

Selenium and Soils in the Western United States

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Selenium has come to the public's attention lately because of news reports from widely divergent areas. At times selenium has been used as a nutritional supplement for both humans and animals, mainly cattle. There have been other reports of poisoning from selenium and concern for its effect on the environment. The purpose of this article is to draw together some of the research from highly specialized areas in an attempt to gain a more well rounded perspective of this natural chemical element. The history of selenium research goes back almost 70 years when selenium was first proven to be the toxic agent responsible for widespread livestock poisoning in the Western United States. Two common livestock diseases which had been around for centuries, "alkali disease" and "blind staggers", were discovered to be the result of livestock foraging on certain plants growing on soils with a high selenium content. Orville Beath, a chemist at the University of Wyoming, found that certain plant species not only grew well in seleniferous soils, but some species could also collect large amounts of selenium in their cells without detrimental effects. However, large, potentially toxic amounts of selenium could be passed on to the animals and humans who consumed vegetation grown in seleniferous soils. Beath called these plants "indicator plants" because their presence indicated that selenium was present in the soil. Research has been ongoing as scientists from a wide variety of backgrounds and disciplines have worked to understand better the chemical behavior of selenium in water, soils, plants, animals and humans. This is especially important, as selenium has been determined to be an essential trace element for optimum human and animal health. However it has also been shown that even small amounts over the normal levels, can lead to chronic or acute toxicity, or selenosis, and have a destructive effect on the environment. This article will give a brief overview of the chemistry of selenium and how it enters the soil, water, plants and animal systems.

Introduction

Selenium is a fascinating, if little studied element on the periodic table. It's chemistry is complex and until fairly recently, little was understood

about the complexity of its chemical behavior and interactions. Selenium is a naturally occurring chemical element found almost everywhere on earth. It is usually found in rocks, where it eventually finds its way into the soil and water systems, then into plants and animals, and eventually into the people who eat those plants and animals. Selenium is a trace mineral absolutely necessary for optimum human and animal health. The RDA (Recommended Daily Allowance) is 50-55 micrograms per day for women, 70 micrograms p/day for men (U.S. Public Health Statement on Selenium, 1996).

Selenium supplements have been promoted as an aid in preventing cancer. It is believed to act much like vitamin E in helping to prevent the damage done to cell tissue by oxidation. At the same time, certain types of selenium compounds, such as selenium sulfide, have been thought to cause cancer. A normal diet containing grains cereals and meat is considered to be sufficient to avoid the harmful effects of insufficient selenium intake. However, even small amounts of 5-10 times the RDA can cause toxicity or chronic selenosis. An overdose of selenium supplements can cause death. Since selenium is a naturally occurring element and so widely prevalent in varying amounts in a variety of soils, plants and animals, a better understanding of selenium chemical interaction in solid, liquid and gaseous form is essential.

The government has also found that, of the 1,430 current or former hazardous waste sites on the National Priorities List, at least 367 have varying amounts of selenium present (ATSDR - Public Health Statement: Selenium 1989). The government considers this noteworthy, since overexposure to selenium can have a detrimental effect on human and animal health. For a complete description of the effects of selenium on human health and a summary of studies that have been done, see the Toxicological Profile for Selenium (NTIS PB97-121032xsp) put out by the U.S. Public Health Service.

Overview and History

Selenium is particularly concentrated in the soils of the drier regions of the world where the soil tends to be more alkaline. In North America, selenium is found in high concentrations across the Great Plains, the Prairie Provinces of Canada, westward to the Pacific, and south into Mexico. It is especially concentrated in the soils of Wyoming and South Dakota. Selenium also occurs in alkaline soils in certain localities in Columbia, Ireland, Israel, South Africa and China. Crop analyses show selenium occurring in Argentina, Venezuela, Spain, Bulgaria, Algeria, Morocco, Australia, New Zealand and in some of the drier regions of the

former Soviet Union.

Martin (1973) gives a brief overview of how selenium poisoning in livestock may have figured in history. The first recorded account may have been by Marco Polo in 1295. Polo wrote about a strange disease that affected pack animals on the border of western China near Turkestan and Tibet. After grazing on plants there, the animals' hoofs began to fall off, a symptom that is now recognized as characteristic of chronic selenosis. Martin also speculates that selenium poisoning may have been a critical factor in the delay of the cavalry scheduled to relieve General Custer at the Battle of the Little Big Horn in Montana. In his official report the officer in charge of the relief troops wrote that the delay was due to a "peculiar sickness" that the horses developed in travelling through what are now known to be seleniferous regions. Orville Beath gives an overview of these mysterious diseases as they occurred in the historical accounts of people settling in geographic areas with seleniferous soils. He notes that, as the occurrences of selenium toxicity in livestock in the western U.S. began to be traced, the soil seemed to be an important factor in the occurrence of disease. All cases investigated were on soils derived from Pierre shale. The disease was focused over the entire area of these soils, but was not evenly distributed (Rosenfeld and Beath 1964). Part of the difficulty and complexity of the problem is that, in a single locality, selenium can be present in soluble, insoluble and gaseous forms.

Chemistry of Selenium

Selenium (Se) was first discovered in Sweden in 1818. Berzelius investigated a residual slime he found forming during the oxidation of sulfur dioxide from copper pyrites and noted the new element (Krief 1988). Krief also points out that, as early as the fourteenth century, Arnold of Villanova had noticed a curious red sulfur deposit which he called "sulfur rubeum" forming on the oven walls after sulfur had been condensed. However it was not until the 1950's that selenium was recognized as being an essential trace mineral in human and animal nutrition. Its chemical adaptability makes the study of selenium's effects on the environment somewhat difficult. Directly below sulfur in the periodical table, and above tellurium, its chemistry is similar to both of these. Selenium (Se) combines with both metals and non-metals, directly and hydrochemically. It can form both organic and inorganic compounds. It is an oxidant as well as a reductant, an important factor in soil formation. Selenium salts resemble the corresponding sulfur and tellurium salts in behavior. Its chemical adaptability accounts for its widespread occurrence in soils, plants, animals and humans. Behaving

chemically like sulfur, selenium quickly becomes toxic in higher doses; five times more poisonous than arsenic. Not only does selenium dosage and accumulation have a narrow range between safety and danger, but the range of optimal beneficial action is very narrow and still has not been determined with certainty.

For a review of the biogeochemistry of selenium and the effects of its presence on plants, animals and humans, see Wilber (1983). For details on the chemistry of selenium compounds and derivatives, see Patai and Rappoport (1986) and Klayman (1973). Klayman includes selenium heterocycles, peptides, amino acids and ketones, along with a discussion of selenium's nutritional importance to plants, animals and humans, and a discussion of its potential as a chemotherapeutic agent.

Selenium in Soils

Selenium is a naturally occurring element found in rocks, soil and water. Its original source was probably volcanic activity. It forms compounds with 16 other elements and is found naturally in igneous rocks, volcanic sulfur deposits, hydrothermal deposits, copper deposits, and in sedimentary rocks such as sandstone, carbonaceous siltstones, phosphorite rocks, limestone, iron, coal and some crude oil deposits. Selenium enters the soil profile through the weathering of selenium-rich rocks. Selenium particles move through the soil until adsorbed on clay particles, iron hydroxides or organic particles. Through water and wind erosion and sedimentation processes these particles are distributed and deposited into top soil. Fungi and bacteria do their part in the oxidation process. Sarathchandra and Watkinson (1980) first reported on a strain of bacteria they had isolated that showed an important step in the biological cycle of selenium. They were able to oxidize elemental selenium into selenite and selenate in the laboratory.

Selenium weathered from rocks under alkaline and oxidizing conditions forms selenates, which are highly toxic. Selenite and selenates are produced by soil microorganisms from less soluble forms of selenium. These forms are highly soluble in alkaline soils, thus facilitating uptake of selenium by certain plants. Rainy regions are less likely to experience the problem from naturally occurring selenium because selenium and other salts have been flushed from the soil profile. Selenium does not occur in sedimentary rocks from the pre-Cretaceous period such as those in the northeastern U.S., or in the coastal regions where the soils are formed by coastal deposits or recent volcanic ash. There are also low-selenium areas in Montana and Idaho where the soil is formed from granites and old metamorphic rock; and areas in Arizona and New

Mexico where the soil is formed from tertiary volcanic rock (Ullrey 1981). These areas also tend to correspond to areas where selenium-deficiency disorders such as white muscle disease tend to occur. Nationwide selenium deficiency in livestock is a far more common occurrence than toxicity. More typically selenium is added to livestock feed as a supplement because the element is lacking in the locally grown forage.

When selenium occurs in alkaline soils (such as those of the Western U.S., the site of the most recent volcanic activity) and becomes oxidized as selenate, the selenium becomes water-soluble. This form is highly toxic and easily leached from the soil and available to plants. In acid soils, whether selenium occurs as a trace element or as selenide (bound to other metals), the selenium is still toxic, but being bound to other metals, it is not actively available to plants to work its way into the food chain.

The concentration of selenium in most normal soils is estimated to be 0.2 ppm (Rosenfeld and Beath 1964). Acute toxicity in animals occurs when the vegetation eaten contains 10,000 ppm. Chronic diseases can occur when the ingested food contains from 5-40 ppm over a sustained period of time. Franke (1934) was the first to show that it was the range plants growing on seleniferous soils rather than the alkali salts or water that was the culprit causing "alkali disease" among livestock. Olson (1973) investigated chronic toxicity in cattle and found that chronic selenosis or "alkali disease" could be produced by prolonged feeding of inorganic selenium. However, his results could not necessarily be duplicated suggesting widespread differences in the susceptibility among cattle and other factors in the biological cycle of selenium uptake and absorption that should be further investigated.

In the meantime chemists and botanists were concentrating their studies on the ability of certain plants to absorb selenium from the soil. For early reviews of the literature see Trelease and Martin (1936), Beath (1937) and Moxon (1937). Absorption by plants depends on the chemical form and solubility of the selenium as well as the moisture content of the soil. Some plants require selenium to grow and possess a high content of seleniferous materials, e.g., *Astragalus* (1000 ppm), *Haplopappus* and *Xylorrhiza* (120 ppm). Other plants may not require selenium for growth, but will accumulate the element if grown in seleniferous soils. The first group are known as primary indicator plants because their presence indicates that selenium is actually present in the soil in potentially large amounts. Plants belonging to the second group, such as alfalfa, western wheatgrass, onions and Swiss chard, are called secondary converter plants. While they can grow in selenium-free soils, they can also grow

well in seleniferous soils and accumulate fairly concentrated, potentially toxic amounts. For a discussion of the effect of selenium dosage on the growth of *Astragalus*, see Broyer et al. (1972), and for selenium's effect on alfalfa and clover, see Broyer et al. (1966).

The total concentration of selenium in soils does not directly determine the concentration of selenium in the plants growing on those soils (Lakin 1972). The chemical bonding and reaction patterns are the critical determining factors since different chemical forms vary in their solubility and subsequent availability to plants (Anderson and Scarf 1983). Van Dorst and Peterson (1984) showed that the chemical forms of selenium present in soils and sediments are closely related to the oxidation-reduction potential and pH of the soil. Soil conditions need to be adequate in terms of pH balance and moisture in order to produce plants adequate to meet the nutritional requirements of the animals and humans who consume the vegetation without the increased levels that could lead to chronic overdose.

Summary

The chief factor in determining the distribution of selenium in the soil is the composition of the geological formation (bedrock) that is exposed on the surface or lies beneath the thin mantle of soil. Soluble organic selenium compounds are released through the decay of seleniferous plants (Beath 1935b). Selenium converter plants can produce areas that are highly seleniferous. The roots of the plant system acts like a pump bringing selenium up from the bedrock, and through decay, deposits selenium on the soil surface in a water-soluble form that is easily available to all other plants. Certain bacteria, fungi and algae are capable of reducing selenites, and probably selenates, to elemental form. Elemental selenium can then be converted, under suitable conditions, into other selenites or selenates changing the nature of the soil (Trelease and Beath 1949).

For a comprehensive assessment of the interdisciplinary nature of the selenium issues, see the 1989 Report to the Governor on Selenium in Wyoming. The Task Force identified several areas where more research is needed. To summarize:

1. More precise determination of both toxicity and deficiency levels of selenium in livestock, wildlife and humans.
2. More basic research to determine how selenium is biocycled through soils, water and plants, and applied research to determine the rate of

selenium volatilization from cured crops such as alfalfa, small grains and grass.

3. Coordination of selenium research and mitigation programs among the Western states and between Federal, State and local authorities.

4. Investigation of the possibility of establishing a Selenium Investigation Network through land grant universities, colleges and other universities to facilitate the dissemination of selenium research, educational materials and mitigation procedures.

In light of the fourth recommendation mentioned above, the University of Wyoming Libraries, as a result of a generous donation by Mary Beath, were able to establish the O.A. Beath Selenium Database in honor of Dr. Beath and his research team. For further information and access to an extensive interdisciplinary bibliography of selenium related research, please connect to <http://www.uwyo.edu/lib/search.htm>.

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