TRANSPORT OF POLLUTANTS CONSIDERED FROM THE POINT OF VIEW OF A SHORT AND MEDIUM RANGE-MATERIAL BALANCE

MICHEL BENARIE, Inst. Nat. de Recherche Chimique Appliquee
B.P 1, 91710 - VERT-le-PETIT (France).

ABSTRACT

Episodical long-range transport is the quasi-instantaneous peak event. It does not express the total dosage of pollutant carried over from the source area to some distant place. The purpose of the present paper is to obtain an average material balance of a pollutant leaving a given area. Available information from the OECD "Long Range Transport of Air Pollutants" is being used for this purpose. The IRCHA is one of the laboratories participating in this project.

Our main sampling station is 37 km from the center of the Paris district. This position allows us to compute, based on emission data from the area and air pollution survey records, the amount of pollutant (total sulfur) leaving the region. We worked out this specific example because we had the first-hand, checked data.

Out of a total emission of about 300 kT SO_2/year (1972 figure), over 50% may be accounted for as remaining inside the 37 km-radius circle. Gaseous and particulate dry deposition mechanisms are considered mainly responsible for this fact. Less than half of the total sulfur emission seems to be transported beyond the 37 km-radius limit. The exact aspect of the deposition function within the national territory is currently being researched.

1. ACKNOWLEDGEMENT

This paper discusses a few aspects and results of the OECD Long Range Transport of Air Pollutants project. Ten European nations participate actively in this program and provide financial support. Their results are being centralized and disseminated by the Norwegian Institute for Air Research. Most of the figures used here come from the OECD project and are largely unpublished. I am expressing herewith my gratitude towards the ten participating laboratories and their staff for the possibility of using a few selected results out of the enormous amount of data gathered.

I am also grateful to Dr. Eric G. Walther of the Charles F. Kettering Foundation, Dayton, Ohio for his assistance in translation of this paper into English.

Episodical long-range transport of pollutants, such as red Sahara dust falling out over Europe, has been known since antiquity. Recently much attention is being paid to episodical long range transport, mainly considering radioactive fallout and acid rains.

2. MATERIAL BALANCE OF THE PARIS REGION

Great attention has hitherto been directed towards "episode analysis" i.e. the scrutiny of the not-to-frequent pollution episodes at remote, slightly polluted stations. If and when such a station records a concentration peak, be it as gaseous pollutant, dry or wet fallout, the cloud can be traced back to its origin. This approach may be termed "receptor-oriented". An alternate way, albeit not original, because it is frequently and almost exclusively used in calculations regarding industrial stacks, is source-oriented. Here, an attempt is made to establish a material balance at and around the emission source.

The Paris district provides a ready example for this approach. It's well-documented emission inventory for 1973 (C.I.T.E.P.A., 1973) amounts to 300 kT SO_2 per year. This emission takes place within a rather well defined, almost circular area of 30 km diameter. No other comparable emission is to be found within 300 km and excepting the North and North-East directions where emissions are nearer, all other directions are altogether free of sources for many hundreds of km and also of geographical relief of any importance.

The area is well-monitored (40 stations) by the Laboratoire d'Hygiène de la Ville de Paris, assisted in this task by other laboratories (EdF; CSTB, etc). One of the OECD-LRTAP ground stations, FO1 is operated by the IRCHA 37 km due South from the center of the district, at VERT-le-PETIT.

The siting of this station is singular, because of the clear possibility of distinguishing between Paris (urban) plume pollution situations and background values. Following from the urban geometry and the wind rose, (information gathered at the Brétigny-sur-Orge airfield, at 6 km distance as well as ours') FO1 is swept by the plume of Paris 13% of the time. Between the 1.1.1972 and 31.5.1974, we could pick out 28 episodes, when the wind and concentration patterns showed clearly that Vert-Le-Petit was for at least 24 hours inside the plume from Paris. During these episodes, the average of the measured SO_2 concentrations was 108 $\mu g\ m^{-3}$. The number of episodes when the plume swept over FO1

for less than 24 hours at one time, was 41 during the same 29 month period. In the absence of a North wind (or a sampling period with a North-wind component) the SO_2 concentration was found on average to be below or near 10 μg m^{-3}. See Table I.

TABLE I

Average concentrations of the SO_2 in the air at FO1 during the summer months of 1973, in the absence of NNE-N-NNW winds, compared with corresponding values at IC1, CH1, NO1 and SF1.

		Monthly average SO_2 conc. in the air μg m^{-3}				
Code	Country**	May	June	July	Aug.	Sept.
FO1	France	12.1	21.3*	9.6	8.1	7.7
IC1	Iceland	9.3	0.8	1.2	1.7	2.4
CH1	Switzerland	3.7	2.5	2.3	2.4	2.2
NO1	Norway	7.2	8.4	8.4	8.7	5.7
SF1	Finland	10.0	6.1	4.6	5.7	5.0

*The relatively high June average is accounted for by a North wind during the day of 13.6.73, when a 24 h mean of 116 μg m^{-3} was recorded.

**See also Table III.

Thus the yearly average at FO1 may be computed as:

$$0.13 \times 108\ \mu g\ m^{-3} + 0.87 \times 10\ \mu g\ m^{-3} = 22.7\ \mu g\ m^{-3}$$

The 1973 experimental average at FO1 was 24.2 μg m^{-3}

The material balance may be established in the following way. The downtown average SO_2 concentration in Paris during the reference period was 154 μg m^{-3}. With a vertical deposition velocity of 0.8 cm s^{-1}, as is assumed throughout the OECD program, taking into account the radial decrease in concentration from 154 to 24 μg m^{-3}, the dry deposition integrates to 110 kT yr^{-1} inside the 37-km-radius circle.

The SO_2 leaves the 37-km-radius circle at the average concentration of 24.2 μg m^{-3}, at an average mixed height of 690 m (Benarie 1975) and a "plume width" of 45 km. This latter dimension was established by recording about 1000 SO_2 concentrations and plotting them against the observed average wind direction, also measured at our laboratory

(Fig. 1). The average plume is quite distinct between compass direction

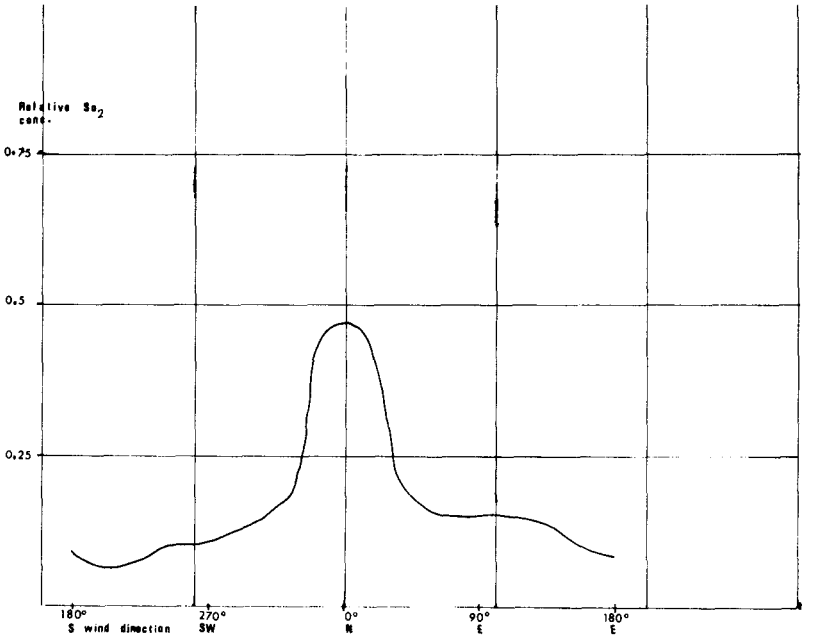

Figure 1. Average SO_2 conc. PARIS divided into the SO_2 conc. at FOl plotted against prevailing wind direction.

of 330° and 40°. This produces an estimate of average plume width of 70°, corresponding to a 45 km front at 37 km radial distance. This estimate is in fair agreement with the St. Louis, Mo. urban plume width measured by Stampfer and Anderson (1975) by aerial sampling. Thus $4.5 \cdot 10^6$ cm (plume width) × $6.9 \cdot 10^4$ cm (plume height) × $24.2 \cdot 10^{-6}$ g m^{-3} (concentration) × $4.1 \cdot 10^2$ cm s^{-1} (average wind speed) × $31.5 \cdot 10^6$ s (year) ≈ $100 \cdot 10^9$ g yr^{-1} = 100 kT yr^{-1}.

Out of the 300 kT yr^{-1} SO_2 emission of the area, 100 kT (≈33%) leave the 37 km radius circle and 110 kT (≈37%) are accounted for by dry and wet deposition inside the area. The remainder, 30% probably undergoes transformation into sulfate during the average residence time (37 km/4.1 m s^{-1} 2.5h) of the emission inside the control area and undergoes partially dry deposition. This figure seems quite realistic in the light of the findings of Benarie et al. (1973) further bibliography and estimates in the reference).

As the average concentration of suspended sulfate at Vert-le-Petit was found to be 13.5 µg m^{-3}, the same reasoning as above gives as an upper estimate of sulfur transport over the 37 km radius boundary, 36 kT yr^{-1} (counted as SO_2). The wet and dry mechanisms account for a deposition of 64 kT yr^{-1} inside the circle. Thus the material balance

(in SO_2 kT yr^{-1}) may be summed up as follows:

	Deposited inside the 37 km radius circle	Transported beyond the 37 km radius circle
Sulfur Dioxide	110	100
Suspended sulfate (as SO_2)	64	36
	174 = 57%	136 = 44%

Total: 310 kT, estimated from the material budget.

Emission: 300 kT, estimated from the source inventory.

This deposition-to-transport ratio is in excellent agreement with that found by Hogstrom (1973) from Uppsala data. He estimated the yearly sulfur deposition originating from "local sources" at about 50 per cent for the Stockholm and Gothenburg areas. To quote Hogstrom: "... high deposition figures are not especially concentrated in the central city area, but occur rather in an area with a radius of 50-100 km around the city".

Attempting to pursue the plume at greater distance, we are handicapped (1) by the scarcity of ground stations; (2) by the appearance of non-background concentrations at the sampling site not caused by the source area (Paris) for which we are attempting to determine a material balance. However, concerning this second objection our purpose is to obtain a maximum estimate of the sulfur leaving the area. Hence the non-background concentrations can only increase this estimate, so it is not of much concern.

At La Crouzille (FO3) we could identify at least one period when wind direction and concentration pattern made the Paris plume clearly identifiable. La Crouzille is 320 km due South from Paris with no obstacles and no important emissions all the way. The annual average SO_2 concentration at FO3 in 1973 was 4.2 $\mu g\ m^{-3}$, while the suspended sulfates were 4.26 $\mu g\ m^{-3}$. From 18.2.74 to 20.2.74, the wind blew on the average at 3.1 to 3.7 ms^{-1} steadily from the northern sector and no precipitation recorded at all. During this period, the following sulfate and SO_2 concentrations were observed: Table 2.

During the three significant days of the episode (18 -20.2) the wind direction did not deviate by more than ± 15° from its mean direction. In these conditions, a 30° plume width at La Crouzille is a good guess; it agrees also with the recent St. Louis study of Stampfer and Anderson (1975). The average sulfur content (accounted for as SO_2) decreased from 148 $\mu g\ m^{-3}$ at FO1 to about 1/4 of this value (=35 $\mu g\ m^{-3}$) at FO3.

Table 2

Sulfur dioxide in the air and suspended sulfate concentrations ($\mu g\ m^{-3}$) observed during February 1974 with a steady North wind blowing from the 17th to the 22nd and no rain.

	February							
	16	17	18	19	20	21	22	23
Paris, average SO_2	135	251	170	180	140	276	216	181
FO1 Vert-le-Petit SO_2*	48	48	123	49	152	37	57	166
Sulfate	0.9	3.6	92	52	42	40	12	13
FO3 La Crouzille SO_2	0	0	19	23	14	14	6	10
Sulfate	2.4	7.1	23	25	20	20	6.5	1.8

At Vert-le-Petit, these averages relate only to the hours during which the North wind was actually recorded. All other figures are for the whole 24-hour sampling period, containing variable wind directions.

We assume, as usual in plume calculations that, at distances which are large compared to the vertical diffusion coefficient and in the presence of a restriciting "lid", the vertical concentration gradients disappear.

With this information, we may formulate the following conditional hypotheses: (1) If the plume does not broaden at all between 37 and 320 km most of the difference 148-35 = 113 $\mu g\ m^{-3}$ was deposited between the two distances. That seems an obvious over-estimation of the deposit, and consequently, an underestimtion of the sulfur leaving the control radius. (2) The effective width of the plume cannot be more than $4 \times 45 = 180$ km, because that would mean that more sulfur leaves the 320 km limit than enters at 37 km, which is obviously impossible. Thus 180 km (which incidentally agrees well with the above 30° estimate, because $\frac{2\pi\ (320\ km)}{12} \approx 170$ km is an upper limit of the width of a plume that meanders as little as possible. In this case, no deposition would have taken place between FO1 and FO3 and all the material entering the 37 km circle would have left the 320 km circle.

As this second hypothesis must overestimate the amount of sulfur leaving the 320 km radius, we can adopt it as the basis of the following estimate. With a plume section of 180 km by 690 m (average mixing height), on the average $4.2 + 2/3\ 4.26 = 7.0\ \mu g\ m^{-3}$ SO_2 are "emitted" throughout the 320 km radius. As the concentration figure contains the (unknown) background sulfur transported from elsewhere than the Paris region, we have a second element of overestimation. A third element of

overestimation follows from the fact that during the period under consideration it did not rain, thus rainy days included, the deposition inside the control circle can only be more, not less than our estimate. With the above data, we estimate that as an upper limit, 115 kT SO_2, (accounting for the SO_2 and the suspended sulfate, i.e. less than 40% of the originally emitted amount) leave the 320 km-circle around the Paris district. The decrease i.e. the deposition between the 37 and 320 km circles does not seem too high but we must bear in mind that the 320 km guess is an overestimate for at least three reasons.

By different reasoning, Raynor et al. (1974) arrive at the same conclusion about New York City: the mean SO_2 concentration is exceeded by local contributions at 70 km from mid-Manhattan and approaches zero at a distance of 112 km.

3. IMPLICATIONS FOR LONG-RANGE TRANSPORT

Admitting as a first estimate the result we derived in the previous section, i.e. that about 150 kT SO_2 per year leave the Paris region, we may ask, how much of it will be available for deposition in some remote area. Some of it will obviously be deposited en route following, on the average, an exponential law. The available best estimate for the decay constant in the exponent is $3 \cdot 10^{-5} s^{-1}$, obtained recently by Eliassen and Saltbones (1975), also from the OECD data. To be rather on the side of overestimation of the remote deposition instead of its probable value, we will consider that the decay constant is equal to zero, i.e. no loss by deposition en route is assumed.

From Northern Central Europe, the end points of trajectories of "particles" (small clouds) released every third day for a period of about one year were calculated following the 850 mb-trajectory by Rodhe (1972). The end points of the trajectories are nearly equally distributed in the four quadrants. For example, we find the following number of end points after 60 hours of travel within 3000 km of the release:

	Quadrant			
Number of 60-hr trajectory ends, after Rodhe (1972)	First	Second	Third	Fourth
	25	19	24	21

We may conclude that there is an approximate directional equipartition on an annual basis. If we admit that the *whole* emission is deposition within the 1000 and 3000 km limits (*no* deposition before; no transport beyond) this circular zone receives on the average an amount of sulfur deposit equivalent to $1.5 \cdot 10^{-2}$ g SO_4 m^{-2} y^{-1}. If we take into account instead of the 150 kT y^{-1} of the Paris area, 50% of the SO_2

emission of France, Great Britain and the Federal Republic of Germany not deposited at short range, i.e. $1/2 \cdot 13400$ kT y^{-1}, this amounts to 0.6 g SO_4 $m^{-2}y^{-1}$ on the average within the boundaries. Not withstanding all the overestimation made, this still is less than the half of the global background (See sect. 5.).

An area of $0.75 \cdot 10^6$ km (roughly the area of Sweden and Norway) within the 1000 to 3000 km limits from Western Europe thus can receive a total yearly deposit of 450 kT sulfate. The 1973 yearly SO_2 emission of these two countries was 1000 kT SO_2, out of which, following the arguments of Sect. 2, 500 kT are deposited at short range, corresponding to 750 kT sulfate. This budget agrees closely with the estimation of Rodhe (1972) "that about half of the sulfur (deposition in Sweden) originates from foreign anthropogenic emission, whilst the other half is caused by Swedish emissions and a natural background".

4. THE PERCENTAGE BREAKDOWN OF THE DRY AND WET DEPOSITION MECHANISMS IN A NUMBER OF GROUND STATIONS

Table 3 presents comparatively the percentage breakdown of the total sulfur deposited (fifth column) for a few ground sampling stations from June 1972 to Dec. 1973. The choice is somewhat haphazard, because of the incomplete measurements and the uncompleted records. Nevertheless, some conclusions seem clear. A group of stations show overwhelming dry SO_2 deposition. These are mostly to be found in the more densely populated areas, and the local SO_2 concentrations must be held responsible for the relatively high dry SO_2 deposition. These network stations are obviously DK2, 3, 4, 5, 6; FOl, NL1, 2, 3, and UKl, 2. It seems surprising but not less clear that ICl, SO4, O5, and SF 1, 2, 3, 4, 5 belong on basis of this statistic also to this group, and thus seem to be influenced by relatively near SO_2 emissions.

On the other hand, in the second group: DKl; NO3; O9; and SO3 the wet mechanism dominates: here the rain precipitates more than 50 percent of the total deposited sulfates.

Table 3 shows that a distinction among ground stations influenced by nearby emission sources can be made on the basis of the ratio of deposition due to the main mechanisms.

Table 3

Percentage breakdown of the sulfate deposition according to the three main deposition mechanisms, June 1972 - Dec. 1973; total deposition in sulfate in g m^{-2} compared with the average emission figures for nearby areas (about 1° by 1°). For the stations marked with an *, fragmentary records (i.e. less than 18 months) were extrapolated.

Station	Dry deposition of SO_2, accounted for as SO_4%	Dry deposition of SO_4, %	Wet deposition SO_4, %	Total deposition of SO_4, gm^{-2} yr^{-1}	Average yearly sulfur emission T $km^{-2}yr^{-1}$
DK 1* Faroe Isl.	30	3	67	3	0
DKZ Hanstholm	60	12	28	4.5	4
DK3 Tange	58	18	24	4.7	6
DK4 Keldsnor	61	18	20	4.4	10
DK5 Gniben	69	16	15	5.0	3
DK6 Dueodde	47	19	33	4.7	1.3
FOl Vert-le-Petit	68	16	15	12.8	30
ICl Rjupnahaed	50	3	47	4.8	0.6
NO3 Finsland	35	7	58	5.0	0.6
NO9 Soyland	25	6	70	6.0	0.6
NLl Wageningen	65	14	21	13.6	30
NL2 Witteven	60	17	23	8.0	18
NL3 Den Helder	58	14	27	9.2	20
SO3* Sjöängen	35	19	46	3	1
SO4* Ryda	49	15	36	5	2
SO5* Bredkälen	44	15	28	6	0
SFl Jomala	62	11	28	5.6	0.2
SF2 Jokioinen	66	7	28	6.8	6
SF3 Puumala	63	8	30	5.5	2
SF4 Ahtäri	50	11	39	4.2	1
SF5 Sodankylä	68	10	32	2.5	0
UKl* Cottered	80	7	13	16	40
UK2 Eskdalemuir	66	10	24	6.0	11

DK = Danemark; F = France; IC = Iceland; N = Norway

NL = Netherlands; S = Sweden; SF = Finland; UK = United Kingdom

5. REGRESSION ANALYSIS

It seems obvious that the material balance method outlined in Section 2 should also be applied to areas other than Paris. Nevertheless, this meets some difficulties. Isolated emission areas in the 10^2 kT yr^{-1} range do not abound in Europe. At least one ground station must

be within a range of clearly distinguishing the plume, as was shown in Fig. 1. This plume should not be confused by other emissions. To meet these criteria, new ground stations may have to be erected, or at least all the OECD results must be accessible in computer compatible form, which is not yet the case.

An attempt which may be made at the present time is to correlate the total per area sulfur deposition rate (fifth column) with the typical nearby regional sulfur emission figures per square kilometer, as reported in the last OECD emission inventories. The regression line

$$\text{Total deposited sulfate } (g\ m^{-2}\ yr^{-1}) = 0.28 \text{ emission } (TSO_{12}\,km^{-2}\ yr^{-1}) + 4.06$$

represents the data with a correlation coefficient of).91, i.e. with the 21 D.F., largely beyond the 0.0001 α level of significance.

There seems to exist a very narrow correlation between neighbouring area emission and total sulfate deposition. The intercept is an estimate of the background deposition in the area. Very exceptional stations report less that this amount. Very remote and anthropogenically uninfluenced stations show values near 4 g SO_4 $m^{-2}yr^{-1}$: DK1, SO3, SF4.

This estimate of the global background level should be compared to Rodhe's (1972) figure, 250 mg S m^{-2} yr^{-1} (=0.75 g SO_4 m^{-2} yr^{-1}) for the wet deposition.

Considering from Table 3 the four relatively umpolluted stations, where the wet precipitation predominates (these are the four stations belonging to the "second group" Sect. 4) one can see that this mechanism accounts on the average for 60% of the total deposition. Thus from Rodhe's estimated figure we arrive at 1.25 g SO_4 m^{-2} yr^{-1}. On the other hand, after Wolaver and Lieth (1972), throughout the anthropogenically uninfluenced areas of the continental U.S. the total deposition extrapolated in the same way as above is between 1.3 and 2.6 g SO_4 m^{-2} yr^{-1}. Thus the present estimate of global background based on European data comes near to the upper limit of Wolaver and Lieth. The data of Selesneva (1966) concur with these findings.

6. CLIMATOLOGICAL EFFECTS ON THE RECEPTOR-ORIENTED OBSERVATIONS

The emission-oriented mass-balance approach has the added advantage of being less sensitive to the prevailing weather conditions during the reference period than episode-analysis. If the meteorological conditions conducive to high pollution were frequent during a given period, a given deposition might look dramatically high, though on the average

it would not be. This point was proven by Munn and Rodhe (1970). These authors demonstrate a remarkable statistical relation between the deposition of chloride and sulfate at Plönninge (south-western Swedish coast) and Flahault (centrally land-locked in southern Sweden. and the frequency of occurence of rainbearing winds in the SE-S-SW-W-NW sectors.

Qualitatively, the agreement is excellent, all the curves showing peaks in the middle fifties, larger peaks in the middle sixties, and minima at the end of fifties. This behavior is in agreement with that found by Eriksson (1970) for the entire European (Scandinavian, Dutch, Belgian, French, and English) network of stations. All these stations show variations more or less in phase. The amplitude of variations is such that at several stations, the deposited sulfur was less by a factor of ten between a minimum and a maximum year. A factor of five is found in most stations. However, five Irish stations agreeing amongst themselves, do not show the maxima and minima observed in all others. This is somewhat bewildering. Perhaps the single, circumspect conclusion to be drawn from the present Sect. 6 is, to point out the danger of evaluating trends or of generalizing from one or two years of receptor-oriented observations. One doesn't know climatologically if this year is a peak or a low. Thus, extrapolation might be far off the target.

7. CONCLUSIONS

It was shown by example, that a credible source oriented material balance of an urban district may be derived. A shortcoming of the argument is that it concerns just one urban district, the Paris region. For the time being, this could not be checked elsewhere, because of the lack of appropriate emission-receptor topography. Work is now being done to obtain more similar material-balances.

The material balance of the Paris region shows, that at a yearly average, not more than half of the sulfur emission leaves the 37 km radius boundary. The material balance at the 320 km radius is more tentative, but at least does not contradict this conclusion.

According to the ratios for the SO_2-sulfate-wet deposition, ground stations seem to group themselves into those which are influenced by nearby sources, and others where wet deposition prevails and sources farther away must be sought.

There exists a very strong correlation in Europe between overall deposition and (nearby) area emission. The intercept of the regression line is near to the global background.

Finally, previous research has shown that the range of wet deposition of sulfates, and also of other material, has changed by a factor of ten over the years. This change is not geographically uniform, and may have an opposite direction in ground stations only a few thousands of

km apart. Thus fallout-research during a few months or years may show up memorable episodes, but not uncover real trends.

REFERENCES

Benarie, M., T. Menard and A. Nonat. 1973. Etude de la transformation de l'anhydride sulfureux en acide sulfurique en relation avec les données climatologiques, dans un ensemble urbain à caractère industriel, Rouen (Text in French) ATM. ENV. 7 p. 403-421.

Benarie, M. 1975. Calculation of the mean yearly mixing height over urban areas, from air pollution data. SCI. TOT. ENV. 3 p. 259-256.

CITEPA. 1973. C. I. 627 and C. I.778

Eriksson, E. 1970. The importance of investigating global background pollution. WMO TECHNICAL NOTE N°106, GENEVA. SWITZERLAND, p. 31-54

Hogstrom, U. 1973. Residence time of sulfurous air pollutants from a local source during precipitation. AMBIO 2 p. 37-41; 90-91.

Munn, R. E. and H. Rodhe. 1970. On the meteorological interpretation of the chemical composition of monthly precipitation samples. Inst. of Meteorology Internat. Meteor. Inst. in Stockholm, REPORT AC-10, 50/1417, 38 pp.

Raynor, G. S., M. E. Smith and I. A. Singer. 1974. Meteorological effects on sulfur dioxide concentrations on suburban Long Island, New York. ATM. ENV. 8 p. 1305-1320.

Rodhe, H. 1972. A study of the sulfur budget for the atmosphere over Northern Europe. TELLUS XXIV, p. 128-138.

Eliassen, A. and J. Saltbones. 1975. Decay and transformation rates of SO_2, as estimated from emission data, trajectories and measured air concentrations. ATM. ENV. 9 p 425-429.

Selesneva, E. S. 1966. On the natural background contamination of the atmosphere and composition of precipitation in the territory of the USSR (Text in Russian) Gidrometeorologitcheskoe Isdatelstvo, Leningrad.

Stampfer, J. F. and J. A. Anderson. 1975. Locating the St. Louis urban plume at 80 and 120 km and some of its characteristics. ATM. ENV. 9 p. 301 - 313

Wolaver, T. G. and H. Lieth. 1972. The distribution of natural and anthropogenic elements and compounds in precipitation across the U.S. Theory and quantitative models. Div. of Ecological Res. E.P.A. Res. Triangle Park, N.C. 75 pp.