Information Paper 3.8.3.2
A Citizen Monitor's Guide to Selenium

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1.0 About this Information Paper

(This section is essentially common to all DQM Information Papers. If you have seen it already, please skip to Section 2 below). This Information Paper is a new type of guidance. It has been created for our new integrated system of guidance and tools for water quality monitoring called "the Data Quality Management (DQM) System". DQM is implemented by the Clean Water Team (CWT) where needed to support collection of reliable data of known quality in a fully documented, scientifically defensible manner. Most DQM materials are delivered in Parameter-Specific Folders, which provide both the traditional "protocol" materials and new, expanded guidance in three types of inter-related documents: Fact Sheet, Information Paper, and Standard Operation Procedures. Background information on the ecological significance of each parameter and the regulatory benchmarks that have been developed for it is summarized in the FACT SHEET. The technical information on measurement methodology provided in this IP with its method-menu. Then there are several detailed standard operating procedures (SOPs) that provide step-by-step instructions for each instrument or kit, as well as instrument-specific Quality Assurance/Quality Control and CCRR directions and data validation checklists.

This Information Paper (IP), a part of the Parameter-Specific Folder for disinfectants and disinfection byproducts (DDB), provides "big picture" technical information on selenium. If you are a Trainer or a Technical Leader of any monitoring project, this may help you select a good method to measure selenium in your water body.

2.0 Introduction

Selenium (Se) is an essential element for humans, animals, and plants in very small concentrations (parts per billion (ppm)). Selenium is a metal found in natural deposits as ores containing other elements. For humans and wildlife the safe between "required" and "toxic" is very narrow.

Selenium is widely distributed throughout the environment, and the processes that control Se distribution are intimately linked to its oxidation state which is affected by pH and redox potential of the media. Its primary source in nature is from volcanic rocks. The secondary natural sources of selenium include metallic sulfides associated with igneous activity and marine shales. Biogeochemical cycling of selenium has resulted in soils rich in Se. Most of the high Se soils are located in arid and semi-arid regions with very low annual precipitation (<2 inches/year).

The greatest use of selenium compounds is in electronic and photocopier components, but they are also widely used in glass, pigments, rubber, metal alloys, textiles, petroleum, medical therapeutic agents, and photographic emulsions. Selenium compounds are released to the environment during the combustion of coal and petroleum fuels; and during the smelting and refining of other metals; through coal, gold, silver, nickel, and phosphate mining; from contaminated landfill leachate; agricultural irrigation, erosion (natural and anthropomorphic); and through oil transport (spills), refining, and utilization.

As a trace element, selenium cannot be eliminated. It moves from one form or environmental compartment to another, often becoming more concentrated in the process. As selenium is released through a variety of industrial and agricultural activities, it can bioaccumulate. It degrades water quality and travels into the food chain, where it reaches fish and birds. Selenium contamination does not result in sudden fish kills but rather causes deterioration and deformity in fish and wildlife over time. Long-term risks from selenium go largely unrecognized, even though it may bioaccumulate and persist in the environment.

For decades constructed wetlands have been used to treat industrial, municipal, and agricultural wastewater nationally and internationally. Although constructed wetlands provide a cost-effective alternative to conventional wastewater treatment they could promote the accumulation of selenium and its bioaccumulation

In order to protect the beneficial uses of water from selenium pollution and to restore damaged ecosystems, a clear understanding of the cause and effect relationship is required. When this cause has been specified alternatives for the control, mitigation or restoration of the ecosystem can be taken.

3.0 Selenium Species

Selenides (Se^{-2}) exist in reducing environments as hydrogen selenide (H_2Se) and as metal selenide. **Elemental selenium** (Se^0) is stable in reducing environments and is typically found in anaerobic sediments. Se^0, is insoluble in water and its chemical oxidation or reduction kinetics are slow. However, Se^0 can be rapidly oxidized to **selenite** or **selenate** by microbial-mediated transformations. Selenate and selenite are both soluble in water and are the most common inorganic oxidation states.

Selenate is considered to be more prevalent than selenite; however, in water samples it is easy to find equal concentrations of both. This issue suggests that other processes, such as biological interactions, adsoprtion-desorption phenomena and physical-chemical parameters, influence the proportion in which selenite is favored in slightly reduced conditions and its salts are less soluble than selenate. It can be reduced to elemental selenium by reducing agents such as ascorbic acid or sulfur dioxide and in acidic environments by microorganisms. Soils have a stronger affinity to absorbed selenite, especially by iron oxides compounds.

Selenate is stable in anoxic environments and its salts are very soluble. It is not as strongly adsorbed, as selenite by soil constituents and the transformations to other selenium species is low. Selenate is also the most mobile form of selenium in aqueous systems, therefore it is the form mostly taken up by plants.

4.0 Selenium and Drinking Water

In 1974, Congress passed the Safe Drinking Water Act. This law requires United States Environmental Protection Agency (EPA) to determine safe levels of chemicals in drinking water which do or may cause health problems. These non-enforceable levels, based solely on possible health risks and exposure, are called Maximum Contaminant Level Goals (MCLG). The MCLG for selenium has been set at 0.05 ppm because EPA believes this level of protection would not cause any of the potential health problems described

Based on this MCLG, EPA has set an enforceable standard called Maximum Contaminant Level (MCL) MCLs are set as close to the MCLGs as possible, considering the ability of public water systems to detect and remove contaminants using suitable treatment technologies. The MCL has been set at 0.05 ppm because EPA believes, given present technology and resources, this is the lowest level to which water systems can reasonably be required to remove this contaminant should it occur in drinking water.

Selenium is an essential nutrient at low levels. However, EPA has found selenium to potentially cause the following health effects when people are exposed to it at levels above the MCL for relatively short periods of time: hair and fingernail changes; damage to the peripheral nervous system; fatigue and irritability. Selenium has the potential to cause the following effects from a lifetime exposure at levels above the MCL: hair and fingernail loss; damage to kidney and liver tissue, and the nervous and circulatory systems.

5.0 Selenium as a Potential Environmental Contaminant

Bioaccumulation can be reach by two processes**: bioconcentration** and **biomagnification**. Bioconcentration, in aquatic ecosystems, is the result of direct uptake of a chemical from the water column or associated sediments. This mechanism can occur due to diffusion, transformation or active transport processes across epithelial or respiratory surfaces. Biomagnification is defined as uptake of a substance by way of the food chain. The chemical is bioaccumulated in lower trophic levels and is passed up the food chain during the feeding and digestive processes of the higher levels. Through each trophic transfer, its concentration increases and results in an accumulation. EPA and the U.S. Fish and Wildlife Service agree that wildlife should be protected from the harmful effects of selenium bioaccumulation.

The toxicity of selenium depends on whether it is in the biologically active oxidized form, which occurs in alkaline soils. These conditions can cause plant uptake of the metal to be increased. It is known that selenium accumulates in living tissues.

Aquatic organisms absorb and reduce **inorganic selenium** during the synthesis of a wide variety of **organic selenide** compounds. Aquatic primary producers concentrate selenium to many times above background water levels. **Biomagnifications** in aquatic food chain may be responsible for higher selenium levels in herbivores and their predators. Most of the time, a substantial portion of the selenium in aquatic ecosystems is in the organic form.

Bioaccumulation in primary producers (algae and aquatic macrophytes) has been well documented. Selenium accumulation by primary producers is thought to be the first step in food-chain uptake. Selenium uptake in these types of organisms has been found to be in competition with sulfur. Experiments with duckweed showed that selenite was absorbed and assimilated approximately three times more readily then selenate, and that biotransformation of Se differed between plants exposed to one form of selenium or the other. The selenium bioaccumulation and transformation are functions of the selenium chemistry of the system, the water quality of the system and the species of primary producers inhabiting the system.

In the early 1980's selenium was identified as a major pollutant in the Kesterson Reservoir Unit of the Kesterson National Wildlife Refuge (now the San Luis National Wildlife Refuge), Merced County, California. Selenium was causing dysfunctions in the reproduction system (teratogenic) impacts on waterfowl due to its bioconcentration, biomagnification and bioaccumulation in the aquatic food chain.

In aquatic systems, selenium concentrates in plankton bioconcentrate in the order of 500 to 2,000 times the selenium concentration in water. Selenium concentrates in sediments, 200-400 times, in the benthic invertebrates 800 to 2,000 times the water concentration; and in fish, depending of the species and tissue sampled in Kesterson from 1,000 to about 35,000 times the water concentration. The selenium concentration levels at Kesterson increased generally from water to sediments, to aquatic plants and from some of the plants to aquatic insects. Most biota at Kesterson bioaccumulated maximum selenium concentrations to levels more than 1,000 times the concentration in water and some more than 5,000 times.

The effects of selenium in fish differs depending on the species, but typically excess selenium result in decreased growth, edema, abnormal development of various tissues including bone, liver, kidneys, and ovaries. High selenium levels result in a significant decrease in blood iron concentrations and red cell volumes. Three main dysfunctions have been observed and studied in freshwater fish with selenosis: 1) Loss of osmotic control; 2) Histopathology and 3) Liver damage.

Selenium poisoning in fish can be `invisible', because, the primary point of impact is the egg, which receives selenium from the female's diet (whether consumed in organic or inorganic forms), and stores it until hatching, whereupon it is metabolized by the developing fish. If concentrations in eggs are great enough (about 10 µg/g or greater) biochemical functions may be disrupted and teratogenic deformity and death may occur while adult fish can survive and appear healthy despite the fact that extensive reproductive failure is occurring.

Selenium concentrations discovered in mosquitofish (*Gambusia affinis*) at Kesterson, were 100 times greater than those from the nearby Volta National Wildlife Refuge. The selenium concentrations in mosquitofish were reported to be 36 to 72 times higher than the national average.

In 2004, EPA proposed a new freshwater **aquatic life criterion** for selenium in fish tissue. The **chronic criterion** was expressed as a concentration in whole-body fish tissue of 7.91 µg/g, dry weight, and if fish tissue samples exceed 5.85 µg/g during summer or fall, fish should be monitored during the winter to determine if selenium exceeds 7.91 µg/g.

The adverse effects of Se on waterfowl at Kesterson were the impacts most exposed by the media. The public was more concerned with the birds because they could see that abnormalities in embryos were often multiple, including missing or abnormal eyes, beaks, wings, legs and feet, as well as exencephaly and hydrocephaly. These deformities were fatal and the mortality of the birds at Kesterson increased. The cause of this phenomenon was attributed to selenium toxicosis.

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