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Assessment of wintertime atmospheric input of European sulfur to the eastern Adriatic(*)

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Summary. — A Lagrangian receptor-oriented long-range transport model has been applied in order to estimate the order of magnitude of the wintertime atmospheric input of sulfur emitted in Europe to the eastern Adriatic. According to the model results, a total of $18.8 \cdot 10^6$ kg of sulfur had been deposited over the $7.2 \cdot 10^4$ km^2 of sea surface during the period 1 December 1991–29 February 1992. This means that on the average about $2.9 \cdot 10^{-6}$ kg m^{-2} of sulfur was deposited on the sea surface per day. The deposition per unit area over the northern part of the domain (which is closer to the strongest pollution sources) was almost twice the input to the southern part.

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1. – Introduction

River input has long been considered as the major source of various chemical elements to the sea. However, in recent years it has become clear that the atmospheric input also plays an important role in the supply of material to the sea. Atmospheric input is particularly important in shelf seas and semi-enclosed seas, which are close to pollution sources, such as the Mediterranean [1,2]. Furthermore, it is well established that many air pollutants could be transported in the atmosphere over the long distances (on synoptic and global scales), before being deposited. Therefore, the contribution of remote emission sources should be taken into account in the assessment of deposition of various pollutants.

Sulfur, as one of the key elements in the chemical actioning of the earth, is also an almost ubiquitous constituent of seawater. Consequently, oceans are the most important natural sources of atmospheric sulfur [3]. During the last century the global sulfur cycle

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has been perturbed by human activities, even over remote ocean regions. This perturbation is primarily caused by the increased fossil fuel combustion [3, 4], *i.e.* increased emission of sulfur dioxide. The importance of anthropogenic sulfur sources on both global and regional scale is also confirmed by the studies of Erisman and Baldocchi [5] and Katsoulis and Whelpdale [6], respectively.

Several facts motivated this study. Adriatic Sea is a small, semi-enclosed sea of eastern Mediterranean. It is located close to highly polluted European regions. Thus, it could potentially be subjected to environmental degradation caused by atmospheric input. Further, some of seawater samples taken from Adriatic Sea are rich with sulfur [7, 8]. Finally, there is a lack of studies investigating the atmospheric input of material to the eastern part of Mediterranean. On the other hand, such studies exist for the western Mediterranean [1, 2].

The fundamental intention of this study was to estimate the order of magnitude of wintertime atmospheric input of sulfur into the eastern Adriatic caused by European emission sources. For this purpose a Lagrangian box model of long-range transport of sulfur [9] was applied. Other models of long-range transport of sulfur compounds in the atmosphere are described elsewhere [10-21].

Winter period (from December to February) is selected since it generally corresponds to the highest anthropogenic sulfur dioxide emissions, and consequently the highest concentrations of sulfur dioxide in air. Therefore, the most unfavorable atmospheric input scenario is expected for this season.

2. – Model overwiev

The description of the model follows the one by Klaić [9]. Well-mixed polluted columns of air in the atmospheric boundary layer are considered. Dimensions of each column are 150 km × 150 km × h, where the column height (*i.e.* mixing height) h varies depending on meteorological conditions. The top of the column acts as a material surface through which no mass transport takes place. Consequently, reservoir layer is not assumed above the column. Columns are followed along specified trajectories, picking up pollutant emissions from the underlying grid.

The mass-balance equations for the pollutants concerned are integrated along each trajectory, taking into account emission inputs, chemical reactions, and dry and wet removal. The equations to be solved for sulfur dioxide and particulate sulfate can be written as

$$\begin{aligned} \mathrm{D}q_1/\mathrm{d}t &= -(v_{\mathrm{d}1}/h + k_{\mathrm{t}} + k_{\mathrm{w}1})q_1 + (1-\alpha-\beta)Q/h\,, \\ \mathrm{D}q_2/\mathrm{d}t &= -(v_{\mathrm{d}2}/h + k_{\mathrm{w}2})q_2 + k_{\mathrm{t}}q_1 + \beta Q/h\,, \end{aligned} \tag{1}$$

where $\mathrm{D}/\mathrm{d}t$ is the total (Lagrangian) time derivative, q_1 and q_2 are concentrations of sulfur dioxide and particulate sulfate (kg m^{-3}, where mass is expressed as the mass of sulfur), $v_{\mathrm{d}1}$ and $v_{\mathrm{d}2}$ are dry deposition velocities (m s^{-1}), and $k_{\mathrm{w}1}$ and $k_{\mathrm{w}2}$ are wet deposition rates (s^{-1}) of sulfur dioxide and particulate sulfate, respectively. Column height h (m) is the height of the box containing the bulk of the polluted air, Q is the sulfur emission rate per unit area (kg m^{-2}s^{-1}), and k_{t} is the rate of transformation of sulfur dioxide to particulate sulfate (s^{-1}). Parameter α represents the fraction of sulfur emission deposited locally, while β denotes part of the sulfur emitted in the form of sulfate. In the current model version they are assumed to be constant: $\alpha + \beta = 0.2$, where $\alpha = 0.15$ and $\beta = 0.05$ [14].

TABLE I. – *Transformation rate of sulfur dioxide to a particulate sulfate (k_t) and dry deposition velocities of sulfur dioxide (v_{d1}) and particulate sulfate (v_{d2}) over the ground (after Renner et al.* [23]*).*

	Cloud cover $< 4/8$				Cloud cover $\geqslant 4/8$		
	Summer		Winter		Summer		Winter
	Day	Night	Day	Night	Day	Night	Day and night
$10^6 k_t$ (s^{-1})	5.8	1.8	1.8	1.8	3.9	1.8	1.8
10^3 v_{d1} (m s^{-1})	6.5	3.9	5.8	0.8	5.8	6.5	5.8
10^3 v_{d2} (m s^{-1})	1.0	0.8	1.0	0.8	1.0	1.0	1.0

Numerical integration of eqs. (1) along the trajectory leads to solutions

$$q_1(t+\Delta t) = A_1/\kappa_1 + [q_1(t) - A_1/\kappa_1]\,\exp[-\kappa_1 \Delta t]\,, \tag{2}$$
$$q_2(t+\Delta t) = A_2/\kappa_2 + [q_2(t) - A_2/\kappa_2]\,\exp[-\kappa_2 \Delta t]\,,$$

where $A_1 = (1-\alpha-\beta)Q/h$, $A_2 = k_t q_1 + \beta Q/h$, $\kappa_1 = v_{d1}/h + k_t + k_{w1}$ and $\kappa_2 = v_{d2}/h + k_{w2}$ are taken as constants over the time interval $[t,\ t+\Delta t]$. In order to provide numerical stability, time step $\Delta t = 15$ min was employed as in the study of Sandnes and Styve [22]. Initial concentrations (*i.e.* concentrations at the start points of trajectories) are set equal to EMEP-modeled (*E*uropean *M*onitoring and *E*valuation *P*rogramme) annual mean concentrations for sulfur dioxide and particulate sulfate [22]. Under this assumption, all trajectories starting in the same 150×150 km^2 grid square pick up equal values of $q_1(0)$ and $q_2(0)$.

Sulfur emissions are assumed to vary linearly over the year, with the maximum and minimum occurring in January and July, where the multiplication factors 1.3 and 0.7 are used, respectively. The parameters h, v_{d1}, v_{d2}, k_t, k_{w1} and k_{w2} are assumed to vary diurnally, depending on relevant meteorological conditions, and they are determined on the basis of routine synoptic observations. Mixing height varied between 500 m and 1700 m depending on stability conditions. As listed in table I, the transformation rate k_t, and deposition velocities over the ground depended on cloud cover, season, and the time of the day as proposed by Renner *et al.* [23]. Over the sea, constant values $v_{d1} = 8 \cdot 10^-$ m s^{-1} and $v_{d2} = 1 \cdot 10^{-3}$ m s^{-1} were employed. Wet deposition rates for both pollutants were calculated from $k_{wi} = W_i P/h$, where W_i is the scavenging ratio of the i-th pollutant ($W_1 = 2 \cdot 10^5$ and $W_2 = 7 \cdot 10^5$), P is precipitation intensity (m s^{-1}) and h is mixing height (m). Full details are given in Klaić [9].

Calculated sulfur dioxide and particulate sulfate concentrations at the receptor points are thereafter enlarged by background values. These values represent either man-made sulfur being in the atmosphere prior to the moment at which the model begins to follow the trajectory, or sulfur of natural origin, that is not included in the emission inventory. As proposed by Szepesi and Fekete [24], values of $1.25 \cdot 10^{-9}$ kg m^{-3} (sulfur dioxide) and $0.80 \cdot 10^{-9}$ kg m^{-3} (particulate sulfate), both expressed as sulfur, are appropriate for the synoptic scale models for Europe.

Trajectories arriving twice a day (00:00 and 12:00 UTC) at selected receptor points are calculated by Petterssen's method [25], as described in the OECD program (OECD [12]). As proposed by Ghim and Seinfeld [26], trajectories are calculated from vertically av-

eraged winds. They are followed 72 hours backwards. Vertical average winds are determined from radiosonde reports taking into account a ground-based layer up to the 850 hPa level. Vertically averaged winds are thereafter objectively analyzed using the "$1/r^2$ aligned" technique [27] with a 350 km radius of influence. For the times between two radiosonde soundings a linear temporal variation of the wind field is assumed.

Total deposition (T) of sulfur per unit area and over the time interval $\Delta\tau$ between the arrival of two consecutive trajectories to a particular receptor point is the sum of dry and wet depositions:

$$T = [v_{\mathrm{d}1}q_1 + v_{\mathrm{d}2}q_2 + \alpha Q + (k_{\mathrm{w}1}q_1 + k_{\mathrm{w}2}q_2)h]\Delta\tau\,. \tag{3}$$

In the deposition calculation $\Delta\tau = 12$ h, and values $v_{\mathrm{d}1}$, $v_{\mathrm{d}2}$, q_1, q_2, Q, $k_{\mathrm{w}1}$, $k_{\mathrm{w}2}$ and h, that correspond to the receptor point at the arrival time of a particular trajectory, are held constant over the interval $\Delta\tau$.

3. – Input data

The model domain covered an area bounded by meridians 30°W and 45°E and parallels 30°N and 75°N. Seven receptor points were selected in the area of interest. Spatial distribution of sulfur emissions per unit time and area was calculated from the EMEP inventory for 1992 [28]. This inventory is based on the official figures submitted by participating countries, and it includes both anthropogenic emissions and natural sulfur emissions from seas. Other natural emissions are roughly taken into account through the background concentrations.

Apart from radiosonde data used in trajectory calculations, meteorological input included surface wind speed, cloudiness and precipitation intensity. Surface data were taken from routine synoptic observations, which were available every 6 hours. The model was run for the 1 December 1991-29 February 1992 period.

4. – Results and conclusion

Figure 1 illustrates the calculated total deposition of sulfur accumulated during the selected winter period. According to the model a total of $18.8 \cdot 10^6$ kg of sulfur was deposited over the 71662.5 km^2 of the sea surface. This gives an average of about $2.6 \cdot 10^{-4}$ kg of sulfur per square meter of the sea surface. However, as shown in fig. 1, the total deposition per unit area decreases toward the south from $3.6 \cdot 10^{-4}$ kg m^{-1} to $1.8 \cdot 10^{-4}$ kg m^{-1}. This means that over the northern part of the eastern Adriatic, that is closer to high emission sources, sulfur deposition is almost twice as large as compared to the input to the southern part.

Above results should be considered as an estimate that is satisfactory on a larger scale. In order to obtain a more detailed spatial distribution of atmospheric input, a more sophisticated parameterization of dry deposition velocities of pollutants concerned should be employed. It is particularly important in the area of interest of this study, since according to the recent study of Park [29], the maximum dry deposition velocities of pollutants occur along the coastline where the friction velocity is large. Therefore the coastal zone can be a potentially high dry deposition region of pollutants. However, according to Erisman and Baldocchi [5], it is still doubtful whether the present state of knowledge and the availability of data allow such a detailed parametrisation.

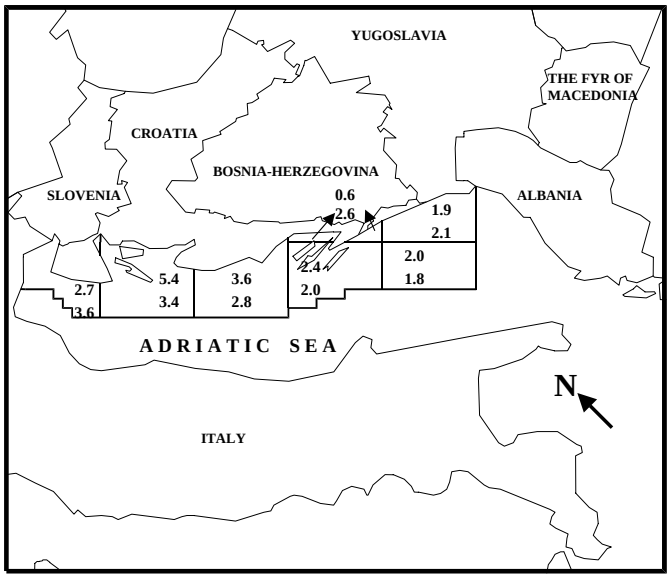

Fig. 1. – Modeled input of sulfur emitted in Europe to the eastern Adriatic accumulated during the 1 December 1991–29 February 1992 period (in 10^6 kg, upper figures). Lower figures represent the accumulated input per unit area (in 10^{-4} kg m^{-2}).

Nevertheless, above results contribute to our understanding of complex problems such as the global sulfur cycle, atmosphere-ocean interactions and the man-made marine pollution. They also confirm the importance of atmospheric input of sulfur emitted in Europe predominantly due to human activities to the pollution of Mediterranean Sea.

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