ON THE ORIGIN OF THE AIR POLLUTION IN A RURAL AREA OF NORTH CHINA

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Abstract

Elemental concentration relationships of atmospheric aerosols in a rural area of north China are examined. It has been found that the concentrations of those elements due to man-made air pollutants, especially S, are high and are comparable with those often found in the heavily industrialized eastern U. S. and western Europe. The low degree of correlation between the variations of the concentration of particulate S and local weather conditions and the relatively smaller range of concentration variation, compared with elements typical of terrestrial dust, suggest that aerosol sulfur pollution has already become a large scale regional problem in north China.

Introduction

As the atmosphere is a superfluid compared to water, air pollutants, in principle, may be transported to remote areas through the atmosphere. Evidence for this has been found elsewhere, especially downwind from polluted continental regions. For example, in the U. S. A. a steady decrease in the concentration of particulate sulfur in Florida from the northwest to the south of the state was observed in 1976 [1]. Analysis of the data has suggested that most of the fine particulate S in the range of 0.5—1 μm diameter, as measured by single orifice cascade impactors, is transported to this peninsular state from the more heavily industrialized states lying to the north rather than generated locally [2]. The excess of fine mode particulate S observed at Bermuda located in the North Atlantic Ocean, some 1000 km away from the North American coast, has been attributed to sulfate from the convension of gaseous SO_2 which is transported through the atmosphere from the continental pollution sources, most possibly in North America [2, 3]. Heintzenberg et al. [4] have recently reported that S concentration in arctic aerosol in winter is as high as 690 ng/m³ compared with the value of 27 ng/m³ in summer and 49 ng/m³ at the South Pole. The arctic haze observed in winter time is considered to be caused by air pollutants transported from western Europe and U. S. S. R. [5]. Asian dusts have been observed occasionally in the deep sea sediment in the central Pacific and in the atmosphere at islands in the Pacific [6]. Now it is widely recognized that the transport of atmospheric pollutants is an intercontinental issue.

Since the 1960's air quality in U. S. cities, as measured by total suspended parti-culate matter in the atmosphere and concentrations of aerosols, has been steadily im-proved while the air quality in the rural areas has deteriorated. One of the reasons is that the cities have built large numbers of tall stacks which allow their pollutants to be carried far away to pollute the rural areas while protecting the cities. With the fast development of heavy industry in China's large cities, a large amount of coal is burned for industry and households, and much of this coal is not very well treated, causing air pollution to become a problem of common concern. Smoke plumes are often visible, and urban air pollution is physically felt by everybody.

In the last few years, we have seen a sharp increase of effort for monitoring and controlling fly ash emissions. Most of this effort has been centered in the large cities, but much less attention has been given to measurements in rural areas. People still think that the air in the countryside is still clean. Actually, according to the present study, as discussed further below, this is generally true for coarse mode aerosols, ex-cept special cases when we have dust storms. Coarse dust contains mainly harmless earth crustal elements and is not dangerous for human health due to its physical pro-perties. However, this is not true for fine mode aerosols which have particle diame-ters < 1 μm. These contain many pollutants such as sulfuric acid and heavy metals from combustion. It is these fine mode aerosol particles that are most harmful to na-ture, agriculture, and public health, due to their physical and chemical properties.
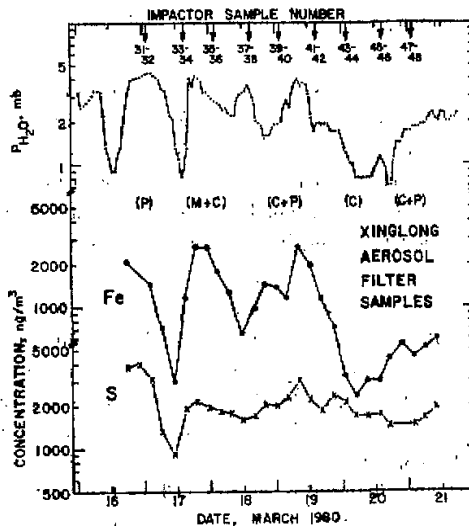

Fig. 1. Variation of concentrations of earth crustal elements represented by Fe and pollut-ant elements represented by S with time in relation to variation of water vapor content

Gaseous sulfur dioxide and its chemical products sulfuric acid and sulfate salts, together with nitrogen oxides and nitric acid from combustion of fuels, are probably the main sources of the atmospheric acidity that causes acid rain and acidifies cul-tivated land. Moreover, small acidic particles which contain H_2SO_4 are able to pass

into a human's respiratory system and can cause both short term and long term health effects, and may even increase the susceptibility to cancer of the lung. In the southeast Atlantic coastal regions of the U.S.A., an area quite far from air pollution sources, public health records show an anomalously high mortality due to lung cancer [7]. This anomaly is highly correlated with a predicted high concentration of H_2SO_4 expected to be formed in a moist marine atmosphere which is mixed with continental air polluted with SO_2 [8].

The present study shows that the concentration of particulate S in fine mode aerosol collected in Xinglong, a rural area some 100 km away from Beijing, is comparable to that often found in the northeast U.S. A recent study has shown that this aerosol probably contains a considerable amount of liquid H_2SO_4 [9], in which many harmful gases can be dissolved. It is these liquid particles containing toxic gases, e.g. SO_2, that may be most harmful to the human lung.

Observations

A comprehensive aerosol sampling program has been carried out at the Xinglong observing station of the Institute of Astronomy, Chinese Academy of Sciences. The station is located in the middle of the Yanshan mountains where the air was believed to be extremely clean when the astronomers selected this location to observe the stars. The samples collected were analyzed in Lund, Sweden and at The Florida State University by PIXE [10]. Many of the results are reported elsewhere [11—13], while the concentration of S, which is the most important pollutant, will be further discussed here.

Table I gives the concentrations of particulate S measured at different locations, mostly with similar sampling devices and chemical analytical techniques. As can be seen from the Table, the concentration of S in Xinglong is of the same order as that in nonurban areas of the northeastern U.S.A. and western Europe, higher than that at rural areas in western U.S.A., and much higher than that found in remote South America. That is to say, air pollution in Xinglong is as serious as that in the northeastern U.S.A.

Figure 1 shows the variation of concentrations of earth crustal elements, represented by Fe, and pollutant elements, represented by S, for the second week of the sampling period when the weather conditions are changeable and most interesting to this study. Plotted on Figure 1 also is the concentration of water vapor in the atmosphere, which is a good indicator of air mass movement. An examination of weather maps of the northern hemisphere has shown that the sampling site had experienced five major weather systems during this period [13]. The variation of concentrations of earth crustal elements, as represented by Fe in Figure 1, roughly follows the pattern of weather changes, but the concentrations of S behave differently. Often when the concentrations of earth crustal elements drop with onset of northerly air flow, no significant changes occur in the concentration of S. On the average, the amplitude of the fluctuation of the concentration of S is much less than that of the earth crustal elements, and the absolute concentration of S remains at a high level for the whole period (except a very short period on March 17). These results suggest that the earth crustal elements may be characterized by local air masses that are defined by

wind direction, wind velocity, temperature, humidity, vertical mixing rate, and local surface conditions, etc., but S may not. Large scale regional parameters must be taken into account to explain the concentration of S. A statistical calculation shows that correlation coefficient for Fe and H_2O is 0.898, but for S, H_2O it is only 0.410.

This is further proved by Figure 2 and Figure 3. Figure 2 shows the elemental weight ratios for earth crustal elements relative to Fe. It is quite obvious that no systematic variation with time can be found, although the weather conditions and the absolute concentrations vary dramatically, as indicated in Figure 1. (A small relative increase in Ti, Mn, and Zn may have occurred at the beginning of March 20.) Figure 2 also shows the weight ratios of the average earth crust as indicated by arrows on the left side of the figure. The averaged weight ratios of Si, Al, K, Ca, and Ti to Fe in Xinglong aerosol are quite close to those of average earth crust, supporting the idea that these elements are mainly from wind blown dust, probably not transported over long distances, and their concentrations are determined by local meteorological conditions and local surface character istics. A statistical calculation has also shown that the concentrations of these elements are strongly correlated to each other.
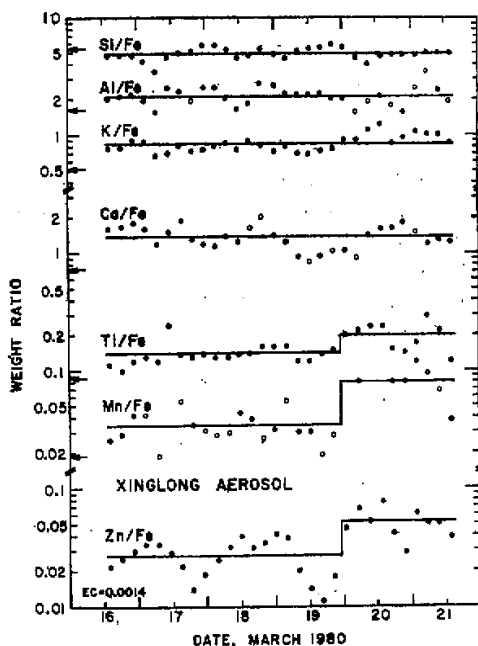

Fig. 2. Variation of elemental weight ratios to Fe of earth crustal elements with time

Figure 3 gives the variation of the weight ratio S/Fe with time. It is obvious that the relative abundance of S in the aerosols of different air masses varies markedly, and generally the ratio is higher for north air flow when the air is believed to be cleaner and lower for the southerly air flow when the air is more polluted. This again indicates that the air pollution by S is distributed over a much larger spatial scale

than is coarse particle terrestrial dust. The concentration of particulate S cannot be simply correlated to local wind direction and other atmospheric conditions. Instead, the overall concentration of particulate S may be determined by the regional total emission rate of SO_2 and the gas-to-particle conversion rate of SO_2 to sulfuric acid, which in turn depends on the atmospheric conditions, e.g. other reactive gas concentrations, temperature, and water vapor content.

The origin of high sulfur concentration in Xinglong aerosol

It is natural to ask why the concentration of particulate S is so high in Xinglong where there are no large pollution sources. To answer this question completely, further comprehensive sampling in the region and serious theoretical study are needed. Perhaps a sophisticated sampling network equipped with samplers capable of measuring both particulate S and gaseous SO_2 has to be set up in the east part of China.

In principle, gas-to-particle conversion of pollution-derived SO_2 and long range transport of sulfate are responsible for the high concentration of particulate S found in Xinglong and other rural areas. It is now commonly recognized that most of the particulate S is in the form of sulfuric acid or sulfate in the atmosphere, the result of conversion from gaseous SO_2 through various chemical reactions. Aerosol particles formed this way are small in size and have longer residence time in the atmosphere than either coarse particles or chemically reactive trace gases. Hence they can be transported to quite remote places.

Almost all the S contained in fossil fuel is emitted to the atmosphere in the form of gaseous SO_2 upon combustion. Gaseous SO_2 is stable in the hot stack plume and carried away by air flow and through diffusion. During transport the SO_2 undergoes complicated chemical changes as it is cooled down. As a result, a portion of SO_2 is oxidized and reacts with water vapor, which always exists in the lower atmosphere, to form fine liquid H_2SO_4 aerosol droplets. The mechanism of oxidation of SO_2 in the atmosphere is still not well understood and the oxidizing agents are not well defined up to now.

Two possible reaction pathways are:

$$SO_2 + OH \rightarrow - - \rightarrow H_2SO_4 \tag{1}$$

$$SO_2 + H_2O_2 \rightarrow H_2SO_4 \tag{2}$$

Reaction (1) occurs in the gas phase with hydroxyl radical whose concentration depends on a series of photochemical reactions. Reaction (2) occurs in the liquid phase with hydrogen peroxide whose concentration depends on many of the same photochemical reactions. Reaction (1) may dominate near pollution sources whereas reaction (2) may dominate at long distances downwind.

SO_2 may be oxidized by reactions involving hydrocarbons or O_3 to form SO_3 which immediately combines with water vapor to form H_2SO_4 in the lower atmosphere. It is also possible that SO_2 gas is absorbed by pre-existing H_2SO_4 droplets and oxidized in the droplets. Whatever the mechanism is, the conversion rate of gaseous SO_2 to particulate sulfuric acid or sulfates is determined by atmospheric parameters, e.g. temperature and water vapor content, as well as the supply of SO_2, concentrations of
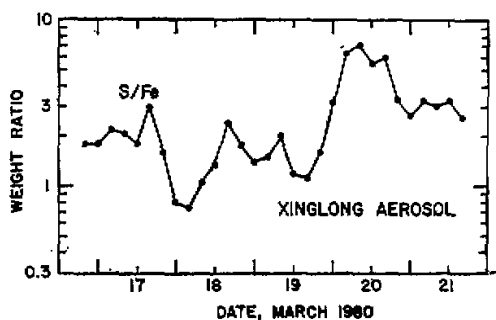
Fig. 3. Variation of elemental weight ratio S/Fe with time

oxidizing agents and catalytic substances. The concentration of particulate S depends on the conversion rate as well as the amount of SO₂ available.
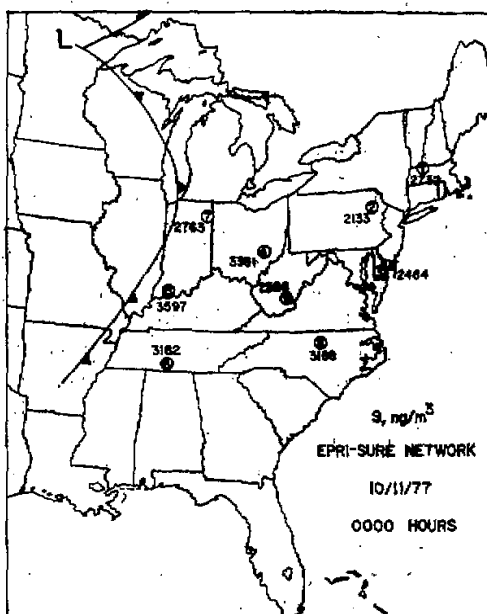

Fig. 4. Spatial distribution of aerosol S concentration in the eastern U. S. A. observed before a cold front passed by

If there should be an isolated SO₂ emission source in a reasonably stable atmosphere, a steady decrease of the concentration of gaseous SO₂ with increase in the distance away from the source would be expected due to dilution and conversion to particles, in addition to removal of SO₂ to the ground. However, the concentration of fine particulate S is expected to exhibit a more complicated pattern of variation, as the conversion rate of SO₂ gas to particulate sulfur may vary from place to place, according to atmospheric conditions which affect the rate, and as the aged particles are

transported from one place to the other. In fact, a maximum in the concentration of the particulate S may occur some distance away from the source, perhaps even as far as a hundred kilometers or more. Indeed, an investigation of the coal-fired Labadie power plant plume has shown that as the measured gaseous SO_2 concentration decreases steadily with increasing distance, the concentration of measured particulate S shows maxima at distances of 150—200 km from the source, and it remains at a high value up to 500 km away from the source [14]. Thus, when the individual emission sources, e.g. power plants, or groups of emission sources, e.g. towns and cities, are dotted sufficiently close in a large region, which is true in eastern U.S.A. and northeastern China, a rather uniform spatial distribution of the concentration of particulate S in this region may be expected, except those parts that are under direct influence of large plumes, even though the emission rates of SO_2 are different from one place to another. This is most likely to happen under rather stable atmospheric conditions. Such evidence has been observed in eastern U.S. states.

Figure 4 shows a result from large scale nonurban network measurements in the northeastern U.S. on October 11, 1977, when a cold front was just about to reach the study region. Sulfur concentrations at all the nine sampling sites in the network are almost the same ranging from 2133 to 3597 ng/m³. Later, when the cold front moved eastwards and gradually passed each sampling site it only caused temporary fluctuation of the S concentrations. After the cold front passed by, the concentration at each site was restored to its normal value [1, 2].

R. B. Husar and D. E. Patterson [14] have recently reported that 75% of SO_2 emitted to the atmosphere from the U. S. is emitted east of the Mississippi River with the highest emission density in the vicinity of the Ohio River Valley partly due to the higher percentage of coal consumption of the total fossil fuel consumption in that region, as shown in Figure 5. The measured concentrations of sulfate, however, show a very different pattern with a much more uniform distribution over a large part of the eastern U. S., as shown in Figure 6. In fact, the annual average of SO_2 concentration in urbanized areas has been decreased by a factor of two from 1964 to 1974, but the sulfate concentrations in rural areas have been increasing steadily [15]. These phenomena are obviously due to long range transport of fine particulate S with transformation of SO_2 during transport.

High and stable concentrations of particulate S observed at Xinglong are probably due to the same reasons described above, although the northeast part of China differs from the eastern U.S. in many ways. There is a similarity, however, in that both regions have a high density of SO_2 emission sources. The annual average emission rate of SO_2 from eastern China may be as large as that from the eastern U.S., as China burns about as much coal as oil burned in the U.S., and coal combustion releases more SO_2 than other fossil fuels such as natural gas and oil products.

Xinglong is situated at the margin of the densely populated north China region, and the high concentration of particulate S observed may probably represent a lower limit to the average S concentration in the northeast part of China. The finding that a short period of generally northern air flow does not change the concentration of S very much, such as those observed on March 19 (although lower concentrations are
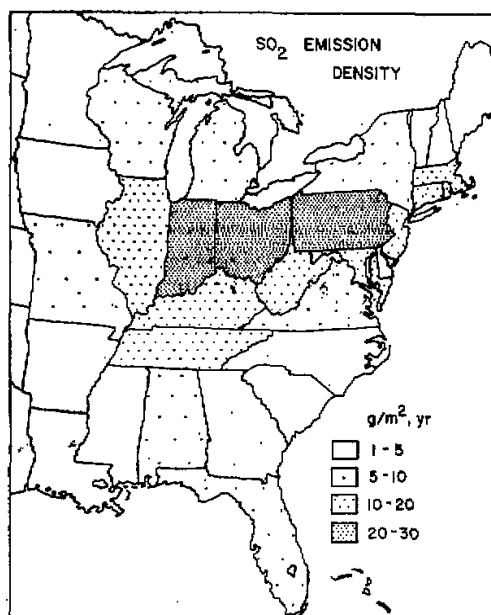
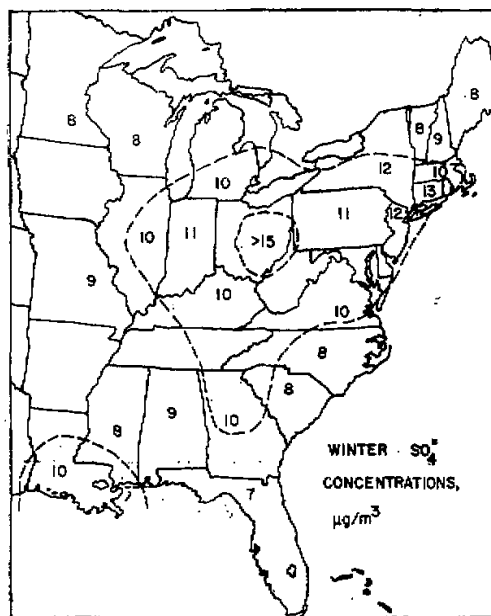Fig. 5. Sulfur dioxide emission density in the eastern U. S. A. [14]

Fig. 6. Sulfate concentration pattern in the eastern U. S. A. [14]

found with a stronger north wind such as that observed on March 17 in Xinglong and that observed on April 1, 1980 on the Great Wall [16]), does indicate that the region that has a high pollution S concentration, that is the phrase "northeast part of China," is very large and should include locations further remote from Beijing than Xinglong.

Although the exact origin of the high concentration of particulate S found in Xinglong aerosol cannot be completely defined with this single sampling program, we feel confident that the air pollution is a large scale regional problem. More sophisticated measurements in rural areas in the east part of China are urgently needed in order to estimate the air quality in the countryside and to make proper air pollution control strategies before the deterioration of air quality has gone too far.

Acknowledgements

Table 1. Comparison of particulate sulfur concentrations at different locations.

Location	Concentration (ng/m^3)	Sampling period	Remarks	Reference
North China:				
Xinglong	2300	March 1980	Rural site, during 2 weeks, mixed air flow conditions	12, 13
Badaling	315	1 April 1980	Rural site on Great Wall, during one day, strong north wind	16
U. S. A.:				
New York, NY	3000	1974—1975	Eastern U. S. A., urban	
Fort Wayne, IN	2500	Oct. 1977	East-Central U. S. A., nonurban	
Pensacola, FL	900	Dec. 1976	North Florida, nonurban	1
Miami, FL	500	Dec. 1976	South Florida, urban	1
Colorado	300	April 1976	Western U. S., Rocky Mountains, rural	
Sweden:				
Ryda Kungsgård	2100	March 1978	Near Stockholm, suburban	
Velen	900	Dec. 1975	Forest area, nonurban	
South America:				
Chacaltaya Mt.	80	March 1977	Remote Bolivian mountain peak	

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华北山区大气污染来源的初步探讨

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提　　要

本文仔细考察了华北一山地采样点获得的大气气溶胶元素浓度随气象条件的变化规律和各元素浓度之间的相互关系；发现，气溶胶中由人为污染物形成的那些颗粒物元素的浓度（特别是硫）相当高，其数值与在高度工业化的美国东北部和西欧的工业城市的观测结果相当；颗粒物硫的浓度的变化与局地天气条件的变化之间相关性很差，整个观测期间硫的浓度波动也不大，这与地壳灰尘元素的变化规律完全不同。这表明，气溶胶硫污染已经成为较大范围的区域性问题，城市污染可能已影响到广大农村和山区。

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