of clearance or removal from the sensitive regions of animal lungs is very important.

Data from the pump-flow system can say nothing about the ultimate fate of soluble components released to the body. It only suggests that the soluble components may be released quickly to the body where any number of possible reactions may occur. The impact of the released components will vary and may depend on the synergistic effects of other pollutants contained in the aerosols (LaBelle and Brieger, 1959). Since many toxic components of aerosols have been shown to be at least partially soluble over a pH range from 3.6 to 7.8, solubilization in the lungs may have significant health effects.

The data derived from the pump-flow system can also be used to make other observations on the initial fate of soluble materials derived from atmospheric aerosols on watersheds. The contribution of dry fallout to the annual flux of certain metals to the forest floor can be significant (Lindberg and Harriss, 1981). Heatley (1982) found that ≅20% of the total lead input and ≅23% of the total cadmium input was contributed by dry fallout to the rural South Carolina Piedmont watershed of Lake Issaqueena. Dry fallout is deposited on the forest canopy and the forest floor, where accumulation occurs. Heatley (1982) found that 93% of the total lead and 98% of the total cadmium from atmospheric input remains in the Issaqueena watershed. The pump-flow data suggests that some of this dry deposition material can be quickly solubilized upon contact with soil moisture or the occurrence of a precipitation event, releasing significant quantities of material to the surrounding environment. A number of fates await this released material, including adsorption or complexation by organic material in the forest litter, uptake by organisms, adsorption by the soil, precipitation with sulfides, or runoff to nearby streams. The ultimate fate of atmospheric deposition will be determined by the chemical, biological, and physical processes in the watershed, but the initial fate of soluble components from atmospheric aerosols will be determined by the dissolution of the deposited material.

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APPENDICES

TABLE A-I

ARTIFICIAL LAKE WATER

The artificial lake water was prepared for a total hardness of 200 mg/ℓ using the following:

111 mg/ℓ $CaCl_2$, and

96 mg/ℓ Na_2CO_3 with the pH adjusted by bubbling CO_2 through the solution to pH 7.8

TABLE A-II

ARTIFICIAL RAIN WATER

Reagent	Concentration (M)	Volume (mℓ)*
$MgSO_4$	0.001	25.0
Kcl	0.001	11.8
$CaSO_4$	0.001	45.0
Na_2SO_4	0.01	13.0
NH_4Cl	0.01	19.7
NH_4NO_3	0.01	9.0
HNO_3	0.01	21.9
H_2SO_4	0.01	24.6

*Volume added to 20 liters.

The artificial rain water formula was prepared by Dr. Robert Talbot using data from the NADP (1979) Station on campus to match precipitation in the Clemson area. Volumes listed in the right column were added to 20 liters of DDD to prepare the solution.

Appendix B

Conditions for Graphite Furnance

The following conditions were used in the determination of trace metals on the Perkin-Elmer HGA-2100 Graphite Furnace (Talbot, 1978) (Nonpyrolytically-coated tubes were used in all cases):

Furnace conditions:

Pb: wavelenth: 283.3 nm
gas flow: interrupt
drying phase: 30 seconds at 125°C
charring phase: 30 seconds at 600°C
atomization phase: 5 seconds at 2300°C
sample size: 20 μℓ
purge gas: Ar

Mn: wavelength: 279.5 nm
gas flow: interrupt
drying phase: 30 seconds at 125°C
charring phase: 30 seconds at 1100°C
atomization phase: 4 seconds at 2400°C
sample size: 20 μℓ
purge gas: Ar

Cd: wavelenth: 228.8 nm
gas flow: interrupt
drying phase: 30 seconds at 100°C
charring phase: 30 seconds at 400°C
atomization phase: 6 seconds at 2200°C
sample size: 20 μℓ
purge gas: Ar

Fe: wavelength: 248.3 nm
gas flow: normal
drying phase: 30 seconds at 125°C
charring phase: 30 seconds at 1200°C
atomization phase: 5 seconds at 2600°C
sample size: 20 μℓ
purge gas: Ar