

An atmospheric selenium budget for the region 30° N to 90° N

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ABSTRACT

Using a mass balance approach, an atmospheric selenium budget for the region 30° N–90° N has been constructed. The atmosphere was assigned four different aerosol burdens corresponding to mean selenium aerosol concentrations in urban, intermediate (rural), remote/continental, and oceanic air. The budget calculations indicate that nearly all atmospheric selenium originates from anthropogenic emissions and biological activity in terrestrial and marine ecosystems. After comparing the sources of selenium to those of sulphur it is concluded that there are many similarities in their atmospheric cycling, but that there are also important differences.

1. Introduction

In recent years interest has grown in the atmospheric cycling of selenium. It is a rather unique element because of the very small difference between levels which are essential to life forms and those which are toxic (NAS, 1976). In regions such as Scandinavia, where selenium levels in soils are low, atmospheric deposition is thought to be the major mechanism for replacing selenium in the terrestrial biosphere (Låg and Steinnes, 1978). Also, it has become evident in recent years that many different types of life forms, under normal metabolic conditions, can release volatile organo-selenium compounds to the atmosphere (Lewis, 1976).

In the atmosphere, selenium exists in both the particulate and vapor phases. Ross (1984) concluded that a portion of the selenium in the vapor phase is due to the relatively high vapor pressure of selenium (0) and chemical reactions on the aerosol surface which convert selenium dioxide to selenium (0). Experimentally, vapor phase selenium is defined as that selenium which is able to pass

through particle collection devices. Pillay et al. (1971), found 60% of the atmospheric selenium in Buffalo, New York, was able to pass through filters which had an efficiency of 100% for aerosols with radii greater than 0.10 μm . Mosher and Duce (1983) found 25% of atmospheric selenium in both urban and remote locations was in the vapor phase. They defined vapor phase selenium as that selenium which was able to pass through 0.20 μm or 0.40 μm pore diameter membrane filters.

Measurements of particulate matter in both remote/continental and marine environments indicate that selenium is highly enriched in the atmosphere with respect to soil dust and sea salt (Zoller et al., 1974; Duce et al., 1975; Adams et al., 1977). An atmospheric enrichment factor (EF) is defined as:

$$EF = \frac{(C_X/C_R)_{\text{air}}}{(C_X/C_R)_{\text{soil or sea salt}}}; \quad (1)$$

R is a reference element which is highly refractory (usually Al or Fe) and X is the element of interest. In marine locations, it is thought that the major source of particulate selenium, and hence the poor

¹ Contribution no. 517.

correlation to sea salt, is particle scavenging and gas to particle conversion of volatile biogenic emissions (Mosher and Duce, 1983).

An atmospheric budget for selenium at the present time would be very useful. It would help to understand the data which originates from many diverse sources, and would indicate where our knowledge is lacking and what type of future measurements should be performed. Also it would provide a chance to compare the major features of the atmospheric cycles of sulphur and selenium. This in itself is an interesting exercise because sulphur and selenium have similar chemistry, and because it has been postulated that selenium can be used as a tracer to help understand the atmospheric cycling of sulphur (Hashimoto and Winchester, 1967; Pillay et al., 1971).

2. An atmospheric selenium budget

2.1. Geographic region

A global selenium budget was not constructed because concentrations of selenium in aerosols, and atmospheric deposition, have been measured almost exclusively between 30° N and 70° N. For simplicity a budget for the region 30° N to 90° N was constructed.

Table 1 lists the physical characteristics of the region 30° N to 90° N. It is one quarter of the earth's total surface area and is equally divided between land and ocean. The land area is 43% of the global total. About 95% of all industrial activity occurs in this region. Industrial regions ($11.4 \times 10^{12} \text{ m}^2$) comprise 24% of the land area between 30° N and 60° N (Ryaboshapko, 1983). This area, less $0.5 \times 10^{12} \text{ m}^2$ to account for urban regions, was designated as the intermediate area.

Table 1. Physical characteristics of the region 30° N to 90° N*†

	30° N–40° N	40° N–50° N	50° N–60° N	60° N–70° N	70° N–90° N	30° N–90° N
Area (10^{12} m^2)						
Oceanic	20.8	15.0	10.9	5.6	11.6	63.9
Continental	15.6	16.4	14.6	13.2	3.8	63.6
Rain flux ($10^{12} \text{ m}^3 \text{ yr}^{-1}$)						
Oceanic	16.6	16.0	10.0	2.9	2.0	47.5
Continental	15.1	12.5	11.1	4.9	0.6	44.2

* Defant (1961).

† Palmén and Newton (1969).

The oceanic area is about 18% of the global total. While atmospheric precipitation is highly variable through latitudinal zones, mean zonal precipitation values are needed to calculate wet deposition. Using precipitation data (Defant, 1961; Palmén and Newton, 1969), zonal rain fluxes for oceanic and continental regions in 10° latitudinal zones were calculated.

2.2. Atmospheric burden

The simplest approach to constructing an atmospheric budget for an element is to treat the atmosphere as a single homogeneous reservoir where a mass balance exists between the sources and the sinks. For selenium, the high spatial variability of atmospheric concentrations precludes the use of a single reservoir. Hence, the atmosphere was assigned four concentrations: urban, intermediate, remote/continental and oceanic.

A summary of the concentrations of selenium in atmospheric aerosols is given in Ross (1984). Fig. 1

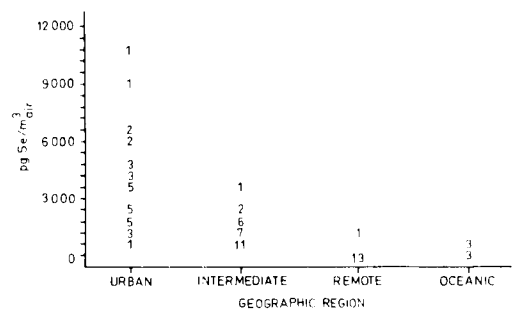


Fig. 1. A summary of observations of atmospheric selenium concentrations on particulate matter between 30° N and 90° N. The numbers represent the number of observations in the given concentration range.

Table 2. *Particulate selenium concentration in surface air between 30° N and 90° N (pg Se m⁻³)*

Region	Number of data points	Mean conc. (S.D.)	Geometric mean conc. (range)
Urban	31	3700 (2300)	3100 (1600–5900)
Intermediate	27	1200 (740)	1100 (610–1900)
Remote/cont.	14	170 (240)	93 (32–270)
Oceanic*	6	290 (180)	240 (110–520)

* Includes measurements from coastal sites on Bermuda and the Shetland Islands.

is a histogram of the distribution of selenium in the atmosphere for oceanic, remote/continental, intermediate and urban areas. The average atmospheric selenium concentration for each region between 30° N–90° N is listed in Table 2. Since there was great variability in the concentrations for a given region, a two-sample *t*-test (99% confidence limit) was performed to insure that there was significant difference between the average concentrations. The results indicate that the selenium concentration in urban air is 1300–3700 pg m⁻³ higher than in intermediate air, and the concentration in intermediate air is 650–1500 pg m⁻³ higher than in remote regions.

Selenium concentrations in samples of atmospheric particulate matter are usually determined by instrumental neutron activation analysis (INAA). With respect to selenium, INAA allows for very low concentrations, on the order of picograms, to be determined with very high precision (Cawse and Peirson, 1972; King et al., 1976; Zoller and Gordon, 1970).

As mentioned previously, an appreciable amount of selenium exists in the vapor phase. We would recommend in future measurements of atmospheric selenium, that a gas trap be included in the experimental design. One could then estimate the total atmospheric burden of selenium with much greater accuracy. Though the partitioning of atmospheric selenium will be dependent on experimental design, the relative significance of various removal processes which are dependent on the phase in which selenium exists could then be assessed.

2.3. Sources of atmospheric selenium

2.3.1. *Anthropogenic emissions.* Selenium emissions from mining and industrial activities (exclud-

ing combustion of fossil fuels) were calculated by multiplying atmospheric emission factors for specific industrial processes (NAS, 1976) by the respective world production (United Nations Statistical Yearbook, 1974). World production values were listed by country; therefore the percent of the atmospheric emissions originating north of 30° N could be determined. Total emissions between 30° N and 90° N are estimated to be 18×10^8 g Se yr⁻¹.

As seen from Table 3 the major source of atmospheric selenium emissions from mining and industrial activities originates from the smelting and refining of metal ores. Our global value of 23×10^8 g Se yr⁻¹ correlates well with the value obtained by Lantzy and Mackenzie (1979) of 20×10^8 g Se yr⁻¹.

The atmospheric selenium flux from the combustion of fossil fuels was calculated by assuming that selenium is equally divided between the particulate and vapor phases after combustion, and that pollution abatement devices are 90% efficient in removing particulate selenium and 0% efficient in removing vapor phase selenium. Vapor phase selenium is defined as that selenium on very fine particulates and/or in the gaseous state. These assumptions are based on the mass balance of two coal-fired power plants (Klein et al., 1975; Kaakinen, et al., 1975).

The concentration of selenium in fossil fuels is highly variable. In the calculation mean concentration values reported by Pacyna (1981, 1982) were used. The amount of coal burned annually was equal to the world production of lignite and hard coal (U.N. Statistical Yearbook, 1974). For the amount of oil burned the world production of residual and distillate fuel oil (U.N. Statistical Yearbook, 1974) was used. The concentration of

Table 3. *Atmospheric selenium emissions from mining and industrial processes (reference year, 1973; emissions are in units of 10⁸ g Se yr⁻¹)*

Industrial process emission factor ⁽¹⁾		World prod. of:	Global emissions	% of emissions north of 30° N ⁽²⁾	Emissions north of 30° N
Mining and milling		ore mined ⁽²⁾			
10 ⁻⁸ g Se (g ore) ⁻¹		(10 ¹² g yr ⁻¹)			
copper	0.75	7.1	small		small
lead	2.4	3.4	small		small
zinc	1.6	4.9	small		small
phosphate	18	98.5	0.18	83	0.16
uranium	18	0.019	small		small
Smelting and refining		metal ⁽²⁾			
10 ⁻⁴ g Se (g metal) ⁻¹		(10 ¹² g yr ⁻¹)			
copper—smelted	1.2	7.7	9.2	69	6.6
refined	1.2	8.5	10.2	79	8.4
lead	0.25	3.3	0.82	89	0.7
zinc	0.20	0.98	0.80	80	0.8
Selenium refining		selenium ^{(3)*}			
g Se (g Se refined) ⁻¹		(10 ⁸ g yr ⁻¹)			
primary	0.14	13	0.18	97	0.17
secondary	0.050	1.3	0.068	100	0.07
End product manufacturing		selenium used in			
g Se (g Se consumed) ⁻¹		industries (%) ^{(3)‡}			
glass and ceramics	0.35	22	1.1	95†	1.0
electronics	0.0010	50	small		small
pigments and paints	0.0075	20	small		small
other	0.50	8	0.56	95†	0.5
Total			23		18

⁽¹⁾ US values; NAS (1976).

⁽²⁾ UN Statistical Yearbook (1974).

⁽³⁾ US Department of the Interior (1981).

* Excluding USSR and FRG.

† Estimates on our part.

‡ US values.

selenium in both types of fuel oil was assumed to be that of crude oil.

Atmospheric selenium emissions from the combustion of fossil fuels were also calculated using emission factors reported by NAS (1976). Table 4 is a summary of both calculations, there is a relatively good agreement, about 40%, between the two estimates. Fossil fuel emissions north of 30° N were determined by looking at the total energy consumption of various countries in the world (U.N. Statistical Yearbook, 1974). It is estimated that about 93% of all fossil fuel consumption occurs north of 30° N.

Bertine and Goldberg (1971) have estimated global selenium emissions from fossil fuel combustion to be 4.2×10^8 g Se yr⁻¹. Their value is

somewhat of an underestimate, because they assumed no selenium was released as a vapor, and there was no enrichment of selenium on the fly ash. Also, they divided world coal production by one half to take into account coke production; whereas 20% may be a more reasonable figure.

Lantzy and Mackenzie (1979), calculated global atmospheric combustion emissions of selenium to be 100×10^8 g Se yr⁻¹. They assumed 90% of all the selenium in fossil fuels is released into the atmosphere after combustion.

2.3.2. *Terrestrial biogenic fluxes.* Biogenic fluxes of selenium to the atmosphere were determined for microbial activity in soils and coastal sediments, and leaf-mediated volatilization from plants. Though it has been demonstrated other life

Table 4. Atmospheric selenium emissions from combustion of fossil fuels (reference year, 1973; emissions are in units of 10^8 g Se yr^{-1})

Fossil fuel	Amount burned ⁽¹⁾ (10^{14} g yr^{-1})	Se conc in fuel ^(2, 3) (p.p.m.)	Emission factor ⁽⁴⁾ (10^{-6} g Se (g fuel) $^{-1}$)	Emissions north of 30° N ⁽⁵⁾	
				(A)	(B)
Hard coal	2.2	3.5	1.4	43	29
Lignite	0.82	2.1	1.4	9.6	11
Fuel oil—distillate	0.50	0.53	0.10	1.5	0.46
—residual	0.82	0.53	0.10	2.4	0.76
Total				56	41

⁽¹⁾ UN Statistical Yearbook (1974).

⁽²⁾ Mean selenium concentrations in coal are from Pacyna (1981).

⁽³⁾ Pacyna (1982), assumed selenium concentration in all types of fuel oil was that of raw petroleum.

⁽⁴⁾ NAS (1976).

⁽⁵⁾ 93% of energy consumption occurs north of 30° N, UN Statistical Yearbook (1974). (A) calculated by assuming 50% of the selenium is in the vapor phase and passes out of the stack and that 50% of the selenium is in the bottom and fly ash; pollution abatement devices remove 90% of the particulate selenium. (B) From emission factors.

forms are capable of releasing volatile organo-selenium compounds into the atmosphere, we felt these contributions to the net biogenic flux are insignificant. As in most calculations of biogenic fluxes the results should be considered only as an order of magnitude estimate.

The task of calculating biogenic fluxes was complicated by several factors. Selenium concentrations in soils, sediments, and plants are highly variable. There seems to be no direct correlation between concentrations in soils and sediments, and biogenic emissions (Chau et al., 1976). Studies of selenium emissions have only been made in the laboratory on a limited number of samples, and in many cases under artificial conditions. Biogenic volatilization rates are dependent on the biological species and the oxidation state of the available selenium for uptake.

Studying the dependence of biogenic selenium emission rates in sewage sludge and soils with respect to the oxidation state of the nutrient selenium, Reamer and Zoller (1980) found selenium was incorporated and volatilized faster than elemental selenium. $(CH_3)_2Se$, $(CH_3)_2Se_2$, and $(CH_3)_2SeO_2$ were detected in the gaseous phase. Doran and Alexander (1977a), using *Corynebacterium* isolated from soils, reported only $(CH_3)_2Se$ being released. The authors also studied the volatilization rate with respect to the speciation

of selenium in the nutrient bath and found selenite was uptaken and volatilized faster than selenate. Elemental selenium showed the smallest volatilization rate. Chau et al. (1976) studying selenium emissions from lake sediments in the Sudbury, Ontario region found $(CH_3)_2Se$, $(CH_3)_2Se_2$, and an unknown volatile selenium compound in the vapor phase. Analysis of their data indicates additions of selenate to the sediment slurries produced larger volatile selenium emissions than additions of equal molar amounts of selenite.

Biogenic selenium fluxes from soils were calculated using a correlation between selenium and sulphur emissions. Direct determination from emission rate data proved futile for the previously mentioned reasons. Selenium fluxes could be estimated using sulphur data because the metabolic pathways which volatilized selenium and sulphur are remarkably similar (Doran and Alexander, 1977a, b; Lewis, 1976).

Mathematically the direct correlation between biogenic selenium and sulphur emissions can be expressed as:

$$d(Se)/dt = (A) d(S)/dt, \quad (2)$$

where the derivatives are the biogenic emission strengths for selenium and sulphur. In order to apply eq. (2), it was assumed that the metabolic pathways which release volatile organo-selenides

and sulphides proceed at the same relative rate. Thus A is merely the ratio of the concentration of selenium to sulphur in micro-organisms (approximately 1×10^{-4}).

Adams et al. (1981) performed a detailed study of total biogenic sulphur emissions from soils in the south-east United States (25°N – 47°N). They found the total biogenic sulphur emissions, for the east-west extension, fit the following empirical equation:

$$\log(Y'_x) = 4.70212 - 0.035588(X). \quad (3)$$

Y'_x has units of 10^6 g S ($6400 \text{ km}^2 \text{ yr}^{-1}$), and X is the north-south grid reference number. Applying eq. (3) to the region of study a sulphur flux of 2.4×10^{12} g S yr^{-1} is obtained. Thus the selenium flux between 30°N and 90°N is estimated to be 2.4×10^8 g Se yr^{-1} .

Lantzy and Mackenzie (1979) calculated a global biogenic soil flux of 30×10^8 g Se yr^{-1} . The authors multiplied a selenium emission rate of 2.26×10^{-9} g Se $\text{cm}^{-2} \text{ yr}^{-1}$ (Chau et al., 1976) by the global surface area less ice. It should be mentioned this emission rate is derived from highly polluted lake sediments and may not be representative of emission rates from unpolluted soils.

Quantitative measurements of vapor phase organo-selenides in the atmosphere have been performed by Jiang et al. (1983). The authors cryogenetically trapped the organo-selenides and determined their chemical form and respective concentrations by means of a gas chromatography-graphite furnace atomic absorption system. Measurements were performed, near aquatic environments, in and around the Antwerp (Belgium) area. $(\text{CH}_3)_2\text{Se}$, $(\text{CH}_3)_2\text{Se}_2$ and $(\text{CH}_3)_2\text{SeO}_2$ were detected in the gaseous phase. Concentrations of all species were highly variable. The authors found no correlation in concentration between dissolved selenium in adjacent waters and ambient air concentrations.

The concentrations as reported by Jiang et al. (1983) can not be used to test our model, because the authors only measured organo-selenides in and around aquatic environments. Furthermore, many of the concentrations were below the detection limit of the analytical system.

Lewis et al. (1974) measured the rate of leaf-mediated selenium volatilization from five different cruciferous plants (cabbage, chinese cabbage, radish, turnips, mustard, and sunflower), and

found it varied between 0.05–0.30% of leaf selenium per hour. The rate was dependent on the plant species, the leaf temperature, the oxidation state of the uptaken selenium, and the pH of the nutrient solution. Studying the volatilization from cabbage leaves in greater detail, the authors found only $(\text{CH}_3)_2\text{Se}$ being released. The emission rate was ten times faster for selenite in the nutrient bath than for selenate. However, the selenium uptake by the plants was the same for both ions.

To calculate a flux from leaf-mediated volatilization it was assumed that 0.05% of leaf selenium per hour is a typical emission rate for all plants and trees. Multiplying this rate by the average dry weight of selenium in plants (0.076 p.p.m.; Ross, 1984) a flux, per gram leaf, of 1.1×10^{-14} g Se s^{-1} is obtained. Table 5 lists the approximate aerial litterfall, per year, of various ecosystems between 30°N and 90°N . It was assumed that leaves compose 75% of the litter fall, and that the average lifetime of a leaf is four months. Hence, it is estimated that the selenium flux from terrestrial biota in the region of study is about 14×10^8 g Se yr^{-1} .

It was stated previously that sulphur and selenium follow similar biochemical pathways. Thus the results are little surprising because a corresponding sulphur flux from leaf-mediated volatilization is not considered when sulphur budgets are constructed. However, Lewis et al (1974) did note that dimethyl-sulphide is released by cabbage leaves. The rate of emission was not mentioned, but the authors noted the biochemical pathway which volatilize selenium and sulphur are similar.

The flux calculations indicate that biogenic selenium emission in the region of study are of the same magnitude as anthropogenic emissions. While laboratory studies are useful, direct measurements of selenium emissions from soils, sediments, and land biota are needed. In addition, simultaneous measurements of sulphur would be extremely useful.

2.3.3. *Volcanic emissions.* There are considered two active volcanic regions on the earth today. The first region is located between 8°S and 15°N and the second region is between 56°N and 65°N . It was assumed half of the global volcanic activity occurs between 30°N and 90°N .

Studies by Lepel et al. (1978), Sedlacek et al. (1982), Phelan et al. (1982), Zoller et al. (1983), and Kotra et al. (1983) indicate that selenium is

Table 5. *Aerial litter fluxes for ecosystems between 30° N and 90° N (adapted from Reiners, 1973)*

Ecosystem	Global area (10 ¹² m ²)	Area between 30° N and 90° N* (10 ¹² m ²)	Aerial litter mass (dry wt.) (10 ² g m ⁻² yr ⁻¹)	Aerial litter flux (10 ¹⁴ g yr ⁻¹)
Swamp and marsh	2	1	10.1	10
Tropical forest	20	0.0	—	—
Temperate forest	18	12	4.0	48
Boreal forest	12	12	2.2	26
Woodland and shrubland	7	4	2.9	12
Savannah	15	0.0	—	—
Temperate grassland	9	8	3.2	26
Tundra and alpine	8	6	1.6	10
Desert shrub	18	8	1.3	10
Extreme rock, ice and desert	24	6	0.005	—
Agricultural land	14	7	3.3	23
Total	147	64		165

* Estimates on our part.

enriched in volcanic plumes compared to fly ash. The enrichment factor (EF_{ash}), in this case, is defined as:

$$EF_{ash} = \frac{(C_X/C_R)_{plume}}{(C_X/C_R)_{ash}} \quad (4)$$

The above authors concluded that selenium is volatilized during volcanic activity, and then condenses onto aerosols in the fine particle range. To calculate selenium emissions from volcanic activity Phenan et al. (1982) recommended that selenium plume concentrations be normalized to those of total sulphur, because they are more closely associated with the release of sulphur than to volcanic ash. The authors performed such a

calculation using data from the Mt. St. Helens plume and obtained a global selenium flux, from volcanic activity, of 1×10^8 g Se yr⁻¹.

Using the method described by Phelan et al. (1982) volcanic selenium emissions north of 30° N were calculated. The results of these calculations are in Table 6. Flux estimates range between 0.2 – 6.2×10^8 g Se yr⁻¹. Further evidence supporting the theory that selenium is volatilized during volcanic activity is the selenium to sulphur ratio in fumarol gases at different temperatures (Suzuoki, 1964). As the temperature of the fumarol gases decreased less selenium was found in the gaseous phase. At temperatures of 450 °C the ratio of selenium to sulphur was about 5×10^{-5} , at temperature around 150 °C the ratio was about 10^{-7} .

Table 6. *Atmospheric selenium emissions from volcanic activity between 30° N and 90° N*

Volcano (year)	Se/S ratio ($\times 10^4$)	Emissions* (10 ⁸ g Se yr ⁻¹)	Reference
Mt. St. Helens (1980)	5.7	2.6	Vossler et al. (1981)
Mt. St. Helens (1980)	0.2	0.4	Pelan et al. (1982)
El Chichón (1982)	0.09	0.2	Kostrá et al. (1983)
Augustine (1976)	3.1	6.2	Lepel et al. (1978)
Nasudake fumaroles ($T = 450$ °C)	0.54	1	Suzuoki (1964) (excluded)
($T = 120$ °C)	0.001	0.002	

* Emissions were calculated by assuming that 50% of all volcanic activity occurs north of 30° N and that yearly sulphur emissions are 4×10^{12} g yr⁻¹ (Cadle, 1975).

2.3.4. *Weathering and wind blown soil dust.* Goldberg (1971) estimated that weathering and the wafting of soil produce 5×10^{14} grams of atmospheric particulates (under $5 \mu\text{m}$ in radius) a year. The concentration of selenium in crustal material was taken to be 0.05 p.p.m. (Mason, 1966). Thus, the global flux of selenium is $2.5 \times 10^8 \text{ g Se yr}^{-1}$. As upper limit, it was assumed the land area between 30°N and 90°N which is capable of producing soil dust is $60 \times 10^{12} \text{ m}^2$ (40% of the global land total). For the region of study the flux is estimated to be $1.0 \times 10^8 \text{ g Se yr}^{-1}$.

2.3.5. *Atmospheric selenium from sea spray.* To calculate the atmospheric flux of selenium from sea spray, it was assumed that the ratio of selenium and sulphur in sea salt aerosols is the same as their ratio in bulk sea water. Also, there is no fractionation of selenium during the production of sea salt aerosols.

The ratio of selenium to sulphur in crustal reference materials is about 1×10^{-4} (Mason, 1966), while in bulk sea water the ratio is 1.5×10^{-7} (Broecker and Peng, 1982). The depletion of selenium in the oceans with respect to sulphur is due to differences in their removal processes. In the ocean the predominant inorganic forms of selenium are selenite and selenate (Wrench and Measures, 1982). These ions are readily absorbed on to metal hydroxide precipitates of iron and manganese, organic matter, and ferric sulphides; sulphate on the other hand is not (Goldschmidt, 1954; Handbook of Geochemistry, 1974).

Measures and Burton (1980) measured selenium concentrations in sea water at sites in the north-eastern Atlantic Ocean. The authors found the profile of selenium concentration with respect to ocean depth was similar to that of a nutrient element; depletion in surface waters and a gradual increase to a constant value at deeper oceanic layers. Total selenium in the first 500 meters ranged between $3.3\text{--}5.1 \times 10^{-8} \text{ g Se (l sea water)}^{-1}$. These concentrations are about 50% smaller than the concentration of selenium in bulk sea water ($1.1 \times 10^{-7} \text{ g Se l}^{-1}$; Goldberg, 1963).

Ryaboshapko (1983) using a mass balance approach estimated the global sulphur flux to the atmosphere from sea salt to be $140 \times 10^{12} \text{ g S yr}^{-1}$. Thus, the corresponding selenium flux is $0.21 \times 10^8 \text{ g Se yr}^{-1}$. For the region of study the selenium sea salt flux is 18% of this value and insignificant in comparison to the other fluxes.

A second estimate of the selenium flux from sea spray was calculated by normalizing selenium concentrations in sea water to those of sodium. The annual sodium flux from the oceans to the atmosphere has been estimated to be $1.5 \times 10^{15} \text{ g Na yr}^{-1}$ (Duce et al., 1983). Taking the sodium concentration in sea water to be $1.1 \times 10^{-1} \text{ g kg}^{-1}$ (Goldberg, 1963) and the selenium concentration in surface sea water to be $4 \times 10^{-8} \text{ g kg}^{-1}$ (Measures and Burton, 1980). The global selenium flux is then estimated to be $5.5 \times 10^8 \text{ g Se yr}^{-1}$. The above calculation provides further evidence that the selenium flux to the atmosphere due to sea salt particle production is small.

2.3.6. *Oceanic biogenic emissions.* To calculate biogenic selenium emissions from the ocean it was assumed in clean marine air that the only sources of particulate selenium is the scavenging of volatile organo-selenides onto aerosols and gas to particle conversion. These assumptions are based on the calculation from the previous section which indicated that sea spray is a negligible source of atmospheric selenium.

The biogenic flux from the oceans in the region of study is estimated to be $9 \times 10^8 \text{ g Se yr}^{-1}$. In the calculation 120 pg m^{-3} (the lower limit of the geometric mean) was used as the particulate selenium concentration in marine air unaffected by continental sources. Also, it was assumed that the residence time of marine aerosols is three days (Kritz and Rancher, 1980), the marine boundary layer is 1000 m, and that there is a steady-state between sources and sinks.

It should be noted that in the region of study there may not be marine air unpolluted by continental aerosols. If this is the case, then the flux calculation is an over estimate. However, if biogenic emissions are the major source of particulate selenium in the marine atmosphere then the temporal and spatial variability of particulate selenium should be closely correlated to the spatial and temporal variability of primary production in the oceans.

2.4. Sinks for atmospheric selenium

2.4.1. *Wet deposition.* Fig. 2 is the plot of the annual mean selenium concentrations in rain water at some rural locations versus the corresponding aerosol concentrations. The least square fit to the data is:

$$\log(R_f) = -0.4716 + 0.6535 \cdot \log(A_f) \quad (5)$$

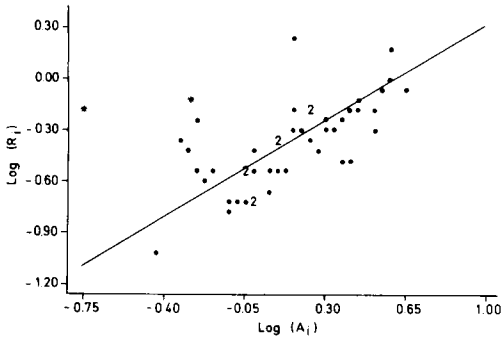


Fig. 2. Concentration of selenium in rainwater ($\mu\text{g Se l}^{-1}$) vs aerosol concentration (ng Se m^{-3}). The stars represent data which have a scavenging ratio (R_i/A_i) greater than two times the geometric mean. These data were not used in the regression calculation. Least square fit to data is:

$$\log(R_i) = -0.4716 + 0.6535 \log(A_i)$$

r^2 is 0.49 for 46 points.

($r^2 = 0.49$; for 46 points), where R_i is the concentration of selenium in rain water ($\mu\text{g Se l}^{-1}$), and A_i is the corresponding aerosol concentration (ng Se m^{-3}). The rain water and aerosol data used in the regression calculation are listed in Ross (1984). Both the soluble and insoluble fractions of selenium have been included in the precipitation values.

To determine the selenium concentration in atmospheric precipitation eq. (5) was used and the geometric mean aerosol concentrations (ranges) listed in Table 2. The rain fluxes for the urban and intermediate regions were determined by assuming the land area for each region is evenly distributed between 30°N and 60°N . Table 7 is a summary of

the calculations of yearly wet deposition of selenium between 30°N and 90°N .

2.4.2. *Dry deposition.* The removal rate of particulate selenium by dry deposition can be written as:

$$S_d = \int_0^\infty V_d(r) C(r) dr \approx \sum_i V_{d_i} C_i \tag{6}$$

where V_d is the "deposition velocity" of the particles, and C the selenium concentration. The "i" refers to the different class sizes. In the above formulation exact knowledge of the mass distribution is needed because V_d is strongly dependent on particle size. In general, when dry deposition is calculated over all particle sizes, coarse particles (greater than $2.0 \mu\text{m}$ diameter) will dominate because of their large deposition velocity. Therefore in the calculation, particulate selenium was only separated into coarse and fine (less than $2.0 \mu\text{m}$ diameter) particulate modes.

The percent distribution of selenium mass for the two size ranges is given in Table 8. For continental regions, the data was taken from Rahn (1971). The oceanic distribution was derived from measurements by Duce et al. (1976). To determine mean particle sizes, the size distribution of selenium mass was assumed to be the same as the overall particle size distribution. Mean particle sizes, as reported by Whitby (1978) for the two size classes are $0.3 \mu\text{m}$ and $6.0 \mu\text{m}$. Deposition velocities, as estimated by Slinn (1977), are 0.005 and 1.0 cm s^{-1} , respectively. The results of the calculation are listed in Table 8.

Peirson et al. (1973), Pattenden (1974) and Cambray et al. (1975) measured the monthly dry deposition of selenium onto filter paper which was placed 1.0 m above the ground and under a

Table 7. Wet deposition of selenium between 30°N and 90°N

Geographical region	Rain flux ($10^{12} \text{ m}^3 \text{ yr}^{-1}$)	$\text{Log}(A_i)$	Se in rain (10^{-6} g l^{-1})	Wet deposition ($10^8 \text{ g Se yr}^{-1}$)
Urban	0.42	0.492 ± 0.278	0.47-1.1	2.0-4.6
Intermediate	9.1	0.028 ± 0.240	0.25-0.51	22-46
Remote/continental	34.7	-1.030 ± 0.458	0.036-0.14	12-49
Oceanic	47.5	-0.628 ± 0.341	0.079-0.22	38-100
Total				74-200

Wet deposition fluxes were calculated using eq. (5) and particulate selenium concentrations in surface air listed in Table 2.

Table 8. Dry deposition of particulate selenium between 30° N and 90° N

Geographic region (area 10 ¹² m ²)	Se mass distribution (in percent)		Dry deposition	
	Fine (<2 μm)	Coarse (>2 μm)	Rate* (g Se m ⁻² s ⁻¹)	Sink (10 ⁸ g Se yr ⁻¹)
Urban (0.5)	50	50	0.80–3.0 × 10 ⁻¹¹	1.3–4.6
Intermediate (10.9)	86	14	0.85–2.6 × 10 ⁻¹²	2.9–8.9
Remote/continental (52.2)	77	23	0.78–6.1 × 10 ⁻¹³	1.3–10
Oceanic (63.9)	75	25	2.8–13 × 10 ⁻¹³	5.6–26

* Assumed mean particle sizes were 0.3 μm for fine particles and 6.0 μm for coarse particles (Whitby, 1978); deposition velocities were taken to be 0.005 and 1.0 cm s⁻¹, respectively (Slinn, 1977). Ranges of the geometric mean particulate selenium concentrations listed in Table 2 were used in the calculations.

protective canopy. For intermediate areas, dry deposition rates from their data are consistent with our value. For urban areas our result is a factor of ten higher. This could be due to an improper mass distribution in the calculation, or the urban locations where the authors measured dry deposition are not representative of typical urban areas.

Estimates of a dry deposition sink for vapor phase selenium were not attempted because there is too little data. Before reasonable estimates can be made, more measurements of vapor phase selenium are needed, and the reactivity of alkyl-selenides in the atmosphere need to be studied.

3. Discussion and conclusions

Table 9 is the summary of our atmospheric selenium budget for the region 30° N to 90° N. Despite the many uncertainties in the calculations the sinks in the budget are comparable to the sources. With respect to the sources of atmospheric selenium, the greatest uncertainties are in the calculations of biogenic emissions. Soil emissions were estimated by assuming a direct correlation between sulphur and selenium emissions. The biogenic flux from terrestrial biota was calculated by assuming all forms of biota release alkyl-selenides to the atmosphere, and at approximately the same rate. Marine biogenic emissions were estimated by assuming the residence times of organo-selenides in the atmosphere are similar to those of reduced sulphur compounds. While these assumptions are based on laboratory studies, field

measurements must be performed to assess their validity in the real world.

Assuming the atmosphere is in a steady state with respect to selenium, the residence time of atmospheric particulate selenium is:

$$T_0 = \frac{M}{S} = \frac{M}{Q}, \quad (7)$$

where M is the total amount of selenium in the atmosphere, S the total sink, and Q the total flux into the atmosphere. Assuming a scale height of 1500–2000 m, and using the geometric mean aerosol concentrations of selenium, the residence time would be around 0.8–4 days. This means that selenium could be transported through the atmosphere several thousand kilometers from its source.

Rodhe and Isaksen (1980) estimate the residence time of sulphur in the first three kilometers to be four days. Ryaboshapko (1983), using a mass balance approach, estimates sulphur has a residence time of 1.5 days. The similarity in the residence times of sulphur and selenium is not surprising, since many of the selenium fluxes were calculated by assuming a correlation exists between sulphur and selenium emission rates.

However, there are important differences in their sources and atmospheric cycles. Sea spray is considered to be a major source of atmospheric sulphate, while it is a negligible source for selenium. Also, the calculations indicate that biota release significant amounts of selenium to the atmosphere. In sulphur budgets land biota is not considered a major source of reduced sulphur compounds.

Table 9. A selenium budget for the global region 30° N to 90° N (units: 10^8 g Se yr⁻¹)

Sources		Sinks	
Anthropogenic emissions from:		Wet deposition over:	
industrial processes	18	land	36–100
fossil fuel combustion	41–56	ocean	38–100
Biogenic emissions from:		Dry deposition over:	
soils	2.4	land	5.5–24
terrestrial biota	14	ocean	5.6–26
marine biota	9		
Volcanic emissions	0.2–6.2		
Soil dust	1.0		
Sea spray	small		
Total	86–107		85–250

The temporal variations in selenium and sulphur aerosol concentrations are also different. Weiss et al. (1971), measured selenium and sulphur concentrations in Greenland ice. The authors found that selenium levels were approximately constant between 800 B.C. to 1965, while sulphur levels increased. The authors explain the differences in trends in terms of the chemical reactivity of sulphur and selenium, which allows sulphur to be mobilized and transferred greater distances. On shorter time scales the particulate selenium concentrations at Chilton, Oxfordshire (Salmon et al., 1977) decreased between 1957 and 1974, while sulphur concentrations increased. We would explain the differences in trends as being due to changes in anthropogenic activity in the region which lowered selenium emissions but increased those of sulphur.

Selenium levels in remote areas of the world should be relatively constant because the residence time of selenium from urban regions is relatively short, and local biogenic sources will be larger than any selenium which is transferred from polluted regions. To verify this hypothesis, measurements of selenium in soils and lake sediments need to be performed. Also, further measurements of selenium in polar ices would be very valuable.

One of the outstanding features of the atmos-

pheric selenium cycle is its atmospheric enrichment, compared to soil dust, in remote regions of the world. Zoller et al. (1974) obtained an enrichment factor for selenium at the South Pole of 16000. Duce et al. (1975), in the north Atlantic, calculated an enrichment factor of 10000. Adams et al. (1977) measuring particulate selenium on Chacaltaya Mountain, Bolivia obtained an enrichment factor between 780–1600. The flux calculations indicate selenium derived from soil dust is a very small part of the total source strength. Therefore, it is not surprising that atmospheric selenium is poorly correlated to soil dust. We explain these high enrichment factors in both continental and marine environments as being due to biogenic emissions.

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