SHORTER CONTRIBUTION

On the residence time of antropogenic sulfur in the atmosphere

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When discussing the circulation of sulfur and other compounds in the atmosphere, especially in connection with the study of dispersion from an antropogenic source, a fundamental quantity to be considered is the residence time of the compound in the atmosphere. This time-scale is obviously a measure of the relative magnitudes of the radius of influence and the effective horizontal transport velocity.

The residence time varies considerably from one source to another depending upon the way the emission takes place and on meteorological factors. The "classical" value of the rate of photochemical oxidation of SO_2 in pure air corresponds to a residence time for SO_2 of 21–42 days (Gerhard & Johnstone, 1955). Although the sulfur is not immediately removed from the atmosphere after the oxidation, the real value of the residence time for antropogenic sulfur is probably considerably lower. The reason is that catalytic processes can increase the oxidation rate considerably (see e.g. Renzetti & Doyle, 1959). Direct measurements of oxidation rates in smoke plumes with high humidity have given time-scales of the order of a few hours (Gartrell *et al.*, 1963). Meetham (1950) used many years measurements of SO_2 (and smoke) in Britain both of the concentration in surface air and the rate of deposition measured in deposit gauges and compared it with the emission. In this way he estimated a residence time for sulfur in the atmosphere of roughly 10 hours.

In the following a very simple investigation is presented of the sulfur deposition in and around the city of Uppsala in Sweden during 12 days in February 1969. A winter situation was chosen because snow samples, which are relatively easy to collect, should contain all that is remowed from the atmosphere (no gas exchange with the sea surface or the vegetation). Furthermore winter situations are more interesting from an air pollution point of view, in that the emission of SO_2 is strongest at that time of the year.

The snow samples were collected with an aluminium spade. The thickness of the snow above a crust level, which was taken as a reference level, was 10–20 cm. This crust was formed during some warm days at the end of January and the beginning of February and the last of these warm days ($T > 0°C$) was 7 February. During the following three days appreciable amounts of snow fell so that what was found in the snow above the crust should indicate what had come down during the time period from 8 February to the sampling day (February 19). Samples were collected at 31 places in Uppsala and out to a distance of 15 km from the center of the town. All samples were collected in open fields at a minimum distance to mainroads of 300 m. At most places double samples were collected and also at a few places further samples were collected in a nearby forest for comparison. Analyses of total sulfur content was made at the International Meteorological Institute in Stockholm by titrating with barium-perchlorate. The winds during the 12-day period were slight to moderate, their directions varying between S, E and N. Based on a mean value of the magnitude of the wind at anemometer level of 3.5 m/sec an effective horizontal transport velocity out from the city was estimated to 5 m/sec. The total amount of precipitation was about 20 mm. The amount of sulfur emitted in the town during the period was approximately 240 tons, one third of which came from a power station having a 40 m chimney.

Although the variations in sulfur deposition was found to be rather large there was a clear decrease in sulfur content during the first kilometers away from the center of the town. If, as a first approximation, radial symmetry is assumed, the deposition $d(r)$ as a function of radius is given as in Fig. 1. Fig. 2 shows the accumulated deposition $D(r) = \int_0^r 2\pi r\, d(r)\, dr$. The material is certainly rather small but it might be of some interest to try to draw a few conclusions from it. The biggest problem when trying

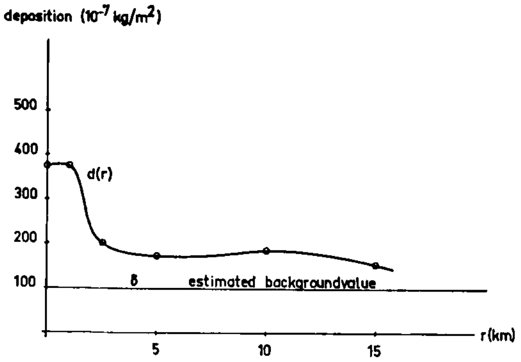

Fig. 1. The deposition of sulfur around Uppsala during the time 8–19 February 1969, as a function of distance from the center of the town. $d(r)$ is the measured amount and δ an estimated background-value.

to interpret Figs. 1–3 is to know how much of the deposition is due to the Uppsala source. The background value is very difficult to estimate and is probably not even a constant. It is however evident from Fig. 2 that within 3 km from the center of the town less than 3‰ of the emitted amount has been deposited and even within 15 km this quotient is smaller than 5%.

Let k be a reaction coefficient for the local deposition, so that the deposition is k times the (vertically integrated) concentration, and let δ be the value of the background deposition. Then an approximate functional relationship between the deposition $d(r)$ and the radius may be represented by

$$d(r) \approx \frac{Mk^2}{2\pi \bar{u}^2} \exp\left(-\frac{kr}{\bar{u}}\right) + \delta \qquad (1)$$

M is the amount emitted at the source and $\bar{u}$ the mean wind velocity. A corresponding relation for the accumulated deposition $D(r)$ is:

$$D(r) \approx M\left[1-\left(1+\frac{kr}{\bar{u}}\right)\exp\left(-\frac{kr}{\bar{u}}\right)\right] + \delta\pi r^2 \qquad (2)$$

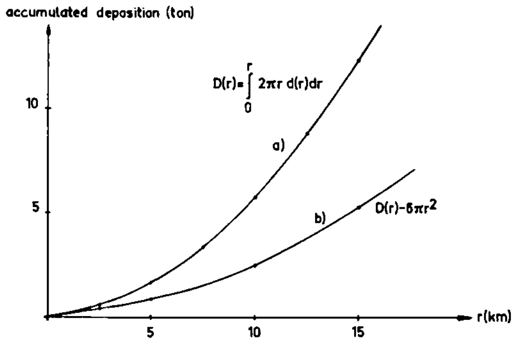

Fig. 2. Accumulated deposition of sulfur (cf. Fig. 1). Curve (a) corresponds to the total deposition while in curve (b) the effect of an estimated background-value has been subtracted.

If $d(r)$ was measured far enough out from the source and M, $\bar{u}$ and δ were known, it would in principle be possible to test the equations (1) and (2) and possibly estimate a k-value. In this case, however, this is not possible since the accuracy of $d(r)$ is too low and it is only measured out to a distance of 15 km which turned out to be very short compared to the length scale of the exponent $\bar{u}/k$.

For further discussion of eq. (2), an extrapolation of the function $D(r)$ has been made in Fig. 3. Curve (a) shows $D(r)$ under the assumption that $d(r)$ is constant ($=d(15\text{ km})$) for $r > 15$ km. In curve (b) an estimated background value of $\delta = 10^{-5}$ kg/m^2 has been subtracted from $d(r)$. The third curve, (c), is only to show the shape of

$$M\left[1-\left(1+\frac{kr}{\bar{u}}\right)\exp\left(-\frac{kr}{\bar{u}}\right)\right]$$

according to eq. (2). Concerning the position in the figure of the curve giving the real value of the integrated deposition from the Uppsala source, nothing more can be said other than that it must lie to the right of curve (a) and very likely also of curve (b).

A lower limit for the residence time T—defined as the distance R within which $\frac{2}{3}$ of the emitted amount has been deposited, divided by the mean transport velocity—for the sulfur emitted in Uppsala during the period can be calculated from Fig. 3. With $R \gtrsim 60$ km and

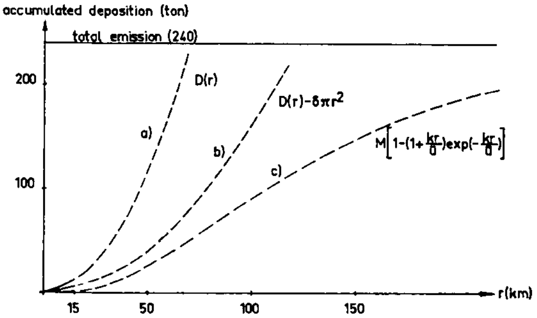

Fig. 3. Extrapolation of the curves in Fig. 2. For further information see the text.

$\bar{u} \approx 20$ km/hour one obtains $T \gtrsim 3$ hours. If also curve (*b*) is situated to the left of the real curve, which is very likely, T is also $\gtrsim 100/20 = 5$ hours. When interpreting these estimated values of a lower limit for the residence time for antropogenic sulfur in the atmosphere it must, of course, be rememberd that they depend on the parameter $\bar{u}$, the estimation of which is somewhat uncertain.

It would be interesting if more detailed investigations of this type could be performed to estimate the strength of the sink mechanisms for antropogenic sulfur and other compounds. A natural extension would be to combine deposition measurements with measurements of concentration in the air and to use longer time periods. For detailed budget calculations it would, of course, be of very much help also to have vertical profiles available. Of special interest in connection with the problem of air pollution on a regional scale would be to compare such investigations, on the one hand, for surface sources—a town with heating in each house—and, on the other, for a point source, corresponding to a town with a big power station.

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