Title

SPATIAL AND TEMPORAL VARIATIONS OF AEROSOL SULFATE AND TRACE ELEMENTS IN A SOURCE-DOMINATED URBAN ENVIRONMENT

Authors

Bizjak, M.
Benner, W.H.
Hansen, A.D.A.

Publication Date

1988-04-01

LBL-24385 c.2
Preprint

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

APPLIED SCIENCE
DIVISION

Submitted to Atmospheric Environment

Spatial and Temporal Variations of Aerosol Sulfate and Trace Elements in a Source-Dominated Urban Environment

M. Bizjak, W.H. Benner, A.D.A. Hansen, D. Hrček,
V. Hudnik, and T. Novakov

April 1988

APPLIED SCIENCE
DIVISION

Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

DISCLAIMER

LBL-24385

SPATIAL AND TEMPORAL VARIATIONS OF AEROSOL SULFATE AND TRACE ELEMENTS IN A SOURCE-DOMINATED URBAN ENVIRONMENT*

M. Bizjak,† W.H. Benner,‡ A.D.A. Hansen,‡ D. Hrček,§
V. Hudnik,† and T. Novakov‡

† B. Kidrič Institute of Chemistry, 61115 Ljubljana, Yugoslavia

‡ Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720

§ Hydrometeorological Institute of Slovenia, 61000 Ljubljana, Yugoslavia

Abstract

Time-resolved measurements of SO_2, sulfate, particulate carbon, and trace metal (Pb, As, K, Mn, Fe, and V) concentrations were performed simultaneously at four locations in Ljubljana, Yugoslavia, during February and April, 1985. During the winter three different sulfate formation regimes are identified: A — morning period coinciding with maximum emissions and high humidity resulting in maximum sulfate concentrations, with the sulfate formation during this period attributed to fast heterogeneous, aqueous oxidation of local SO_2 involving combustion products; B — late evening period with low humidity and high emissions when most sulfate is primary; C — the remainder of the day when sulfate appears to be of a regional origin and formed by a combination of heterogeneous and homogeneous processes. During the nonheating season, the sulfate appears to be of regional origin.

---

*The portion of this work done at LBL was supported by the Director, Office of Energy Research, Office of Health and Environmental Research, Physical and Technological Research Division of the U.S. Department of Energy under contract no. DE-AC03-76SF00098. The work performed in Ljubljana was supported by the Community for Scientific Research of Slovenia, and by U.S. Environmental Protection Agency through the joint U.S.-Yugoslav Board on Scientific Cooperation.

Introduction

Both local and regional sources contribute to the aerosol sulfate in urban environments. Local sources include primary sulfate produced by the oxidation of fuel sulfur to S(VI) during the combustion process, and secondary sulfate produced by oxidation of sulfur dioxide in the local atmosphere. Regional sulfate is formed by the oxidation of SO_2 released farther upwind. The relative contribution of these sulfate sources to the urban atmosphere depends on the spatial distribution of sources, the meteorology and topography, and the concentrations of oxidants, oxidative catalysts, and other reactive species. For example, in the eastern United States, where most major SO_2 sources are located outside urban areas, conversion processes during transport produce regional aerosol sulfate, whose concentrations vary little between the cities and the surrounding areas (Altshuller, 1980, 1987). Consequently, under such circumstances sulfate produced locally in the city is of relatively minor importance. In contrast, local sulfate may be important in many urban situations where significant SO_2 sources are within the local area, and when concentrations of pollutants may reach very high levels because of stagnant meteorological conditions and temperature inversions.

The measurements described in this study were performed in Ljubljana, Yugoslavia, a city of approximately 300,000 inhabitants 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 residential boilers and home furnaces. In the winter of 1983-84, we conducted a study in Ljubljana with analysis of 24-hr aerosol samples collected at a single central city location (Bizjak *et al.*, 1986). During that study frequent periods of atmospheric stagnation occurred, often accompanied by urban fog and persistent subfreezing temperatures. Under these conditions, favorable for aqueous heterogeneous processes, we have observed the highest aerosol sulfate formation, corresponding to the conversion of up to 20% of the

SO_2. We have also found circumstantial evidence that this sulfate is of local origin. These conclusions agree with those reached by Benarie *et al.* (1973), who studied wintertime air pollution in the industrial Rouen region. These authors have determined SO_2 oxidation rates to be between 6 and 25% hr^{-1} and have attributed the sulfate formation to catalytic action of suspended solid particles.

The new field experiments described in this paper, carried out during February and April, 1985, were designed to differentiate local and regional sulfates. Measurements were performed simultaneously at four locations, providing city-wide temporal variations on the concentrations of SO_2, particulate sulfate, carbon, trace metals (Pb, As, K, V, Mn, and Fe), and meteorological parameters.

Results obtained in this study show that during high pollution episodes in winter (February), three separate sulfate formation processes can be distinguished. Depending on meteorological conditions and source emission intensity, these result in the formation of local secondary, local primary, and regional aerosol sulfate. In contrast, during nonheating periods when local SO_2 emissions are decreased, the sulfate is principally of regional origin. Although the measurements reported in this paper were performed during only two days in February and three in April, 1985, we believe that these do not describe isolated events but are representative of a systematic wintertime pattern in this source-dominated region. It is also likely that similar manifestations of fast, local sulfate formation can be found in other regions where coal is extensively used for space heating, particularly during cold winter days when consumption of this fuel is highest. The winter of 1985 was exceptionally cold in most of Europe; and severe SO_2, smoke, and sulfate pollution episodes were observed throughout the continent, including neighboring Hungary (Mészáros *et al.*, 1987).

Experimental Details

Ground-level aerosol samples were collected at four sites with synchronized sequential samplers. The locations of sampling sites are shown in Fig. 1 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 sequential samplers (about 2 m above ground) were heated so the sampled air was 5 °C above ambient air temperature. During fog episodes the heating of the air stream evaporates fog droplets; therefore the total aerosol, including any material incorporated into fog droplets, was collected. A metal shield placed above the sampler inlet prevents the precipitating droplets from entering the sampler. The aerosol was sampled at a flow rate of 40 liters min^{-1}. Sampling times were usually set to collect eight 2-hr samples from 0800 to 2400 hr, and two 4-hr samples starting at 2400 and 0400 hr. The samples were collected on 25-mm diameter quartz fiber filters (Pallflex type 2500 QAO) that had been prefired at 700 °C to remove combustible carbon.

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 followed by conductometric CO_2 and SO_2 determination (Wösthoff Co. C and S analyzer). The April samples were more lightly loaded, and the entire filter had to be used for the C and S analysis; trace metal data were therefore not obtained for these samples. During our previous studies in Ljubljana, the analysis of filters for total sulfur by combustion and for water-soluble sulfate (mostly present as ammonium sulfate) by ion chromatography yielded results that were in excellent agreement (Bizjak *et al.*, 1986). We therefore assume that the particulate sulfur, S_p, is in the form of sulfate. Previous work also demonstrated that the total particulate carbon, C_p, is equivalent to primary carbon (*i.e.*, soot) during winter at this location (Bizjak *et al.*, 1984).

During the February sampling period, the Slovenian Hydrometeorological Institute continuously monitored SO_2 concentrations adjacent to the four aerosol sampling sites (Monitor Labs SO_2 analyzers) and recorded meteorological variables including wind speed and direction, temperature, and relative humidity. During the April sampling period, these measurements were not made.

The meteorological conditions for the February sampling period can be summarized as follows: February 18 was clear with no temperature inversion. February 19 and 20 were foggy in the city but clear in the surrounding mountains. The low-lying city fog persisted until about 1000 hrs on both days. A temperature inversion existed on February 19 and 20 during part of the night and morning, but not during the rest of the day. The temperature inversion was stronger on February 20 than on February 19. Because of such meteorological conditions, significant buildup of airborne pollutants occurred on February 20.

Results and Discussion

In this section we will first examine the evidence for local sulfate formation by examining the spatial and temporal variations of SO_2, sulfate, and tracer elements. This approach uses the fact that SO_2 sources are not evenly distributed throughout the city. The highest emissions during winter are in the city center (site CC), where in older buildings much of the coal is burned in individual stoves that are usually stoked in the morning and evening. In the outer residential districts (site RS), the emissions are lower because of lower population density and the prevalence of central heating. Locally generated sulfate should, under stagnant atmospheric conditions, exhibit a spatial inhomogeneity similar to that of primary species produced by the combustion of sulfurcontaining fuels. In contrast, when the emissions from local sources are greatly diminished (April), a greater spatial homogeneity of sulfate concentrations can be expected.

Figure 2 shows half-hour average SO_2 concentrations at the four sites for February 19 and 20, 1985. SO_2 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 reflects the distribution of SO_2 sources and the pattern of daily fuel consumption.

Temporal variations of sulfate concentrations at the four sites for February 19 and 20 are shown in Fig. 3. Spatial distribution of peak sulfate concentrations resembles that of SO_2. This is particularly pronounced in the February 20 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 peak sulfate and SO_2 concentrations is indicative of the local origin of these sulfate particles.

Diurnal concentration variations for February 20 of As, K, and Pb (*i.e.*, the tracer elements for the principal fuels coal, wood, and gasoline, respectively) are shown in Fig. 4. The diurnal and spatial variations of the coal tracer (As) follow very closely those of sulfate. K and Pb concentrations also show 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. 5), strongly resemble those of sulfate and As and, to a lesser degree, SO_2, K, and Pb.

This apparent relationship between sulfate and primary emission species can have at least two explanations: either most sulfate is primary or it is produced by an SO_2 oxidation process in the urban atmosphere. In the following discussion, we will demonstrate 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 sulfate, SO_2, carbon, and tracer elements. The data for February 20 from the four sites are tabulated in Table I. That most of the sulfate is not primary is evident from the particulate to gaseous sulfur ratios (S_p/S_g). (S_g is the SO_2 concentration expressed as sulfur.) These range on the average from ~ 0.05 to ~ 0.20. The variability of these ratios 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 ratios with those determined for stack emissions of various source types at this location. A recently determined average S_p/S_g source ratio for coal and oil burning is ~ 0.02 (Bizjak *et al.*, 1987). This value is considerably lower than practically all ambient ratios, thus demonstrating that atmospheric SO_2 oxidation to sulfate does take place.

Further insight into the nature of the SO_2 oxidation process is gained by considering details of the diurnal variations of meteorological parameters and chemical species. Figure 6 shows variations of relative humidity, ambient temperature, SO_2, sulfate, particulate carbon, and S_p/S_g and S_p/C_p concentration ratios for February 20 at site CC. Three separate sulfate formation regimes can be distinguished from the data presented in Figure 6 and Table I. These correspond to:

A — The morning period (0800-1000), which coincides with maximum emissions; the S_p/S_g ratio increased by 115% between the 0400-0800 and 0800-1000 periods, corresponding to an apparent oxidation rate of $57\%\,\mathrm{hr}^{-1}$.

B — The late evening period (2000-2400) when the S_p/S_g ratios were of the order of a few percent and similar to the values obtained from stack sampling.

C — During the rest of the day, a gradual increase of the S_p/S_g ratios is seen, corresponding to apparent oxidation rates of $\sim 6\%\ hr^{-1}$ and $\sim 10\%\ hr^{-1}$ for the time periods between 0000 and 0800, and 1000 and 2000 respectively.

During the time periods corresponding to these regimes, different sulfate formation mechanisms could take place.

In the following we shall first discuss the observations relating to regime A — *i.e.*, the apparent local sulfate formation during morning hours. The local nature of this sulfate is suggested by its spatial inhomogeneity, which is similar to that of SO_2. The fact that the morning sulfate peak coincides with the SO_2 increase but the evening SO_2 peak does not demonstrates that the intense morning sulfate peak is caused not only by the SO_2 increase. The lack of exact correspondence between SO_2 and sulfate is also evident from the difference in the duration (or width) of their respective morning peaks (Fig. 6). The SO_2 concentration remained essentially constant during the 4-hr period (0800-1200 hr), 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 1000-1200 hr, sulfate decreased by about a factor of three from the preceding 0800-1000 hr time period. Between 0800 and 1000 hr, the S_p/S_g and S_p/S_g ratios are at maximum values, indicating enhanced sulfate formation during this period. Why is the sulfate formation particularly pronounced during the 0800-1000 period but not the 1000-1200 period? The answer to this question is in the meteorology.

The data in Fig. 6 show that the relative humidity was $> 90\%$ during the night and part of the morning, sharply decreasing after 1000 hr. From visual observations at the sampling site, we know that during the morning hours there was dense ground fog. However, the fog dissipated after 1000 hr and did not recur for the rest of the day. 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 suggest an aqueous oxidation mechanism. Such a mechanism would be much less efficient between 1000-1200 hr than between 0800-1000 hr 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 time periods. From the considerations presented thus far we can conclude that during regime A sulfate is formed locally by a fast aqueous process that coincides with the onset of morning emissions of SO_2 and other combustion products.

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

We may first eliminate the possibility of catalysis by transition metals. Figure 7 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 those 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. Although photochemical oxidants were not monitored at our sites, it is very unlikely that high ground-level concentrations of oxidants would be produced under winter conditions with dense fog. Measurements of gas-phase H_2O_2 and O_3 concentrations performed elsewhere in Europe (Po Valley, Italy) under similar foggy conditions in winter show that these are negligible (Fuzzi *et al.*, 1986; Lind and Lazrus, 1986). We therefore assume that photochemically generated oxidants do not contribute significantly to the formation of local morning sulfate.

From the evidence presented so far, we are inclined to hypothesize that the rapid SO_2 oxidation observed in the morning period is caused by incomplete combustion products in the presence of liquid water droplets (Brodzinsky *et al.*, 1980; Chang *et al.*, 1981; Novakov, 1984; Benner *et al.*, 1985). Field evidence supporting this hypothesis was obtained by Eatough *et al.* (1984), who observed rapid sulfate formation when the plume of an oil-burning power plant impacted on a fog bank. A direct laboratory proof for the occurrence of aqueous SO_2 oxidation byproducts of incomplete combustion was recently obtained by Benner and Novakov (1987) from cloud chamber experiments. These experiments were designed to simulate the conditions when a plume of freshly generated soot particles interact with liquid water droplets. These authors have observed rapid SO_2 oxidation to sulfate ($>$ 100% hr^{-1}) when water droplets are nucleated on combustion-generated soot particles in the presence of SO_2, other combustion products, and gaseous ammonia. Sulfate formation was either negligible or minimal in the absence of ammonia, liquid water droplets, or soot particles. (Ammonia is abundantly present in the European atmosphere [Buijsman *et al.*, 1987]. We are unaware of an ammonia emissions inventory for this specific location. However, high concentrations of ammonium sulfate and other ammonium salts were measured in Ljubljana [Puxbaum *et al.*, 1985]. Another significant source of particle alkalinity at the sites of this study is the coal fly ash.) These results are in qualitative agreement with our ambient observation of rapid sulfate formation during the morning high emission period. We note that the emissions at our study site are mostly from low chimneys, and therefore fast mixing of ambient air, including ammonia with the plume constituents is expected.

Most of the above discussion is relevant to the processes responsible for the formation of high concentrations of sulfate during morning hours (regime A). As we have mentioned, at other periods of the day different SO_2 oxidation mechanisms may be involved. For example, regime B is characteristic of primary sulfate emissions because ambient S_p/S_g ratios are low, similar to those obtained from source samplings. Sulfate concentrations during this time period are low in spite of very high gaseous SO_2 concentrations. The relative humidity was $\sim$ 70%; from visual observations we know that there was no fog during this period. Such conditions were therefore not conducive for aqueous SO_2 oxidation.

During the rest of the day (regime C), a gradual increase in the S_p/S_g ratios was observed. Two separate atmospheric conditions existed during this regime: a high humidity and foggy period from 0000 to 0800; and a low humidity, clear air interval between 1200 and 2000. Judging from the S_p/S_g and S_p/C_p ratios, SO_2 oxidation did take place during both periods. It is plausible to assume that heterogeneous aqueous oxidation occurred during the former period and that a homogeneous process or processes took place during the latter. An assessment of the actual mechanisms is impossible at this time, however, because of the lack of pertinent — particularly gas phase — data. It is of interest to note, however, that 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 supercooled water droplets and therefore at reduced oxidation rates.

From the above discussion we conclude that during different periods of the day aerosol sulfate could be formed by different processes. These could involve local SO_2 oxidation (regime A), local sulfate emissions (regime B), and possibly oxidation of regional SO_2 (regime C). The latter possibility is suggested by the fact that the sulfate concentrations are relatively homogeneously distributed throughout the city during time periods corresponding to regime C (see Table I).

The above discussion is based on the February data, typical of heavy winter pollution with air stagnation and foggy days. During the April sampling period, an entirely different picture was observed. 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 $> 90\%$ 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%. Sulfate and particulate carbon concentrations measured at the same sites as in February are shown in Table II. 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. 8, 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, because of greatly reduced SO_2 emissions in the city, ambient sulfate probably comes from regional sources. Differences in diurnal variations between February and April are also indicative of the differences in sulfate formation chemistry during the two sampling periods. While there is strong evidence that the February sulfate was produced largely by nonphotochemical mechanisms, April sulfate is most likely produced by photochemical oxidants. This possibility is suggested by the midday sulfate and S_p/C_p maxima (Fig. 8).

Conclusions

Time-resolved measurements of SO_2, sulfate, particulate carbon, and trace metal (Pb, As, K, Mn, Fe and V) concentrations were performed simultaneously at four sites in Ljubljana, Yugoslavia, in February and April, 1985. The data are used to distinguish local from regional sulfate and to infer some possible mechanisms of sulfate formation at this location. Spatial inhomogeneity of local SO_2 sources during the winter heating season is reflected in a similar inhomogeneity of peak sulfate concentration, indicating its local origin.

During winter days with stagnant air and low temperature inversion, three different sulfate formation regimes were identified: A — morning period coinciding with maximum emissions and high humidity resulting in maximum sulfate concentrations; the sulfate formation during this period is attributed to fast heterogeneous, aqueous oxidation of local SO_2 involving combustion products (soot). B — late evening period with low humidity and high emissions when most sulfate is primary. C — the remainder of the day, when sulfate appears to be of a regional origin, formed by a combination of heterogeneous and homogeneous processes. The estimated SO_2 conversion rates were 57% hr^{-1} for regime A and between 6 and 10% hr^{-1} for regime C.

During the April measurement period when the local SO_2 emissions are greatly diminished, the sulfate was homogeneously distributed throughout the city at all times. This finding is indicative of regional sulfate formation.

References

Altshuller A. P. (1980) Seasonal and episodic trends in sulfate concentrations (1963-1978) in the eastern United States. *Environ. Sci. Technol.* **14**, 1337-1349.

Atshuller A. P. (1987) Relationship between direction of wind flow and fine particle sulfur concentrations within and upwind of St. Louis, MO. *Atmospheric Environment* **21**, 1023-1032.

Benarie M., Menard T. and Nonet A. (1973) Etude de la transformation de l'anhydride sulfureux en acide sulfurique en relation avec les données climatologiques, dans un ensemble urbain a caractère industriel Rouen. *Atmospheric Environment* **7**, 403-421.

Benner W. H., McKinney P. H. and Novakov T. (1985) Oxidation of SO_2 in fog droplets by primary oxidants. *Atmospheric Environment.* **19**, 1377-1383.

Benner W. H. and Novakov T. (1987) A cloud chamber demonstration of heterogeneous SO_2 oxidation by combustion products. Lawrence Berkeley Laboratory Report LBL-24038.

Bizjak M., Hudnik V., Gomiscek S., Hansen A. D. A. and Novakov T. (1984) Aerosol studies in Ljubljana under conditions of combustion-derived winter pollution. *Sci. Total Envir.* **36**, 377-382.

Bizjak M., Hudnik V., Hansen A. D. A., and Novakov T. (1986) Evidence for heterogeneous SO_2 oxidation in Ljubljana, Yugoslavia. *Atmospheric Environment,* **20**, 2199-2204.

Bizjak M., Lengar Z. and Hudnik V. (1987) Technical report on stack solid particle and SO_2 emission measurement. B. Kidrič Institute of Chemistry Report KIBK-DP-617.

Brodzinsky R., Chang S.-G., Markowitz S. S. and Novakov T. (1980) Kinetics and mechanisms for the catalytic oxidation of sulfur dioxide on carbon in aqueous suspensions. *J. Phys. Chem.* **84**, 3354-3358.

Buijsman E., Maas H. F. M. and Asman W. A. H. (1987) Anthropogenic NH_3 emissions in Europe. *Atmospheric Environment* **21**, 1009-1022.

Chang S.-G., Toossi R. and Novakov T. (1981) The importance of soot particles and nitrous acid in oxidizing SO_2 in atmospheric aqueous droplets. *Atmospheric Environment* **15**, 1287-1292.

Eatough D. J., Arthur R. L., Eatough N. L., Hill M. W., Mangelson N. F., Richter B. E. and Hansen L. D. (1984) Rapid conversion of $SO_2(g)$ to sulfate in a fog bank. *Envir. Sci. Technol.* **18**, 855-859.

Fuzzi S., Orsi G., Nardini G. and Facchini M. C. (1986) Chemical composition of fog droplets and other physico-chemical measurements. Report of the Heterogeneous Atmospheric Chemistry Project, Istituto FISBAT-C.N.R, Bologna (Italy), pp. 7-10.

Lind J. and Lazrus A. (1986) Measurements of hydrogen peroxide vapor at S. Pietro Capofiume. Report of the Heterogeneous Atmospheric Chemistry Project, Istituto FISBAT-C.N.R, Bologna (Italy), pp. 27-31.

Mészáros E., Mersich I. and Szentimrey T. (1987) The air pollution episode of January 1985 as revealed by background data measured in Hungary. *Atmospheric Environment* **21**, 2505-2510.

Novakov T. (1984) The role of soot and primary oxidants in atmospheric chemistry. *Sci. Total Envir.* **36**, 1-10.

Puxbaum H., Weber M. and Pech G. (1985) Occurrence of inorganic acidic components of four source-dominated sites in Europe. In *Proceedings of the Symposium on Heterogeneous Processes in Source-Dominated Atmospheres,* Lawrence Berkeley Laboratory Report LBL-20261, pp. 49-50.

TABLE I

Concentration variations of major pollutants and S_p/S_g and S_p/C_p ratios at four sites on 20 February 1985. Sampling start times correspond to local clock time. Sampling sites: CC = city center; IR1 - IR2 = mixed industrial-residential; RS = residential.

Site CC										
$\mu g\ m^{-3}$										
C_p	98	135	255	190	77	43	63	137	148	121
S_p	14	24	90	33	18	10	10	31	12	20
SO_2	440	500	865	900	335	165	190	390	970	895
$ng\ m^{-3}$										
As	45	41	83	99	32	12	27	50	48	41
K	1350	910	1520	1750	990	590	750	1620	1510	1560
Pb	1230	1040	2530	1550	790	530	800	2180	1630	1180
Mn	55	34	69	64	89	30	24		170	220
Fe	2580	3450	4300	3070	2310	1410	1560	2220	3490	4010
V	23	46	71	33	22	20				
S_p/S_g (%)	6.4	9.6	20.7	7.3	10.7	12.0	10.5	15.8	2.4	4.4
S_p/C_p (%)	14.3	17.7	35.0	17.3	23.3	23.2	15.8	22.6	8.1	16.0
Site IR1										
$\mu g\ m^{-3}$										
C_p	86	107	136	232	100	47	54	133	131	85
S_p	15	17	17	42	23	10	8	15	15	12
SO_2	380	365	575	835	445	250	295	600	620	500
$ng\ m^{-3}$										
As	30	45	60	91	51	15	29	43	32	18
K	820	1060	1900	2160	1350	690	720	860	910	710
Pb	450	1370	1630	2060	880	370	660	1710	1130	470
Mn	135	200	690	730	655	735	565	40	36	140
Fe	3350	5500	10200	11200	7400	3250	5100	2050	2300	4400
V	85	98	105	58	36	37		22	21	145
S_p/S_g (%)	7.9	9.2	5.9	10.0	10.3	7.9	5.4	5.0	4.8	4.8
S_p/C_p (%)	17.4	15.9	12.5	18.1	23.0	21.2	14.8	11.3	11.4	14.1
Start hour	**0**	**4**	**8**	**10**	**12**	**14**	**16**	**18**	**20**	**22**

Site IR2										
$\mu g\ m^{-3}$										
C_p	128	120	146	135	68	39	67	168	174	
S_p	18	30	42	24	16	12	11	35	17	
SO_2	475	340	420	500	290	130	190	600	625	
$ng\ m^{-3}$										
As	35	31	44	49	23	16	41	51	46	
K	1030	880	1810	1400	950	510	550	1390	1540	
Pb	600	960	1000	830	560	230	420	1470	2200	
Mn	62	55	94	76	89	18	19	20	37	
Fe	8600	9150	7400	3800	2300	1750	2100	9650	12600	
V		46	130	47						
S_p/S_g (%)	7.6	17.6	19.6	9.6	11.0	18.3	11.6	11.6	5.4	
S_p/C_p (%)	14.0	25.0	29.0	17.8	23.0	30.0	16.4	20.0	9.8	
Site RS										
$\mu g\ m^{-3}$										
C_p	122	130	168	101	85	61	91	174	130	121
S_p	16	16	18	20	10	10	11	21	12	17
SO_2	375	330	430	355	340	275	310	460	475	340
$ng\ m^{-3}$										
As	42	37	29	41	28	17	32	76	60	30
K	1530	1220	1410	1650	1030	690	1270	1550	990	1820
Pb	1430	1180	1600	940	720	530	1150	2360	1350	1360
Mn	269	99	53	117	86	59	44	29	18	40
Fe	4700	3800	3250	3400	2100	1750	4050	2500	1250	2300
V	55	78		93	68	44	62	46		24
S_p/S_g (%)	9.4	9.6	8.4	11.2	5.8	7.3	7.1	9.2	5.1	10.0
S_p/C_p (%)	13.1	12.3	10.7	19.8	11.7	16.4	12.1	12.0	9.2	14.0
Start hour	**0**	**4**	**8**	**10**	**12**	**14**	**16**	**18**	**20**	**22**

TABLE II

Particulate carbon (C_p) and sulfur (S_p) concentrations measured at four sites during the period 8-10 April 1985. Starting times (local time) of each filter are indicated.

C_p, μg m^{-3}															
CC2	10	15	2	3	26	13	4	3	5	8	25	13	7	6	3
IR1	6	4	3	7	18	12	4	3	8	11	17	17	7	5	6
IR2	6	7	7	8	18	18	6	4	5	10	18	11			
RS	12	7	11	5	15	12	6	4	6	8	9	8	9	3	
S_p, μg m^{-3}															
CC2	2.2	3.6	0.9	1.3	3.6	6.5	2.6	2.9	2.1	2.2	3.5	3.1	2.9	2.4	1.3
IR1	3.1	2.8	1.8	2.1	3.1	3.2	2.7	1.4	3.4	3.2	6.8	8.8	4.5	3.4	4.8
IR2	4.6	3.4	4.3	1.4	5.4	6.3	5.7	3.7	3.0	2.6	4.1	1.8			
RS	4.3	4.1	4.2	2.1	3.0	4.3	4.6	2.8	2.3	2.8	2.9	3.7	2.7	1.9	
Start hour	12	15	18	21	3	9	12	15	18	21	3	6	9	12	15
Date	8 April 1985				9 April 1985						10 April 1985				

Figure Captions

Figure 1

Map of Ljubljana showing the locations of the sampling sites: CC = city center, IR1 and IR2 = mixed industrial and residential districts, RS = residential area.

Figure 2

Half-hour average SO_2 concentrations measured at the four sites on 19 and 20 February 1985. Peak concentrations decrease from the city center to the outlying residential areas.

Figure 3

Diurnal variations of sulfate concentrations at the four sites for 19 and 20 February 1985. Peak sulfate concentrations are highest in the city center (CC) and lowest in the suburban location (RS).

Figure 4

Diurnal variations of As, K, and Pb concentrations at the four sites for 20 February 1985.

Figure 5

Diurnal variations of particulate carbon concentrations at the four sampling sites on 19 and 20 February 1985. The morning carbon peaks decrease from the city center (CC) to the outlying areas, similar to sulfate concentration peaks.

Figure 6

Diurnal variations of air temperature, relative humidity, SO_2, sulfate and carbon concentrations at the city center on 20 February 1985. Maximum S_p/S_g and S_p/C_p ratios are observed during the morning increase of primary emissions. These coincide with the last hours of the high humidity period.

Figure 7

Diurnal concentration variations of Mn, Fe, and V measured on 20 February 1985 at CC, IR1, and RS sites. Concentrations of these metals do not correlate with sulfate concentrations.

Figure 8

Concentration variation of particulate sulfur and carbon averaged over all sites for the 8-10 April 1985 period. S_p/C_p ratios show midday maxima. Carbon peaks precede sulfur peaks, indicating different sources of these species.

XBB 873-2004

Figure 1

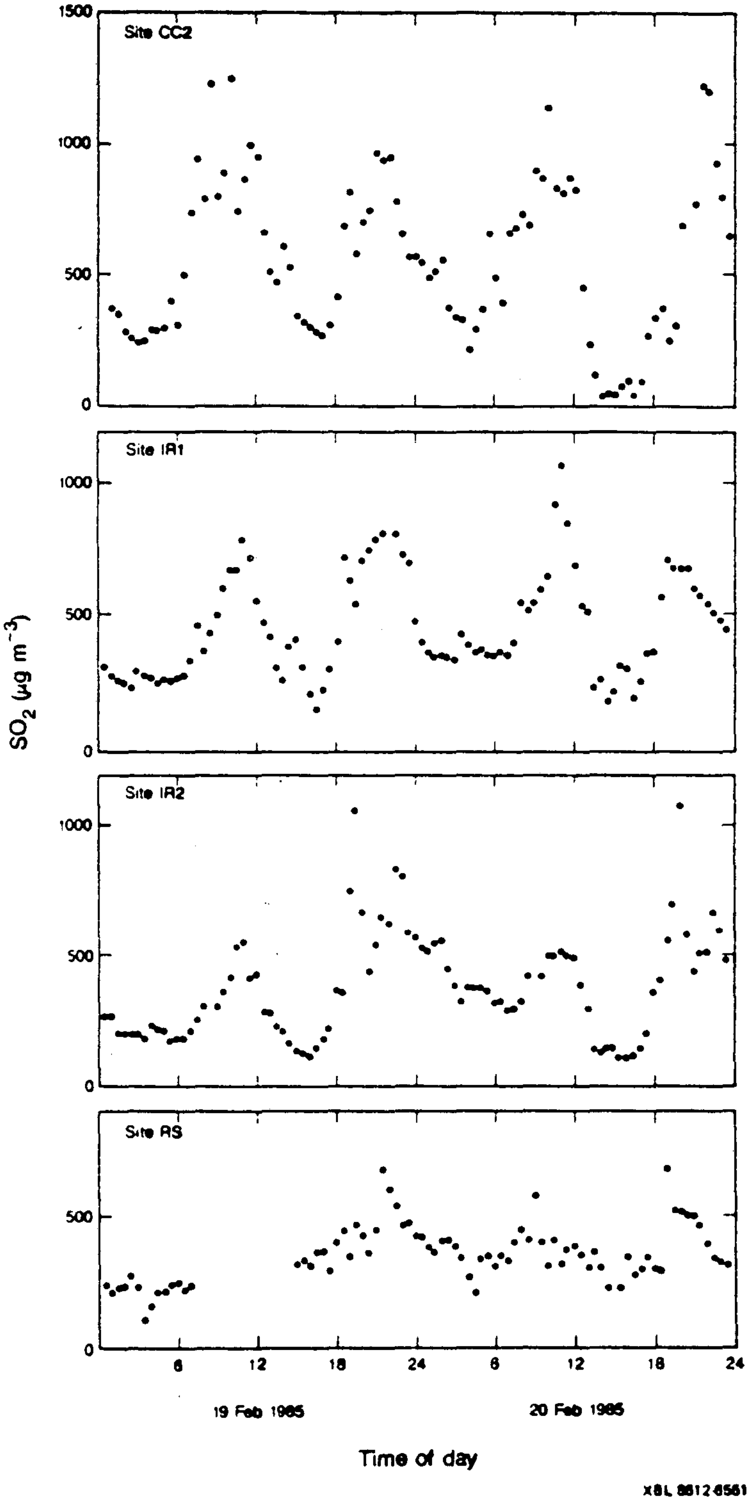

Site CC2
Site IR1
Site IR2
Site RS
1500
1000
500
0
SO$_2$ (μg m^{-3})
6
12
18
24
19 Feb 1985
20 Feb 1985
Time of day
XBL 8812-6561

Figure 2

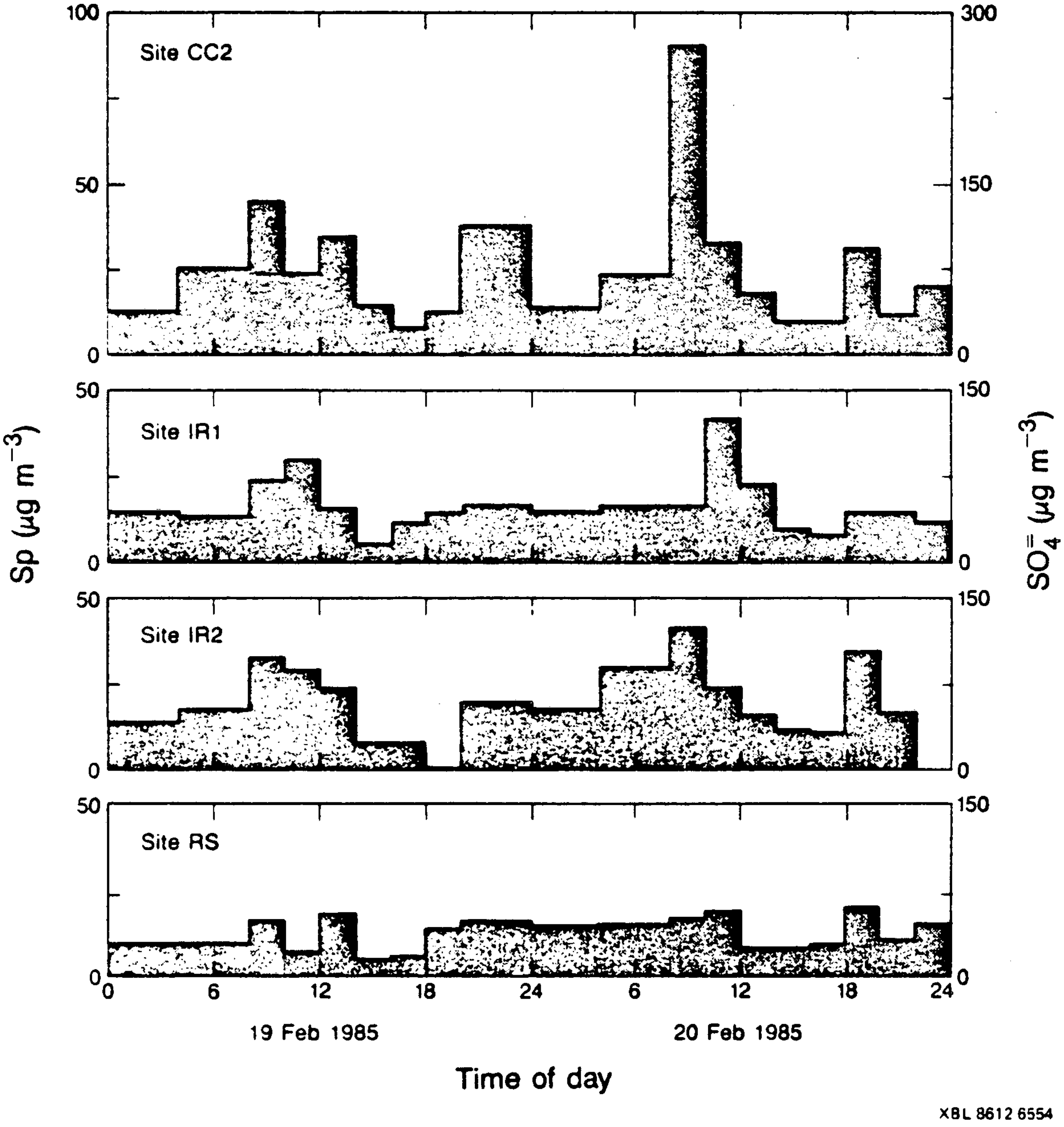

Site CC2
Site IR1
Site IR2
Site RS
100
50
0
300
150
0
Sp (μg m^{-3})
$SO_4^=$ (μg m^{-3})
0
6
12
18
24
6
12
18
24
19 Feb 1985
20 Feb 1985
Time of day
XBL 8612 6554

Figure 3

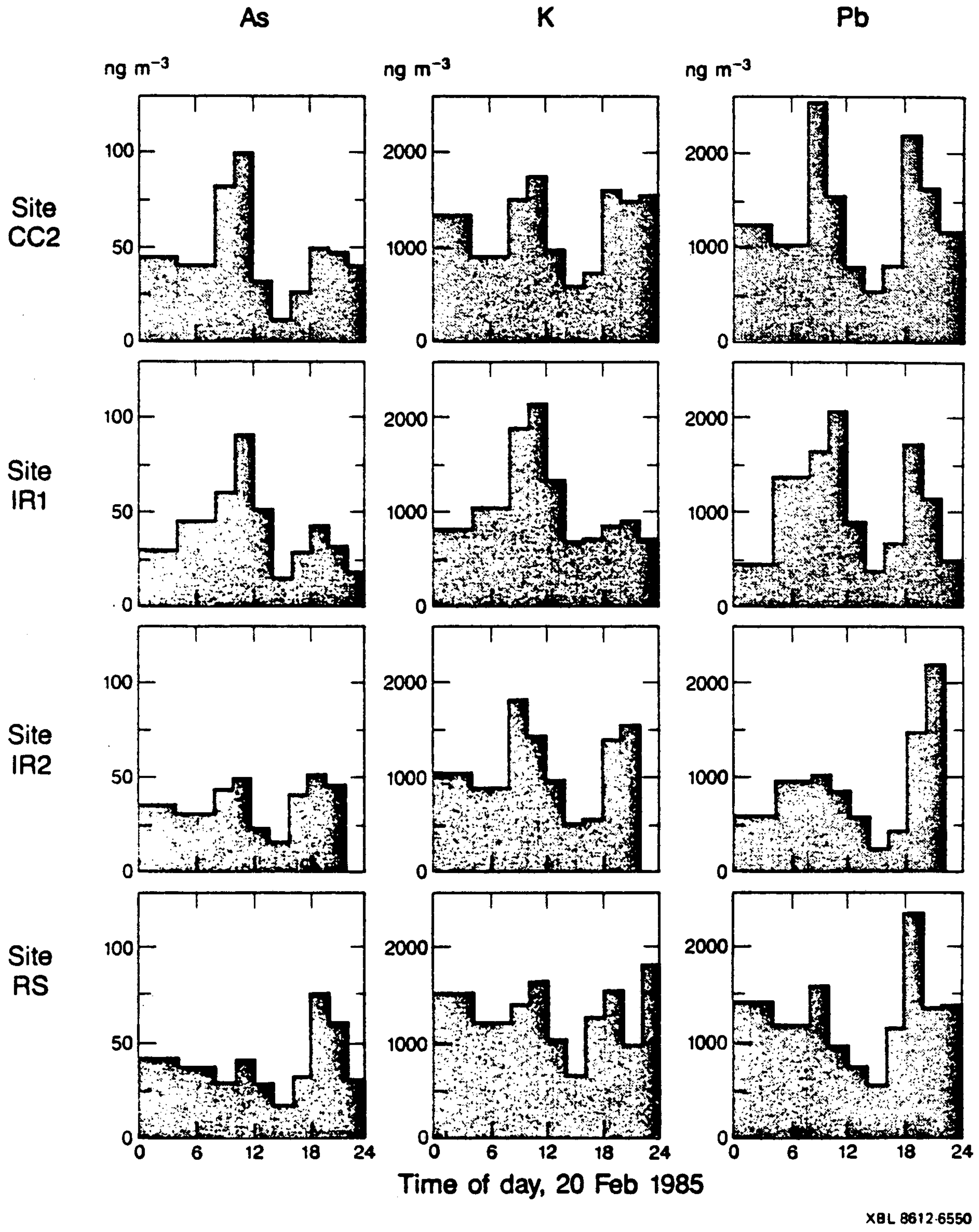

As
K
Pb
ng m^{-3}
ng m^{-3}
ng m^{-3}
Site CC2
Site IR1
Site IR2
Site RS
0
50
100
0
1000
2000
0
6
12
18
24
Time of day, 20 Feb 1985
XBL 8612-6550

Figure 4

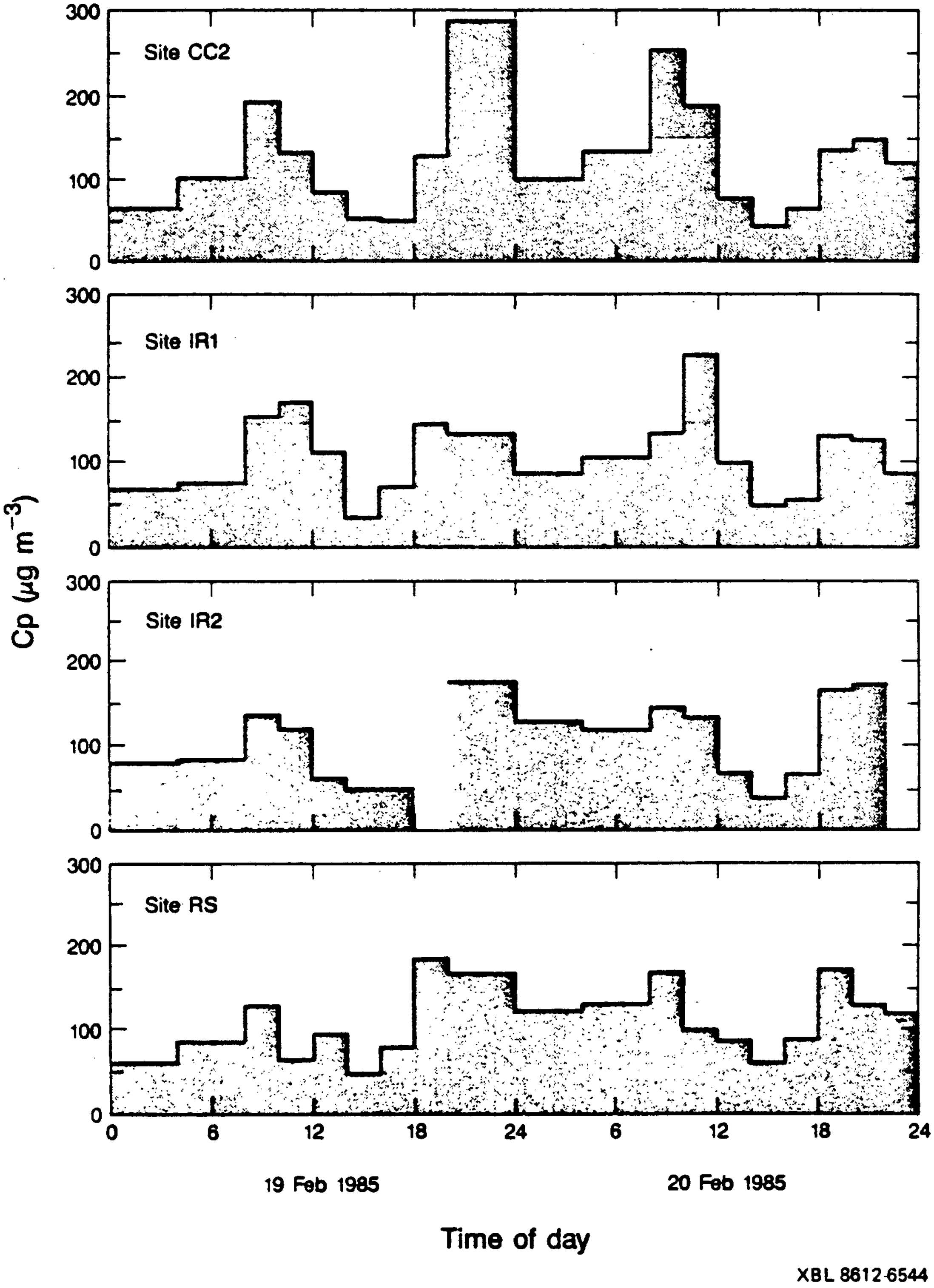
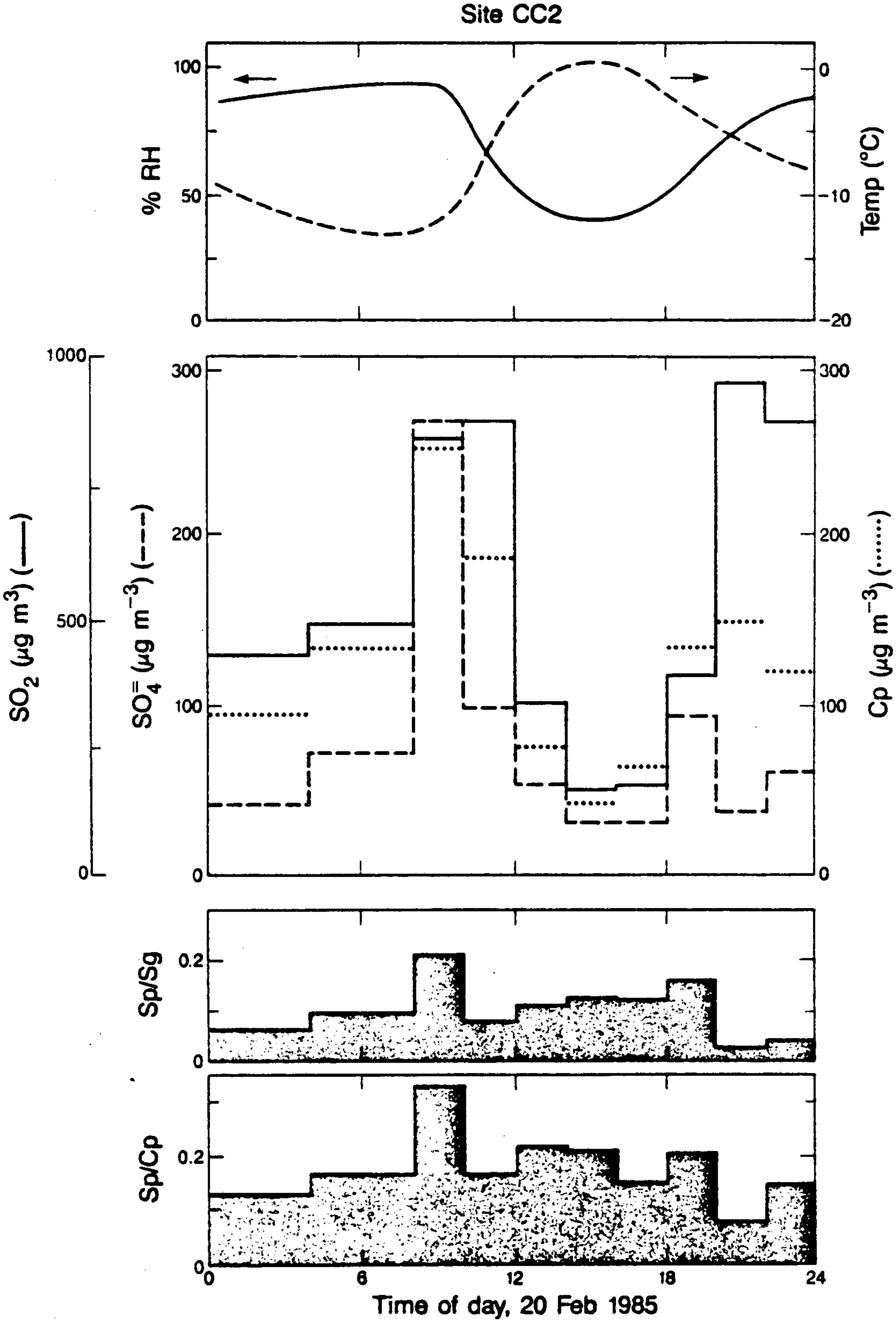

Site CC2
Site IR1
Site IR2
Site RS
Cp (μg m⁻³)
0
100
200
300
0
6
12
18
24
6
12
18
24
19 Feb 1985
20 Feb 1985
Time of day
XBL 8612-6544

Figure 5



XBL 873-1072

Figure 6

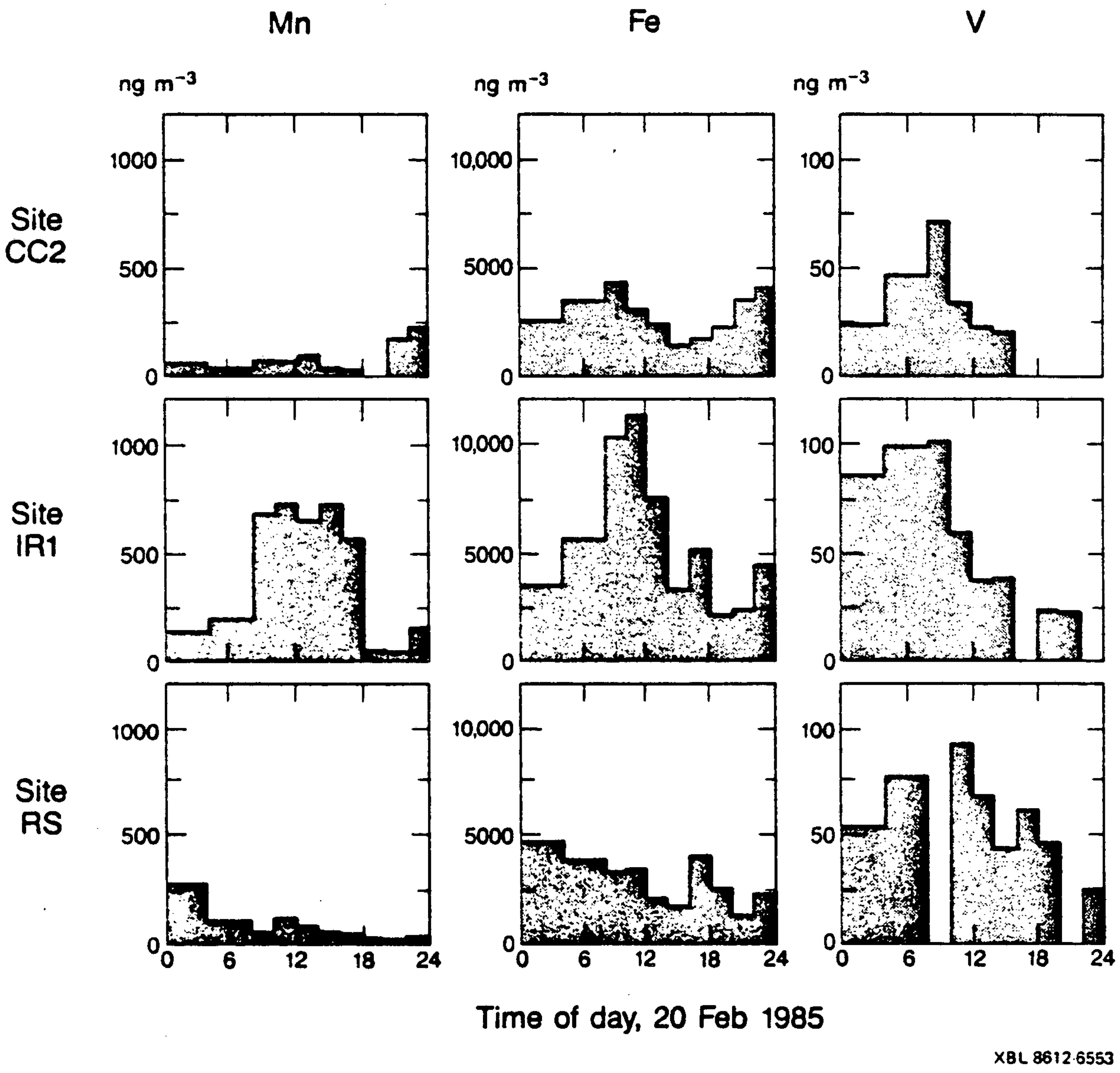

Mn
Fe
V
ng m^{-3}
ng m^{-3}
ng m^{-3}
Site CC2
Site IR1
Site RS
1000
500
0
10,000
5000
0
100
50
0
0
6
12
18
24
Time of day, 20 Feb 1985
XBL 8612-6553

Figure 7

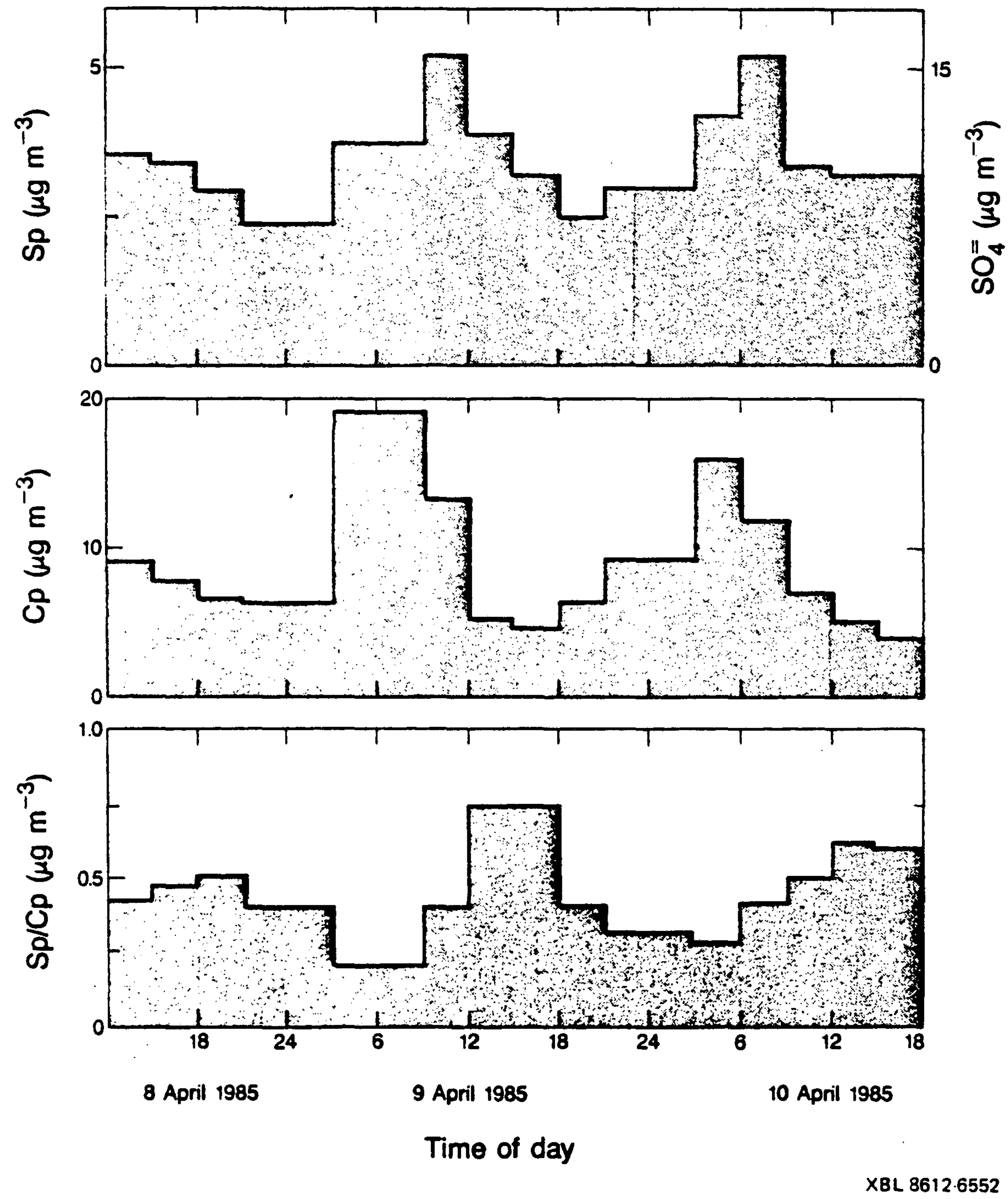

Sp (μg m^{-3})
SO$_4^=$ (μg m^{-3})
5
0
15
0
Cp (μg m^{-3})
20
10
0
Sp/Cp (μg m^{-3})
1.0
0.5
0
18
24
6
12
18
24
6
12
18
8 April 1985
9 April 1985
10 April 1985
Time of day
XBL 8612-6552

Figure 8

LAWRENCE BERKELEY LABORATORY
TECHNICAL INFORMATION DEPARTMENT
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720