## Title

THE ROLE OF ANALYTICAL CHEMISTRY IN ASSESSING ATMOSPHERIC EFFECTS OF COMBUSION



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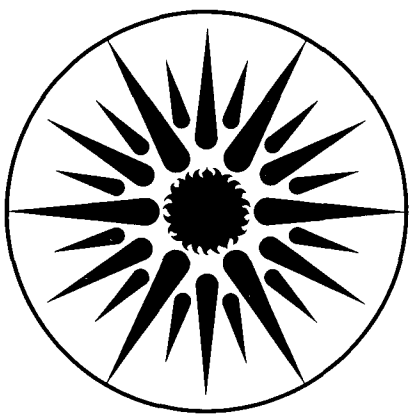

**APPLIED SCIENCE DIVISION**



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# THE ROLE OF ANALYTICAL CHEMISTRY IN ASSESSING ATMOSPHERIC EFFECTS OF COMBUSTION*

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**Abstract**

This paper discusses sampling and analysis strategies designed to distinguish local and regional sulfate and to identify heterogeneous $SO_2$ oxidation in an urban heavily polluted atmosphere. The role of analytical chemistry will be illustrated by reviewing the results of a multi-year international cooperative study conducted principally in Ljubljana, Yugoslavia. The analytical results, when combined with physical measurements and meteorological data, have enabled us to assess the role of combustion effluent in $SO_2$ oxidation and to infer the interrelationship between the chemical and physical properties of the atmosphere. The conclusions from field measurements about the $SO_2$ oxidation process were verified by laboratory cloud chamber experiments designed to simulate the conditions encountered in a source-dominated atmosphere.

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## Introduction

Combustion is the principal form of the world's energy production and utilization. Chemical species released into the atmosphere from combustion processes are recognized as the principal cause of a number of adverse environmental effects. Effects of $CO_2$ and aerosols on global climate, acid deposition, and urban smog, and effects of pollution of forest, vegetation, and human health are some of the well-known examples.

Air pollution by combustion products is not only a local or regional problem but also a global one. The so-called Arctic haze[1] is one example of global aerosol pollution. It is now evident that the entire Arctic is polluted during winter and that the sources of this pollution are not located within the Arctic region but rather in New England, Europe, and Central U.S.S.R.[2] Chemical analyses of the Arctic haze aerosols have shown that it contains a variety of constituents including metals, sulfate,[2] and carbonaceous material.[3] Based on the analytical results, it is now clear that the Arctic haze is not a natural phenomenon but is caused by combustion products brought into the region by long-distance transport.[2] A definitive proof for the combustion-derived origin of this aerosol was the discovery of large concentrations of black soot particles, which are produced solely by incomplete combustion of fuels.[3] This finding also demonstrates the large extent of poor, uncontrolled combustion going on around the globe.

This example of Arctic pollution is one illustration of a fundamental need of atmospheric chemistry to understand the relationship between sources and receptors. I have already alluded to the crucial role of analytical chemistry in establishing this relationship. The other equally important objective of atmospheric chemistry is to understand the formation and transformation of pollutants after these have been released into the atmosphere. These transformations occur both close to and away from sources, depending on the meteorological conditions, pollutant dispersion, and physical and chemical properties

of the atmosphere. Understanding these complex processes is impossible without analytical chemistry and without the involvement of analytical chemists in the overall objective of a particular atmospheric project. Sampling design and analytical techniques must suit specific research objectives, and conversely the capabilities of existing analytical techniques will determine the type of sampling platforms (ground-based or airborne), the kind of samplers to be used, their geographical locations, the time resolution of sampling, the sampling calendar, the use of real-time instruments, etc.

It is obvious that one can talk about the role analytical chemistry plays in atmospheric chemistry only within the framework of more specific objectives. It is therefore my intent to present the results from some specific atmospheric projects and, in doing so, to describe the analytical approaches that were actually used.

These projects are directed toward understanding heterogeneous processes occurring in heavily polluted source-dominated atmospheres. There are important reasons to study source-dominated regions: These constitute an important input to the global atmosphere, and most of the world's population live in such environments. Furthermore, because of inadequate combustion conditions, the emission of some pollutants is disproportionate to per-capita energy consumption. Finally, high ambient concentrations should provide particularly good conditions for the study of heterogeneous processes. It is worth mentioning in this context that most field studies in the past were conducted in regions with stringent air pollution controls. Because of this, the concentrations of atmospheric chemical species were usually low, often close to the detection limits of analytical and other measurement methods used. As we will show, this did not happen in our studies.

The role of heterogeneous chemical processes in the atmosphere has only relatively recently attracted the attention of the atmospheric science community. Heterogeneous processes refer to chemical and physical effects involving gaseous species that interact

with the solid or liquid surface of atmospheric particles (dry and wet aerosol particles, fog and cloud droplets) and solid or dissolved material within aqueous droplets. Homogeneous processes involve only gas-phase reactants, although the products of these reactions may be suspended particulate material. The differentiation of these pathways and the assessment of conditions favoring each pathway are of the utmost importance in understanding not only local and regional atmospheric chemistry but also chemical cycles and their effects on the global atmosphere.

Most effort in atmospheric chemistry in the past was devoted to studies (laboratory, field, and modeling) of homogeneous reactions with considerably less emphasis on heterogeneous processes, resulting in a serious gap in knowledge about the relative importance of heterogeneous reactions. One reason for this disparity is that heterogeneous reactions are more difficult to study. However, they can be expected to be most significant and pronounced in source-dominated atmospheres, especially during cold seasons when the concentrations of gaseous and particulate species are at a maximum and there are frequent occurrences of fog.

Only a joint effort of research groups specializing in various aspects of atmospheric chemistry, analytical chemistry, atmospheric physics, and meteorology can successfully address a complex subject such as heterogeneous chemistry. Because of this a group of scientists from Austria, Germany, Italy, Yugoslavia, and the United States have initiated a cooperative project to specifically study the heterogeneous atmospheric chemistry at two sites in Europe - the Po Valley in Italy and Ljubljana, Yugoslavia.

In this paper I will attempt to demonstrate how a cooperative international effort, using relatively simple and analytical methods, was able to (1) demonstrate the formation of local sulfate by heterogeneous atmospheric reactions, and (2) provide direct field and laboratory evidence for the involvement of combustion products in $SO_2$ oxidation to sul-

fate.

## Objectives of Study

The broader objectives of the collaborative studies at the Ljubljana and Po Valley sites were:

1. To determine the relative importance of heterogeneous processes in the formation of suspended sulfate, nitrate, and organic species.
2. To identify empirically the most important heterogeneous mechanisms of sulfate, nitrate, and organic species formation during photochemical and nonphotochemical conditions.
3. To assess the major sources of $H_2O_2$ and other oxidants under photochemical and nonphotochemical ambient conditions.
4. To estimate transformation rates for different heterogeneous mechanisms (principally the $SO_2$ to sulfate and $NO_x$ to nitrate) during summer and winter periods.
5. To develop an appropriate theoretical understanding of empirically identified heterogeneous mechanisms.

Various activities directed toward these research goals took place at both sites between 1984 and the present. In this paper, I will review only the results from Ljubljana, particularly those relevant to sulfate formation. These results are the product of a joint effort involving the Chemistry Institute B. Kidrič, Ljubljana; the Institute of Analytical Chemistry, Technical University of Vienna; the Institute for Experimental Physics, University of Vienna; and Lawrence Berkeley Laboratory, University of California at Berkeley.

The specific objectives of our studies in Ljubljana were (1) to establish whether local sources contribute to urban sulfate, (2) to identify the heterogeneous $SO_2$ oxidation processes, (3) to assess the role of nonphotochemical oxidants and catalysts in sulfate

formation, and (4) to investigate the relationship between $SO_2$ oxidation and products of incomplete combustion of fossil fuels. Our approach to these questions involved a combination of field and laboratory investigations. The field data have enabled us to postulate a hypothesis about sulfate formation in such atmospheres that was then tested in a series of laboratory experiments.

Sulfur dioxide can be oxidized in the atmosphere by many chemical pathways that can be classified in several ways. For example, a distinction can be made between oxidation processes that involve homogeneous reactions, when all reactions are in the gas phase, and the processes that involve a multiphase heterogeneous system of gases, liquid droplets, and solid particles. Because $SO_2$ oxidation by molecular oxygen alone is a slow process, oxidants and/or catalysts are needed to promote sulfate formation. Depending on the sources of these oxidants and catalysts, $SO_2$ oxidation processes can be further subdivided into photochemical and nonphotochemical processes. The principal photochemically generated oxidants are HO, $HO_2$, $O_3$, and $H_2O_2$. HO and possibly $HO_2$ are involved in homogeneous reactions, while $O_3$ and especially $H_2O_2$ are the most important oxidants in aqueous $SO_2$ oxidation processes.[4] Because of their photochemical origin, these oxidants are most important during summer, particularly during daylight hours. During winter, the role of these photochemical oxidants is diminished and often negligible. During such nonphotochemical periods, $SO_2$ oxidation is believed to involve catalysts such as water-soluble Fe(III) or Mn(II) ions[5] and soot particles.[6] The reactions catalyzed by these catalysts are aqueous heterogeneous reactions, which occur either in fog or cloud droplets or on wet aerosol particles.

It is important to distinguish the sulfate aerosol by its origin, i.e. how much of it is produced during long-range transport as opposed to local production. Both local and regional sources contribute to the aerosol sulfate in urban atmospheres. Local sources

include primary sulfate, produced by the oxidation of fuel sulfur to $SO_3$ during combustion, and secondary sulfate, produced by oxidation of $SO_2$ in the urban atmosphere itself. Regional sulfate is formed by oxidation of $SO_2$ released farther upwind from a variety of regional sources. It is obvious that a better understanding of the relative contributions of these sulfate sources and the mechanisms of their formation is important for both practical and fundamental scientific reasons.

## Sampling and Analytical Methods

The criteria for the field sites most likely to provide optimal conditions for achieving the above objectives can be defined as follows. For observing local sulfates, it is important that $SO_2$ sources are predominantly within and not outside the urban area. For example, in the eastern United States where many studies have been performed, most major sources are located outside urban areas. Conversion processes during transport produce regional sulfate, whose concentrations vary little between the cities and the surrounding areas. Under such circumstances, sulfate produced in the city is of relatively minor importance.[7] Other conditions favorable for the observation of local sulfate are meteorology and topography. Local sulfate should be easier to detect under stagnant conditions and when the topography tends to confine the pollutants over the city. Heterogeneous processes will be favored if the atmosphere contains liquid water droplets, i.e. during periods of radiation fog. High concentrations of pollutants will make the required measurements easier by improving the signal-to-noise ratio. To study nonphotochemical processes, it is desirable that pollutant emissions are seasonally modulated with maximum concentration in winter when photochemical activity is at a minimum. We note that in the United States, because of the extensive use of air conditioning, $SO_2$ emissions from power generation are evenly distributed throughout the year. Finally, for an assessment of the relation of sulfate to incomplete combustion, the study area should ideally

have a predominance of low-temperature combustion sources with minimum emission controls.

The urban atmosphere in Ljubljana meets all these criteria. Ljubljana is a city with a population of approximately 300,000, located in a basin surrounded on three sides by mountains. During the winter, the principal $SO_2$ source is coal burning for space heating in home furnaces and larger residential boilers. Sulfur dioxide sources are not uniformly distributed throughout the city. The highest emissions from these sources are in the city center, where in older buildings coal is burned in individual stoves. In the outlying districts, the emissions are lower because of lower population density and the prevalence of central heating. Because of the meteorology and topography, frequent stagnation and temperature inversions occur during winter, resulting in the accumulation of pollutants in the city atmosphere. During adverse meteorological conditions, the pollutant concentrations reach a very high level. Peak $SO_2$ concentrations frequently reach 1 mg $m^{-3}$. These days of high pollution are often accompanied by urban fog and persisting subzero temperatures. Sulfate and $SO_2$ reach extreme levels during winter when photochemical activity is low. Large soot concentrations at this location result from incomplete, poorly regulated combustion.

Analytical chemistry, sample collection, data analysis, and data interpretation must be viewed as integral parts of the objective of atmospheric chemistry, which is to understand the formation, transformation, transport, and removal of atmospheric species. Each specific objective, such as identifying the heterogeneous processes, requires the design of specific sampling and analysis strategies. We must also realize that chemical and physical properties of the atmosphere are strongly interrelated. Therefore chemical measurements should be supplemented with measurements of the physical properties of the atmosphere such as temperature, humidity, wind fields, liquid water content, and physical properties

of particulate species, including size distribution, optical properties, and morphology. For a complete understanding of atmospheric chemistry information about source emissions, their chemical composition, and their physical properties are also needed. Finally, all data gathered in a field study must ultimately be used to infer the atmospheric chemical processes.

It is obvious that only cooperative projects involving many research groups and scientific disciplines can tackle problems of such complexity. A number of sampling, analysis, and measuring techniques were deployed at the site. Tables I-III list the capabilities and the participating institutions that were used in this study. The choice of chemical species to be analyzed and the selection of sampling intervals and actual measurement sites were dictated by the objectives of the project and by practical considerations. The limitations to an ideal approach are many, including financial, manpower, and logistical considerations. Because of this, not all sampling and analysis methods listed in Tables I-III could be used simultaneously. Another limiting factor is related to the general unpredictability of weather conditions suitable for certain types of observations and measurements. To get representative data under a variety of meteorological conditions, measurements have to be performed over protracted time periods, usually involving periods of several months per year. As a consequence, a large number of samples have to be analyzed by the most efficient and cost effective methods, which provide the most useful, though sometimes limited, output.

To achieve a balance between the number of samples collected and the practical considerations about analyzing these samples, two types of measurement and analysis programs are commonly used - routine and intensive. Routine programs usually involve daily sample collection at one site only, complemented by rudimentary meteorological and routine air quality measurements. The collected samples can then be analyzed for a few key

constituents to provide a minimal data base. The analysis of this data base provides an overall characterization of the atmosphere and may result in a hint or a key insight about a possible atmospheric chemical process or mechanism. Collected samples can be stored and thus be available for subsequent in-depth analysis by more advanced and complex techniques.

Intensive or episodal sampling and measuring periods usually last from several days to a few weeks. These are chosen according to the best available meteorological forecasts to encompass a period or episode of interest to the project, such as the occurrence of fog, temperature inversion, or high photochemical activity. During intensive periods, an attempt is made to have all available sampling and measuring devices in operation at the same site or sites and to obtain much more detailed results than during routine sampling programs.

In the following example, the results of both types of sampling and measuring programs will be presented. Twenty-four-hour aerosol samples and $SO_2$ concentrations were routinely collected at one site (Hydrometeorological Institute) from 1981 to 1984. All collected samples were analyzed for particulate carbon and sulfur, water-soluble anions, and elemental composition. Intensive sampling was performed in February and April 1985 at five locations simultaneously. Two-hour time resolution aerosol samples were analyzed for elemental and ionic composition. Real-time (1-min average) $SO_2$ concentrations, relative humidity, temperature, and wind speed and direction were obtained at all five locations in parallel with the aerosol sampling. General regional meteorological data were provided by the Slovenian Meteorological Service.

These measurements have provided a data base sufficient to conclude that heterogeneous $SO_2$ oxidation does take place and to empirically describe the principal features of the oxidation mechanisms. A list of other measurements employed during some

sampling periods includes: (1) sulfate concentrations (and $NH_4^+$, $NO_3^-$, $Cl^-$, etc.) as a function of particle size; (2) tracer elements for various fuels so that the relationship between sulfate (a secondary species) and inert source tracers could be studied; (3) catalysts and oxidants that may be involved in $SO_2$ oxidation; (4) liquid water content, especially important for heterogeneous chemistry; (5) gaseous $SO_2$ and $NH_3$ concentrations; and (6) meteorological parameters. Some of the results, however, are still being evaluated and therefore have not been included in this paper.

## Results from Field Studies in Ljubljana

*Routine samplings, 1981-1984.* Sampling was performed at the Hydrometeorological Institute in central Ljubljana. Meteorological data consisting of wind speed and direction, temperature, and relative humidity were collected at the site. Twenty-four-hour average $SO_2$ concentrations were determined by a conventional titration method[8] and smoke was determined by reflectance.[9]

Two kinds of 24-hr ground-level aerosol filter samples were collected: total samples, i.e. without size segregation, and size-segregated samples corresponding to cutoffs of $<$ 0.3 $\mu$m and $<$ 2.0 $\mu$m. The total aerosol samples were collected on 47-mm diameter quartz fiber filters (Pallflex type 2500 QAO, prefired for 6 hr at 700 °C to remove combustible carbon) and on cellulose membrane filters (Millipore type RATF, 1.2-$\mu$m pore size). The flow rates used were 6.7 $m^3$ $min^{-1}$ for both filters. The air inlet chamber (approximately 10 liters capacity) was heated to prevent condensation. Twenty-four-hour size-segregated samples were collected on the quartz afterfilters of two single-stage impactors. The impactors operated at a flow rate of 8.5 l $min^{-1}$.

The exposed quartz filters were analyzed for total C and S by combustion followed by relative conductometric determination of $SO_2$ and $CO_2$ at Ljubljana.[10] Portions of the

same filters were also analyzed for total C at Berkeley by a combustion technique with coulometric $CO_2$ detection.[11] Millipore filters were analyzed for sulfur and trace elements by x-ray fluorescence (XRF) using an energy-dispersive spectrometer.[12] Aerosol S data used in this study are those determined by combustion, which were judged to be more accurate than the XRF data because of the self-absorption of S x-rays in these heavily loaded samples. The combustion S results agreed within ±5% with water-soluble sulfate as determined by ion chromatography.

Analysis of the data obtained during the period of routine sampling has demonstrated[13,14] that during winter (1) particulate carbon is essentially primary soot, (2) total atmospheric sulfur (particulate and gaseous) is mostly produced by fossil fuel combustion, (3) between 5% and 20% of $SO_2$ is converted to sulfate, and (4) aerosol sulfate is most likely produced by heterogeneous oxidation of locally emitted $SO_2$.

Carbonaceous particles in the atmosphere consist of two components - black carbon (also called graphitic or elemental carbon) and organic carbon. The organic carbon can be subdivided into primary and secondary fractions. In combustion-generated pollution, the sum of black and primary carbon is synonymous with soot.[15] Secondary carbon is produced in the atmosphere, most likely by photochemical reactions. Black carbon is the principal light-absorbing species of the aerosol and is responsible for the gray or black coloration of the filter deposits.[16] It can easily be determined by either light absorption or reflection. The OECD "smoke" method,[9] routinely used throughout Europe, is actually a measure of the black carbon concentration.

That most of the particulate carbon is primary combustion-generated soot is evident from Fig. 1, where "smoke" concentration (determined on Whatman filters) is plotted against total carbon measured by combustion of quartz filter samples.[13] From the good correlation between these two sets of measurements, we conclude that soot is the

dominant form of particulate carbon. A secondary organic aerosol, if present in appreciable amounts, would increase the total carbon but, because it lacks the black absorbing component, would not contribute to sample blackness. Black carbon is a convenient tracer for incomplete combustion and will be used in this context throughout this paper.[15] Because a good correlation between this species and total carbon was observed during the entire study, total carbon can also be used as a tracer for combustion products. A simple application of this tracer is shown in Fig. 2, where total sulfur (the sum of $SO_2$ and aerosol sulfate) from a number of 24-hr measurements taken between September 1981 and April 1982 is plotted against total carbon. The good correlation between total sulfur or carbon implies that atmospheric sulfur is coemitted with soot carbon from the same sources.[13]

Analytical results on 24-hr samples have also provided us with a preliminary insight into sulfate formation chemistry at this site. The seasonal pattern of pollutants in Ljubljana is illustrated in Figs. 3a and b, where biweekly $SO_2$ and particulate sulfur, $S_p$, concentrations are plotted as a function of time during the 1981/82 sampling season.[14] The particulate sulfur to gaseous sulfur ratios, $S_p/S_g$, and the particulate sulfur to carbon ratios, $S_p/C_p$, for this period are shown in Figs. 3c and d. It is evident from this figure that the highest pollutant concentrations are during winter months.

The $S_p/S_g$ ratio, which can be viewed as a measure of $SO_2$-to-sulfate conversion, is about four times higher in the summer ($\sim 0.4$) than in the winter ($\sim 0.1$), indicating a different chemistry during the two seasons. During summer and early fall, the $SO_2$ conversion (most likely by a photochemical mechanism) is more efficient than during winter. However, because of the high concentrations of $SO_2$ in winter, even a less efficient, nonphotochemical mechanism produces the highest absolute sulfate concentrations. The variations of $S_p/C_p$ ratios are qualitatively similar to the variations of $S_p/S_g$

ratios.

A closer examination of the $S_p/C_p$ and $S_p/S_g$ ratios show that, in addition to the summer-winter differences, there also seems to be a clear difference in these (biweekly) ratios between Nov.-Dec. and Jan.-Feb., with the latter period having higher values. The differences in sulfur chemistry between these two winter periods are even more obvious when 24-hr data are considered.[14] In Fig. 4, daily particulate sulfur concentrations are plotted against $SO_2$ and particulate carbon concentrations for Nov.-Dec. 1981 and Jan.-Feb. 1982. During Nov.-Dec. a very good correlation with C (Fig. 4b) is seen, but there is essentially no correlation with $SO_2$ (Fig. 4a). The situation is reversed during Jan.-Feb. when a good correlation is observed with $SO_2$ (Fig. 4c) but not with carbon (Fig. 4d). Note that the line corresponding to the fit to the Nov.-Dec. data also represents the lower limit for $S_p/C_p$ ratios in the subsequent period, indicating enhanced sulfate formation during the latter part of the winter.

It is unlikely that the differences between the Nov.-Dec. and Jan.-Feb. periods could be attributed to the differences in photochemical activity. January and February had many more overcast and foggy days than November and December and therefore had a lower ultraviolet radiation intensity. The data in Table TableIV[14] imply that the differences in sulfur chemistry are not directly related to concentrations of $SO_2$ and catalytically active species. In this table the average concentrations of $SO_2$ and aerosol C, S, and other elements are listed for three periods (9-18 November 1981, 23-30 December 1981, and 15-21 January 1982) characterized by increasing $S_p/C_p$ and $S_p/S_g$ ratios. Table IV shows that there are not significant differences in concentrations of catalytically active species, such as C, Mn, V, and Fe, corresponding to periods of low and high $S_p/C_p$ ratios.

The most significant changes in trace element concentrations were observed for Cl. Its concentration decreased drastically as the sulfate concentration (and $S_p/C_p$ and $S_p/S_g$ ratios) increased. To a much lesser degree, a similar trend was also observed for Br. The apparent loss of Cl could be indicative of an aqueous chloride + acid reaction resulting in the formation of volatile HCl as originally proposed by Robbins et al.[17] This observation is one of the indications that the enhanced sulfate formation in the Jan.-Feb. period is caused by a mechanism involving liquid water droplets or wet aerosol particles.

This view is supported by an examination of the relative humidity and ambient temperature data.[14] The average 24-hr relative humidity was high, usually exceeding 80%, and the wind speed was generally low ($\sim$ 1 m $sec^{-1}$) during both the Nov.-Dec. and Jan.-Feb. periods. The only drastic difference in meteorology corresponding to low and high $S_p/C_p$ ratios was the ambient temperature. This is seen from Fig. 5, where $S_p/C_p$ ratios, average daily relative humidity, and temperature are plotted for December 1981 and January 1982. This figure shows that the high $S_p/C_p$ ratios during January correspond to periods with high humidity and persistent subzero temperatures. These results are con-

sistent with earlier results obtained elsewhere in Europe.[18]

In our view, this observation represents the manifestation of a heterogeneous liquid-phase mechanism of $SO_2$ oxidation. Under conditions of high humidity, low wind speed and low temperature would enhance condensation of water droplets on combustion nuclei. Such conditions, when accompanied by temperature inversion, are known to favor the formation of urban fog.

The effect of high humidity and low ambient temperatures on enhanced sulfur formation observed from 1981/82 data has been confirmed during the winter of 1983/84 with size-segregated sampling.[14] This is illustrated in Fig. 6, where $S_p/C_p$ and $S_p/S_g$ ratios (for particle diameters $< 2$ $\mu$m), average temperature, relative humidity, and $SO_2$ concentrations for February 1984 are shown. The second half of the month showed a pronounced increase in the $S_p/C_p$ and $S_p/S_g$ ratios. During this period the average daily temperatures were consistently below 0 °C. The increase in the $S_p/C_p$ and $S_p/S_g$ ratios occurred after the relative humidity exceeded approximately 65%. Such dependence on relative humidity has been shown to be characteristic of heterogeneous reactions. It should be noted that during this period, the $SO_2$ concentration remained approximately constant; and therefore the apparent increase in sulfate production is related entirely to the physical changes in the atmosphere, i.e. the liquid water content.

Twenty-four-hour $S_p$ and $C_p$ concentrations corresponding to $< 0.3$ $\mu$m and $< 2.0$ $\mu$ size cuts for the same sampling period are shown in Fig. 7,[14] with approximately 70% of particulate S in the size range greater than 0.3 $\mu$m. Similar observations are valid for particulate C. The fact that S is predominantly found in the size fraction larger than 0.3 $\mu$m suggests that aerosol sulfate is formed by aqueous heterogeneous reactions. The possible involvement of combustion-derived particles in sulfate formation is suggested by the similarity between the size-segregated C and S concentration patterns.

The observations described thus far can be qualitatively explained as follows: water may condense on soot (or other) particles in a plume, forming a layer of liquid water on the particle. The $SO_2$ in the plume will be dissolved in this layer and oxidized to sulfate by one or more oxidation mechanisms. If ambient conditions, such as relative humidity and temperature, do not favor additional water condensation during transport to the receptor site, the entire oxidation would occur, possibly in the first phases of plume development. However, if atmospheric conditions favor additional condensation, particle-associated liquid water would continue to exist during transport. Good correlations with $SO_2$ are more likely to be found when the liquid water content is high and droplet lifetime long because the dissolved S(IV) concentration would be more proportional to the ambient $SO_2$ concentrations. With these data no specific $SO_2$ oxidation mechanism could be identified. However, at the time these results were evaluated, it was felt that there were sufficient indications that products of incomplete combustion could play a role in sulfate formation. More definitive proofs of this were derived from intensive field programs and from laboratory simulations.

*Intensive sampling (1985).* The purpose of the intensive sampling performed 19-20 February and 8-9 April 1985 was (1) to identify the locally generated sulfate, (2) to establish whether $SO_2$ oxidation takes place, and (3) to empirically identify the sulfate formation mechanisms. Measurements were performed simultaneously at four locations, providing city-wide temporal variations on the concentrations of $SO_2$, particulate sulfate, carbon, and trace metals (Pb, As, K, V, Mn, and Fe). Figure 8 shows the location of these sites on a map of the city of Ljubljana. Site CC was in the city center, IR1 and IR2 were in mixed industrial-residential areas, and RS was in a residential area.

The inlets to the samplers were heated to 5 °C above ambient temperature to evaporate fog droplets and thus collect the total (fog + interstitial) aerosol.[19] Sampling times

were usually set to collect eight 2-hr samples from 0800 to 2400, and two 4-hr samples at 2400 and 0400. The samples were collected on 25-mm diameter quartz fiber filters.

The heavily loaded filters collected in February were divided into halves; one half was analyzed at Berkeley for trace metals by x-ray fluorescence, the other at Ljubljana for total C and S by combustion. The April samples were more lightly loaded, and the entire filter was used for the C and S analyses; therefore trace metal data were not obtained for these samples. During the February sampling period, the Slovenian Hydrometeorological Institute continuously monitored $SO_2$ concentrations adjacent to the four aerosol sampling sites and recorded meteorological variables including wind speed and direction, temperature, and relative humidity. During the April sampling period, these measurements were not made.

I will first describe the results that demonstrate that winter sulfate in Ljubljana is largely local.[20] The approach uses the fact that $SO_2$ sources are not evenly distributed throughout the city. As mentioned before the highest emissions during winter are in the city center (site CC), and lowest in the outer residential districts (site RS). Locally generated winter sulfate should exhibit a spatial inhomogeneity under stagnant atmospheric conditions similar to that of primary combustion-generated species. In contrast, when the emissions from local sources are greatly diminished (April), a greater spatial homogeneity of sulfate concentrations can be expected.

Temporal variations of $SO_2$ and sulfate concentrations at the four sites for 19-20 February are shown in Figs. 9 and 10. Sulfur dioxide concentrations (peaking in excess of 1.2 mg $m^{-3}$ in the city center) exhibit pronounced morning and evening maxima that are highest in the city center and decrease toward the suburbs in the sequence CC, IR1, IR2, and RS. This clearly is the reflection of the distribution of $SO_2$ sources and the pattern of daily fuel consumption. Spatial distribution of peak sulfate concentrations resembles that

of $SO_2$. This is particularly pronounced in the 20 February data during the morning period corresponding to maximum morning $SO_2$ emissions. The highest 2-hr sulfate concentrations were measured at the city center, and lowest at the residential suburban site. The similarity between the spatial distributions of sulfate and $SO_2$ is indicative of the local origin of sulfate particles.

Diurnal concentration variations for 20 February of As, K, and Pb (i.e. the tracer elements for the principal fuels coal, wood, and gasoline respectively) are shown in Fig. 11. The diurnal and spatial variations of the coal tracer (As) follow very closely those of sulfate. K and Pb concentrations also shown a degree of spatial inhomogeneity, although less pronounced than $SO_2$, As, and sulfate. This is to be expected, however, because coal, not wood or gasoline, is the principal source of atmospheric sulfur. Concentrations of particulate carbon, a tracer for incomplete combustion (shown in Fig. 12), strongly resemble those of sulfate and As and, to a lesser degree, $SO_2$, K, and Pb.

This relationship between sulfate and primary emission species can have at least two explanations: either most sulfate is primary or it is produced by a rapid $SO_2$ oxidation process in the urban atmosphere. Rapid oxidation is required to preserve the relationship between secondary sulfate and primary emission species. In the following discussion, it will be demonstrated that the latter is the more likely explanation.

Evidence for atmospheric $SO_2$ oxidation is obtained by considering the details of the diurnal variations of meteorological parameters and chemical species.[20] Fig. 13 shows variations of relative humidity, ambient temperature, $SO_2$, sulfate, particulate carbon, and $S_p/S_g$-$S_p/C_p$ concentration ratios for 20 February at site CC. The most obvious conclusion from these data is that sulfate does not primarily depend on $SO_2$ concentrations. The morning sulfate peak coincides with the $SO_2$ increase; however, the evening $SO_2$ peak is not accompanied by an equivalent sulfate concentration increase. The lack of exact

correspondence between $SO_2$ and sulfate is also evident from the difference in the duration (or width) of their morning peaks. The $SO_2$ concentration remained essentially constant during the 4-hr period (0800-1200), while the sulfate peak was confined to the first two hours of this period (0800-1000). In spite of the persisting large $SO_2$ concentrations between 1000 and 1200, sulfate decreased by about a factor of three from the preceding time period (0800-1000).

The lack of correspondence between $SO_2$ and sulfate is indicative of atmospheric conversion because primary sulfate should constitute a relatively constant fraction of $SO_2$ emissions. A direct proof for atmospheric $SO_2$ oxidation to sulfate is obtained by comparing the ambient $S_p/S_g$ ratio with those determined for stack emissions of various source types at this location. The recently determined average $S_p/S_g$ source ratio for coal and oil burning is 0.02.[21] This value is considerably lower than practically all ambient ratios, thus demonstrating that atmospheric $SO_2$ oxidation to sulfate does take place. Sulfate concentration variations show a better correspondence with particulate carbon concentrations (Fig. 13). This is evident from the $S_p/C_p$ ratios, which are relatively constant throughout the day with the exception of the 0800-1000 period when the sulfate is significantly enriched with respect to carbon. Between 0800 and 1000, the $S_p/C_g$ ratio is also at maximum value, indicating sulfate formation during this period.

The question I want to address next is why the enhanced sulfate formation is particularly pronounced during the 0800-1000 period but not the 1000-1200 period in spite of the fact that both $SO_2$ and carbon concentrations remained high. The answer to this question is in the meteorology. The data in Fig. 13 show that the relative humidity was about 90% during the night and part of the morning, sharply decreasing after 1000. From visual observations at the sampling site, we know that during the morning hours there was dense ground fog. The fog dissipated after 1000 and did not reoccur for the rest of

the day.[22] Therefore the maximum morning emissions occurred during both foggy and nonfoggy conditions. A sulfate peak, however, was observed only during the high-humidity, foggy period. These facts obviously suggest an aqueous oxidation mechanism. Such a mechanism would be much less efficient between 1000-1200 than between 0800-1000 because of the decreased liquid water content. Aqueous reactions would therefore produce different sulfate amounts even if the $SO_2$, catalyst, and oxidant concentrations were the same during these two periods. Because of low ambient temperatures (reaching -13 °C at the time of the sulfate concentration peak), aqueous $SO_2$ oxidation reactions have to proceed in super-cooled water droplets unless much of the oxidation occurs at higher temperatures in plumes.

We now examine the various candidate aqueous heterogeneous reaction mechanisms that may be responsible for this local oxidation of $SO_2$. These may include catalytic oxidation by transition metal ions, aqueous reactions with photochemical oxidants, and oxidation reactions involving products of incomplete combustion.[6,23] Although a complete assessment of these mechanisms is impossible with the available data, several mechanisms can be ruled out.

We may first eliminate catalysis by transition metals. Figure 14 shows the variations of Mn, Fe, and V at sites CC, IR1, and RS. We see that none of these variations correlates with those of sulfate at the same sites. In fact, the lowest trace metal concentrations were measured at site CC, which had the highest sulfate concentrations.

Second, we consider ozone and other photochemically generated oxidants. To produce the observed increase in sulfate of $\sim$ 200 $\mu$g m$^{-2}$ above the nighttime levels, an ozone concentration of at least 30 ppbv would be required. Although ozone monitoring at the sites was not performed, it is very unlikely that these concentrations would be produced under winter conditions of overcast sky and dense fog. Measurements of $H_2O_2$ and

$O_3$ concentrations performed in the Po Valley, Italy,[24] show that these are negligible in winter. We therefore assume that photochemically generated oxidants are not a significant factor under conditions such as those encountered in February in Ljubljana.

From the evidence presented so far, we are inclined to hypothesize that the apparently fast wintertime $SO_2$ oxidation is caused by incomplete combustion products in the presence of liquid water droplets.[6,23] A direct proof for the feasibility of aqueous $SO_2$ oxidation by soot and other products of incomplete combustion was recently obtained from cloud chamber experiments.[25] These will be described below, after mentioning the results from the April period.

During this sampling period, an entirely different picture was observed from that in February. The principal differences were in meteorology, the concentration of species, and their spatial and temporal variations. The April measuring period was characterized by calm days with temperatures ranging from a low of about 10 °C to a midday high of about 20 °C. Nighttime relative humidities were $> 92\%$ on April 8 and 9 and about 75% between April 9 and 10. The daytime relative humidities for the three days were between 63 and 38%. The sulfate concentrations were much lower during this period and, in contrast to February, homogeneously distributed throughout the city during most of the day. Particulate carbon was spatially more inhomogeneous than sulfate. From Fig. 15, where sulfate and carbon diurnal variations averaged for all sites are shown, it is evident that the sulfate and carbon peaks do not occur at the same time. Carbon peaks occurred only in the morning and preceded the sulfur peaks by 3-4 hr, indicating that carbon and sulfate originated from different sources. Carbon particles originate mostly from traffic; while ambient sulfate is likely coming from regional sources because of greatly reduced $SO_2$ emissions in the city. Differences in diurnal variations between February and April are also indicative of the differences in sulfate formation chemistry during the two sam-

pling periods. While there is strong evidence that the February sulfate was produced by a nonphotochemical mechanism, April sulfate is most likely produced by photochemical oxidants. This possibility is suggested by the midday sulfate and $S_p/C_p$ maxima (Fig. 15).

*Laboratory demonstration of heterogeneous sulfur dioxide oxidation by combustion products.* The field results described above have led us to postulate the following hypothesis. Substantial sulfate formation (with the sulfate present mostly in the form of ammonium salts) occurs under nonphotochemical conditions when pollutant concentrations are high and the physical properties of the atmosphere favor formation of fog droplets or wet aerosol particles. The $SO_2$ is oxidized by a heterogeneous, aqueous process (or processes) in the presence of combustion-generated oxidants and/or catalysts. The oxidation process is fast, occurring essentially immediately after the combustion effluent interacts with liquid water.

If this hypothesis is correct, enhanced sulfate formation should be observed in the laboratory when water droplets are nucleated on combustion-generated particles in the presence of $SO_2$ and other combustion products. Such experiments were recently performed at Berkeley with a mixing-type cloud (fog) chamber coupled to a propane combustor.[25] Rapid, efficient $SO_2$ oxidation is observed when the chamber atmosphere contains liquid water droplets, soot particles (and other combustion products), and ammonia. If any one of these ingredients is absent, either no or very low sulfate formation occurs. These results substantiate the hypothesis and are consistent with ambient observations and demonstrate the role of combustion products in $SO_2$ oxidation.

Figure 16 shows a schematic representation of the experimental apparatus used in these experiments, which consists of a combustor (not shown), a dilution manifold, and the cloud chamber. The combustor is a propane torch enclosed in a glass cylinder maintained at a slight positive pressure. $H_2S$ was added to propane to simulate fuels with

varying sulfur content (0-2.7% S by weight). This addition increases the fuel sulfur content and therefore the amount of primary sulfate generated by the flame. This primary sulfate when incorporated into soot particles also increases their cloud nucleation potential and therefore the likelihood for the occurrence of heterogeneous aqueous reactions.

Additional $SO_2$ and $NH_3$ can be introduced into the system through a dilution manifold as indicated in Fig. 16. Particulate and gaseous effluent from the combustor is diluted with filtered room air before entering the chamber. The fraction of combustion effluent reaching the dilution manifold can be varied by adjusting the flow between the combustor and the main dilution tube. In this way the concentrations of $SO_2$, $NH_3$, and carbon particles delivered to the chamber could be varied to encompass the concentration ranges found in polluted ambient air. The concentration ranges in the chamber were 0.1-9 ppm $SO_2$ and 100-1000 $\mu$g C $m^{-3}$. When $NH_3$ was used in the experiments, its concentration was kept constant at 2.5 ppm.

The diluted stream of gaseous and particulate species was humidified and introduced into the chamber through a slightly heated tube in the center of the perforated bottom plate at a flow rate of 1.2 ml $min^{-1}$. Cold mixing air ($t_c$ = -13 °C, flow rate 10.5 l $min^{-1}$) was introduced into the chamber through this plate. When the temperature of the chamber air is lower than the dew point (typically 48 °C) of the humidified input air stream, dense cloud nucleated on combustion particles forms in the chamber. The cloud temperature at the center of the chamber was approximately 20 °C. An upward net flow of 14.5 l $min^{-1}$ was maintained in the chamber due to the aspiration through two aerosol samplers. Under such flow conditions, the calculated transit time in the chamber is about 3 min.

Aerosol samples for chemical analyses were collected on heated quartz filters from the top part of the chamber. The chamber aerosol was extracted through heated stainless

steel tubings to evaporate the water droplets and to minimize sulfate artifact formation from to water condensation on the filters. One of the two sampling tubes was equipped with a mesh impaction droplet separator made of polypropylene mesh (100 $\mu$m fibers, 96% void volume).[26] The 50% droplet cut point was estimated to be about 2.5 $\mu$m. Particles that penetrate through this separator are the interstitial aerosol. The particles collected without size segregation are referred to as the total aerosol, consisting of evaporated cloud droplets and the interstitial aerosol.

The chemical composition of primary particles (i.e. before they have entered the chamber) was determined by analyzing filter samples collected from the dilution train. The filter holder was preceded by a diffusion drier/denuder to keep the artifact sulfate formation at a minimum. The concentration of particles expected in the chamber was calculated from the measured dilution factors. These are referred to as input concentrations. Sulfur dioxide concentrations were determined by passing the air from the dilution train through bubblers containing a 0.01 M solution of $H_2O_2$. $NH_3$ concentrations were not directly determined but estimated from the measured flow rates. Liquid water content was determined in a few experiments by weighing the cloud water collected by the mesh impactor. The average liquid water content in these experiments was about 1.6 g $m^{-3}$.

The water-soluble filter extracts and the bubbler solution were analyzed for anions by ion chromatography. The black carbon content of filter samples was determined optically by the laser transmission method. The ratio of total to black carbon concentration for some of the filter samples was determined by thermal temperature-programmed evolved gas analysis. The data were corrected by this ratio (black C/total C = 0.51) and expressed as total carbon.

Two sets of experiments were performed. In the first series of measurements, the chamber atmosphere consisted of liquid water droplets, $SO_2$, and diluted combustion

effluent only. The second series was performed in an analogous manner but with the addition of gaseous ammonia. The results without $NH_3$ show that cloud processing of the input aerosol did not result in the formation of additional sulfate, as evidenced by the similar values of input and output S/C ratios. That the sulfate in these experiments is essentially primary is also suggested by the fact that interstitial sulfur is a major fraction of the total particulate sulfur.

In contrast to the experiments without ammonia, increased in-cloud $SO_2$ oxidation was observed when $NH_3$ was supplied to the system. The effect of cloud processing on sulfate formation is demonstrated by the results shown in Fig. 17. In this figure the sulfate concentrations of the input, interstitial, and total aerosol, and the cloud water (difference between total and interstitial) are plotted against the input carbon particle concentration.

The data in Fig. 17 show that input sulfate concentrations are generally low and independent of carbon concentration. The output sulfate is markedly higher even for the run when the only source of sulfur is $H_2S$ in the fuel. Substantially higher sulfate concentrations were measured for all runs when additional $SO_2$ was introduced to the system. It is obvious from these data that the sulfate concentrations show a definite dependence on input soot concentrations. No such dependence on $SO_2$ concentrations was observed. The lowest sulfate concentration was detected in the absence of carbon particles.

That oxidation under these conditions involves an aqueous process or processes is also evident from the fact that most sulfate is found in the cloud droplets and not in the interstitial aerosol. This is in contrast with the results of experiments without ammonia when the sulfate was found to be essentially primary and confined to the interstitial particle size range. Another finding of our experiments is that $SO_2$ oxidation is fast because the residence time of the species in the chamber is several minutes. Nevertheless, a very high fraction of $SO_2$ was oxidized during this short time. This corresponds to oxidation rates

estimated to be well in excess of 100% $hr^{-1}$.

The principal role of ammonia in aqueous $SO_2$ oxidation is in controlling the pH of the droplets and thus the equilibrium between the dissolved S(IV) species and the gaseous $SO_2$.[27] Most $SO_2$ oxidation mechanisms are pH dependent, with oxidation rates increasing with the pH of the solution. Such dependence is also evident from the present data. Furthermore, these experiments demonstrate that higher sulfate formation occurs in the chamber when carbon particles are also present. (On the average about 13% of carbon by mass is incorporated in droplets.) This is indicative of the catalytic action of carbon particles and is at least qualitatively in agreement with the known pH dependence of this catalytic oxidation process.[6] Because $[SO_2] > [NH_3]$, it is assumed that the droplets were acidic and thus the carbon reaction could proceed.

## Conclusions

The results described in this paper illustrate how relatively simple analytical methods when used with appropriately designed field and laboratory measurements can provide valuable information about sulfate formation in polluted source-dominated urban environments. The results of this international multiyear field study conducted in Ljubljana, Yugoslavia, provided strong evidence that under adverse wintertime meteorological conditions (air stagnation, temperature inversion, and fog), most of the ambient sulfate is locally produced by a heterogeneous, aqueous process. The field evidence also suggests that the oxidants and/or catalysts for this oxidation are products of incomplete combustion, coemitted with $SO_2$ into the atmosphere. These conclusions were verified by laboratory cloud chamber experiments involving combustion products and designed to simulate the conditions encountered in a source-dominated atmosphere.

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Table I. Aerosol samplers.

| Sampler | Laboratory[a] |
|---|---|
| Low-volume dual-filter sampler (quartz, Millipore, or Teflon) | LBL |
| Two-stage impactor afterfilter sampler (quartz) $D_p < 2\mu m$; $D_p < 0.3\ \mu m$ | LBL |
| Heated inlet total (fog + aerosol) sampler | LBL |
| Low pressure impactors | |
| LPI 25 (11 stages) 15 nm $< D_p <$ 16 $\mu$m | |
| LPI 30 (9 stages) 0.06 $\mu$m $< D_p <$ 16 $\mu$m | UV |

[a]LBL - Lawrence Berkeley Laboratory; UV - University of Vienna.

Table II. Aerosol analysis methods.

| Species | Method | Laboratory[a] |
|---|---|---|
| Total C | Combustion with coulometric $CO_2$ detection (quartz) | LBL |
| | Combustion with relative conductometric $CO_2$ detection (quartz) | KIBK |
| Black C | Laser transmission (quartz) | LBL |
| | Transmission (quartz) | KIBK |
| | OECD "smoke" (Whatman) | HMZ |
| Anions ($Cl^-$, $NO_3^-$, $SO_4^{2-}$, etc.) | Ion chromatography | KIBK, LBL |
| Cations ($NH_4^+$, etc.) | Ion chromatography | LBL |
| Total S | Combustion with relative conductometric $SO_2$ detection | KIBK |
| Elemental | X-ray fluorescence - Al, Si, S, Cl (Millipore); K, Ca, Ti, Mn, Fe, Cu, Zn, Se, Br, Sr, Pb (Millipore or quartz) | LBL |

[a]LBL - Lawrence Berkeley Laboratory; KIBK - B. Kidric Institute of Chemistry; HMZ - Hydrometeorological Institute

Table III. Gas-phase measurements.

| Species | Method | Laboratory[a] |
|---|---|---|
| $SO_2$ | Pulsed fluorescence | HMZ |
| $NO_x$ | Chemiluminescence | HMZ |
| $O_3$ | Chemiluminescence | HMZ |
| $SO_2$ | Colorimetric | KIBK |
| $SO_2$ | Diffusion denuder | TU |
| HCOOH | Diffusion denuder | TU |
| $CH_3COOH$ | Diffusion denuder | TU |
| $NH_3$ | Diffusion denuder | TU |
| HCl | Diffusion denuder | TU |
| $HNO_3$ | Diffusion denuder | TU |

[a]HMZ - Hydrometeorological Institute; KIBK - B. Kidric Institute of Chemistry;
TU - Technical University.

Table IV. Average concentration of $SO_2$, principal elements, and $S_p/C_p$ and $S_p/S_g$ ratios.

| | Concentrations ($\mu g\ m^{-3}$) | | |
|---|---|---|---|
| | 9-18 Nov. 1981 | 23-30 Dec. 1981 | 15-21 Jan. 1982 |
| $SO_2$ | 256 | 402 | 399 |
| C | 81 | 104 | 82 |
| S | 10.4 | 18.2 | 27 |
| Cl | 1.2 | 0.5 | <0.01 |
| K | 1.3 | 1.0 | 2.0 |
| Ca | 3.6 | 0.33 | 0.06 |
| V | 0.05 | 0.03 | 0.06 |
| Mn | 0.18 | 0.09 | 0.17 |
| Fe | 2.1 | 1.1 | 3.2 |
| Se | <0.01 | <0.01 | <0.01 |
| Pb | 1.9 | 1.3 | 1.2 |
| Br | 0.58 | 0.32 | 0.17 |
| | | Ratios | |
| $S_p/C_p$ | 0.13 | 0.17 | 0.34 |
| $S_p/S_g$ | 0.08 | 0.09 | 0.14 |

## Figure Captions

1. Correlation between "smoke" (black carbon) and total carbon concentrations for 24-hr samples collected between September 1981 and April 1982 (from Ref. 13).

2. Correlation between total (particulate + gaseous) 24-hr atmospheric sulfur and particulate carbon (from Ref. 13).

3. Bi-weekly concentrations of $SO_2$ particulate sulfur ($S_p$), particulate to gaseous sulfur ratios ($S_p/S_g$), and particulate sulfur to particulate carbon ratios ($S_p/C_p$) for the 1981-1982 sampling season (from Ref. 14).

4. Correlations of 24-hr particulate sulfur ($S_p$) with $SO_2$ and particulate carbon ($C_p$) for the November-December 1982 and January-February 1982 periods (from Ref. 14).

5. Dependence of the particulate sulfur to carbon ratio on mean relative humidity and ambient temperature for the December 1981-January 1982 period (from Ref. 14).

6. Dependence of 24-hr particulate sulfur ($S_p$) to particulate carbon ($C_p$) and gaseous sulfur ($S_g$) ratios on mean daily relative humidity, temperature, and $SO_2$ concentration for February 1984. The data are for the $< 2$-$\mu$m size cut (from Ref. 14).

7. Twenty-four-hour concentrations of particulate sulfur ($S_p$) and carbon ($C_p$) corresponding to particle size cuts of $< 2$ $\mu$m (solid line) and $< 0.3$ $\mu$m (dashed line) for the period December 1983 to March 1984 (from Ref. 14).

8. Map of Ljubljana, Yugoslavia, indicating the locations of sampling sites for intensive measurements in February and April 1985.

9. Diurnal variations of $SO_2$ concentrations during 19 and 20 February 1985 at the four sites.

10. Particulate sulfate concentration variations for the same period shown in Fig. 9.

11. Diurnal concentration variations of As, K. and Pb for 20 February 1985.

12. Total particulate carbon concentration variations at the four sites during 19 and 20 February 1985.

13. Diurnal variations of temperature, relative humidity, sulfate, particulate carbon, and $S_p/S_g$ and $S_p/C_p$ ratios during 20 February at the city center site.

14. Diurnal variations of Mn, Fe, and V at three sites during 20 February 1985.

15. Concentration variations of particulate sulfur, carbon, and $S_p/C_p$ ratio for the 8-10 April 1985 period.

16. Schematic representation of the cloud chamber used in $SO_2$ oxidation experiments (from Ref. 25).

17. Concentrations of sulfate (expressed as S) in the total, cloud, and interstitial aerosol after cloud processing, plotted as a function of input carbon concentration. The input sulfate concentrations are also indicated (see text).

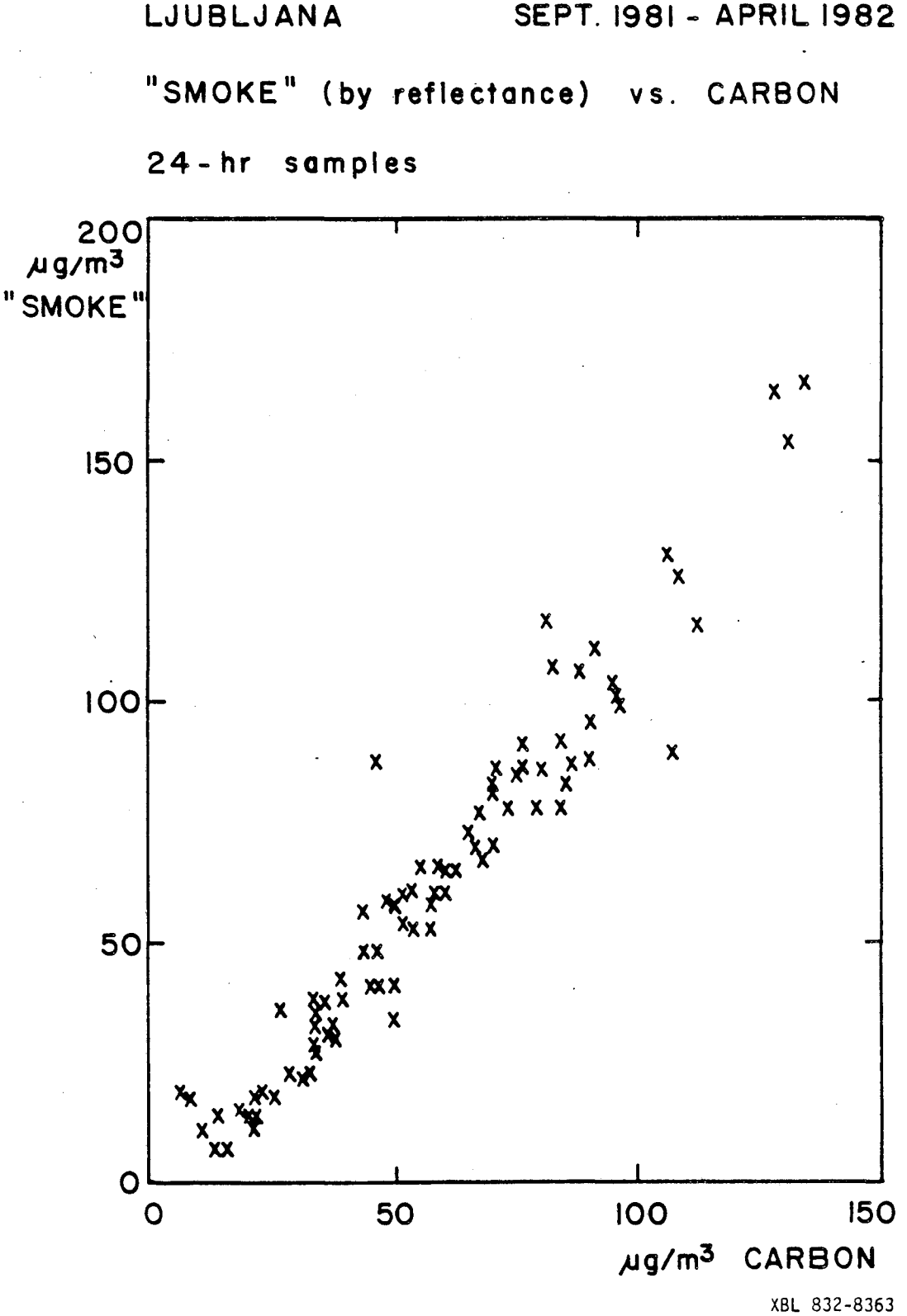
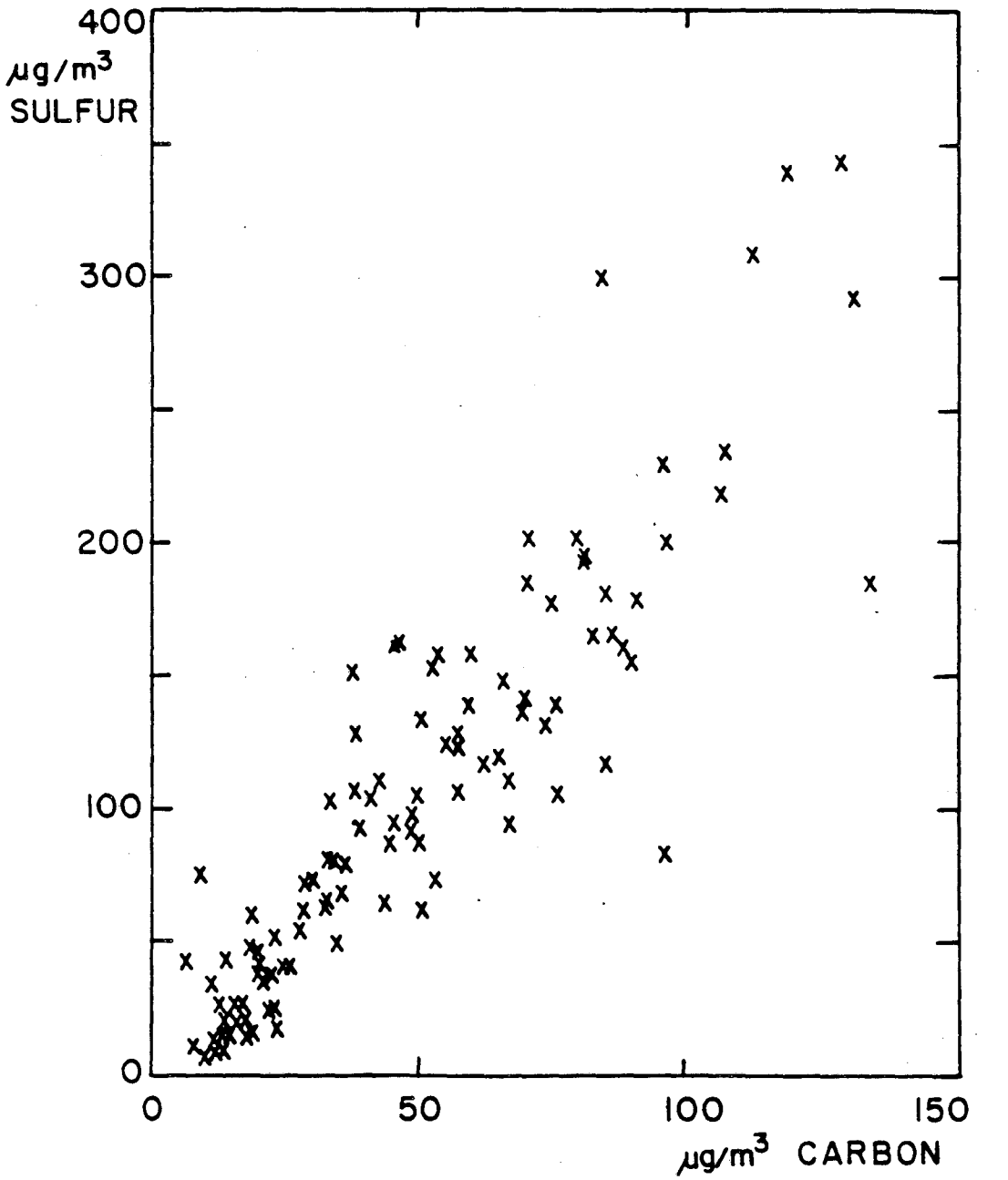

LJUBLJANA SEPT. 1981 - APRIL 1982
"SMOKE" (by reflectance) vs. CARBON
24-hr samples
200
μg/m3
"SMOKE"
150
100
50
0
0
50
100
150
μg/m3 CARBON
XBL 832-8363

Figure 1

LJUBLJANA SEPT. 1981 - APRIL 1982

TOTAL SULFUR (gas + particle) vs. CARBON

24-hr samples




XBL 832-8366

Figure 2

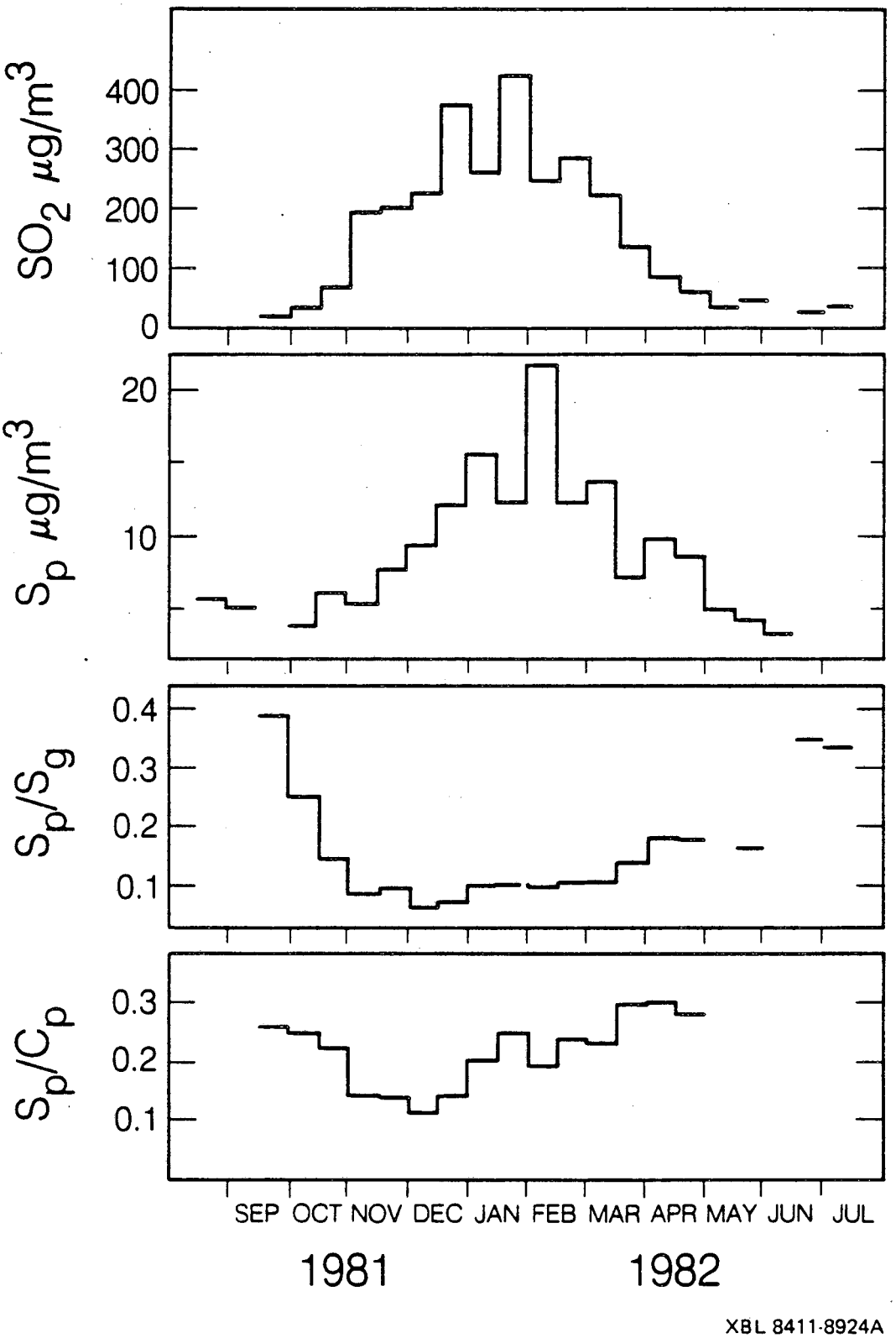

$SO_2$ μg/m$^3$
400
300
200
100
0
$S_p$ μg/m$^3$
20
10
$S_p/S_g$
0.4
0.3
0.2
0.1
$S_p/C_p$
0.3
0.2
0.1
SEP OCT NOV DEC JAN FEB MAR APR MAY JUN JUL
1981
1982
XBL 8411-8924A

Figure 3

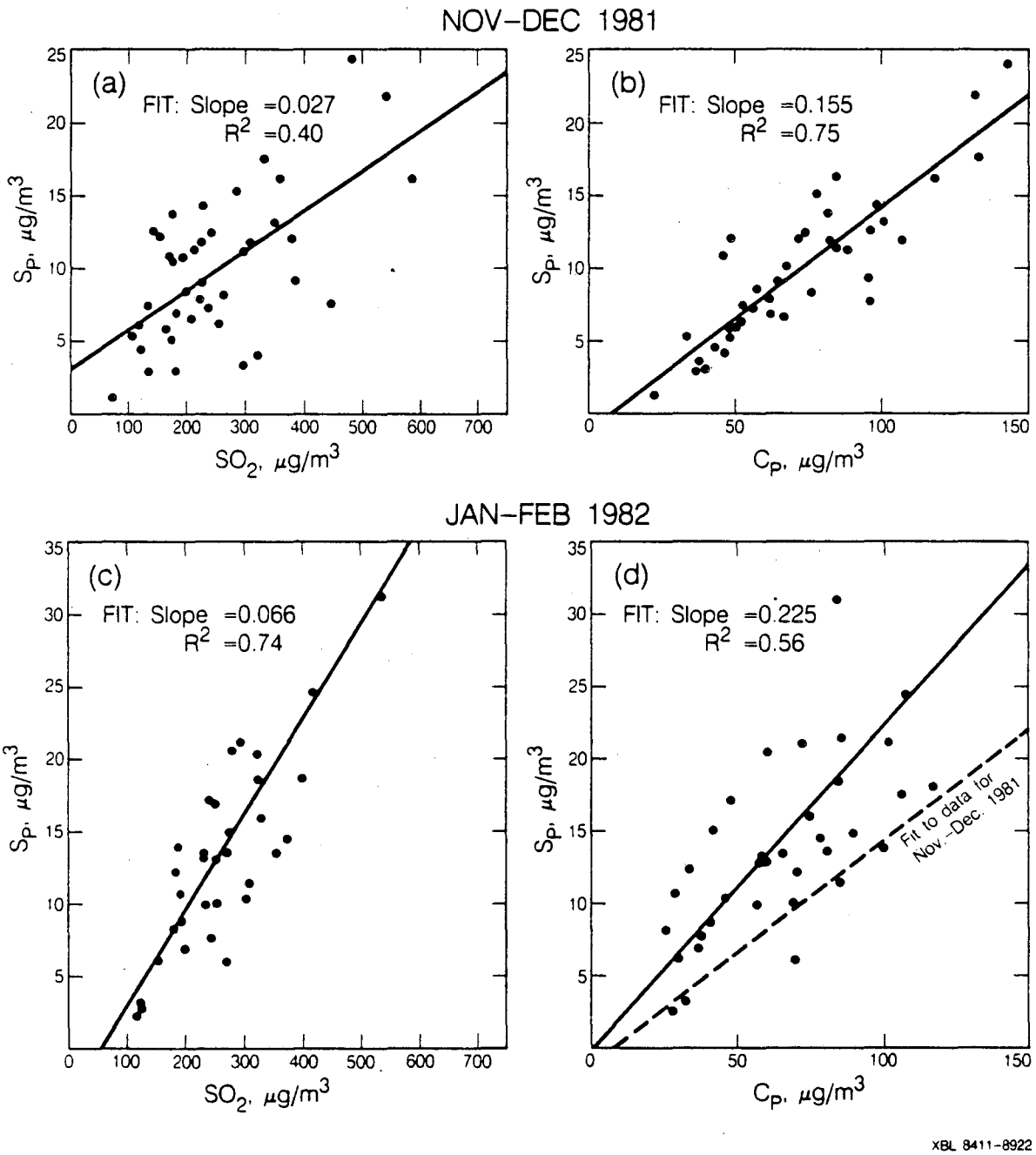

NOV–DEC 1981
(a)
FIT: Slope =0.027
$R^2$ =0.40
$S_P$, μg/m$^3$
$SO_2$, μg/m$^3$
(b)
FIT: Slope =0.155
$R^2$ =0.75
$S_P$, μg/m$^3$
$C_P$, μg/m$^3$
JAN–FEB 1982
(c)
FIT: Slope =0.066
$R^2$ =0.74
$S_P$, μg/m$^3$
$SO_2$, μg/m$^3$
(d)
FIT: Slope =0.225
$R^2$ =0.56
Fit to data for Nov.-Dec. 1981
$S_P$, μg/m$^3$
$C_P$, μg/m$^3$
XBL 8411-8922

Figure 4

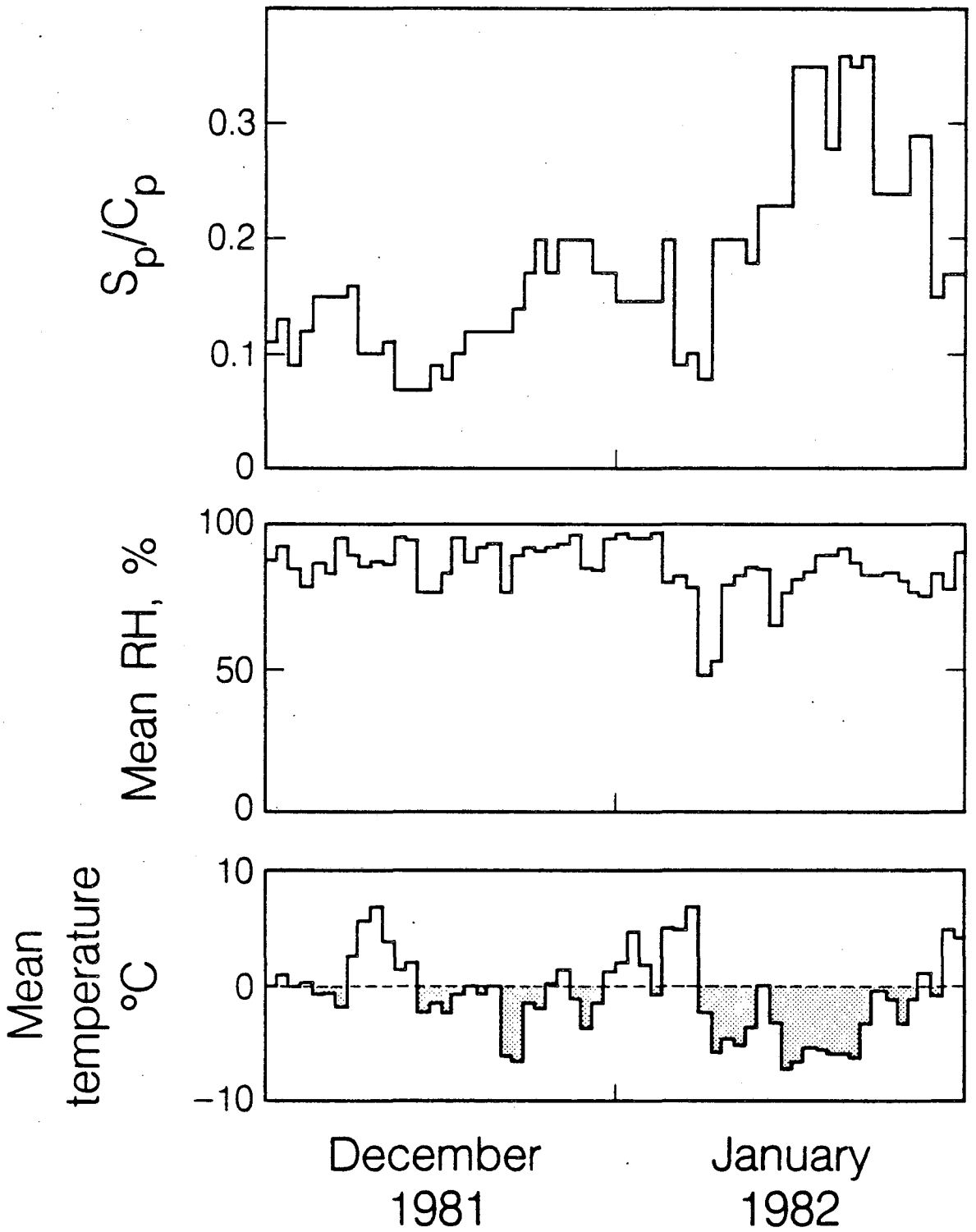

$S_p/C_p$
0.3
0.2
0.1
0
Mean RH, %
100
50
0
Mean temperature °C
10
0
−10
December 1981
January 1982
XBL 859-12125

Figure 5

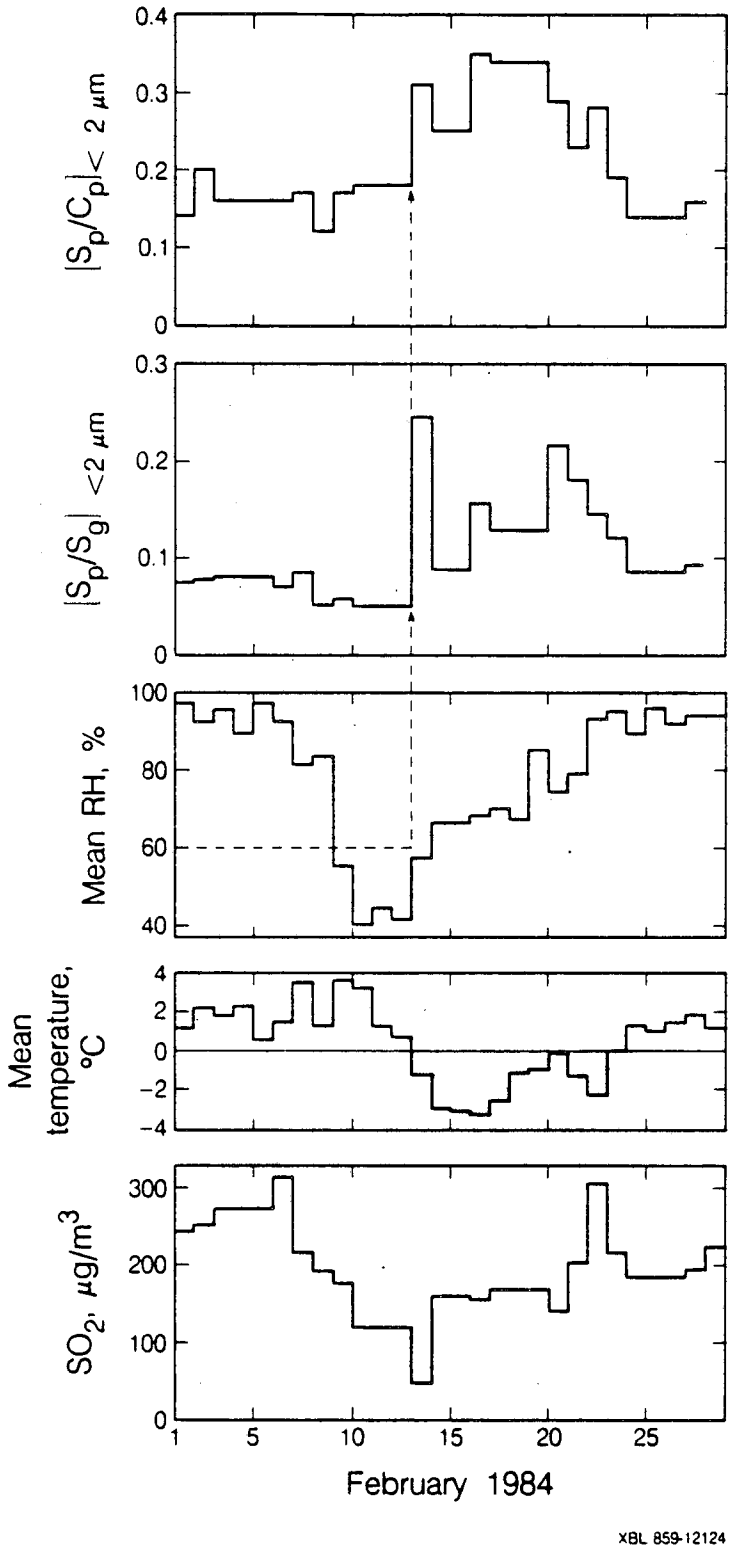
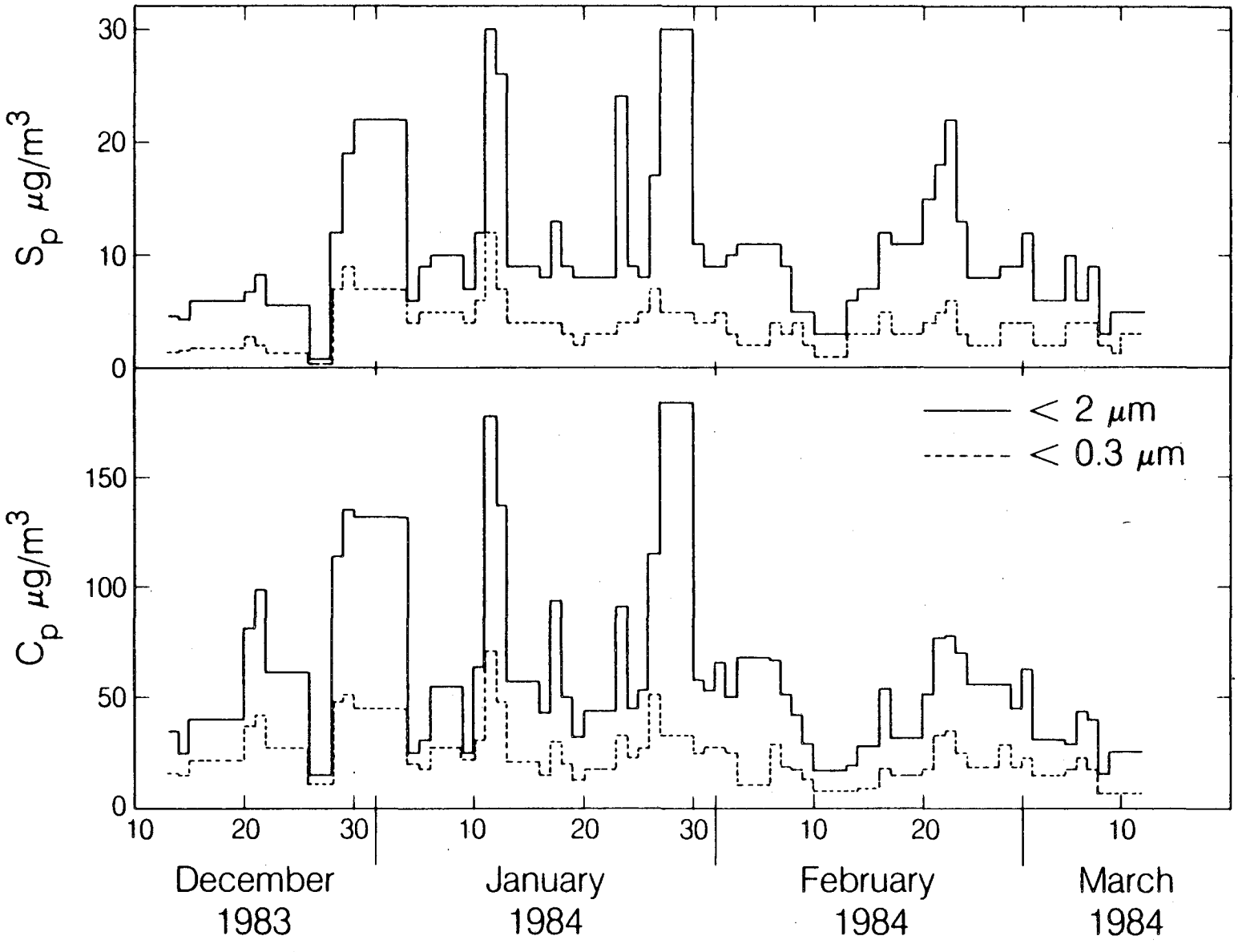
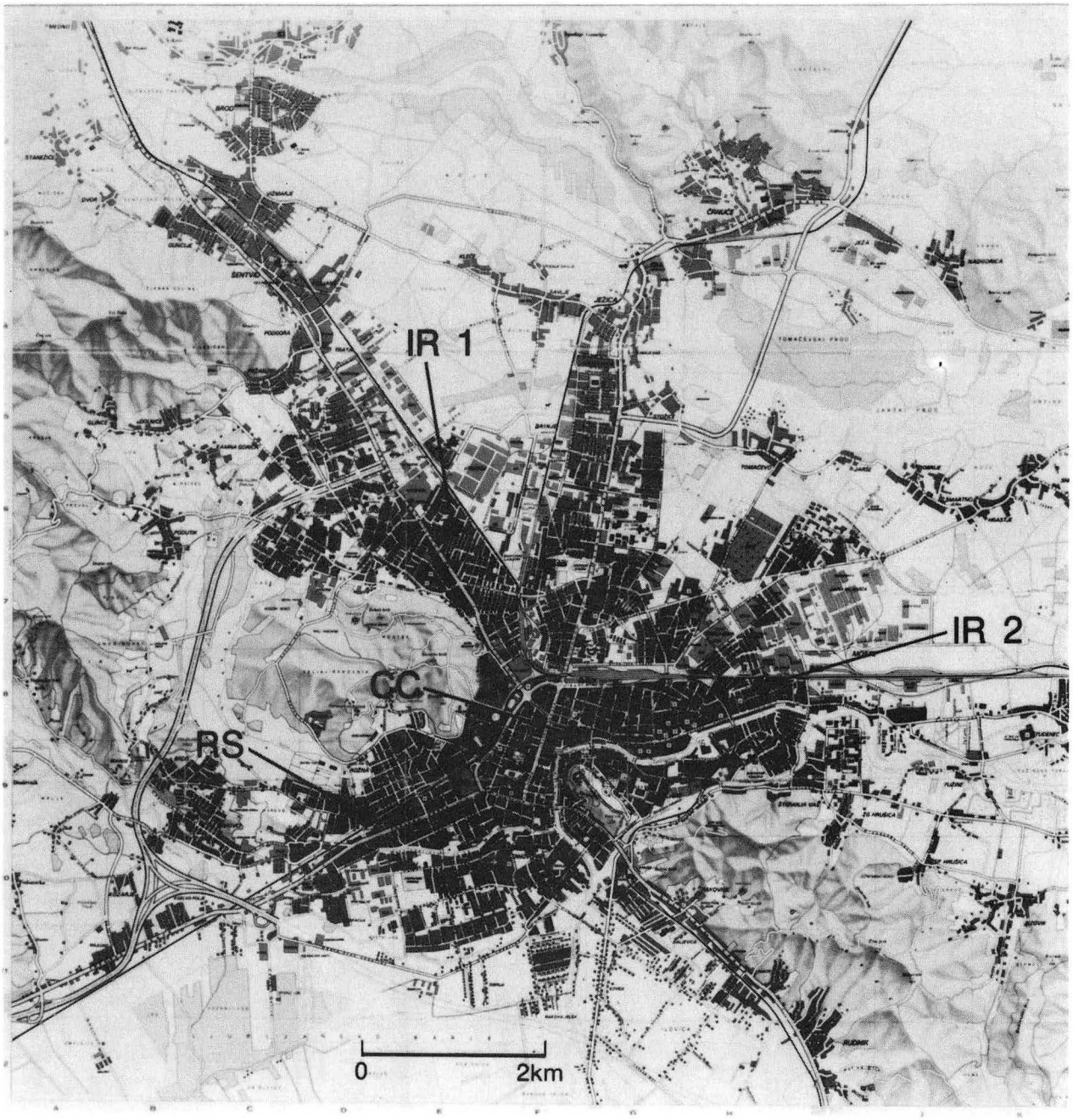

0.4
0.3
0.2
0.1
0
$|S_p/C_p|< 2\ \mu m$
0.3
0.2
0.1
0
$|S_p/S_g|\ <2\ \mu m$
100
80
60
40
Mean RH, %
4
2
0
−2
−4
Mean temperature, °C
300
200
100
0
$SO_2$, $\mu g/m^3$
1
5
10
15
20
25
February 1984
XBL 859-12124

Figure 6




XBL 859-12126

Figure 7




XBB 873-2004

Figure 8

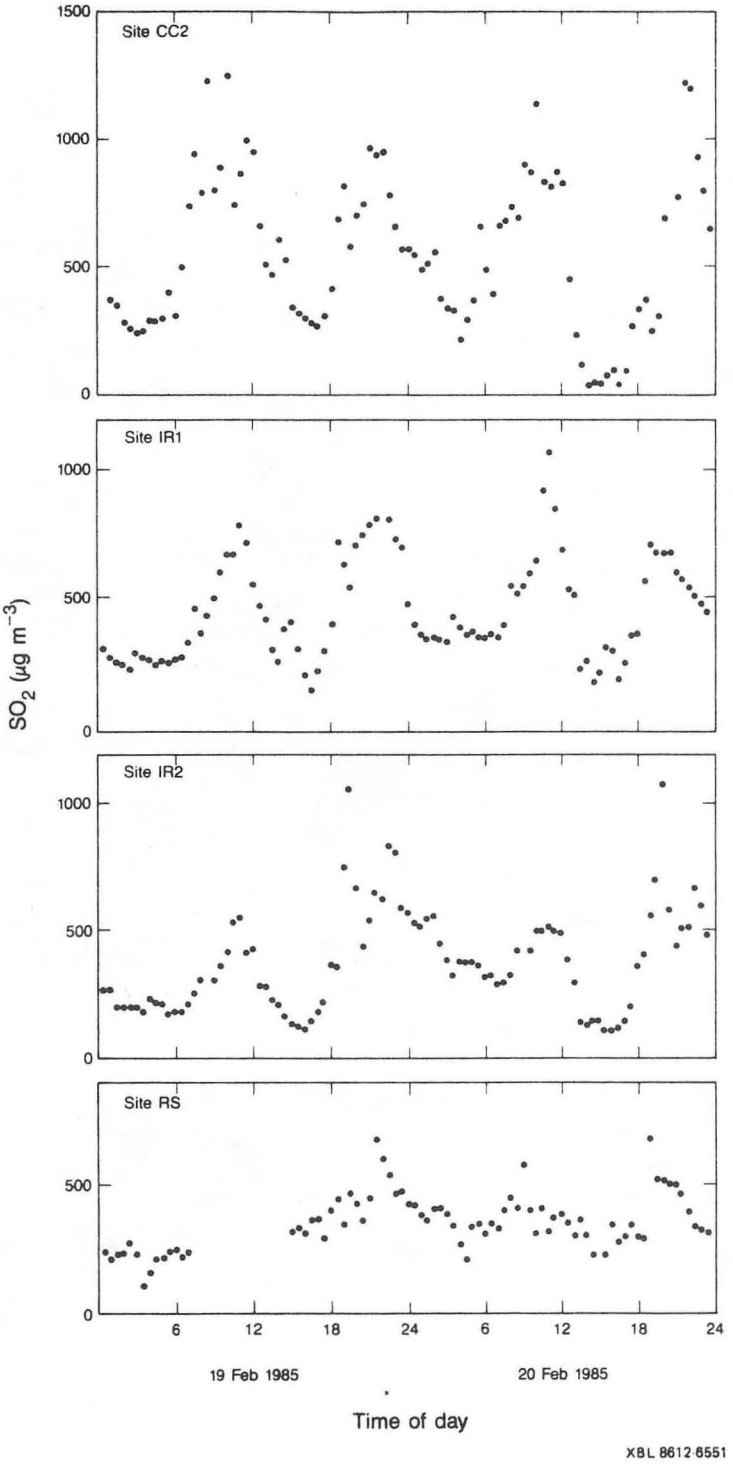

Site CC2
Site IR1
Site IR2
Site RS
1500
1000
500
0
$SO_2$ ($\mu g\ m^{-3}$)
6
12
18
24
19 Feb 1985
20 Feb 1985
Time of day
XBL 8612-6551

Figure 9

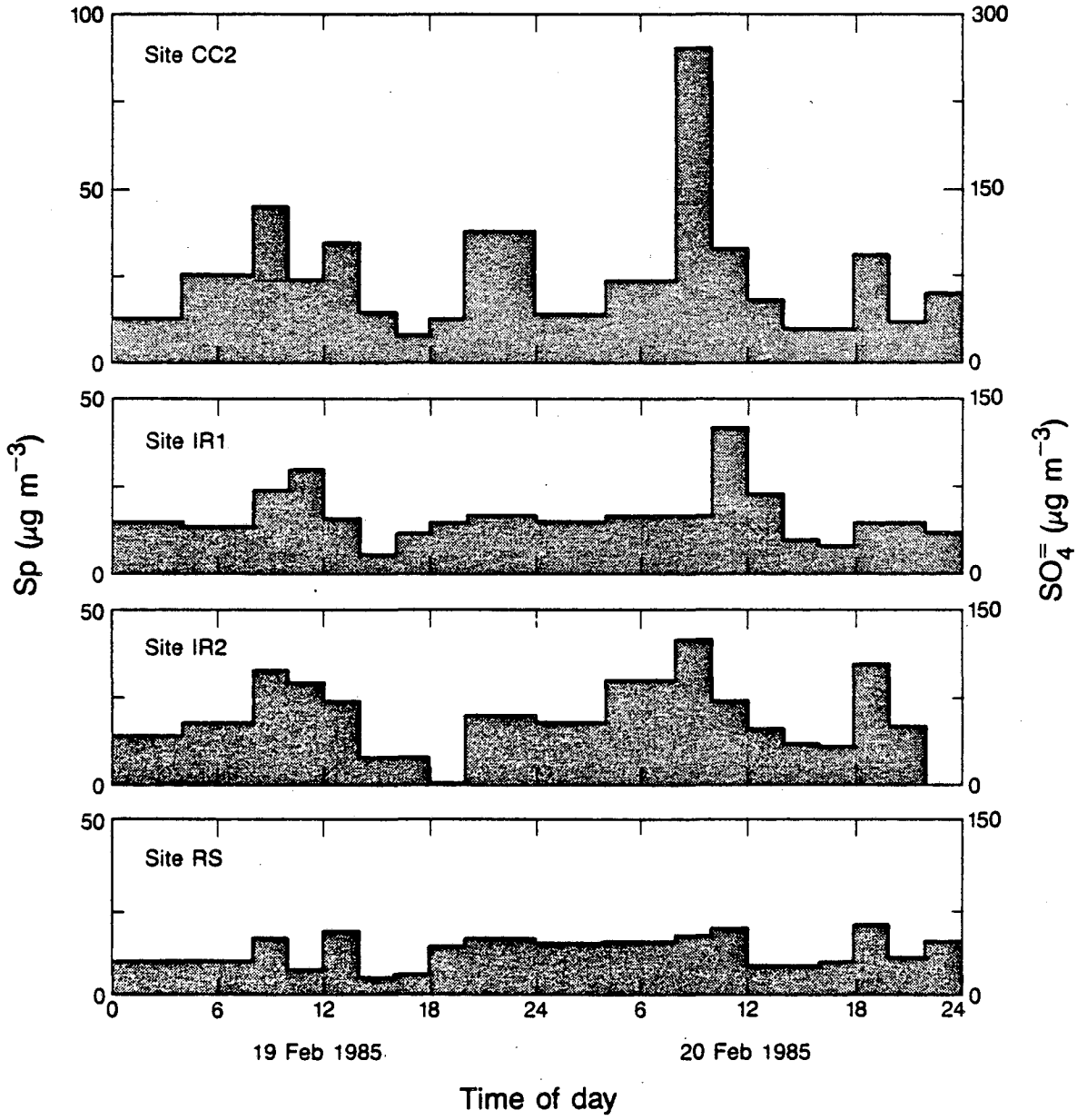

Site CC2
Site IR1
Site IR2
Site RS
100
50
0
300
150
0
Sp (μg m⁻³)
SO4= (μg m⁻³)
0
6
12
18
24
19 Feb 1985
20 Feb 1985
Time of day
XBL 8612-6554

Figure 10

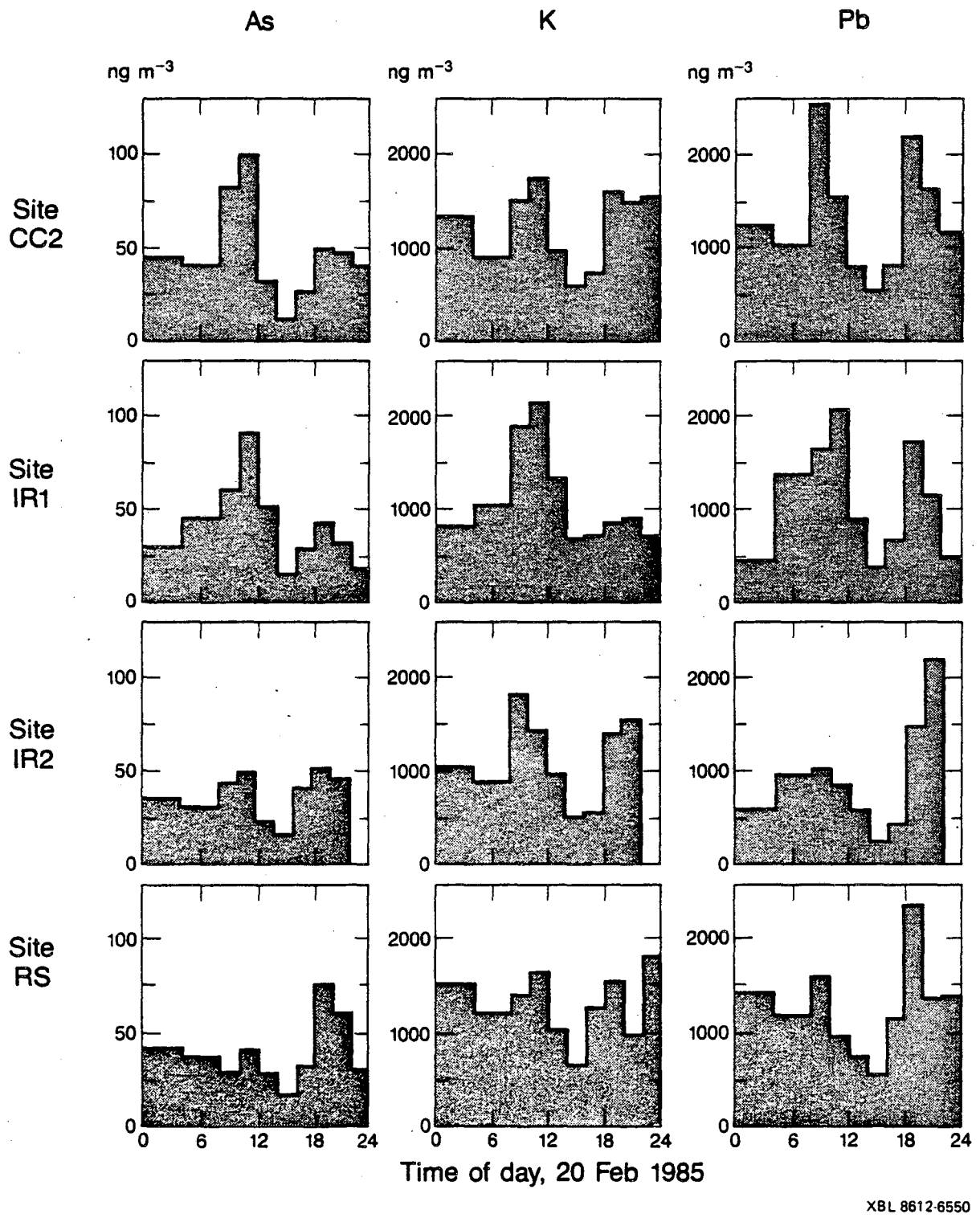

As
K
Pb
ng m⁻³
Site CC2
Site IR1
Site IR2
Site RS
0
50
100
1000
2000
0
6
12
18
24
Time of day, 20 Feb 1985
XBL 8612-6550

Figure 11

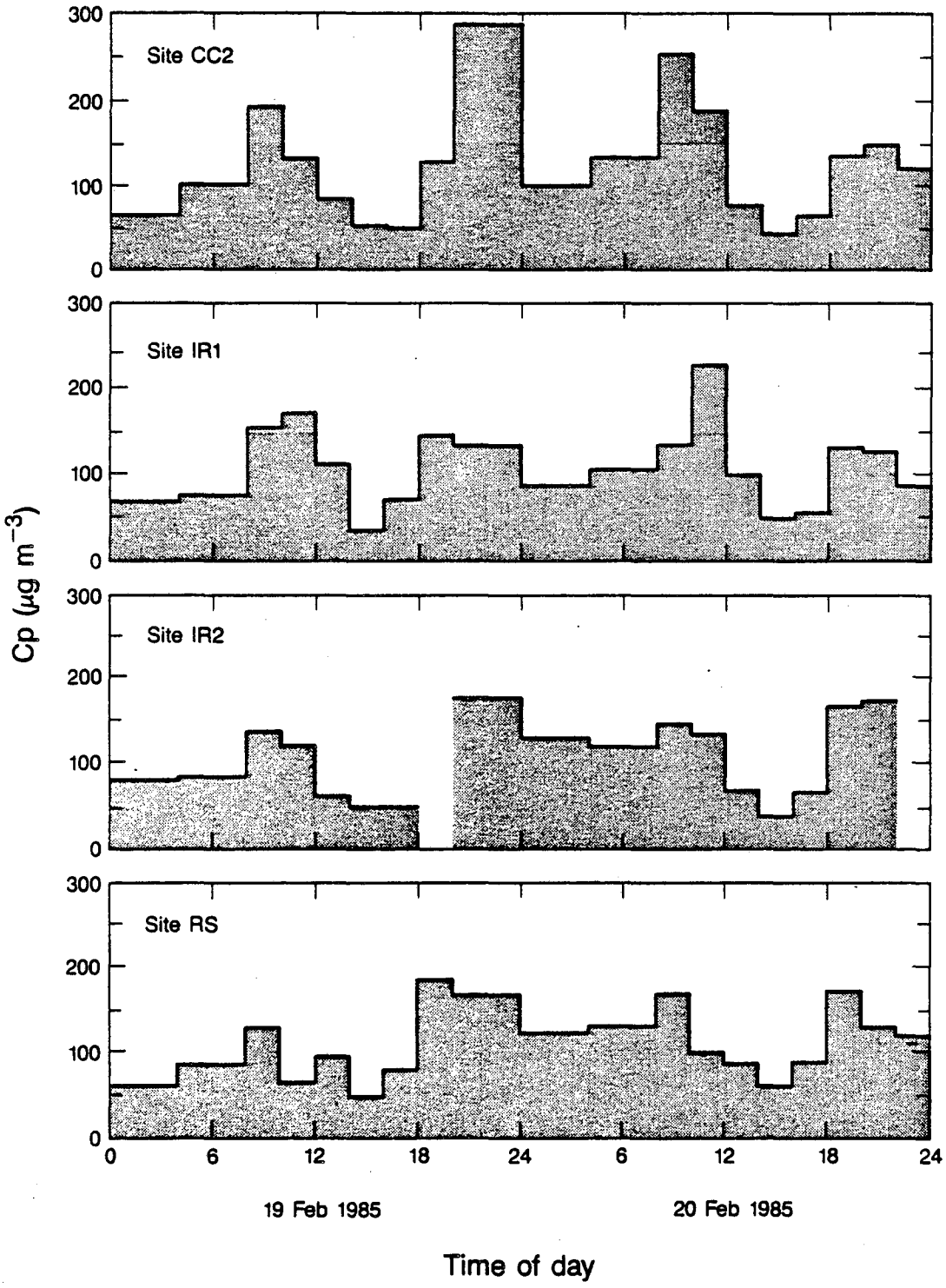

Site CC2
Site IR1
Site IR2
Site RS
300
200
100
0
Cp (μg m⁻³)
0
6
12
18
24
6
12
18
24
19 Feb 1985
20 Feb 1985
Time of day
XBL 8612-6544

Figure 12

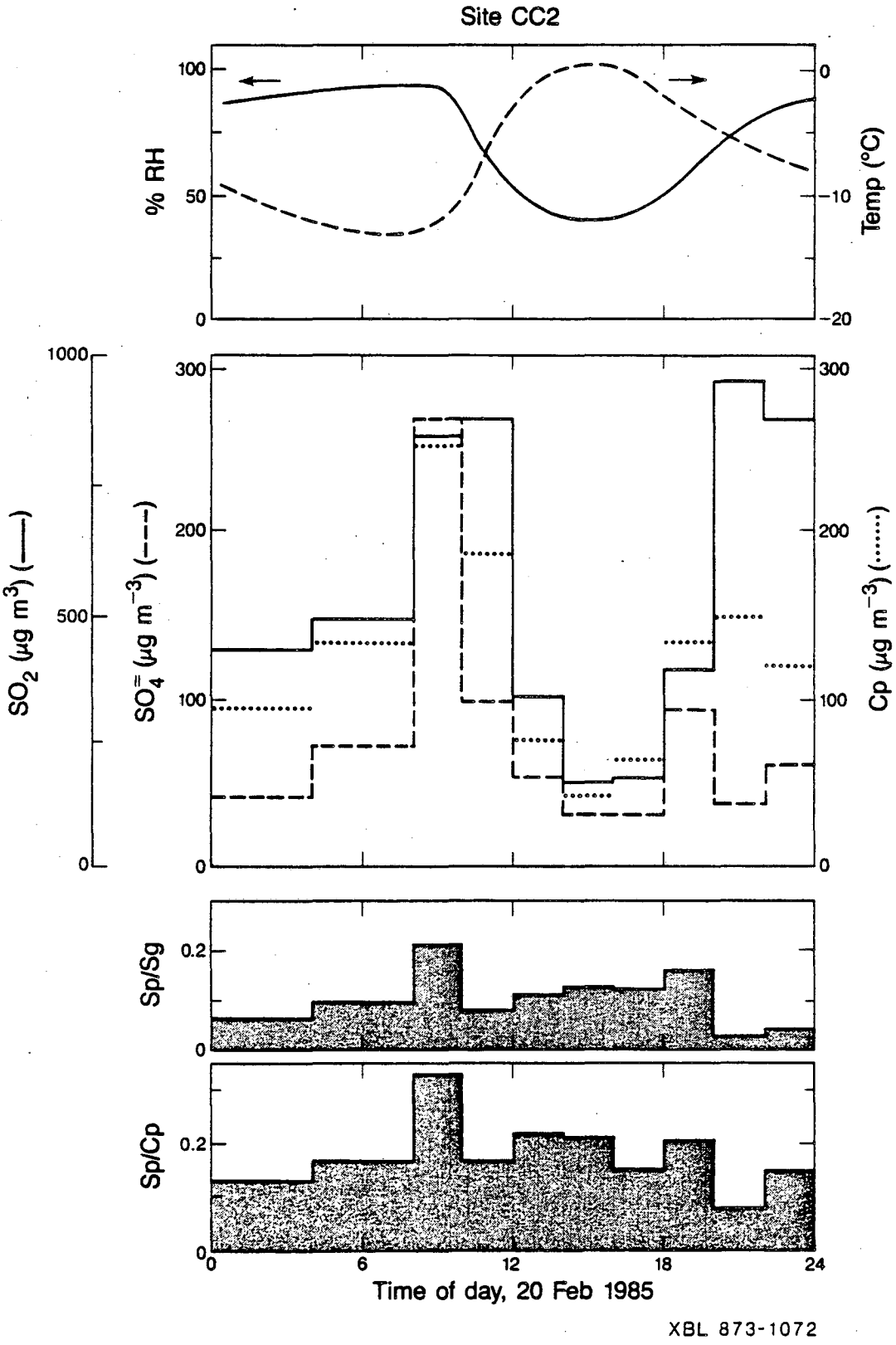

Site CC2
% RH
Temp (°C)
100
50
0
0
−10
−20
$SO_2$ (μg $m^3$) (——)
$SO_4^=$ (μg $m^{-3}$) (– – –)
Cp (μg $m^{-3}$) (.....)
1000
500
0
300
200
100
0
Sp/Sg
Sp/Cp
0.2
0
0
6
12
18
24
Time of day, 20 Feb 1985
XBL 873-1072

Figure 13

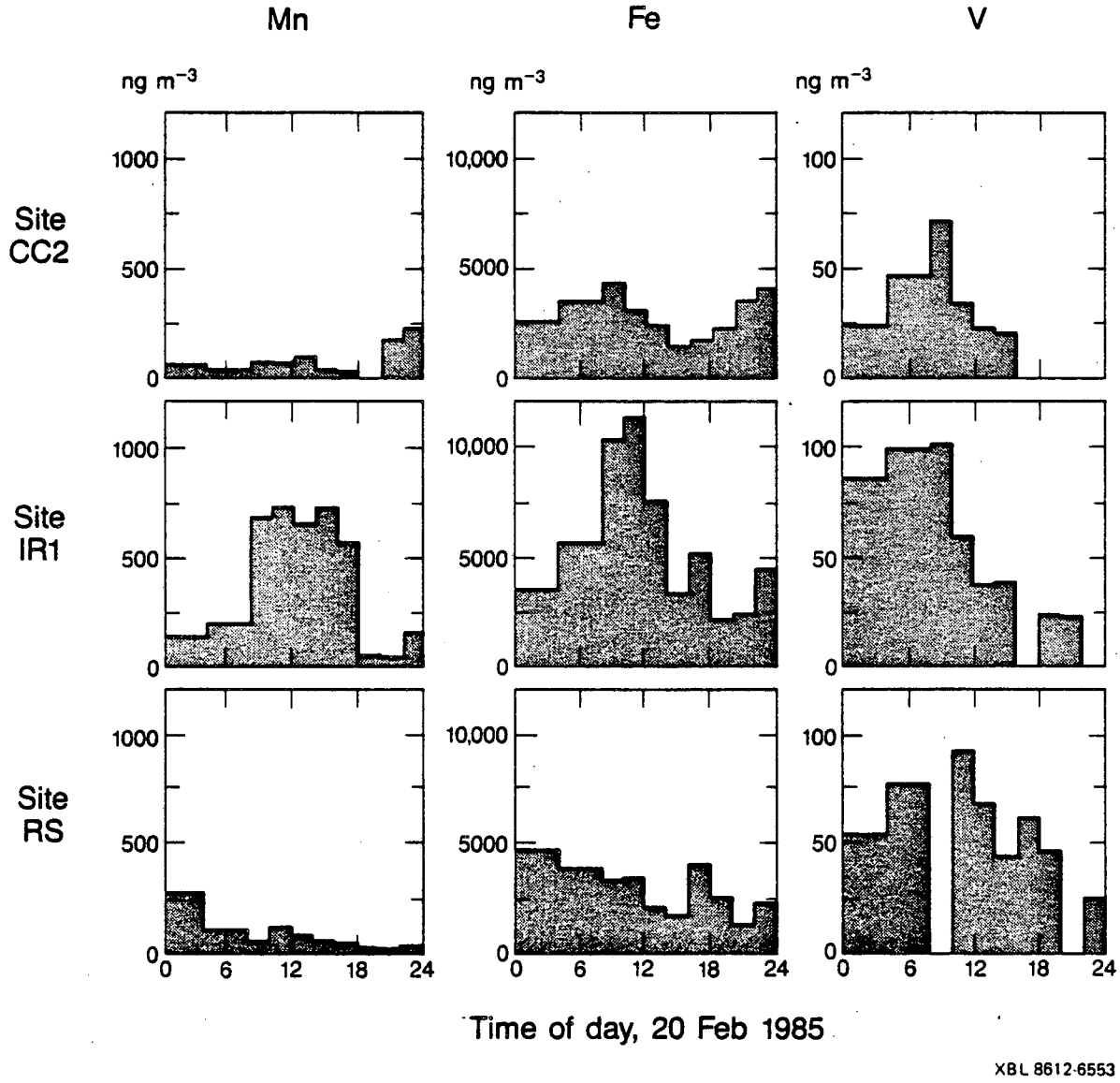
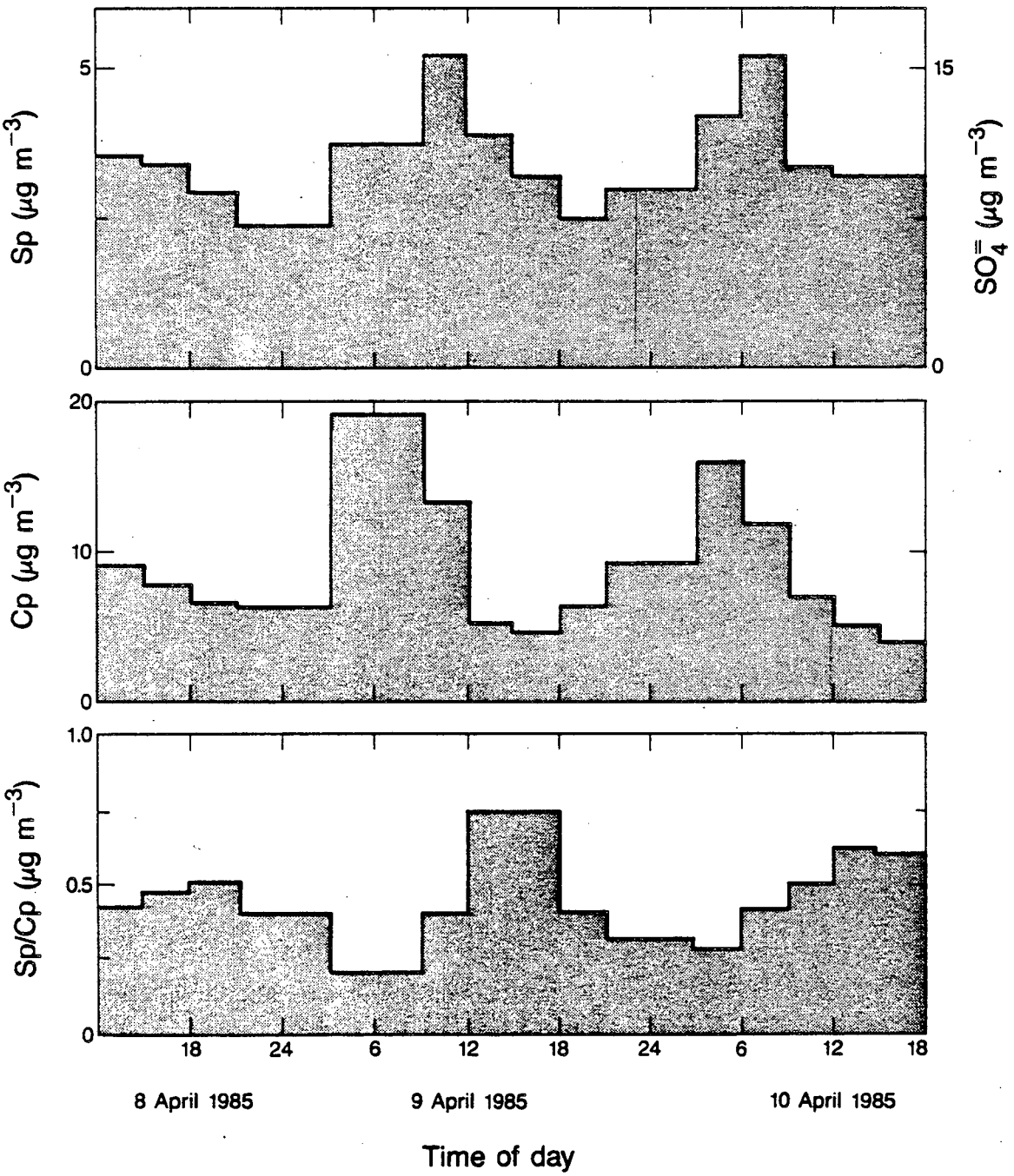

Mn
Fe
V
ng m⁻³
ng m⁻³
ng m⁻³
Site CC2
Site IR1
Site RS
1000
500
0
10,000
5000
100
50
0 6 12 18 24
Time of day, 20 Feb 1985
XBL 8612-6553

Figure 14




XBL 8612-6552

Figure 15

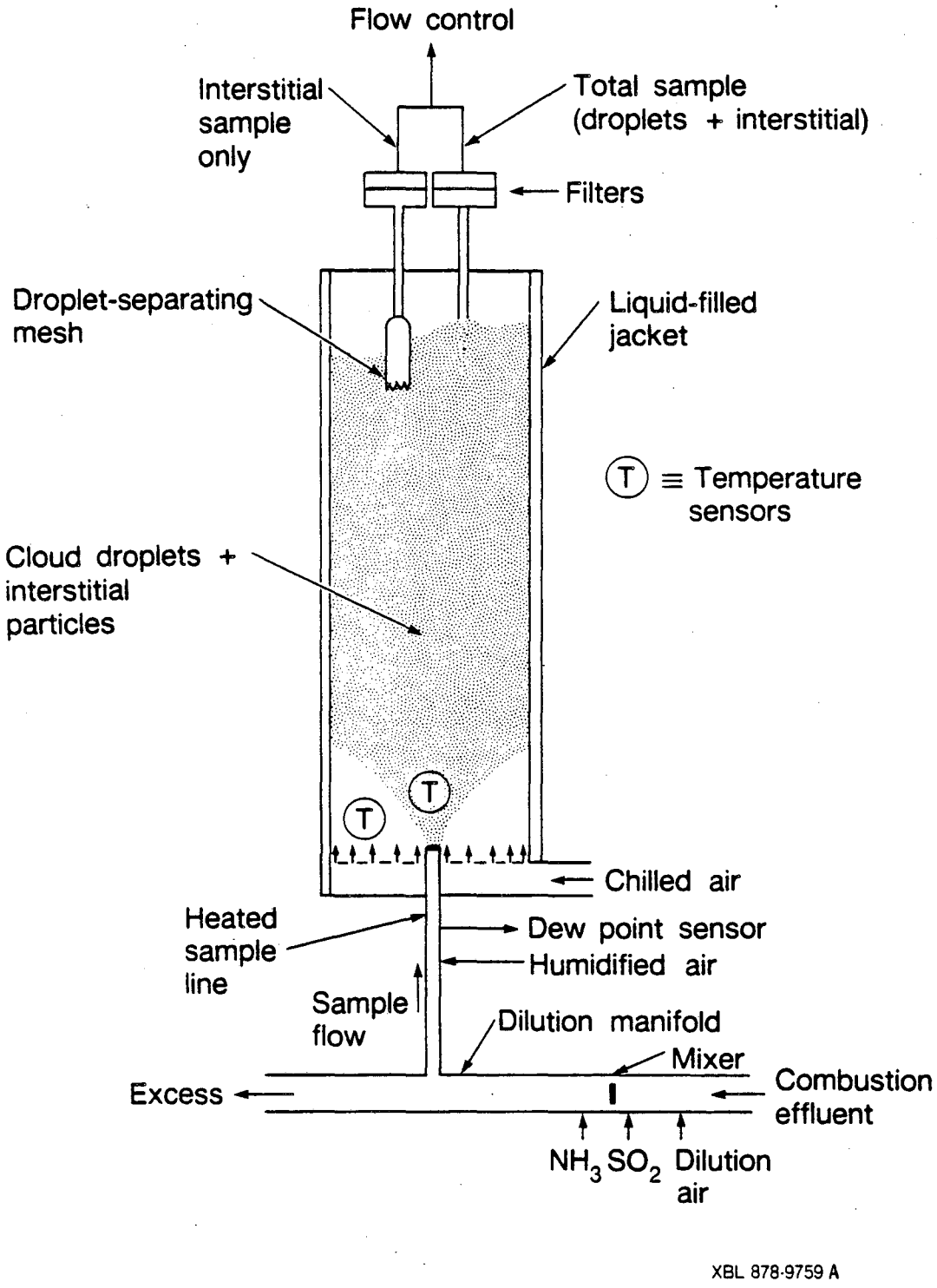

Flow control
Interstitial sample only
Total sample (droplets + interstitial)
Filters
Droplet-separating mesh
Liquid-filled jacket
T ≡ Temperature sensors
Cloud droplets + interstitial particles
T
T
Chilled air
Heated sample line
Dew point sensor
Humidified air
Sample flow
Dilution manifold
Mixer
Excess
Combustion effluent
NH3 SO2 Dilution air
XBL 878-9759 A

Figure 16

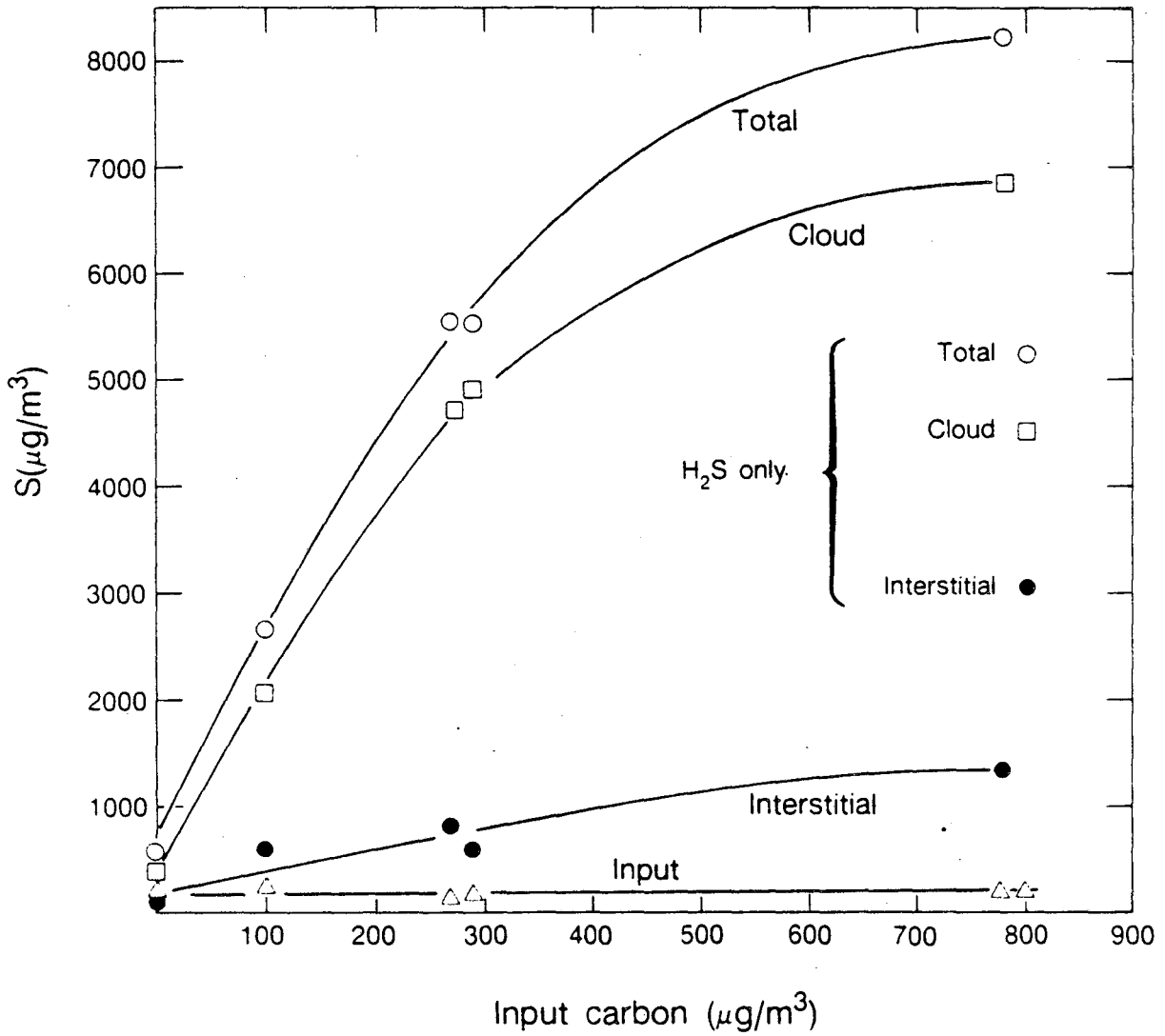

8000
7000
6000
5000
4000
3000
2000
1000
S(μg/m³)
100
200
300
400
500
600
700
800
900
Input carbon (μg/m³)
Total
Cloud
Interstitial
Input
H₂S only
Total
Cloud
Interstitial
XBL 879 9756

Figure 17

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