Transactions on Ecology and the Environment vol 29 © 1999 WIT Press, www.witpress.com, ISSN 1743-3541

A methodology for examining the long-range transport and the source-receptor relationships for acidic pollutants

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Abstract

A receptor-oriented methodology was applied to study the source-receptor relationships for sulfur dioxide, particulate sulfate and non-sea salt sulfate collected at a background site in France. In this methodology, chemical data and air parcel backward trajectories were combined to produce concentration field maps of likely contributing sources. The sources were essentially identified outside France in known European regions of high emissions of SO_2. The quantitative relationships between the computed concentration maps and the European emissions of SO_2 are examined performing a correlation analysis. Satisfying correlations were found between the sulfur species and the SO_2 emitted above 100 meters, while weaker correlations were found between these same species and the SO_2 emissions below 100 meters. The results of this study mean that the occurrence of high sulfur concentrations at once in gas, particles and in precipitation at Morvan are mainly caused by the long range transport of anthropogenic SO_2 and SO_2's secondary species. The SO_2 emitted above 100 meters seems to be the major cause of episodes of high SO_2 concentrations, particulate SO_4^{2-} concentrations and non-sea salt SO_4^{2-} concentrations in precipitation at the receptor site.

1 Introduction

It is now well-admitted that acidification is a consequence of transboundary transport of man-made pollutants. The knowledge of the sources of emissions that lead to acid deposition at a given area is necessary to establish the international control strategies aiming to decrease anthropogenic emissions. The determination of these so-called source-receptor relationships is considered as a key question in the problem of acid deposition (Seinfeld[1]).

The receptor-oriented methodology initialized by Ashbaugh *et al.*[2] associates chemical data with meteorological data (backward trajectories). This methodology has been successfully improved and applied to various atmospheric compounds to find their source areas (Cheng & Hopke[3] ; Zeng & Hopke[4] ; Seibert *et al.*[5] ; Gao *et al.*[6] ; Plaisance *et al.*[7]; Stohl[8] ; Plaisance *et al.*[9]).

In the present study, we intend to examine the source-receptor relationships for sulfur dioxide, particulate sulfate, and sulfate in precipitation measured at a background site in France. With this aim, the Seibert *et al.*[5] methodology is applied to produce concentration field maps of likely influential sources. A previous study has shown that the methodology created by Seibert *et al.*[5] is an efficient tool to study the source-receptor relationships influencing precipitation recorded at a background site (Charron *et al.*[10]). The source locations likely responsible for sulfur compounds in precipitation and ambient gas and particles will be compared with European emissions of SO_2.

2 Data and method

2.1 Data description

Data sets used in this study correspond to daily samples collected at a background station belonging to both French MERA (MEsure des Retombées Atmospheriques) and EMEP (Co-operative Programme for Monitoring and Evaluation of the Long Range Transmission of Air Pollutants in Europe) networks. This station is located in Morvan massif (elevation 620 m, latitude 47°16' N, longitude 04°05' E) far from the main urban and industrial emission areas according to the criteria required by EMEP. SO_2 and particulate SO_4^{2-} data correspond to concentrations of 353 samples collected from January 1994 to December 1994. These samples were collected using an in-line bubbling method for absorption of the gaseous SO_2 and pre-filter for collection of the particles. 395 precipitation samples were collected from January 1992 to December 1995 by wet-only precipitation collector. All analyses are performed by ion chromatography with conductimetric detection. Sampling and analysis protocols in the French network are described by Coddeville *et al.*[11]. The dynamic validation procedure established by Plaisance *et al.*[12] has permitted to eliminate some precipitation samples which have a considerable ion and specific conductivity imbalance. Na^+ concentrations are used to calculate the non-sea salt SO_4^{2-} in precipitation samples through the ratio in seawater $SO_4^{2-}/Na^+ = 0.12$.

The Météo France 3-D trajectory model developed by Martin *et al.*[13] is used in this study. 3-D trajectories have been calculated from linear spatial and temporal interpolations of the wind fields achieved by the European Centre for Medium Range Weather Forecast (ECMWF). Each concentration of particulate sulfate and sulfur dioxide is combined with the four air parcel back trajectories given per day and calculated at 925 hPa pressure level at the receptor site. Cheng & Hopke[3] have shown that 925 hPa level provide reasonable results for regional transport of airborne particles. The choice of the backward travel times is based on the average lifetimes defined by Wojcik & Chang[14]. Sulfur dioxide is associated with 38-h air parcel back trajectory and particulate SO_4^{2-} with 54-h air parcel back trajectory (both with 1-h segments). Each daily precipitation data is combined with one 72-h air parcel back trajectory (1-h segments) ending at the receptor site at 850 hPa pressure level. The 850 hPa pressure level for the trajectory ending at the receptor site is used to describe the transport of pollutants contained in precipitation (Casado *et al.*[15]). The start and end times of precipitation events are given by a reference gauge installed near the collector. The precipitation samples which cannot be associated with only one trajectory (daily samples corresponding with several rain events and rain events divided into two daily samples) are eliminated.

2.2 method

Concentration field maps for SO_2, particulate SO_4^{2-} and non-sea salt SO_4^{2-} in rain are computed using the following formula (eqn 1) established by Seibert *et al.*[5]:

$$\log\overline{C}_{ij} = \frac{\sum_{l=1}^{M} n_{ijl} \times \log C_l}{\sum_{l=1}^{M} n_{ijl}} \tag{1}$$

where (i,j) are the indices of the grid cell, l the index of the trajectory, M the total number of trajectory, C_l the concentration observed on the receptor site (nss-SO_4^{2-} in rain, particulate SO_4^{2-} or SO_2) and n_{ijl} the number of one-hour endpoints of the trajectory l into the ij-th cell. n_{ijl} corresponds to the hourly time spent in the grid cell (i,j) by the trajectory l.

The grid cells counting less than 10 endpoints and the isolated grid cells (i.e. with neighbouring cells without computed concentration) are not treated. The confidence of these grid cells is considered as too low. The displacement error of 3-D trajectories is mainly due to the interpolation of the wind velocity and increase with the backward travel time (Kahl & Samson[16] ; Stohl *et al.*[17]). Then, we expect a displacement error higher than the grid cell size (150 ×150 km^2) after travel times beyond 38 hours. So, a smoothing (eqn 2) is applied to the whole of cell values for SO_2, particulate SO_4^{2-} and nss-SO_4^{2-} in precipitation.

$$\overline{C_{ij}}^{S} = \frac{\left(\sum_{p=1}^{8} C_p + \overline{C_{ij}}\right)}{9} \qquad (2)$$

where $\overline{C_{ij}}^{S}$ is the ij-cell smoothed concentration, $\overline{C_{ij}}$ is the ij-cell computed concentration (from eqn 1) and C_p with p=1 to 8 the computed concentrations (from eqn 1) of the ij-cell's neighbouring cells. In the methodology, a high $\overline{C_{ij}}^{S}$ value means that air masses passing through cell (i,j) give, on average, events with this concentration value at the receptor site.

The relationships between the computed concentration fields and the emissions of SO_2 above and below 100 meters established by EMEP for 1993 (Barrett *et al.*[18]) are examined performing a correlation analysis.

3 Results and interpretation

The results are presented in the EMEP map of Europe divided into 150 km by 150 km grid cells. Figures 1 to 3 represent concentration field maps for SO_2, particulate SO_4^{2-} (p-SO_4^{2-}) and non-sea salt SO_4^{2-} (nss-SO_4^{2-}) in precipitation respectively. The three maps show similar patterns. The highest computed concentrations are attributed to continental areas and the lowest to marine areas. These results mean that the highest concentrations of sulfur compounds recorded at Morvan are associated with air masses coming from Eastern Europe and the lowest concentrations with air masses coming from the Atlantic ocean. The contribution of SO_2 resulting from the reaction of dimethyl sulfide with oxidizing free radicals is negligible compared with the anthropogenic contribution. The part of marine sulfate (calculated from the ratio SO_4^{2-}/Na^+ in seawater) is weak. The non-sea salt SO_4^{2-} has represented on average about 91±11% of the SO_4^{2-} in precipitation collected at Morvan between 1992 and 1995. Moreover, the p-SO_4^{2-} field map (Fig.2) does not show substantial differences with the SO_2 and the nss-SO_4^{2-} concentration field maps.

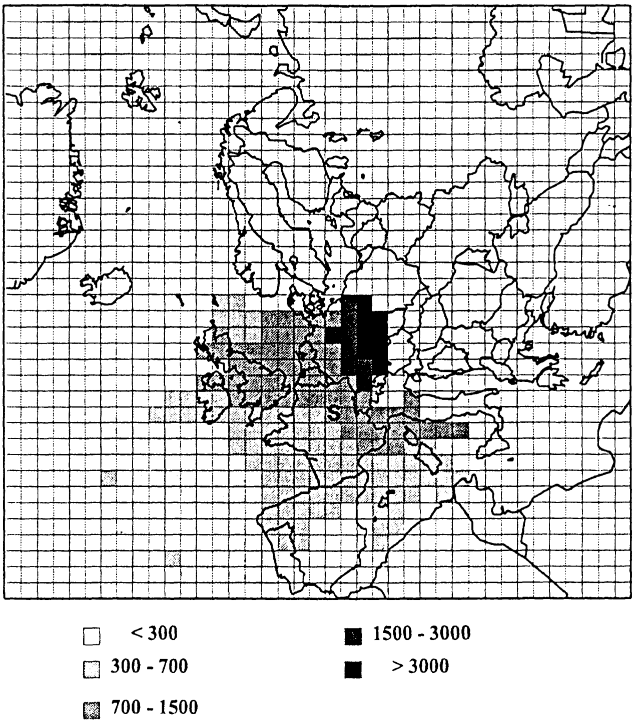

Figure 1: SO_2 computed concentration field map for the receptor site (symbol S on the map). Unit: ng sulfur per m^3. Grid cell size is 150 km × 150 km.

SO_2, p-SO_4^{2-} and nss-SO_4^{2-} concentration fields clearly point out the same area located at Polish-Czech-German border area (namely « Black Triangle »). This known region of high emissions of SO_2 seems to be responsible at once for high SO_2 concentrations (>3 μgS.m^{-3}), high particulate SO_4^{2-} concentrations (>2 μg.m^{-3}) and high nss-SO_4^{2-} concentrations in precipitation (>50 μmole.L^{-1}) at Morvan.

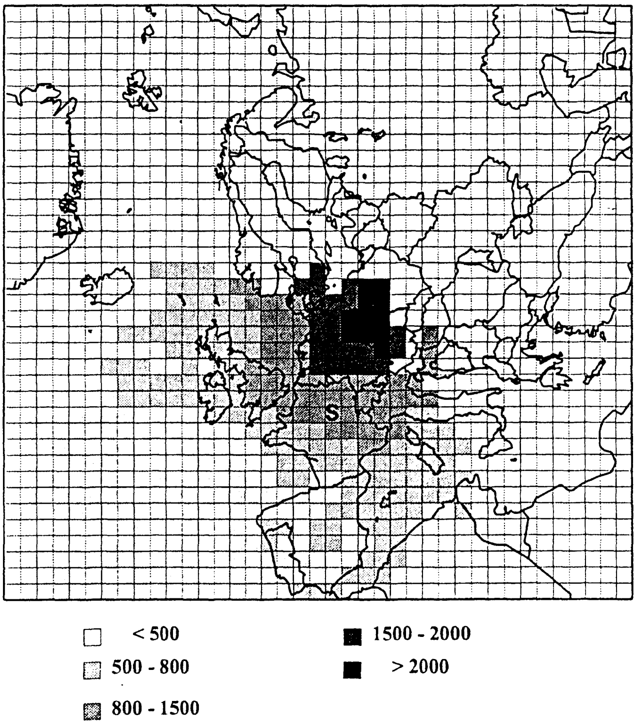

Figure 2: particulate SO_4^{2-} computed concentration field map for the receptor site (symbol S on the map).Unit: ng sulfur per m^3. Grid cell size is 150 km × 150 km.

The high concentrations of non-sea salt SO_4^{2-} (Fig. 3) also can be seen in a part of Poland, Slovakia and Hungary. Areas of high emissions of SO_2 located in England, Spain or Italy seem to weakly influence the concentrations of these sulfur species measured at Morvan. A possible explanation could be the large precipitation amounts in mountainous and coastal areas which wash out the air masses coming to France. Large precipitation amounts entailing large depositions in mountainous and coastal areas have been reported by Van Leeuwen *et al.*[19].

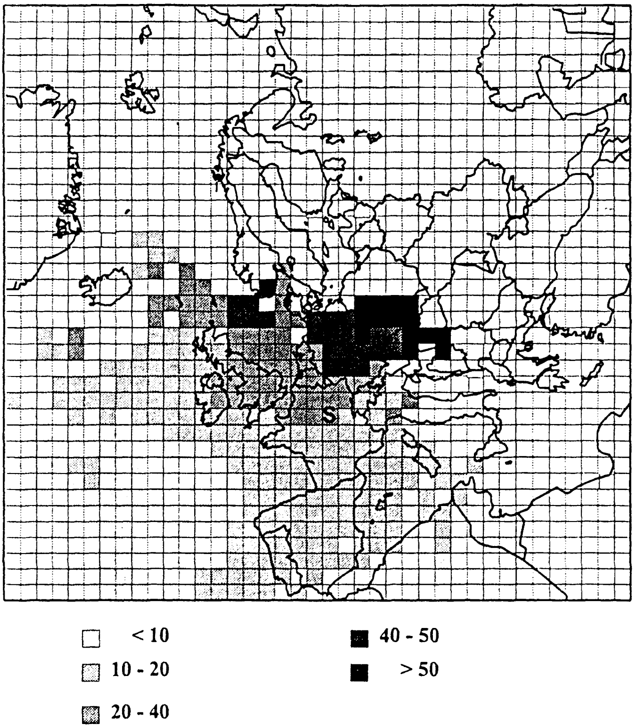

Figure 3: nss-SO_4^{2-} computed concentration field map for the receptor site (symbol S on the map).Unit: µmole.L^{-1}. Grid cell size is 150 km × 150 km.

Linear regression analysis has been used to examine the quantitative relationships between the logarithm of the emissions of SO_2 and the logarithm of the computed concentration fields.

Table 1: Results of the regression analysis applied to the logarithms of computed concentrations vs. of the logarithms of SO_2 emissions (above and below 100 m).

linear regression	correlation coefficient	value in the Anova table
Gas		
$\log(\mathbf{SO_2}) = 2.78 + 0.11 \log(\mathbf{SO_2{<}100m})$	0.294	0.004
$\log(\mathbf{SO_2}) = 2.37 + 0.38 \log(\mathbf{SO_2{>}100m})$	0.648	< 0.001
Particles		
$\log(\mathbf{p\text{-}SO_4^{2-}}) = 2.89 + 0.06 \log(\mathbf{SO_2{<}100m})$	0.227	0.017
$\log(\mathbf{p\text{-}SO_4^{2-}}) = 2.52 + 0.31 \log(\mathbf{SO_2{>}100m})$	0.666	< 0.001
Precipitation		
$\log(\mathbf{nss\text{-}SO_4^{2-}}) = -4.79 + 0.10 \log(\mathbf{SO_2{<}100m})$	0.267	0.002
$\log(\mathbf{nss\text{-}SO_4^{2-}}) = -5.07 + 0.30 \log(\mathbf{SO_2{>}100m})$	0.632	< 0.001

Similar correlation coefficients have been found for the three sulfur compounds and, on the one hand, SO_2 above 100 m and, on the other hand, SO_2 below 100 m (see table 1). Stronger correlations have been found with the SO_2 emissions above 100 meters compared to the SO_2 emissions below 100 meters. This result suggests that the SO_2 emitted above 100 meters (e.g. from factory chimneys) is the main source of ambient SO_2, particulate SO_4^{2-} and SO_4^{2-} in precipitation at Morvan. The SO_2 emitted above 100 meters seems to be more efficiently transported into the atmosphere over long distances. Satisfying correlation coefficients about 0.6 have been found with the SO_2 emitted above 100 meters. These medium correlation coefficients can come from non-considered factors (removal processes) and from uninfluential areas. The consideration of removal processes (wet and dry deposition) occurring during the air masses travels would improve the determination of quantitative relationships.

4 Conclusion

A receptor-oriented methodology has been applied to SO_2, particulate SO_4^{2-} and non-sea salt SO_4^{2-} measured in precipitation to examine the long-range transport and the source-receptor relationships responsible for high concentrations events measured at Morvan. The influential sources of sulfur compounds measured at the Morvan station are found to be essentially located outside of the country that underlines the substantial impact of long-range transport of SO_2 and SO_2's secondary species. Almost the same areas of high emissions of SO_2 located in Eastern Europe have been revealed to be at the origin of high SO_2 concentrations, high particulate SO_4^{2-} concentrations and high SO_4^{2-} concentrations in precipitation at the receptor site.

Linear regression analyses were used to compare quantitatively the computed concentrations and the European emissions of SO_2. Satisfying correlations are found between the computed concentrations and the emissions of SO_2 above 100 meters. The SO_2 emitted above 100 meters is determined as the main source of sulfur compounds at Morvan.

Lastly, receptor-oriented methodology is an efficient tool to exame the source-receptor relationships responsible for high sulfur compounds collected at once in gas, particles and precipitation. Such a methodology could be used to evaluate emission control strategies.

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