

Biogeochemical Cycling of Iodine and Selenium and Potential Geomedical Relevance

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Introduction

An increasing number of the 92 naturally occurring elements on Earth are now known to be essential to humans and other vertebrate species. In addition to the ten main constituents (H, N, O, Na, Mg, P, S, Cl, K, Ca), twelve elements present in trace quantities are generally accepted to have necessary functions in the human body. These essential trace elements are Mn, Cr, Fe, Co, Cu, Zn, Se, Mo, F, bromine (Br), Si, and I. Most of these elements are present in human serum at levels orders of magnitude lower than their mean concentrations in the Earth's crust (e.g., Mn and Cr are less than 10^{-6} of average rock composition), except for I and Se, which occur in similar concentrations in human serum and in rocks. This indicates that the pathways of these two elements to humans are basically different from those of other essential trace elements. There is now substantial evidence to suggest that the marine environment is an important source of I and Se to humans and other terrestrial species through biogeochemical cycling involving atmospheric transport.

The Ocean as a Source of Elements to Humans and Livestock

The dissolved matter in ocean water is enriched relative to the earth's crust in a few elements (e.g., Na, Mg, S, Cl, Br) but depleted in most others. Some elements, such as I and Se, are strongly enriched in ma-

rine organisms relative to their concentrations in sea water. Fish and other marine food may constitute an important source of these elements to humans. It has become increasingly evident, however, that atmospheric transport of substances from marine to terrestrial systems may constitute an alternative pathway of some essential elements to humans and livestock.

Elements may be released from the ocean surface as:

- Seasalt aerosols (Na^+ , Mg^{2+} , Cl^- , SO_4^{2-} , etc.)
- Biogenic gases (CH_3S , CH_3I , etc.)

In addition, some elements may be enriched in surface-active material present on the surface of the ocean (Dean 1963) either from atmospheric deposition of particulate material or from enrichment in marine biota from which the material is derived. When bubbles burst on the ocean surface, this micro-layer may be enriched on salt particles formed and thus be preferentially released to the atmosphere.

The importance of the marine environment as a source of cation supply to coastal areas in Norway was convincingly demonstrated in a study of forest soils by Låg (1968). Later work in Norway on natural surface soils (Njåstad et al. 1994) and lake waters (Allen and Steinnes 1986) has confirmed that atmospheric cycling

processes play an important role in supplying elements such as Na and Mg to the terrestrial surface in coastal regions. Similarly, the concentrations of halogens (Cl, Br, I) in natural surface soils were shown to be several times higher near the coast of mid-Norway than in areas east of the Caledonian Mountain Range where the marine influence is small (Låg and Steinnes 1976). A similar geographical trend was shown for Se, which is present in the ocean at a level of only $0.1 \mu\text{g L}^{-1}$ (Låg and Steinnes 1974, 1978), and it was hypothesized that there might be a marine source for the excess Se in the coastal soils.

In the following, the present knowledge on the biogeochemical cycling of I and Se in relation to the marine environment is briefly reviewed, and some possible geomical consequences are indicated.

Iodine

It has been obvious for a long time that iodine must be released from the ocean in another form than seasalt aerosols. Whereas the Cl/I ratio in ocean water is about 3×10^5 , it is generally 100–1000 times lower in precipitation samples collected in marine air (Seto and Duce 1972) and another factor of 10 lower in natural surface soils (Låg and Steinnes 1976). Different hypotheses for the nature of the separation process causing iodine enrichment in the marine atmosphere relative to the sea water have been presented. Miyake and Tsunogai (1963) proposed a photochemical oxidation of iodide to elemental iodine in the surface layer of the sea. On the other hand, an observation that the iodine in the atmosphere is to a great extent present in organic form (H.I. Svensson and E. Eriksson, cited in Bolin 1959) led Dean (1963) to suggest that iodine may be enriched in the organic surface microlayer and correspondingly enriched on the salt particles formed when bubbles break through the surface. More recent research has indicated that the main source of iodine in the marine atmosphere may be CH_3I produced by biological activity in the surface water (Whitehead 1984).

Selenium

As far as is known, the first indication that the ocean might be a source of selenium to the terrestrial environment came from an investigation by Låg and Steinnes (1974, 1978). In a study on the geographical

distribution of trace elements in the humus layer of forest soils, they found that the Se concentration near the coast of mid-Norway was as much as 5 times higher (1.0 versus 0.2 ppm) than in areas of eastern Norway shielded from oceanic influence by high mountains. Låg and Steinnes (1974) put forward the hypothesis that the excess Se observed in the coastal surface soil may have been supplied by precipitation, with the marine environment as a source.

At first sight, this hypothesis might seem rather unlikely since the Se concentration in ocean water is very low, about $0.1 \mu\text{g L}^{-1}$ (Cutter and Bruland 1984). Further studies in Norway on natural soils (Steinnes 1991), agricultural soils (Wu and Låg 1988), and ombrogenous peat (Steinnes 1997) and in Sweden on forest soils (Johnsson 1989) verified and reinforced the original findings by Låg and Steinnes (1974). Studies of atmospheric deposition of Se based on analysis of terrestrial mosses (e.g., Steinnes et al. 1992) confirmed a strong coast-inland gradient, as illustrated in Figure 8.1. Investigations of Se in peat cores from ombrotrophic bogs showed that the same trend was evident before the Industrial Revolution (Steinnes 1997). Although the selenium in the sea water could hardly be a source of excess Se in coastal areas as such, the possibility of a biologically driven cycling of Se, in a similar way as indicated above for I, could not be excluded. It was already known that Se is enriched in marine food chains (Lunde 1968).

Thus, there is strong evidence from research carried out in Norway that the ocean is a significant source of Se to coastal terrestrial areas, presumably through biogeochemical cycling processes. More recent evidence from marine studies appears to confirm this hypothesis:

- Cutter and Bruland (1984) determined the concentration level of Se in the ocean to be of the order of $0.1 \mu\text{g}^{-1}$, and that organic selenide made up around 80 % of total dissolved Se in ocean surface waters.
- Mosher et al. (1987) observed anomalous enrichment of Se in marine aerosols, and found that the Se concentration was related to primary productivity in the sea.

- Cooke and Bruland (1987) studied the speciation of dissolved Se in surface water, and observed the formation of volatile organoselenium compounds, mainly dimethyl selenide, $(\text{CH}_3)_2\text{Se}$. On that basis they hypothesized that outgassing of dimethyl selenide may be an important removal mechanism for dissolved Se from aquatic systems.
- Amouroux and Donard (1997) observed emission of Se to the atmosphere via biomethylation processes in the Gironde estuary, France.

Altogether, these observations appear to confirm that biological processes in the surface ocean water provide a dominant source of atmospheric Se supply to coastal regions.

Still, one important question remains to be answered in order to close the natural biogeochemical selenium

cycle: What are the chemical transformations of Se when it leaves the ocean until it is supplied to the terrestrial surface and eventually is bound in the surface soil? This knowledge is also relevant with respect to another important issue: to what extent does Se derived from the marine environment enter terrestrial food chains? More research needs to be done to answer these questions.

Potential Geomedical Relevance

An extensive discussion of the geomedical importance of the above findings is beyond the scope of this chapter. From the literature, however, there are numerous examples that deficiency problems related to I and Ss are evident in many populations around the world (Låg 1990). These problems are more prominent in certain geographical areas than in others, and often related to predominant consumption of locally derived food.

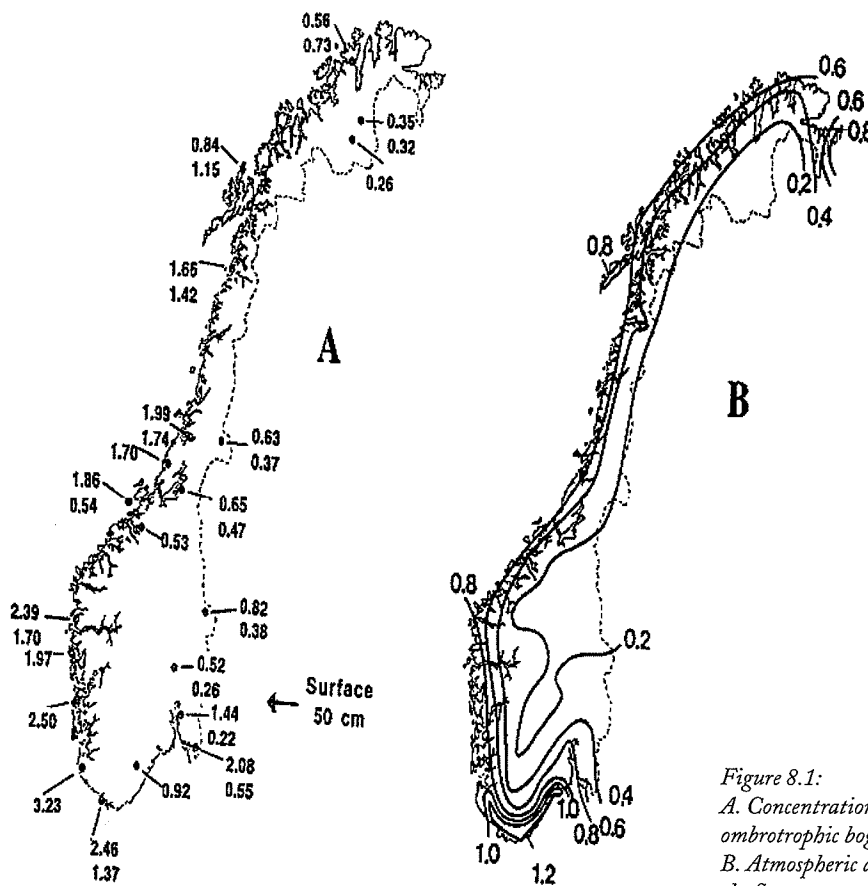


Figure 8.1:

A. Concentrations of selenium (ppm dry weight) in Norwegian ombrotrophic bogs in the surface peat and at 50 cm depth.
B. Atmospheric deposition of selenium in Norway as illustrated by the Se concentration (ppm dry weight) in naturally growing moss.

For example, some populations may live in territories where the bedrock contains too little quantities of I and Se. The soil in these areas may not provide sufficient amounts of these elements to prevent deficiency problems in the people, and in their domestic animals, if they are dependent on locally grown plants. Problems related to I and Se deficiency may therefore be more widespread, especially in developing countries, than has been so far anticipated.

Conclusions

Iodine and selenium are released from the ocean surface through volatile organic substances resulting from biogenic processes in the water. These elements are also enriched in surface soils, peats, and lake waters in coastal areas of Norway relative to corresponding areas farther inland. On the basis of these observations and evidence from international marine research, it is argued that biogeochemical cycling of I and Se from the ocean may be a significant source of these elements to the coastal terrestrial environment in general. Since these biologically essential elements often occur in very low concentrations in crustal rocks, the atmospheric supply of I and Se could be a significant geomedical factor in many areas of the world, and deficiency problems would most likely occur in regions far from the ocean.

References

- Allen, R.O. and Steinnes, E., 1986. A contribution to the geochemistry of lakes in Norway. *NGU Bulletin*, v.409, p.35-48.
- Amouroux, D. and Donard, O.F.X., 1997. Evasion of selenium to the atmosphere via biomethylation processes in the Gironde estuary, France. *Marine Chem.* v.58, p.173-188.
- Bolin, B., 1959. Note on the exchange of iodine between the atmosphere, land and sea. *Int. J. Air Poll.* v.2, p.127-131.
- Cooke, T.D. and Bruland, K.W., 1987. Aquatic chemistry of selenium: Evidence of biomethylation. *Environ. Sci. Technol.* v.21, p.1214-1219.
- Cutter, G.A. and Bruland, K.W., 1984. The marine biogeochemistry of selenium: A re-evaluation. *Limnol. Oceanogr.* v.29, p.1179-1192.
- Dean, G.A., 1963. The iodine content of some New Zealand drinking waters with a note on the contribution from sea spray to the iodine in rain. *N. Z. J. Sci.* v.6, p.208-214.
- Johnsson, L., 1989. Se levels in the mor layer of Swedish forest soils. *Swed. J. Agric. Res.* v.19, p.21-28.
- Låg, J., 1968. Relationships between the chemical composition of the precipitation and the content of exchangeable ions in the humus layer of natural soils. *Acta Agric. Scand.* v.18, p.148-152.
- Låg, J., ed., 1990. *Geomedicine*. CRC Press, Boca Raton. 278 pp.
- Låg, J. and Steinnes, E., 1974. Soil selenium in relation to precipitation. *Ambio* v.3, p.237-238.
- Låg, J. and Steinnes, E., 1976. Regional distribution of halogens in Norwegian forest soils. *Geoderma* v.16, p.317-325.
- Låg, J. and Steinnes, E., 1978. Regional distribution of selenium and arsenic in humus layers of Norwegian forest soils. *Geoderma* v.20, p.3-14.
- Lunde, G., 1968. Activation analysis of trace elements in fishmeal. *J. Sci. Fd. Agric.* v.19, p.432-434.
- Miyake, Y. and Tsunogai, S., 1963. Evaporation of iodine from the ocean. *J. Geophys. Res.* v.68, p.3989-3993.
- Mosher, B.W., Duce, R.A., Prospero, J.M. and Savoie, D.L., 1987. Atmospheric selenium: Geographical distribution and ocean to atmosphere flux in the Pacific. *J. Geophys. Res.* v.92, p.13277-13287.
- Njåstad, O., Steinnes, E., Bølviken, B. and Ødegård, M., 1994. National survey of element composition in natural soil. Results for samples collected in 1977 and 1985 obtained by ICP emission spectrometry. Report NGU 94.027, Geological Survey of Norway, Trondheim, 113pp (In Norwegian).
- Seto, F.Y.B. and Duce, R.A., 1972. A laboratory study of iodine enrichment on atmospheric sea-salt particles produced by bubbles. *J. Geophys. Res.* v.77, p.5339-5349.
- Steinnes, E., 1991. Influence of atmospheric deposition on the supply and mobility of selenium and cadmium in the natural environment. In Låg, J., Ed., *Human and animal health in relation to circulation processes of selenium and cadmium*, pp. 137-152.
- Steinnes, E., 1997. Trace element profiles in ombrogenous peat cores from Norway: evidence of long range atmospheric transport. *Water, Air, Soil Pollut.* v.100, p.405-413.
- Steinnes, E., Rambæk, J.P. and Hanssen, J.E., 1992. Large scale multi-element survey of atmospheric deposition using naturally growing moss as biomonitor. *Chemosphere* v.25, p.735-752.
- Whitehead, D.C., 1984. The distribution and transformation of iodine in the environment. *Environ. Internat.* v.10, p.321-339.
- Wu, X. and Låg, J., 1988. Selenium in Norwegian farmland soils. *Acta Agric. Scand.* v.38, p.271-276.