Chapter 2

AN ANALYSIS OF SELENIUM LEVELS IN SAN FRANCISCO BAY AND RELATED TREATMENT AND REMOVAL PROCESSES

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Introduction

San Francisco Bay and its surrounding wetlands serves as a critical sanctuary for many migratory and endangered species of wildlife and functions as a productive estuary. The pollution threats to the Bay, including hazardous wastes and raw sewage, are now exacerbated by increasing levels of the toxic trace element selenium (Se) that leaches out of agricultural soils in the Central Valley and empties into the Bay via the San Joaquin River, smaller tributaries, and possibly through underground aquifers (Green, 1985). The industrial discharges from refineries in the North Bay and municipal discharges from the South Bay electronics industry also contribute to the Se levels in the Bay. Although Se runoff and discharges into the Bay have caused irreversible damage to some important species (Ohlendorf et al., 1986), the environmental community has responded to the problems and has developed several treatment models that emphasize the prevention of further Se contamination. The purpose of this paper is to evaluate some of the current methods of removing Se from wastewater and to document some of the Bay's physical and environmental features that add to the increasing levels of Se in the Bay.

Past Studies

There are no past studies of Se levels in the Bay nor of treatment processes for removing Se from wastewater. Recent studies of Se levels in Bay birds and fish indicate that Se is bioaccumulating in organisms at high trophic levels, causing harm to those organisms (Ohlendorf et al., 1986; Greenberg and Kopec, 1985). Studies of Se in soils indicate Se mobility in soil water that contributes to toxification of Central Valley soils and possibly other soils (Presser and Barnes, 1985).

Selenium in the Bay

Selenium is a trace element essential to most organisms in small amounts, but it becomes toxic in two to three orders of magnitude, a relatively small proportion of increase in comparison with most toxic compounds (Burau, pers. comm., 1985). A recent study by the U.S. Geological Survey (USGS) at Kesterson National Wildlife Refuge, the terminus for much of the irrigation runoff for San Joaquin Valley agriculture, indicates Se-related deaths, deformities, and reproductive failure in thousands of birds and fish (Hoffman et al., 1985). The study shows levels of Se exceeding all tolerance limits and indicates rates of embryonic deaths at 15 times the normal rate for unhatched eggs.

The devastating effects of Se toxicity at Kesterson warrant concern for the potential for similar toxification of the Bay, which shares an exposure to drainage water, although not at the same levels, and also harbors many of the same migratory birds and species of fish. A recent study of two San Francisco Bay bird populations, the greater scaup and the surf scoter, reveals Se concentrations in the birds' livers as high as the levels in Kesterson waterfowl (Ohlendorf et al., 1986). These birds, which feed on Bay shellfish, are particularly vulnerable to toxification because they feed on species that take up and concentrate heavy metals and other pollutants. A population study over the last four years of these birds in Bay wetlands indicates a population decline of 80-90 percent in scoter numbers and a drop of 50 percent in scaups (Ohlendorf et al., 1986). The decline in populations has not been linked to Se directly, but this possibility is under investigation by the USGS and the U.S. Bureau of Reclamation. Se is also being studied as the cause of the decline in other Bay species such as the striped bass, the Dungeness crab, clams and harbor seals.

Bay Vulnerability to Toxics

Although all water systems collect toxic substances and thus harmful levels may accumulate in sediments and in filter-feeding organisms, the geochemistry and water flows of an estuary facilitate greater accumulation of suspended toxics than other aquatic systems such as lakes and rivers (Klaverkamp et al., 1983). The composition of Bay sediments, the circulation patterns of the estuary, and the capacity for bioaccumulation by filter-feeding organisms concentrates the Se and other pollutants that can toxify the Bay.

Because much of California's soils and sediments contain Se in high amounts, it is expected that Bay sediments also contain high levels of this element. The waters that flow in and out of the Bay vary in density, salinity and temperature. The Bay receives saline dense water from the ocean and fresh lighter water from rivers (Conomos, 1979). Mixing of ocean and fresh water creates a 'trap' for suspended particles, including Se. The settling out of particles reduces the amounts of Se that would normally be carried to the ocean, where Se would be less available to filter-feeding organisms (Young, 1985).

The deposited Se is taken up by microbial and plant life on the Bay floor. These plants and bacteria concentrate Se in their tissues and become toxic to organisms that feed on them, including fish and crabs. When Se is absorbed into tissues, it is metabolized into amino acids which are more effectively incorporated into the diets of birds and mammals than are the inorganic forms of Se, selenate and selenite

(Burau, 1985). The suspended forms of Se which are taken up by filter-feeding organisms are concentrated into the organisms' tissues at levels up to 4,000 times the amount present in the water, making filter-feeding organisms a threat to populations that feed on them (Green, 1985).

Selenium Levels Measured in San Francisco Bay

Selenium levels in the Bay can be attributed to refinery discharges and municipal runoff, as well as to agricultural wastes and levels in the sediments. The major industrial use of Se is in making photocells for electronics firms (Horne, pers. comm., 1986). Refineries generate Se wastes from the materials used in the process of treating crude oil. Table 1 shows some Se levels discharged from municipal sewage treatment plants and from Bay refineries.

Source	Effluent	Se Concentration	Mass Loading
Chevron	18.5 MGD[a]	16 ug/ L	1100 g/day
Exxon	2.3	7	61
Pacific	.25	38	36
Shell	3.2	10	1300
San Jose	123	2	930
Palo Alto	28	2	211
Sunnyvale	17.6	1	66

[a] MGD= Million Gallons per Day.

Table 1. Selenium Levels in Major Bay Discharges.

The EPA standard for fresh water is 35 µg/L.

Source: Munley, unpublished data.

Table 1 also shows the Environmental Protection Agency (EPA) standard for Se in fresh water, as a comparison with the Se levels in the effluents. Presently, the EPA has no established estuarine standards; the EPA ocean standards for Se are higher than for freshwater, but because the Bay is considered more of a freshwater system than an oceanic one, the freshwater standards are more accurate for comparison with Bay discharges.

Selenium Removal Processes

In the past few years, several methods for removing Se from water have been developed, including pressure mechanisms, biological uptake, and chemical precipitation of Se compounds. These methods focus on concentrating Se ions and compounds into a waste sludge that can be treated, leaving the residual wastewater free of contaminants, and available for reuse. The most advanced methods include reverse osmosis and biological uptake.

Reverse Osmosis - Reverse osmosis treatment is a process that separates wastewater into two streams, a purified water stream and a waste sludge stream (EPA, 1981). A pressure gradient is created on the two sides of a semi-permeable membrane, allowing only pure water to pass through the membrane, whereas the water molecules attached to the wastes are unable to cross. The waste stream is transferred to evaporation ponds where other treatment processes, including sedimentation and algal accumulation, further concentrate the pollutant into a sludge that can be recycled or disposed of.

The California Department of Water Resources operates a pilot plant at Los Banos that uses reverse osmosis to desalinate and detoxify agricultural wastes in the San Joaquin Valley (Willey, 1985). The process involves several stages of pretreatment that use marsh ponds with aquatic plants to trap particles that might clog the membrane. The ponds also absorb chemicals, which reduces the concentration of toxics remaining in the water, and thus decreases additional chemical treatments necessary for removal of trace toxics. The test plant began operation in December, 1985, but has stopped several times due to equipment failure. A proposal by the Environmental Defense Fund estimates that six reverse osmosis plants, modelled after the Los Banos facility, and each handling 25 million gallons a day at a cost of $20 million a plant, could manage the wastewater in the San Joaquin area, removing Se and other toxics from the waterways leading into the Bay (Willey, 1985).

The main advantage to reverse osmosis is that it concentrates a waste stream without requiring the addition of coagulating chemicals. Adding chemicals complicates the treatment process and increases environmental risks and economic costs. Another advantage is that reverse osmosis may meet its own energy requirements, because the evaporation ponds containing the briny wastes can produce electricity (Willey, 1985).

There are several disadvantages to reverse osmosis treatment. Membranes are sensitive to clogging and require extensive pretreatment to remove large particles. The process creates high volumes of waste that must be treated, stored, and disposed of, and the equipment for this is expensive. Evaporation ponds require large land areas, up to several acres, which may be unavailable or costly. The process may be ineffective at trapping other toxics, such as boron.

The most significant environmental costs involve ecological dangers associated with open ponds containing heavy metals. Groundwater contamination is possible, but lining the ponds should prevent seepage. The appeal of open ponds as a resting site for migratory birds creates a potential for harmful uptake of waters containing high concentrations of toxics (Ohlendorf, pers. comm., 1985).

Biological Treatment - There are many approaches to biological treatment, ranging from algal absorption of heavy metal to the use of several kinds of organisms in the detoxification of a complex waste stream. Most biological treatments use an organism that can ingest toxics and bioaccumulate them. This paper will focus on two processes that use algae and bacteria to treat Se-laden water.

A type of biological treatment for Se presently practiced in the Westlands District of the San Joaquin Valley by Binnie Co. uses algae in ponds to accumulate water contaminants (Willey, pers. comm., 1985). The algae are then removed, leaving a less-concentrated wastewater. The cleaner waste stream facilitates the precipitation of Se by the addition of coagulating chemicals. Se is finally filtered from the pond and is treated to form the insoluble Se metal. The remaining water is drained through polyester tubes, trapping residual Se particles, making the water available for reuse. Binnie Co. estimates an operation potential of one million gallons per day, dropping Se levels from 400 parts per billion (ppb) to 6 ppb (Carter, 1985).

The treatment developed by Binnie Co. is applicable to other wastes than those contaminated by Se and therefore has potential for widespread industrial applications. Because the algae remove the bulk of the contaminant, the water can be treated for specific contaminants more easily than if the stream were complex and saturated with pollutants.

Some of the limitations of this treatment include the creation of high volumes of waste, large land requirements for ponds, and the high costs of operation. The ecological threats created by open ponds are the same as for reverse osmosis treatment. Another potential environmental danger could result from the improper disposal of biological wastes, such as algae, that would expose organisms to toxic wastes in the food chain.

A biological treatment process developed by Alex Horne at UC Berkeley proposes a combination of anaerobic algae and bacteria to convert suspended Se to a concentrated and insoluble metal form (Horne, pers. comm., 1986). The process mimics natural algal and bacterial reactions observed in the Kesterson ponds, that have concentrated up to 75 percent of the suspended Se into mud and sediments.

In the first phase of the treatment process, algae absorb Se and other metals from water and carry these toxics to bottom sediments as the algae die. Then, in the absence of oxygen, the Se and metals are taken up by bacteria and rendered into insoluble compounds. The key to this process is that anoxic waters do not support the zooplankton that normally feed on dying algae, concentrating the Se and making it available to other organisms in the food chain. The bacterial uptake, however, makes Se insoluble and inaccessible to most organisms.

The most important controls in this process are in keeping the waters anoxic and preventing zooplankton from colonizing. The main method for maintaining anoxic waters is to stop light from penetrating into the ponds, thus preventing conditions for zooplankton growth and oxygen buildup. Methods of blocking light include using black plastic covers or dense plant matter that does not give off oxygen underwater, such as duckweed (Horne, pers. comm., 1986). Since blocking sunlight will also prevent algal growth, the process may involve two ponds, one in which to grow algae, and one to support the decaying algae and toxics. Horne estimates that the treatment process may require pond sizes one fiftieth the size of ponds used for Se water evaporation treatment.

One advantage to this treatment system is that it mimics the natural treatment, minimizing input requirements such as chemicals and equipment. Thus, there are lower costs and potential for equipment problems. This process also reduces land requirements for pond sites. The main disadvantage involves the difficulty in keeping ponds anoxic and free of zooplankton. In practice, this process may require additional inputs to keep the zooplankton from surviving. The potential for groundwater seepage of toxics into aquifers and the risks associated with open ponds are the potential environmental dangers of this process.

Other Removal Processes - Coagulation and precipitation is a pond treatment that requires the addition of chemicals that induce particle coagulation and sedimentation (EPA, 1981). Other treatment processes, such as reverse osmosis or biological uptake, are needed to reduce the toxicity of the Se in the final effluent. In terms of Se treatment, this removal process is more a pretreatment process than a complete removal system, because the chemicals do not remove enough of the Se and other toxics to make the water safe for most organisms (Munley, pers. comm., 1985).

Ion exchange treatment removes undesirable ions from wastewater by using a resin that 'exchanges' the wastewater ions with a group of substitute ions (EPA, 1981). After the wastewater is pretreated to remove solids, it passes through a resin until all exchange sites are filled, and the contaminant appears in the effluent. This process is difficult to apply to Se treatment on a large scale because not all forms of suspended Se can be exchanged, and thus some particles remain in the water and require further treatment (Maneval et al., 1985).

Discussion

If Se and other heavy metals must eventually be removed from Bay discharges, it is important to recognize the constraints in applying removal processes to Bay industrial and municipal sites. It is to Bay industrial and municipal sites. It is difficult to assess the applicability of the various Se removal processes because each of these processes is still in an experimental stage and each contains many operational problems. The most difficult problems that would result from use of the processes include high volumes of wastewater requiring treatment, pretreatment needs and costs for the processes, large land requirements for ponds, and large volumes of hazardous waste sludge.

The high volumes of Bay discharges would require treatment systems designed to handle such large volumes of wastewater on a daily basis. Presently, treatment processes such as reverse osmosis and biological uptake are unable to treat water at very high volumes, although the potential is there.

Both reverse osmosis and biological uptake treatment require extensive pretreatment, such as chemical precipitation and accumulation in ponds, before the actual Se removal can take place. For a Bay system, the pretreatment would be costly and slow, reducing the potential for an efficient and continuous removal. The processes also require large land areas for pond sites, which may not be a major cost when the processes operate in the Central Valley but would be a considerable cost in the Bay Area, where land prices are extremely high. Other treatment processes, such as coagulation and precipitation, also require large land areas for pond sites.

Any treatment process will generate a concentrated waste sludge, which will be considered a hazardous waste and will require a permit for handling, storage and disposal. Reverse osmosis effluent, when concentrated, still contains high volumes of water which make its disposal both messy and costly (Horne, pers. comm., 1986). Biological treatment also generates biological hazardous wastes which are a large danger to the ecosystem. One problem that may develop in the future is that the wastes will no longer be taken to landfill, and the treatment will have to change to reduce wastes and recycle them, in addition to concentrating the wastes initially.

Conclusion

The Bay and its surrounding wetlands are a critical environment for many organisms, and their sensitivity to toxic effects creates a need for the prevention of potential harm to the ecosystem. Se has become a concern because its toxic effects at Kesterson and in the Bay indicate the threats to the environment associated with this element. Presently, Se is entering the Bay from many sources, including rivers, refineries and industrial discharges. Because Se is not fully understood, in terms of routes of entry into the Bay, and its reactions with organisms, control of Se levels is essential for the protection of the Bay. Because Se is not the only pollutant in the Bay, its toxic presence is only one indicator of the harm that is occurring in this important ecosystem.

The present treatment processes for Se are varied and have potential for treating Se-contaminated effluents and possibly other waste streams as well. The need for a combined waste removal technology must be stressed, because no pollutant acts in isolation; pollution problems must be treated as a whole. The Bay must be preserved, and in order to do so, many of its pollutants, including Se, must be treated or removed at the source.

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