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Accidental release of hydrogen sulfide in Nagylengyel, Hungary on November 14, 1998 – A trajectory study

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The movement of air parcels polluted due to an accidental release of H_2S close to the Croatian border is examined. Emission started on November 13, 1998 at around 2330 UTC. Trajectories starting at 0000 UTC were calculated by a dynamic method which provides realistic nonlinear variations of the wind field in space and time. Pressure gradients were calculated from the ECMWF surface pressure forecasts using two finite-difference schemes: centered and off-centered. According to one-day forward trajectories, polluted air was transported over Hungary, Slovakia and Ukraine. Furthermore, measurements of daily mean SO_2 concentrations in the air for 5 locations in Croatia confirm that concentrations were not affected by the accidental emission.

Keywords: H_2S, accidental release, trajectory study

Introduction

According to the media, on November 14, 1998 an accidental release of hydrogen sulfide (H_2S) and carbon dioxide (CO_2) occurred in southwestern Hungary, about 40 km from the Croatian border. It was caused by a worn-out sealing joint at bore hole of unknown elevation situated close to the Nagylengyel ($\varphi = 46°\ 38'$, $\lambda = 17°\ 11'$). Emission began on 13 November around 2330 UTC and lasted for several hours. Consequently, about 5000 inhabitants of Sárhida, Bak and Bocföld were evacuated (Croatian Embassy in Budapest, 1998).

The aim of this study is to investigate wether Croatia and Bosnia-Herzegovina have been affected by the hazardous cloud. Since CO_2 is a heavy gas, it will remain in the vicinity of an emission source. On the other hand, it is well known that H_2S under atmospheric conditions reacts further to form sulfur dioxide (SO_2) (Mészáros, 1981; Finlayson-Pitts and Pitts, 1986; Jacobson, 1999). Chemical conversion of H_2S to SO_2 (see Appendix) occurs in the atmosphere within a few hours. The residence time of the SO_2 in the atmos-

phere is about 2 days (Mészáros, 1981). Thus SO_2 can travel long (synoptic scale) distances in the atmosphere before being deposited or chemically transformed to particulate sulfate (Fisher, 1975; Eliassen, 1980; Eliassen et al., 1982; Endlich et al., 1984; Ellenton et al., 1985; Renner et al., 1985; Tarrason and Iversen, 1992; Klaić, 1996). Therefore, air parcel trajectories describing the movement of polluted air within the atmospheric boundary layer were calculated.

Trajectory calculation and input data

Trajectories

Two-dimensional trajectories starting at Nagylengyel were calculated by the method proposed by Chen and Smith (1987). This method is based on a dynamic approach which, as compared to a kinematic one, is able to diagnose transport more accurately due to its ability to provide realistic, nonlinear variations of the wind field in both space and time (Warner et al., 1983). Other dynamic and/or kinematic methods of trajectory calculation are described in the number of studies. Petterssen's kinematic method (1956) is employed in the calculation of two-dimensional isobaric trajectories (OECD, 1979; Eliassen et al., 1982; Ferenczi and Labancz, 1993; Klaić and Cvitan, 1993). ApSimon et al. (1985) and Ellenton et al. (1985) also use kinematic methods, while Petersen and Uccellini (1979) and Ihász (1992) calculate isentropic trajectories based on dynamic approach. On the other hand, descriptions of three-dimensional trajectory models could be find in the studies of Haageson et al. (1990), Rolph and Draxler (1990), Bonelli et al. (1992), and Kotamarthi and Carmichael (1993).

The following is a short description of the model of Chen and Smith. A material surface slightly above the ground is considered. By definition, no fluid particles cross this surface. Frictional effects are neglected. Yet the surface is assumed low enough so that its pressure field resembles that at sea level. The impermeability of the earth's surface makes it approximately a material surface of the fluid. From given initial position and horizontal velocity vectors ($\boldsymbol{X}_0$, $\boldsymbol{V}_0$) of an air parcel, trajectory can be computed from the horizontal momentum and position equations assuming a known time-dependent sea level pressure field $p(\boldsymbol{X},t)$:

$$\begin{aligned} \frac{\mathrm{d}\boldsymbol{V}}{\mathrm{d}t} + f\boldsymbol{k}\times\boldsymbol{V} &= -\frac{1}{\rho}\nabla p \\ \frac{\mathrm{d}\boldsymbol{X}}{\mathrm{d}t} &= \boldsymbol{V}\,. \end{aligned} \tag{1}$$

Employing the one-sided forward-in-time numerical scheme, (1) can be discretized as:

$$\begin{aligned} \boldsymbol{V}^{n+1} &= \boldsymbol{V}^{n} - \left(\frac{1}{\rho} \nabla p^{n} + f\boldsymbol{k} \times \boldsymbol{V}^{n} \right) \cdot \Delta t \\ \boldsymbol{X}^{n+1} &= \boldsymbol{X}^{n} + \boldsymbol{V}^{n} \cdot \Delta t \\ t^{n} &= n\,\Delta t \end{aligned} \qquad (2)$$

where $\boldsymbol{V}(t)$ is the horizontal velocity vector of the parcel, ρ is the parcel density (assumed constant), $\boldsymbol{X}$ is the horizontal position vector of the parcel, $\boldsymbol{k}$ is the unit vector in the vertical, $f(\boldsymbol{X})$ is the Coriolis parameter, $p(\boldsymbol{X},t)$ is the specified pressure field, n is the index of a time steps, and Δt is the time step increment.

Trajectory positions may thereafter be expressed in term of latitude (φ) and longitude (λ), where φ and λ are given in degrees. Thus

$$\begin{aligned} \lambda^{n+1} &= \lambda^{n} + \frac{180}{\Pi R_z \cos\varphi} u^{n} \Delta t \,, \\ \varphi^{n+1} &= \varphi^{n} + \frac{180}{\Pi R_z} v^{n} \Delta t \,, \end{aligned} \qquad (3)$$

where u^n and v^n are the components of the horizontal velocity vector $\boldsymbol{V}^n$ at the n^{th} point of a trajectory (that corresponds to a transport time $n\Delta t$), and R_z is the radius of the earth (R_z = 6371 km). In order to avoid possible numeric instabilities time step used in the calculation was Δt=10 min.

Pressure gradients

Pressure gradients were determined from surface pressure fields predicted by the ECMWF (**E**uropean **C**enter for **M**edium-Range **W**eather **F**orecast) model that were provided to us by the Croatian MHS (**M**eteorological and **H**ydrological **S**ervice). Four-day pressure forecasts with output every 6 hours and the horizontal resolution of 0.5 × 0.5 were analysed over the area within 0E and 37E and 35N and 55N. Forecast reliability decreases from about 90% for the day one to about 60% at the day four. Over the 6-h interval between the two predicted values pressure was assumed to vary linearly, and thus parcels moved through a pressure field that was changing smoothly in time.

The pressure gradient at a grid point (i, j) was thereafter computed by a finite-difference approach using two schemes (Bluestein, 1992). One was the centered-in-space scheme

$$\left(\frac{\partial p}{\partial x}\right)_{i,j} \approx \frac{p_{i+1,j} - p_{i-1,j}}{2\,\Delta x}, \qquad \left(\frac{\partial p}{\partial y}\right)_{i,j} \approx \frac{p_{i,j+1} - p_{i,j-1}}{2\,\Delta y}, \tag{4}$$

whereas the other was the off-centered differencing scheme:

$$\left(\frac{\partial p}{\partial x}\right)_{i,j} \approx \frac{p_{i+1,j} - p_{i,j}}{\Delta x}, \qquad \left(\frac{\partial p}{\partial y}\right)_{i,j} \approx \frac{p_{i,j+1} - p_{i,j}}{\Delta y}, \tag{5}$$

where Δx and Δy are the spatial increments in the x and y direction, respectively. Pressure gradients were computed at a relatively fine resolution ($\approx$ 50 km $\times$ 50 km) compared to, for example, EMEP (**E**uropean **M**onitoring and **E**valuation **P**rogram) model for the long-range transport of pollutants which employs 150 km $\times$ 150 km grid (Barrett et al., 1995). Due to the computer memory limitations the pressure gradient at any nongrid point was set equal to the gradient computed at the closest grid point. For the same reason, the spatial increments $\Delta x = \Delta y = 100$ km were employed.

Initial conditions

All trajectories originated at 0000 UTC at Nagylengyel ($\varphi = 46° 38'$, $\lambda = 17° 11'$). The initial time of every trajectory calculation corresponds to the beginning of the 4-day forecast. The initial velocity for each trajectory was assumed geostrophic.

Results and conclusion

Figures 1 and 2 illustrate trajectories starting at 0000 UTC for the 14 and 15 November 1998, respectively, shown in a polar stereographic projection. For the first day, trajectories that originated about half an hour after the beginning of the accidental release were followed 24 hours forward in time. For the second day, trajectories were computed for only 6 hours, since the emission of H_2S had already stopped. According to both 0600 UTC and 1200 UTC ECMWF weather forecast maps for November 14, windfield in the area of interest had a northward component. Therefore, trajectories were initiated only at 0000 UTC.

For November 14 very similar pathways were obtained for both the centered and off-centered differencing scheme. According to both trajectories, due to the dominantly western wind component, air was transported over

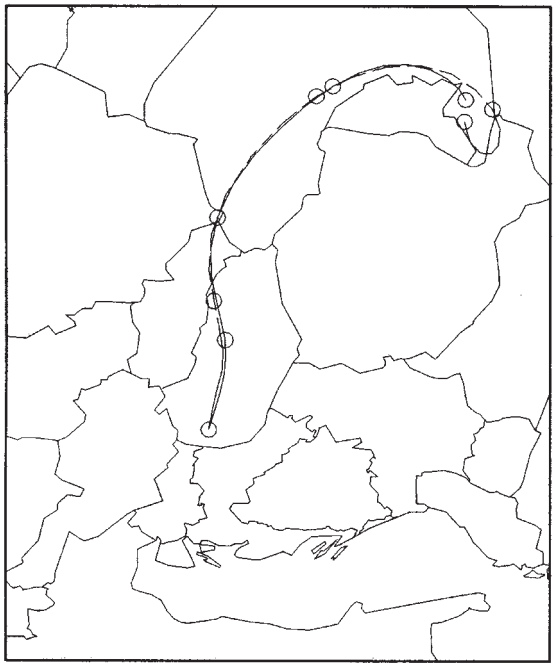

Figure 1. One day forward trajectories starting at Nagylengyel (φ = 46° 38', λ = 17° 11') at 0000 UTC for November 14, 1998. Solid and dashed lines correspond to the centered and off-centered differencing schemes, respectively.

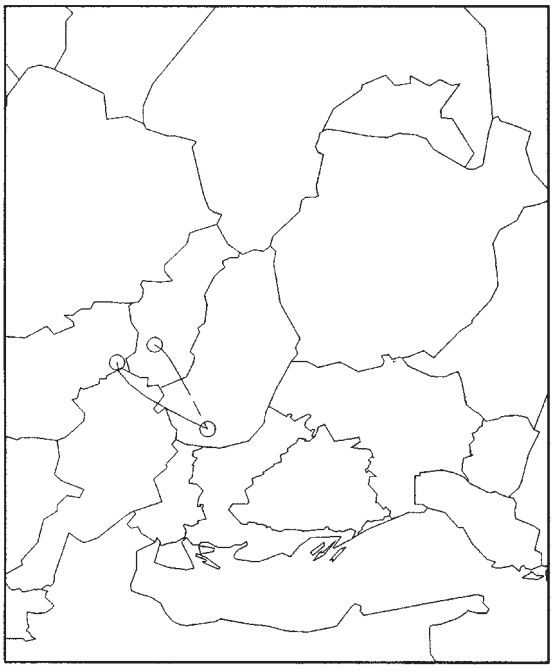

Figure 2. Six hours forward trajectories starting at Nagylengyel (φ = 46° 38', λ = 17° 11') at 0000 UTC for November 15, 1998. Solid and dashed lines correspond to the centered and off-centered differencing schemes, respectively.

Hungary, southeastern Slovakia and the southwest Ukraine. In the afternoon of November 14, the northern component gradually increased, causing the transport of the air almost along the border between Ukraine and the eastern Moldova.

During the first six hours of the next day air parcels were carried northward. However, the difference between the two trajectories was more pronounced than on the previous day. (After six hours of transport time the distance between two end points of the trajectories was about 100 km.) Therefore, the centered-scheme trajectory ended in the Czech Republic, whereas the off-centered scheme end point was in Slovakia. We believe that a discrepancy betwen the two November 15 trajectories comes from the use of two different discretizations of the pressure gradient term. (One should note that all four trajectories are calculated from the day one of the ECMWF forecast.)

According to computed trajectories one may conclude that the accidental emission did not affect Croatia and Bosnia-Herzegovina. This is in agreement with the measurements of daily mean $S0_2$ concentrations in the air obtained at 5 locations in Croatia by the MHS and the Institute for Medical Research and Occupational Health (Figure 3). (Unfortunately, measurements in the domain along the trajectories were not available.) Two locations (Puntijarka and Zavižan) are in natural environment, whereas the remaining three (Grič, Maksimir and Ksaverska) are in urban area of Zagreb. Maksimir is far from the local pollution sources. Therefore recorded concentrations are

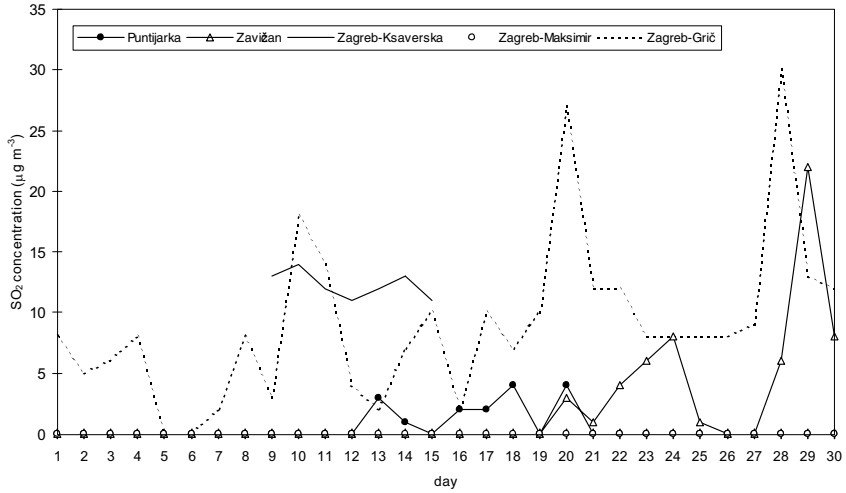

Figure 3. Daily mean SO_2 concentrations in air ($\mu g\ m^{-3}$) for Zavižan (44° 49' N, 14° 59' E), Puntijarka (45° 54' N, 15° 58' E), Zagreb-Grič (45° 49' N, 15° 59' E) and Zagreb-Maksimir (45° 49' N, 16° 02' E) for November 1998. Also, shown is the data for Zagreb (location Ksaverska cesta 2) for the period 9 November–15 November 1998.

allways much lower as compared to other two Zagreb locations. Figure 3 shows that the concentrations measured on November 14 and a few following days did not exhibit any unusual increase.

Ground level concentrations caused by emitted pollutants were not calculated since the necessary input data, such as emission and source characteristics (mass of emitted pollutants, duration of emission, source height and diameter, effluent temperature and exit velocity), was unknown.

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Appendix

In the air, H_2S reacts with hydroxil radical (OH) to form hydrogen sulfide radical (HS) by (Jacobson, 1999)

$$H_2S + OH \longrightarrow H_2O + HS.$$

HS reacts with ozone (O_3), nitrogen dioxide (NO_2), and oxigen (O_2). The HS–O_3 and HS–NO_2 reactions produce HSO. HSO further reacts with O_3 and NO_2, producing HSO_2 in both cases. HSO_2 combines with O_2 to form SO_2 and HO_2. The HS–O_2 reaction is

$$HS + O_2 \longrightarrow SO + OH.$$

SO is rapidly oxidized to SO_2 by

$$SO + O_2 \longrightarrow SO_2 + O.$$

SAŽETAK

Akcidentalna emisija H_2S u Nagylekgyelu, Madžarska, 14. studenog 1998. – Analiza putanje

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Ispitano je gibanje česti zraka koja je onečišćena zbog akcidentalne emisije H_2S u blizini hrvatske granice. Emisija je započela 13. studenog 1998. oko 2330 UTC. Putanje kreću u 0000 UTC, a izračunate su dinamičkom metodom koja uvažava realistične nelinearne prostorne i vremenske promjene polja vjetra. Gradijenti tlaka izračunati su iz prognostičkih ECMWF prizemnih polja tlaka, korištenjem dviju shema: centralne i necentralne. Obje jednodnevne putanje unaprijed ukazuju da se onečišćeni zrak kretao iznad Madžarske, Slovačke i Ukrajine. Nadalje, mjerenja srednjih dnevnih koncentracija SO_2 u zraku na pet lokacija u Hrvatskoj, potvrđuju da akcidentalna emisija nije utjecala na koncentracije.

Ključne riječi: H_2S, akcidentalna emisija, analiza putanje

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