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Some characteristics of the long-range transport of sulphur dioxide in Croatia and Slovenia

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The application of a Lagrangian box-model for the calculation of sulphur dioxide concentrations in Yugoslavia is described. Modeled concentrations are then used to estimate dry and wet depositions of the pollutant concerned. Further, two days with high and one with low concentrations, recorded and calculated for the Croatia and Slovenia, are selected. These cases are illustrated by 30-hour backward 850 hPa air trajectories.

Neke karakteristike daljinskog transporta sumpor-dioksida u Hrvatsku i Sloveniju

Opisuje se primjena boks-modela u Lagrangeovom koordinatnom sustavu na proračun koncentracija sumpor-dioksida u Jugoslaviji. Iz modeliranih koncentracija proračunava se suho i mokro taloženje promatranog polutanta. Dva dana s viskom i jedan s niskom izmjerenom i izračunatom koncentracijom sumpor-dioksida u zraku ilustriraju se u 30-satnim 850 hPa trajektorijama unazad.

1. Introduction

The synoptic-scale transport of pollutants in the atmospheric boundary layer has been in the centre of interest for the last few decades. Two different approaches of models giving results on a daily basis are possible, depending on the way of integration of the mass-balance equation within the boundary layer. In Eulerian models (Chang et al., 1987; Simpson et al., 1990; Kotamarthi and Carmichael, 1990) integration is performed in a geographically fixed grid. Such models can generally incorporate three-dimensional mathematical descriptions of processes affecting atmospheric pollutants. However, they require detailed information about the meteorological parameters in the boundary layer as input. These can be obtained either by extensive measurements or by complex model-

ing on the mesoscale. In addition, some numerical problems are associated with the integration of advection terms in the Eulerian mass-balance equation.

In the Lagrangian framework, the integration of the mass-balance equation is carried out along trajectories in a numerically simple manner. Due to the computational simplicity, these models can include a detailed description of a complicated air chemistry. The model of Eliassen et al. (1982), for example, incorporates about chemical reactions between 40 different species. Nevertheless, the Lagrangian approach usually assumes a fairly simple meteorology, associated with the concept of a vertically homogeneous air parcel, that maintains its integrity from source to receptor. This assumption is considered as one of the main shortcomings of most of the Lagrangian models. However, a more sophisticated approach with a vertical structure was described recently by Renner et al. (1985). In that model the boundary layer is divided in a surface and mixing layer, the latter being subdivided in three levels. At the present stage the model was not used for the calculation of real pollutant concentrations which could be verified by measurements, at any receptor point. On the contrary, it was used to describe the fate of emitted sulphur dioxide for several hypothetic emission scenarios.

The movement of the air parcel is represented by the horizontal wind velocity, that is most often assumed to be independent of height. The choice of suitable advecting wind depends on the available routine meteorological observations on a synoptic scale. As a result, the existing Lagrangian models use different advection winds. Eliassen and Saltbones (1983) calculate two-dimensional trajectories on the 850 hPa surface using observed winds from radiosonde soundings. Ellenton et al. (1985) compute horizontal trajectories from modified surface geostrophic winds, taking advantage of the relatively fine space and time resolutions of routine surface observations. In the model of ApSimon et al. (1985) a power law approximation is used within the mixing layer to attain the geostrophic wind speed at the top of the mixing layer. In the multi-level model of Renner et al. (1985), a log-type profile of the wind in the surface layer is assumed, while in the mixing layer the wind profile has a form of the power law. A log-type profile is based on the Monin-Obukhov similarity theory.

During its travel along the trajectory, the pollutant in the air parcel is subjected to vertical dispersion, dry and wet deposition and chemical transformation. Further, the air parcel picks up the pollutant as it passed above the area sources. The Lagrangian long-range transport model has to incorporate all these processes in a realistic way, and yet has to be sufficiently simple to apply.

In this paper the application of simple one-layer Lagrangian model of long-range transport of sulphur dioxide to Yugoslavia is described. Further, in order to get some information on long-distance sources, two days with high and one day with low sulphur dioxide concentrations recorded and calculated for Croatia and Slovenia, are illustrated by 850 hPa backward air trajectories.

2. Model overview

The description of the model follows the one by Klaić (1990). A well-mixed air parcel is considered, which moves within a ground based atmospheric boundary layer with a height-independent advection wind. The movement of the parcel is represented by a trajectory. Under the assumption of a well mixed parcel, the concentration of the pollutant is independent of the height. Further, the top of the parcel acts as a material surface through which no mass transport takes place, and the air density variations are ignored.

The time variation of pollutant concentration is described by the mass-balance equation. For sulphur dioxide this may be written:

$$Dq/dt = -(v_d/h + k_t + k_w)\, q + (1 - \alpha - \beta)\, Q/h \tag{1}$$

where D/dt = total time derivate
q = sulphur dioxide concentration (kg m^{-3} as S)
v_d = dry deposition velocity of sulphur dioxide (m s^{-1})
k_t = transformation rate of sulphur dioxide to sulphate (s^{-1})
k_w = wet deposition rate of sulphur dioxide (s^{-1})
h = mixing height (m)
α = part of sulphur emission deposited locally
β = part of sulphur emission emitted in the form of sulphate
Q = sulphur emission per unit area and time (kg m^{-2} s^{-1}).

The numerical integration of equation (1) along the trajectory leads to the sulphur dioxide concentration estimation in the receptor point:

$$q(N\,\delta t) = q(0)\exp\left(-\sum_{i=0}^{N-1} k_i\,\delta t\right) + \sum_{i=0}^{N-1}(1 - \alpha - \beta)\, Q_i/h_i \exp\left(-\sum_{j=0}^{N-1} k_j\,\delta t\right) + q_b \tag{2}$$

where $q(N\delta t)$ = sulphur dioxide concentration in the receptor point (kg m^{-3} as S)
$q(0)$ = sulphur dioxide concentration in the start point of trajectory (kg m^{-3} as S)
$k_i = (v_{di}/h_i + k_{ti} + k_{wi})$ = decay rate at i-th trajectory position (s^{-1})
δt = time step (s)
N = number of time steps
q_b = background concentration added to represent either man-made sulphur that has spent more than t seconds in atmosphere, or sulphur of natural origin that is not included in the emission inventory (kg m^{-3} as S).

The dry deposition of sulphur dioxide is estimated by applying deposition velocity to the calculated concentration q and adding the part of sulphur dioxide

Table 1. Values of the model parameters (after Klaić, 1990).

Parameter	Symbol	Units	Value			
Deposition velocity	v_d	cm s^{-1}	Over the ground			
			Clear	Cloudy		
			0.65	0.58	summer day	
			0.58	0.58	winter day	
			0.38	0.65	summer night	
			0.08	0.58	winter night	
			Over the sea 0.80			
Transformation rate of sulphur dioxide to sulphate	k_t	s^{-1}	Winter 10^{-6}	Summer $5 \cdot 10^{-6}$	Spring $3 \cdot 10^{-6}$	Fall $3 \cdot 10^{-6}$
Wet deposition rate of sulphur dioxide	k_w	s^{-1}	$3 \cdot 10^{-5}$			
Mixing height	h	m	Stable 600	Neutral 1100	Unstable 1700	
Part of sulphur emission deposited locally	α	none	0.15			
Part of sulphur emission emitted in the form of sulphate	β	none	0.05			
Sulphur dioxide concentration in the start point of trajectory	$q(0)$	kg m^{-3} as S	estimated from mean concentration field measured over Europe			
Background concentration	q_b	μ g m^{-3}	0.2			
Sulphur emission per unit area and time	Q	kg m^{-2} s^{-1}	emission inventory			

emission deposited locally. The dry deposition D per unit area over the time interval δt may be written:

$$D = (v_d\, q + \alpha Q)\, \delta t \qquad (\text{kg m}^{-2} \text{ as S}) \tag{3}$$

Ideally, the wet deposition should be calculated from the amount of pollutant removed from the atmosphere by each precipitation event. However, due to incomplete knowledge of the complicated chemical and physical processes leading to wet deposition and the absence of precipitation data available, the wet deposition W, per unit area over the time interval δt was estimated for a day with precipitation using a very simple parametrization:

$$W = k_w\, q\, h\, \delta t \qquad (\text{kg m}^{-2} \text{ as S}) \tag{4}$$

In the calculations, accepted values of the model parameters were chosen as discussed in Klaić (1990). The parameter values are shown in Table 1.

3. Model application

The model was applied to the region covering Yugoslavia for the period from 2 to 14 April 1977. 850 hPa trajectories were calculated by Petterssen's method (Petterssen, 1956), as described in the OECD programme (OECD, 1979). Trajectories were arriving four times a day (0000, 0600, 1200 and 1800 GMT) at 35 receptor points situated in Yugoslavia and the surrounding countries. Due to the computer restrictions (PC/XT, 640 KB), trajectories were followed 30 hours backward, although a longer time period would have been preferable, since sulphur dioxide residence time in the atmosphere is about 2 days (Eliassen and Saltbones, 1975; Seinfeld, 1975). Trajectory positions were given every 2 hours in the 150×150 km^2 grid covering Europe. In the same grid of 864 square elements, emissions and meteorological data necessary for the determination of model parameters, were taken. One should note that other choices of receptor points enable the application of the model to different regions.

The spatial distribution of emissions employed in model calculation was estimated from NILU (1986) data. Figure 1 shows emissions data over the part of Europe which is of particular interest for most of the trajectories arriving to Croatia and Slovenia.

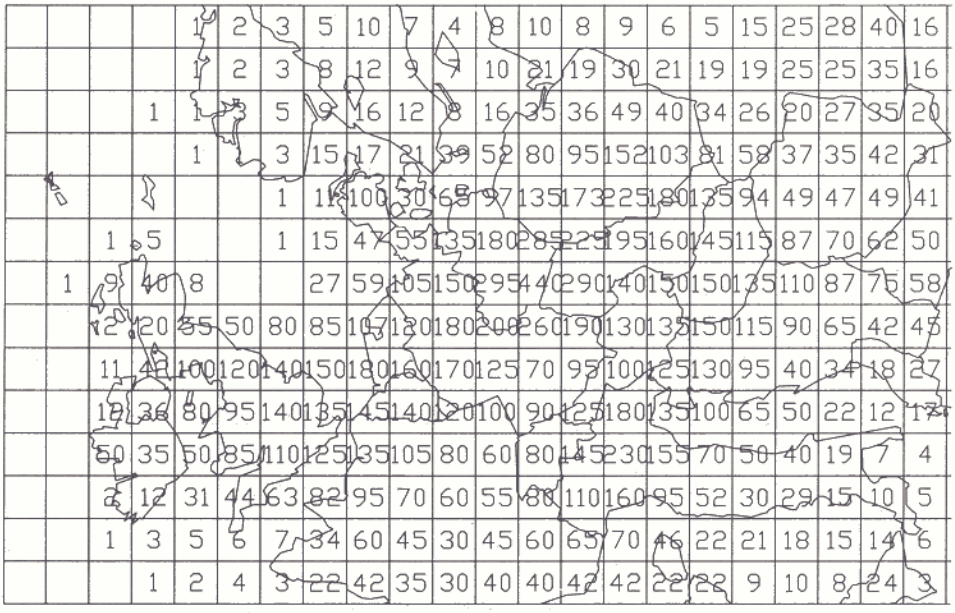


Figure 1. Spatial distribution of sulphur-dioxide emissions (Q in equation 2; units: 10^6 kg y^{-1} as sulphur). Emissions are based on the inventory published NILU (1986). Only a part of data employed in the calculation is shown.

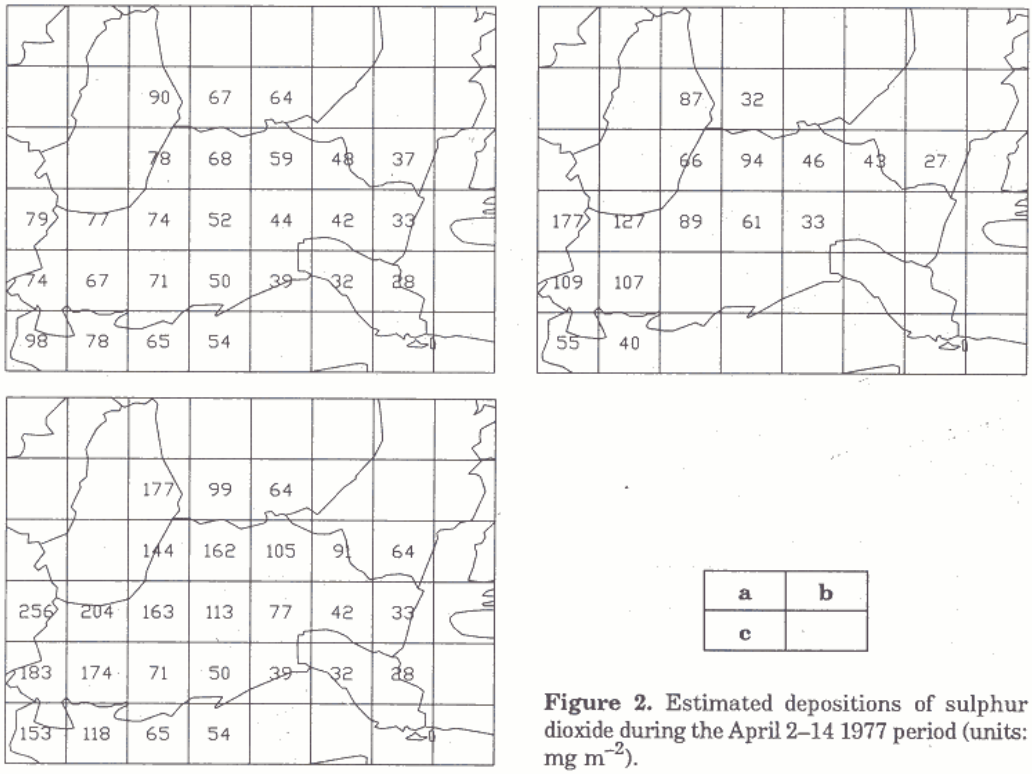


Figure 2. Estimated depositions of sulphur dioxide during the April 2–14 1977 period (units: mg m^{-2}).

The highest calculated concentrations are related to northwest Yugoslavia. Concentrations are higher in the inland than in the coastal areas and they generally decrease in the southeast direction. This field and a comparison between the calculated and the recorded concentrations available at measuring sites are described in Klaić (1990).

Figures 2a–2c illustrate the model of estimated dry, wet and total depositions of sulphur dioxide for the period of study. These values have been obtained under the assumption of height-independent sulphur dioxide concentrations. The shapes of the deposition fields are similar to the shape of the calculated concentration field, having the highest values in northwest Yugoslavia.

4. Long-range transport to Croatia and Slovenia

Several measuring sites, all situated in Croatia and Slovenia, were reporting sulphur dioxide concentrations during the period of study. These were Zagreb-Maksimir, Velenje, Domžale, Maribor, Ptuj, Kočevje, Novo Mesto and Koper. Since none of the sites was situated in a purely natural environment, recorded concentrations were caused by both local and remote pollution sources. However, most of the stations reported two more or less equally expressed concentra-

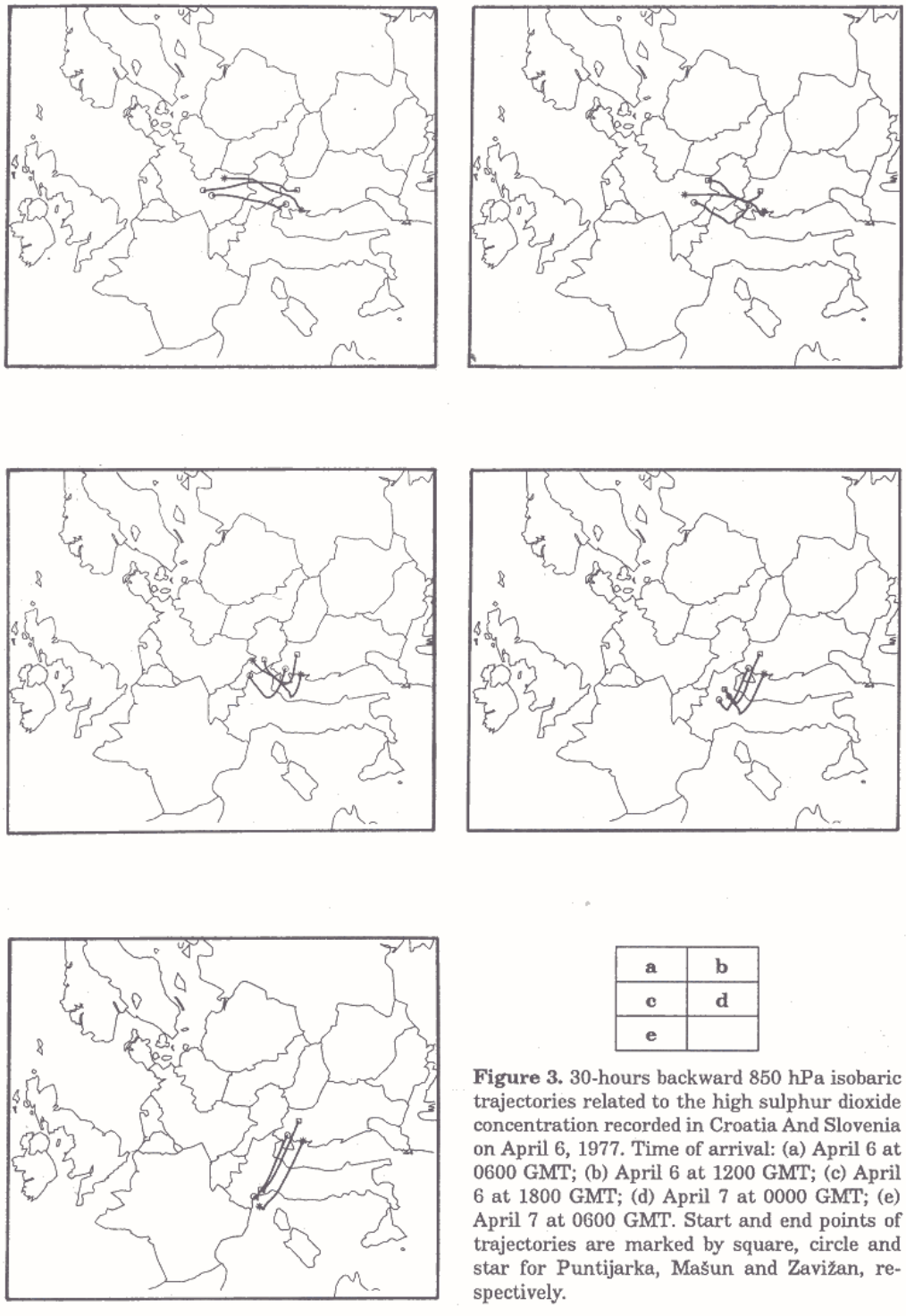
Table 2. Extreme values of measured daily mean sulphur dioxide concentrations (units: $\mu g\ m^{-3}$).

Measuring site	Measured daily mean sulphur dioxide concentration		
	6 April 1977	9 April 1977	13 April 1977
Domžale (46° 07'N 14° 36'E)	80	30	90
Kočevje (45° 38'N 14° 52'E)	100	70	110
Novo Mesto (45° 49'N 15° 10'E)	50	10	80
Koper (45° 33'N 13° 45'E)	60	40	60
Zagreb-Maksimir (45° 49'N 16° 02'E)	59	26	83
Maribor (46° 34'N 15° 09'E)	50	40	70
Ptuj (46° 26'N 15° 52'E)	70	20	60
Velenje (46° 22'N 15° 07'E)	20	20	50

tion maxima, one on 6 April and the other on 13 April, while the minimum value was recorded on 9 April (Table 2). Moreover, the modeled concentrations for those sites expressed similar behavior. This indicated that an influence of long-distance pollution sources on Croatia and Slovenia was noticeable during the period of study. In order to locate the possible remote sources, the days with extreme concentrations were further examined by backward trajectories arriving at three receptor points: Puntijarka (45° 54'N 15° 58'E), Zavižan (44° 52'N 14° 59'E) and Mašun (45° 49'N 14° 22'E).

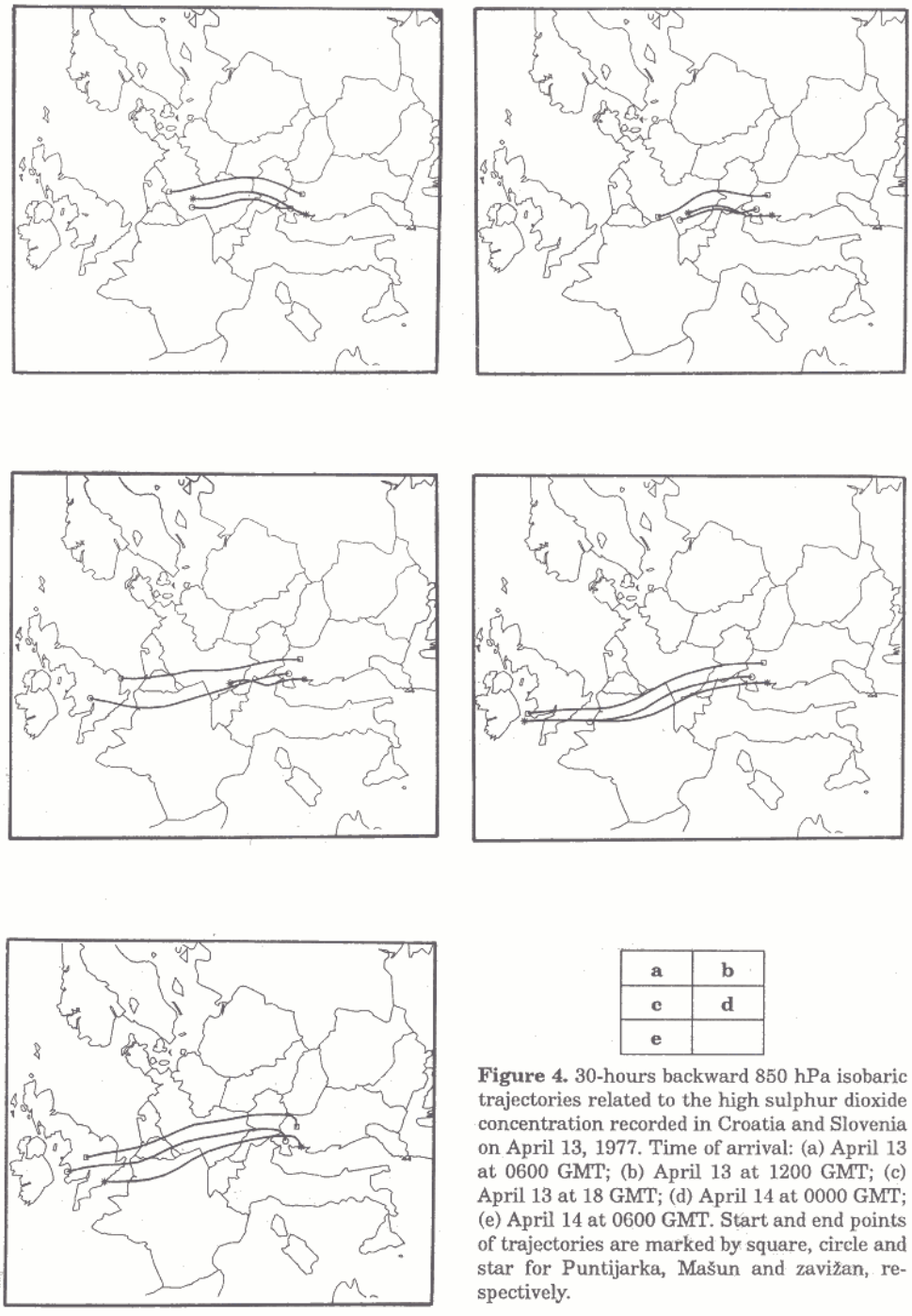
Since both the measured and calculated concentrations represent daily mean values covering the period from 0600 GMT of the observed day to 0600 GMT of the day after the observed day, each day was illustrated by five trajectories. Three of them arrived at the receptor point at 0600, 1200 and 1800 GMT of the day concerned, while the other two arrived at 0000 and 0600 GMT of day after. Figures 3 and 4 show the trajectories related to the days with increased sulphur dioxide concentrations, while the trajectories for the day with low concentrations are show in Figure 5.

The first case of high concentration (Figure 3) shows that in the beginning air masses were transported from the southern part of West Germany. Gradually the western component of the air flow became dominant, causing the transport of air masses from northern Italy. In the second case (Figure 4), the air masses originated in the central part of West Germany. Later, the wind velocities grew stronger, carrying the air from southern Great Britain, above north-eastern France and south-western West Germany, toward Croatia and Slovenia. One may see that in both cases the air masses were passing above the areas characterized by a relatively high sulphur dioxide emission (Figure 1). Figure 4 (c) deserves a further comment, since the trajectory arriving at Zavižan considerably differs from the other two. This illustrates the uncertainty which is inherent in the determination of true boundary-layer trajectories. Part of this uncertainty arises from the rough temporal and spatial resolution of input meteorological data available, while part of it is due to the computational method.



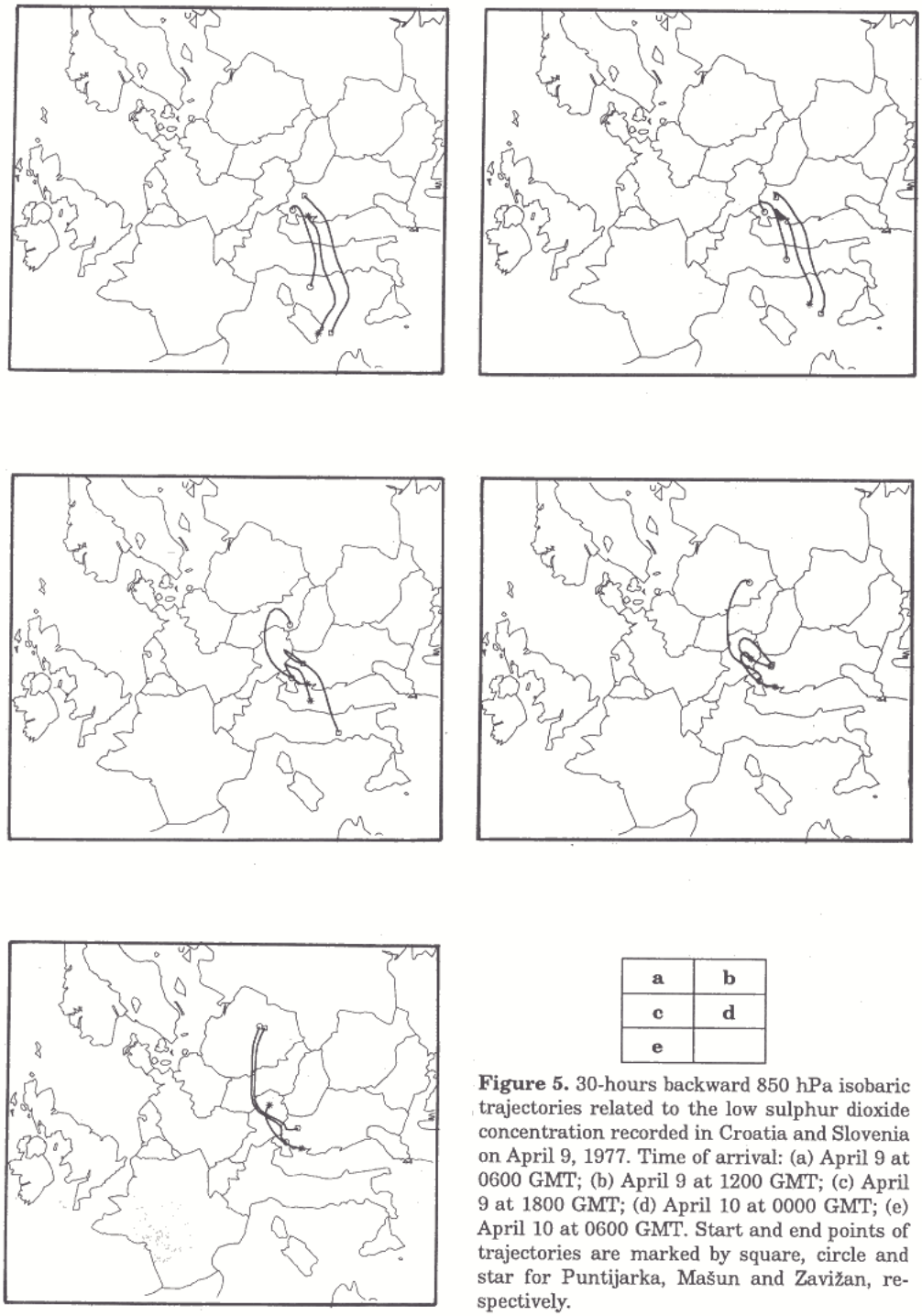
a	b
c	d
e	

Figure 3. 30-hours backward 850 hPa isobaric trajectories related to the high sulphur dioxide concentration recorded in Croatia And Slovenia on April 6, 1977. Time of arrival: (a) April 6 at 0600 GMT; (b) April 6 at 1200 GMT; (c) April 6 at 1800 GMT; (d) April 7 at 0000 GMT; (e) April 7 at 0600 GMT. Start and end points of trajectories are marked by square, circle and star for Puntijarka, Mašun and Zavižan, respectively.



a	b
c	d
e	

Figure 4. 30-hours backward 850 hPa isobaric trajectories related to the high sulphur dioxide concentration recorded in Croatia and Slovenia on April 13, 1977. Time of arrival: (a) April 13 at 0600 GMT; (b) April 13 at 1200 GMT; (c) April 13 at 18 GMT; (d) April 14 at 0000 GMT; (e) April 14 at 0600 GMT. Start and end points of trajectories are marked by square, circle and star for Puntijarka, Mašun and zavižan, respectively.



a	b
c	d
e	

Figure 5. 30-hours backward 850 hPa isobaric trajectories related to the low sulphur dioxide concentration recorded in Croatia and Slovenia on April 9, 1977. Time of arrival: (a) April 9 at 0600 GMT; (b) April 9 at 1200 GMT; (c) April 9 at 1800 GMT; (d) April 10 at 0000 GMT; (e) April 10 at 0600 GMT. Start and end points of trajectories are marked by square, circle and star for Puntijarka, Mašun and Zavižan, respectively.

On the day with low sulphur dioxide concentration (Figure 5), in the beginning the air flow was south-westerly, transporting the clean Mediterranean air masses above central Italy, where sulphur dioxide emission is two to three times weaker than in the northern part of the country. Later, the flow became less straightforward, forcing the air (except in the case of Mašun) to circulate above NW Yugoslavia and Austria. In the end, the north-eastern wind component became stronger, transporting the masses from central Poland, over Czechoslovakia and Austria.

Since sulphur dioxide is one of the main acidifying agents of precipitation on the large scale, the illustrated cases roughly agree with a previous examination (Klaić and Lisac, 1988), where it was shown that air flows from NW and SW directions are related to the highest and the lowest precipitation acidity recorded in the north-western part of Croatia.

5. Conclusion and further development of the model

The results presented show that a simple one-layer Lagrangian model reflects the mechanism of long-range transport of sulphur dioxide. The model allows the estimation of sulphur dioxide concentration and dry and wet deposition fields over an arbitrary region on a daily basis. Further, a detailed insight in the pathways of air masses is possible, which is of particular interest to the study of highly polluted episodic cases caused by remote sources.

However, in future work the model should be improved to a certain extent. Trajectories should be followed at least 48 hours backward. In trajectory calculation a more recent method could be employed, the method proposed by Chen and Smith (1987), which takes the advantage of the relatively fine space and time resolution of routine pressure observations. The model could easily be extended to the long-range transport of sulphates by adding the mass-balance equation for atmospheric sulphates with an adequate dry and wet deposition parametrization. In that case, trajectories should be followed several days backward, since sulphates live longer the in the atmosphere than sulphur dioxide. Instead of a constant wet deposition rate, a correction, as a function of the precipitation intensity, could be introduced. For this purpose, an empirical relation given by Iversen et al (1990) could be tested. Further, instead of time-independent sulphur dioxide emission, a more realistic seasonal variation should be assumed. Also, a diurnal cycle of mixing height should be introduced due to diurnal variability of stability conditions. (At the present stage of the model only day-to-day variations related to the stability conditions were assumed.)

A more sophisticated approach would require a multi-layer model, in which the mixing layer is divided into at least two sublayers, related to the lower (domestic) and higher (industrial) emission sources, respectively. In that case, a dry deposition of the pollutant should be assumed only in the lower sublayer. However, such on approach is associated with a detailed emission inventory on

the synoptic scale, which is not available. Further, it would imply a more complicated calculation of the air flow, including the mechanism of exchange of the pollutant between the lower and upper sublayer. It would also require a more detailed input of meteorological data. Although these demands would complicate operative work with the model, its applicability would be extended from a synoptic to a regional scale without any alteration of the algorithm.

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