The drainage of agricultural wastewater from the rich San Joaquin Valley — a problem that has vexed farmers, scientists, and politicians for many years — reached a climax early this year, when a halt was ordered in the delivery of federal irrigation water to 42,000 acres of land in the Westlands area of the Valley. Behind this action was the detection of high levels of selenium in Kesterson Reservoir, terminus for the 80-mile-long San Luis Drain, which carries saline wastewater from the Westlands Irrigation District to Kesterson. Built in 1971, the 12 shallow evaporation ponds at Kesteron supported a variety of fish and wildlife. Mortalities and deformities attributed to accumulated selenium attracted national attention.

In this article, Dr. Richard Burau, Professor of Soil Chemistry in the Department of Land, Air, and Water at UC Davis, reviews what is known about selenium and how it enters the food chain.


Dick Venne

Kesterson Reservoir

Environmental chemistry of selenium

Richard G. Burau

Some selenium in the diets of higher organisms is healthy

Selenium is an essential trace element for animals and humans, but at elevated levels of dietary exposure, it causes toxicity. It is not known to be essential for plants. In animals, selenium is a component of glutathione peroxidase, which detoxifies peroxides as well as superoxide and hydroxide free-radicals, preventing damage to tissues, especially cell membranes. In this respect, selenium complements a function of vitamin E. It is possible that selenium also has other functions, including participation in the mitochondrial electron transport system in muscles.

Deficiency, expressed most readily in animals as "ill-thrift" disease or as the more severe "white muscle" disease, occurs in calves and lambs on both sides of the Sacramento Valley and the northern Coast Range as well as in the San Joaquin Valley of California. Livestock deficiency problems are most often associated with forages that are low in selenium because they are grown on leached, acidic soils with higher levels of free iron oxides.

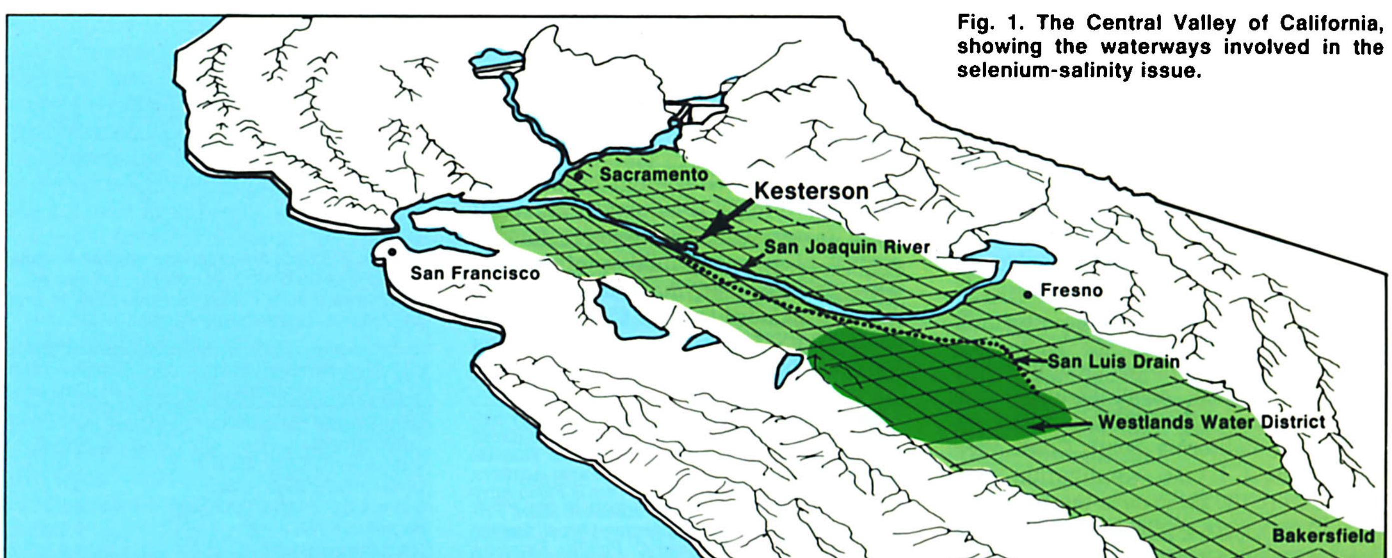

Fig. 1. The Central Valley of California, showing the waterways involved in the selenium-salinity issue.

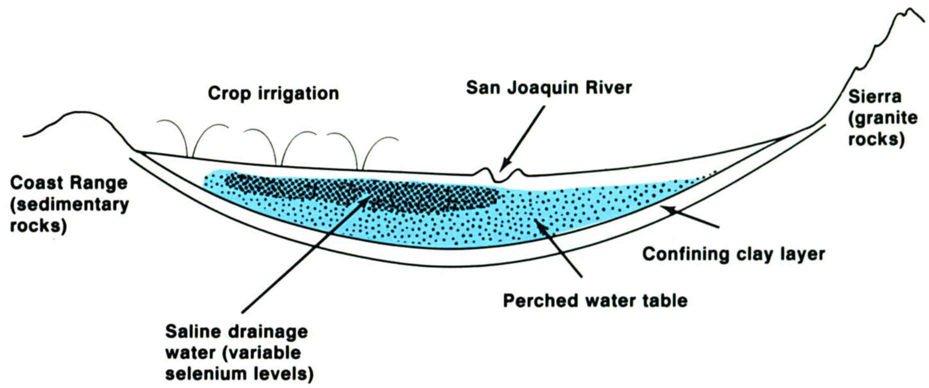

Fig. 2. Cross-section of the San Joaquin Valley. Selenium from Coast Range sedimentary rocks eroded into the fans on the west side of the Valley, from which it was leached by irrigation into groundwater.

Geochemistry

Atmospheric deposition of selenium, especially in the vicinity of coal-fired industrial or power-generating plants, is significant in some soil-plant systems. In most soils, however, the selenium content of the parent rock and the amount of annual rainfall are the two most important determinants of soil selenium levels: higher parent material levels and lower rainfall contribute to the formation of soils with higher selenium contents. Magmatic rocks have the lowest selenium content (10 to 50 parts per billion [ppb]), while sedimentary rocks are generally higher in selenium. Shales have the highest selenium contents (500 to 28,000 ppb).

Worldwide, the average soil concentration is 400 ppb, but high-selenium soils of the Great Plains area of the United States, where selenium in forage has caused toxicity in domestic animals, range from 6,000 to 28,000 ppb selenium. The soils of this region are derived from the Cretaceous-age Pierre Shale, they tend to be alkaline, and the climate is semi-arid. Soil alkalinity is a frequent concomitant of high selenium levels in soils. In Wales and Ireland, selenium has leached from Avonian shales to the extent that the associated low-lying, highly organic soils now contain 30,000 to 300,000 ppb.

On the west side of the San Joaquin Valley, shallow groundwater areas with high levels of selenium have received sediments of Cretaceous-age shale formations from the east side of the Coast Range (fig. 1). The hypothesis of Dr. Ivan Barnes of the U.S. Geological Survey is that these sediments acquired their selenium at the time of their deposition as seleno-sulfides of iron. Later, when these sediments were uplifted and exposed to oxidative conditions, the selenium was released as selenite and selenate salts, while the sulfur appeared as sulfates. These materials then eroded into the fans, but the generally low rainfall caused evapoconcentration of the salts at the rim of the San Joaquin Valley basin and also caused their inefficient transfer into the San Joaquin River and thus into the ocean by way of the Delta.

Aquatic chemistry

Fresh and marine waters around the world average 0.2 and 0.1 ppb selenium, respectively, although levels in seepage water in areas of seleniferous soil (high available selenium) are two to three orders of magnitude greater than these values. The recommended limit in water for domestic consumption is 10 ppb. (The selenium concentration in the city water supply of Davis, California regularly equals or exceeds this value.) A recent survey sampling by the U.S. Geological Survey of shallow wells and subsurface agricultural drainage waters on the west side of the San Joaquin Valley has shown relatively low or moderate selenium levels (less than 10 ppb) in samples from the area around and to the north of Kesterson Reservoir. In contrast, samples from regions to the south, in the area of the Panoche Creek fan (in the Westlands district) have ranged into the hundreds of parts per billion (fig. 2). The highest value reported in a single water sample from the area was over 4,000 ppb.

When these high-selenium waters were brought to the surface and drained into Kesterson Reservoir, selenium was taken up by aquatic biota including marsh plants, phytoplankton, zooplankton, and insects that contribute to the diets of higher forms of wildlife in the area (fig. 3). The selenium acquired by both terrestrial and aquatic photosynthetic organisms is tranformed biochemically into organic or carbon-linked selenium (RSe), especially selenoanalogues of sulfur-containing amino acids, such as seleno-cystine, selenocysteine, and seleno-methionine. It is well known that higher life forms take up these or other more elaborate peptide or protein forms of selenium from their diets into their tissues more effectively than they take up inorganic forms such as selenite or selenate. The working hypothesis of U.S. Fish and Wildlife Service scientists is that this food-chain transfer mechanism has caused selenium toxicity in aquatic birds in the Kesterson area, which is expressed not only as hatchling deformities and death but also as toxicity symptoms in adult fowl. There is little doubt that selenium, in one form or another, is the toxic principle causing these problems.

Geobiochemistry

As previously noted, selenium deficiency in livestock is widespread in California. It is often stated in the literature that, in domestic livestock, selenium deficiency is more common around the world than selenium toxicity. Selenium deficiency in humans due to dietary insufficiency is quite rare, although children have died in China in areas affected by "Keshan disease," which is believed to be selenium deficiency. There is an extensive, worldwide literature on dietary levels in domestic animals (sheep, cows, horses, and chickens) that give rise to symptoms of toxicity as well as deficiency. Deficiency is likely if the selenium concentration in food is less than 50 ppb; selenium sufficiency is likely in the range of 100 to 1,000 ppb, but the toxicity threshold is from 3,000 to 5,000 ppb. By comparison, the literature on selenium response in wild animals is relatively sparse.

Plant roots take up selenium from soil water in either the selenate or the selenite ionic forms. Quantities in the soil solution are governed by the solubilities of adsorbed forms and by the biological transformation of organic forms (fig. 4). Approximately 25 genera of plants are classed as selenium accumulators. These include *Astragalus* (milkvetch, rattleweed, locoweed), *Stanleya* (prince's plume), and *Haplopappus*, which have an

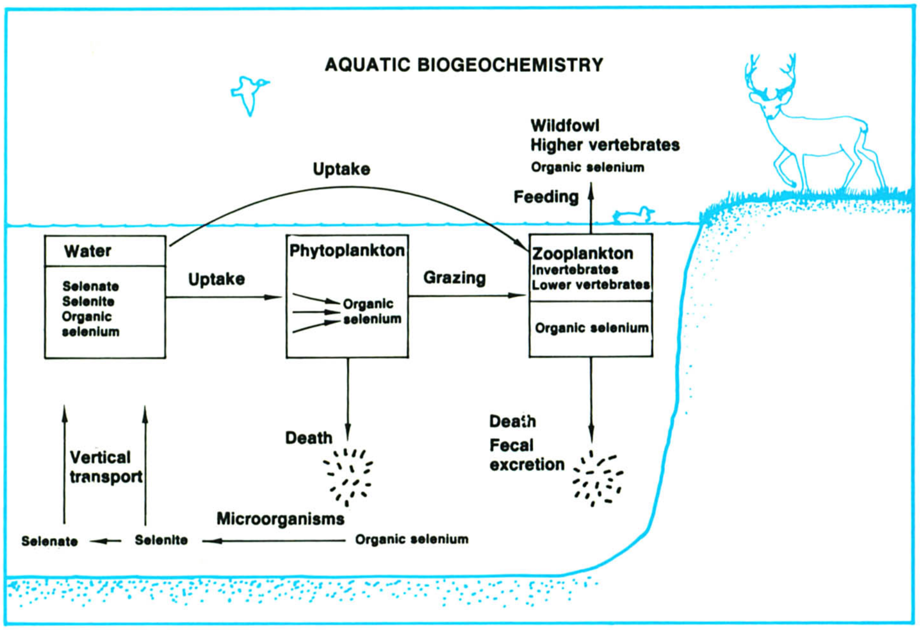

Fig. 3. Aquatic organisms, such as marsh plants, phytoplankton, zooplankton, and insects, take up inorganic selenium and transform it into organic forms, which are more easily taken up by higher life forms.

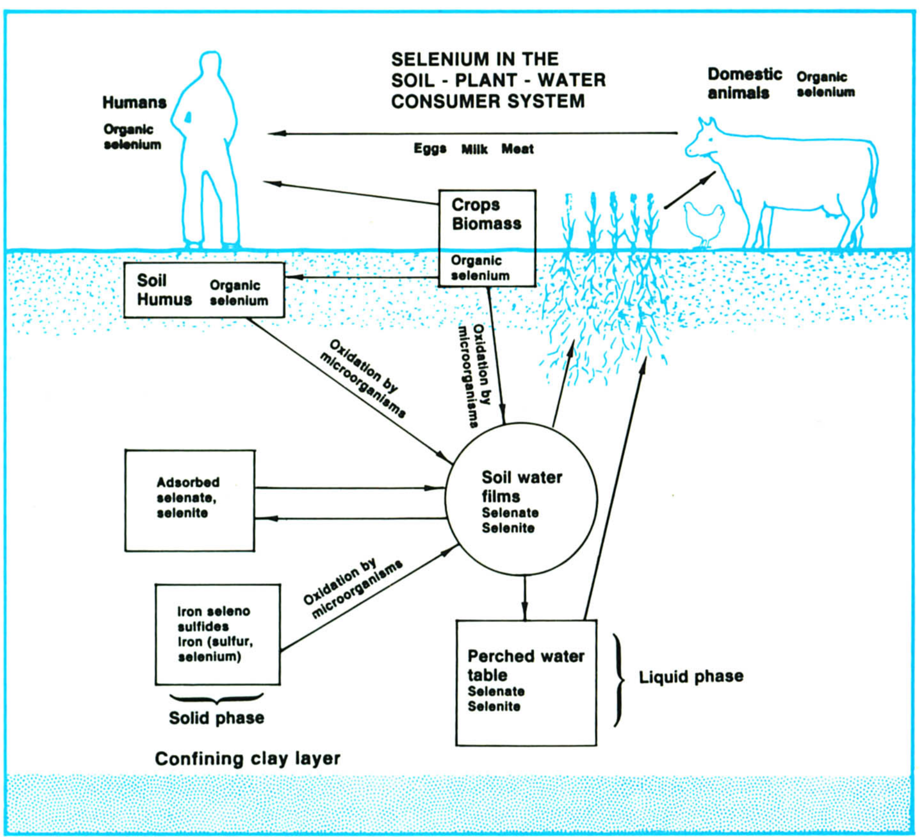

Fig. 4. Plant roots take up selenate or selenite forms of selenium from the soil water. The selenium concentration in the soil solution depends on the solubility of the forms of selenium present and the biological transformation of organic forms.

extraordinary ability to acquire selenium, sometimes 100-fold greater than other plants growing on the same soil. Because of the disagreeable odors their foliage emits, however, these plants are seldom important in causing toxicity, except where animals are forced by near starvation to consume them.

Most instances of selenium toxicity in domestic livestock are from consumption of ordinary (as opposed to selenium-accumulator) forages and feeds grown on seleniferous soils. Selenium levels in plants are positively correlated with levels in soils (total or extractable), but uptake is also positively affected by pH and soil temperature. Concentrations of selenium tend to be higher in the grains and seeds, although some plants such as maize are reported to have similar concentrations throughout their anatomy.

Human toxicity from high selenium levels in the diet derived from food grown on seleniferous soils is relatively rare. Adults in the United States consume approximately 170 micrograms of selenium per day from all sources, and the recommended dietary allowance is 50 to 200 micrograms a day. If one consumed 2 liters of water per day containing 10 ppb of selenium, selenium ingestion would be 20 micrograms per day from this source. A recently completed study of selenium in human diets in China reported no toxic symptoms in individuals taking in 750 micrograms of selenium a day or less, but those consuming 5,000 micrograms a day or more consistently showed one or more symptoms of toxicity. The most frequently observed symptoms were loss of hair or nails and skin lesions. In addition to these visible symptoms, there are analytical techniques to indicate the level of a person's dietary exposure. Selenium level in hair is one of the best indicators, but blood as well as urine analysis is also useful.

In the situation reported by the Chinese study, a local drought had forced the peasants to consume more locally grown vegetables as well as maize, all of which increased the dietary intake of selenium. Species of Cruciferae were particularly high in selenium, although they did not approach the acquisition rates of accumulator species.

It is most important to recognize that there are levels of selenium in the food and water supply of all higher organisms that are healthy and not toxic. Our knowledge on selenium effects on domestic animals and humans is quite good, but we are not similarly blessed with data for wild animals, especially those in aquatic systems.

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