

Conceptual Model for Selenium Cycling in the Great Salt Lake



Prepared for the Division of Water Quality
of the Utah Department of Environmental Quality

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This document describes a conceptual model for selenium cycling in the Great Salt Lake. The document consists of four parts:

- A) Introduction to the problem & Overview (page 1)
- B) The framework of the model and underlying assumptions (page 7)
- C) Visual depiction of conceptual model (page 17)
- D) Relevant references supporting the model framework (page 22)

Introduction to the problem & Overview

During the Fall of 2005 a panel of nationally recognized scientists in the area of selenium environmental toxicology and geochemistry was convened to work with local scientists and engineers to develop a conceptual model to guide development of investigations in support of determining an open water selenium standard for the Great Salt Lake. The expert panel included Dr. Anne Fairbrother (U.S. Environmental Protection Agency), Dr. Joseph Skorupa (U.S. Fish & Wildlife Service, Dr. William Adams (Rio Tinto, Inc), Dr. Theresa Presser (U.S. Geological Survey), and William Wuerthle (U.S. Environmental Protection Agency). The local scientists and engineers who worked with the expert panel in development of the conceptual model were Drs. William Johnson and Jack Adams (University of Utah), and Drs. Michael Conover & Wayne Wurtsbaugh (Utah State University).

Motivation

The motivation to determine a selenium standard for the open water of the Great Salt Lake (GSL) derives from public concern for a plan to allow disposal of reverse osmosis (RO) concentrate in the GSL. The concentrate would contain elevated concentrations of major and trace elements, including selenium.

Existing GSL selenium standard

The open water of the GSL is protected for its current beneficial uses through the application of the narrative criteria clause which states that it is unlawful “to discharge ... any waste or other substance in such a way as will be or may become offensive ...or cause conditions which produce undesirable aquatic life or which produce objectionable tastes in edible aquatic organisms; or result in concentrations or combinations of substances which produce undesirable physiological responses in desirable resident fish, or other desirable aquatic life, or undesirable human health effects”. Due to the highly individual nature of the Great Salt Lake, the Utah Department of Environmental Quality (DEQ) has not yet identified numeric water quality standards specific to the Great Salt Lake.

Conceptual model to guide standard development

The development of an open water standard for selenium requires a working knowledge of the biological significance of existing selenium concentrations in the Great Salt Lake, as well as a

working understanding of the likely trajectories of these concentrations over time given existing and proposed loads to the system. This “working knowledge” is being represented in a conceptual model that accounts for selenium in various “stocks” in the system (e.g. water, sediment, biota) and the “flow” of selenium between stocks (e.g., precipitation and settling, volatilization, bioconcentration). The conceptual model is presently descriptive, but will serve as the basis for a semi-quantitative model that will be fed by data accumulated during subsequent investigations.

Loads

The existing selenium loads to the GSL are not well characterized. The most prevalent source of selenium nationally is irrigation of marine deposits of Cretaceous to Tertiary age. Marine deposits of Cretaceous to Tertiary age are not prevalent in the Great Salt Lake Basin (Hintze, 2005), and are restricted mainly to the Bear River Watershed. However, the Bear River is the dominant source of water to the GSL and since the GSL is a terminal lake, evaporative concentration of selenium increases the risk of elevated selenium concentrations within the GSL system. Other actual and potential sources of selenium to the GSL include mine tailings and refinery wastes, respectively.

Challenges to analytical methodologies

The hypersaline water of the Great Salt Lake presents an exceptional challenge to existing analytical techniques used to measure selenium in water. A preliminary “round robin” survey of samples from several depths (one location) demonstrated that only a limited set of analytical methods can reliably quantify selenium in this system. The round robin, which was based on a single sampling location, is encouraging in that it indicates that approximately 0.5 ppb selenium exists in the water column; a value that is not expected to yield deleterious effects in biota. However, it must be stressed that the open water of the Great Salt Lake cannot be represented by a sample from a single location, or a particular time, as elaborated below.

Accumulated record

The degree to which selenium is sequestered in non-bioavailable compartments or forms in the GSL is central to the assessment of the long-term effects of selenium loads to the GSL. The long-term accumulation of selenium in the GSL is recorded in its accumulating sediments. Collection and analysis of sediment cores from lakes and reservoirs provides a record of long-term water quality trends. Measurable concentrations of most trace elements and selected organic compounds are often associated with fine particulates in the water column, which settle and may accumulate at the lake bottom. The U.S. Geological Survey (USGS) lake cores in Farmington Bay show pre-1900s selenium concentrations around 0.4 µg/g, with increases of 4- to 5-fold thereafter (Dr. David Naftz, personal communication). The cause of the increase has not been investigated, and may reflect either increased selenium loads, or selenium loss from the deeper (older) sediments with time. The significance of potential increased selenium accumulation depends on the long-term bioavailability of accumulated selenium. Hence, the goal of understanding the distribution of existing and additional selenium loads within the GSL system requires the development of a conceptual model that comprehensively describes selenium cycling within the existing GSL ecosystem. The conceptual model is needed to guide prediction of how pathways may vary with climate-induced changes (e.g. salinity, redox conditions, etc.),

and to provide metrics indicating the degree of confidence with which the various components of the cycle are understood.

Dynamics of the GSL ecosystem

Comprehensive determination of selenium cycling in this system requires an understanding of the following attributes of selenium cycling that will be elucidated in the conceptual model:

- a) The storage compartments of selenium in the system
- b) The residence times of selenium within these compartments
- c) The fluxes of selenium between these compartments
- d) The pathways between these compartments.

The comprehensive conceptual model for selenium cycling in the GSL system allows decision makers to identify areas where improved understanding of processes is required prior to determination of a standard for the open water of the GSL. However, the complexity of the GSL system will likely identify more potential investigations than can be supported financially or completed in the time allotted. Hence, decision makers will need to rank identified areas of need relative to the ultimate goal of support of beneficial use of the GSL system. There are two major considerations in development of the conceptual model:

- a) The GSL system is spatially diverse, being comprised by four distinct bays and two layers. The limited connections between the bays yield major differences in salinity among their waters. These bays are also frequently stratified vertically. Gilbert Bay has a deeper anoxic zone that does not "turn over" on an annual basis and is more saline than the overlying shallower zones. Farmington Bay also frequently has a deep brine layer that is believed to be mixed periodically during strong wind events (Wayne Wurtsbaugh, personal communication). Due to variation in salinity (and hence density) with depth, the flow between spatial compartments can be bi-directional flow, such that the deeper hypersaline layer flows oppositely to the overlying water.
- b) The GSL system is temporally dynamic, due to seasonal and inter-annual variations in runoff from the Wasatch and Uinta Mountains to the east. Variability in runoff controls salinity, shoreline location, and lake depth. Due to the shallowness of the GSL, wind events are also important drivers of flow between compartments in the GSL. Wind events also influence vertical mixing of the deep anoxic layer into the overlying water column. Greater than 60% of the lake area is oxic, but a significant portion is underlain by an anoxic deep brine layer. In Farmington Bay, a wind event was observed to mix the deep brine layer into the total water column making the entire water column anoxic for two days (Wayne Wurtsbaugh, personal communication). The lateral extent of the deeper anoxic zone appears to expand and shrink on a seasonal basis, potentially exposing sediments to a combination of chemically reducing and oxidizing conditions on an annual basis. The temporal dynamics of selenium cycling in the GSL system is also biologically driven since the abundances of particular organisms shift from season to season.

Biogeochemical fluxes

The vertical spatial variability of the GSL system requires special consideration since it is likely across this vertical gradient that selenium moves from the geochemical to the biological system. In short, microorganisms in the water column “make their living” by facilitating the trade of electrons between elements. In this process, selenium may be chemically reduced when an oxidized form of selenium sorbs to a particle and settles to the deeper anoxic zone. In contrast, reduced selenium may be oxidized when reduced forms are re-suspended into the oxic zone. The same issue applies to lake area variations, which may expose anoxic sediment to air, or may submerge oxic sediment beneath the anoxic deep brine layer. The deeper anoxic zone in the GSL has some of the highest sulfate reduction rates measured in a natural system (**Dr. David Naftz, USGS, personal communication**), suggesting that transformation of selenium in this system is significant (based on the similarities of selenium and sulfur chemistry).

A potential release mechanism of selenium from the GSL and sediments is the buoyant transport (upward) of bubbles of reduced volatile selenium (e.g. methylated selenides). The flux of volatile selenium in the Great Salt Lake is unknown. The rate of this transfer is likely temporally variable in response to variations in salinity and temperature, each of which control speciation and the solubility of organic selenium species.

Into the food chain

The tie between biogeochemical cycling and the food chain occurs at the level of microorganisms. Brine shrimp and brine fly larvae are expected to take up selenium via the microorganisms on which they feed. The brine shrimp and brine flies are in turn the major food sources to birds in the open water. Hence, the development of an open water standard involves the execution of surveys to measure selenium concentrations in water, microorganisms, brine shrimp, and brine flies. Notably, preliminary monthly data taken during the summer by Dr. Bill Adams (**Rio Tinto**) suggests factor of two increases in selenium concentrations in brine shrimp at the south end of the Great Salt Lake during the month of July. This period roughly coincides with depleted $\delta^{15}\text{N}$ (the heavy isotope of nitrogen) measured by Dr. David Naftz (**USGS, personal communication**). Possible reasons for the observed large seasonal shift could be a seasonal change in food source from green to blue green algae or a shift to a benthic food source growing on the extensive areas of stromatolites/bioherms in the GSL.

Toxic endpoints

The development of an open water standard must of course occur with reference to sensitive species at the top of the food chain, i.e. birds in the case of the Great Salt Lake. Among the birds present on the Great Salt Lake, three species were chosen: one as a representative of migratory species, and two as representatives of species that breed on the Great Salt Lake.

Eared grebes were chosen to represent migratory species on the basis that The Great Salt Lake and Mono Lake are the only two lakes in the western U.S. supporting the population of eared grebes in the fall season. Furthermore, while they reside on the Great Salt Lake, the eared grebes eat only brine shrimp (99.7% of diet) (**Dr. Michael Conover, personal communication**). Viability of offspring is likely not a sensitive endpoint for this species since the high rate of Se depuration for birds likely resets their selenium concentration within weeks of change in diet, and egg laying occurs about 90 days following departure from the Great Salt Lake (in the fall). Since eared grebes must consume on the order of 13,000 shrimp per day during their stay to support their

migration from the Great Salt Lake (Dr. Michael Conover, personal communication), a potential selenium toxic endpoint for this species is inadequate build-up of mass for migration. However, in other avian species, e.g. mallards, the level of selenium required to impair adult health has been demonstrated to be higher than that required to impair reproduction (Dr. Joseph Skorupa, personal communication), suggesting that resources should be focused on the toxic endpoints associated with reproduction.

Avocets/stilts and northern shovelers were chosen to represent species that breed on the Great Salt Lake. Their diet contains a high concentration of brine flies, brine shrimp, or corixids, thereby making them most at-risk relative to other over-wintering birds in terms of selenium burden. Furthermore, sufficient numbers of eggs can be easily obtained for these species, and in the case of avocets/stilts their foraging area restricted to relatively short distances. A disadvantage of avocets is their relatively low sensitivity to Se. An advantage of shovelers is that toxicity data from mallards may be transferable. A disadvantage of shovelers is that a portion of the population may be year round, but other portions may be transient, and they may not rely heavily on the Great Salt Lake for diet since they nest at the interface between fresh and salt water.

Momentum

The conceptual model illustrates the critical pathway of selenium from water, to microorganisms, to brine shrimp and brine flies, to birds, and to their eggs. Surveys of selenium concentrations within these “stocks” will yield bio-accumulation factors for selenium between these “stocks” and will thereby support the back-calculation of an open water standard. An interim standard can likely be developed over the course of a single year. However, based on the conceptual model, the confidence in this standard would be greatly enhanced by surveys performed over multiple years in order to account for characteristic year-to-year variation in the Great Salt Lake system. In order to better predict the long-term trajectories of selenium concentrations in this system, additional surveys are needed to determine selenium loads to the system in a fashion that accounts for year-to-year variation. Furthermore, selenium particulate fluxes into and out of sediment, and selenium vapor fluxes upward through (and exiting) the system, need to be examined in order to determine the significance of accumulated sediments as long term sinks or sources of selenium.

Framework of the model and underlying assumptions

The conceptual model for selenium cycling in the Great Salt Lake system includes two major domains:

- 1) trophic transfer of selenium upward through the food chain
- 2) biogeochemical cycling of selenium “below” the food chain, which is dynamically influenced by hydrologic processes (variations in runoff and evaporation).

For both domains, the boundary of the conceptual model coincides with the effective boundaries of Gilbert Bay, i.e. the open water of the Great Salt Lake west of Farmington Bay, west of the Weber River input, and south of Promontory Point (Bear River Bay) and the North Arm.

This boundary places wetlands processes outside the boundaries of the conceptual model. However it is well recognized that wetlands processes govern the concentration of selenium entering into Gilbert Bay from Farmington Bay and other areas outside the boundaries of the conceptual model.

An important consideration is the potential export of selenium from within the conceptual model boundaries to wetlands during high stands of the Great Salt Lake. The effects of this “violation” of the model boundaries are mitigated by the following conditions:

- 1) during high stands of the Great Salt Lake the present wetlands become hypersaline and effectively become equivalent to the open water of the Great Salt Lake (the freshwater-hypersaline interface is moved outward)
- 2) the open water selenium standard will likely be maintained at a level that is less than the selenium standard for the wetlands. If this condition is not met, then export of selenium to wetlands during high stands must be further considered.

Given these conditions, the conceptual model boundaries allow the mass transfer of selenium and water to Gilbert Bay to be idealized one-way (into Gilbert Bay). This simplification allows the complexities of selenium cycling in the wetlands to be considered separately from the complexities of selenium cycling in Gilbert Bay.

The conceptual model that follows focuses on selenium cycling in Gilbert Bay.

Trophic transfer of selenium within food chain

The food chain in the Great Salt Lake system is relatively simple. For birds, food sources available directly from the lake are restricted to brine shrimp, brine shrimp cysts, brine flies, brine fly larvae, and water column insects (i.e. corixids).

Although corixids are known from freshwater environments, corixids can be found in Gilbert at salinities up to 160 g/L (salinity). Although many of the corixids observed at high salinities have likely have been washed in from less saline environments, observations demonstrate corixids may be present in significant numbers in the saline waters of Gilbert Bay (Wayne Wurtsbaugh, personal communication).

Simplifying assumptions are required to define compartments and physical mass transfer processes in a tractable model. Below we articulate simplifying assumptions that yield a tractable, albeit still complex, model.

Simplifying assumptions

- 1) The Se cycle can be separated into trophic transfer “within” the food chain versus physical mass transfer and chemical transformation “below” the food chain. The underlying assumption is that exposures to Se for organisms “higher” than phytoplankton in the shallow layer and periphyton and bacteria in the littoral sediment are predominantly via diet. Hence, the conceptual model treats direct physicochemical partitioning of selenate and selenite to “higher” organisms as negligible relative to uptake of organic selenium via predation. This assumption is justified by the fact that dietary exposure is the dominant route of exposure for many organisms (Toll et al., 2005; Brix et al., 2005).
- 2) An exception to the above assumption is physicochemical uptake of selenate and selenite by plants, which in turn influences aqueous selenium concentrations. The conceptual model boundaries effectively eliminate the need to consider influences of plants on selenium cycling. In contrast, the influence of plants is likely a very important consideration in selenium cycling in Farmington Bay.
- 3) Dietary uptake of Se by “higher” organisms is predominantly in the form of organic Se. Dietary uptake of inorganic Se is negligible for “higher” organisms.
- 4) Incorporation of inorganic Se into the food chain occurs predominantly at the level of periphyton and bacteria in the littoral sediment and phytoplankton in the shallow layer.
- 5) Only phytoplankton in the shallow layer, and periphyton and bacteria in the littoral sediment, are grazed by brine shrimp and brine fly larvae. Hence, the phytoplankton in the shallow layer, and periphyton and bacteria in the littoral sediment act as the gateway between the geochemical cycling and the food chain. The bacteria in the deep brine layer and anoxic sediment mediate Se cycling, but are not directly significant to higher food chain organisms.
- 6) Brine shrimp diet may vary dynamically. Potential food sources for brine shrimp other than phytoplankton include purple sulfur bacteria located at the interface between the Shallow Layer and Deep Brine Layer, and bioherm algae located on the lake bottom where the deep brine layer is absent (Littoral Sediment). The purple sulfur bacteria are photosynthetic and oxidize H_2S exsolved from the Deep Brine Layer, and may therefore also oxidize volatile selenium compounds and accumulate selenium. That brine shrimp foraging is dynamic is suggested by measured peak selenium concentrations in brine shrimp during July (Bill Adams of Rio Tinto) which qualitatively corresponds to depletion of ^{15}N in brine shrimp (measured by Dave Naftz of USGS). These changes are likely coincident with depleted phytoplankton concentrations (as a result of brine shrimp grazing the phytoplankton). The combined observations suggest that the brine shrimp graze on other food sources during July; or alternatively, the phytoplankton are depleted in selenium during July. Brad Marden (Artemia Association) suggests that weekly monitoring is needed, since brine shrimp and algae populations fluctuate significantly on a weekly basis.
- 7) A tentative link is also included between phytoplankton and birds. Joe Skorupa (USFWS) has expressed discomfort with the absence of an avian species that exploits the

phytoplankton directly. This tentative link is added as a reminder of the need to assess this absence. However, Mike Conover suggests that no GSL birds eat single-cell phytoplankton because these organisms are just too small. Some algae species form dense colonies (floating mats, etc.), that are sufficiently large (several grams wet weight) for some ducks that are primarily herbivores (e.g., wigeon) and geese to pick up and eat. These algae species probably do not occur in the pelagic areas of the GSL. The algae can be significant at times in Farmington Bay. However, in most herbaceous birds, algae make up only a small part of their diet due to lack of nutritional value.

Among the birds present on the Great Salt Lake, three species were chosen as representative of migratory species, and species that breed on the Great Salt Lake. The food supply for most birds (corixids, brine flies, brine shrimp) collapses in November when the GSL becomes too cold. Many species, e.g. grebes, stilts, avocets, plovers, phalaropes, and gulls leave by December. Some species, e.g. ring-billed and California gulls and ducks (e.g., common goldeneyes) over-winter on the GSL and probably migrate directly to the breeding ground. Birds that breed on the Great Salt Lake include avocets, stilts, Franklin's gulls, California gulls, and snowy plovers.

Grebes

Eared grebes were chosen as a "sentinel" species on the basis that while on the GSL, they only eat brine shrimp (99.7% of diet). Feathers, corixids and brine flies each make up about 0.1% of their total diet according to research by Mike Conover, and work by Don Paul. Their length of stay on the GSL is known from Mike Conover's data.

Toxic endpoint

The most sensitive endpoint is considered to be mass wasting, since it may result in unsuccessful migration. Reproductive impairment is likely not a sensitive endpoint for this species since the high rate of Se depuration for birds likely resets Se concentration within weeks of change in diet, and egg laying occurs about 90 days following departure from the Great Salt Lake (in the fall). Reproductive impairment is not considered a sensitive endpoint for grebes that use the Great Salt Lake in the spring due to the short residence time of the birds on the lake during this period.

The level of Se to impair adult health is higher than that required to impair reproduction. Heinz (1996) provides a summary of mallard work, and recommends a dietary value of 10 ppm, dw, to protect adult mallards from adverse effects. Ohlendorf (2003) reported that the dietary EC10 for reproductive impairment in mallards was 4.87 ppm, dw, with 95% confidence boundaries of 3.56 - 5.74 ppm, dw. Given that the value of 4.87 ppm is an EC10, not the expected LOAEL, and that one really should allow for inter-species variability in sensitivity. Dr. Skorupa advocates using the lower confidence boundary value of ca. 3.5 ppm. He suggests that this is consistent with Wilber's (1980) comprehensive review of selenium toxicology in *Clinical Toxicology*, 17:171-230, wherein he noted that the chronic toxic dose for "hens" ranged from 3.5 - 10 ppm. Presumably part of the variation in that range is due to different endpoints evaluated by different studies and also presumably the reproductive endpoints would have yielded the lower boundary of the range cited by Wilber (1980). Dr. Skorupa indicates that all parties agree now that the EC10 for mallard egg hatchability data is about 12 ppm (Adams et al. 2003; Ohlendorf, 2003). Furthermore, Ohlendorf (2003) reported that the 95% confidence

boundary on that EC10 estimate was 6.4 - 16.5 ppm, dw. For the same reasons as outlined above, Dr. Skorupa advocates an EC10 of about 6 ppm. He suggests that the wisdom of this is further reinforced by a recent paper that reported about an EC15 control-adjusted effect in egg hatchability for spotted sandpipers at an average egg selenium concentration of 7.3 ppm, dw (Harding et al., 2005).

The bird most likely to be at-risk from loss of mass (or decreased gain of mass) due to selenium effects while on the GSL is the eared grebe:

- 1) some of the highest Se concentrations at Kesterton reservoir were found in this species
- 2) they eat only brine shrimp, brine flies, and corixids while on the GSL
- 3) these birds are always at the edge of what is nutritionally possible (i.e., having enough energy to migrate from the GSL to the Salton Sea)
- 4) there are mass downings of eared grebes migrating from the GSL during some years that result in the deaths of thousands of grebes. The cause of these downings is not clear, however some attribute the downings to snow storms (Jehl, 1993).

Uncertainty in depuration rate

Selenium accumulation and depuration rates are rapid. Studies indicate that it would take about 2.5 months (71 days) for waterfowl to return to background selenium levels once they leave a source, but they would be below effects levels of 10 ppm (w:w) in about 8 - 10 days (e.g. Heinz et al., 1990; Yamamoto et al., 1998; Heinz, 1996; Wilson et al., 1997).

However, selenium accumulates to high levels in preen glands and does so fairly rapidly (e.g., from ca. 4 ppm ww to ca. 20 ppm ww in ca. 60 days in one study of small shorebirds). The feathers concurrently also increase rapidly in Se content from preen gland (uropygial gland) secretions being applied to the feathers. Selenium concentrations in these feather must have been introduced via the exterior since the feathers were fully grown (i.e., hard penned) and therefore no longer had any vascular connection to pathways for metabolic (i.e., internal) deposition of Se (e.g. Goede and De Bruin, 1986; Goede and DeBruin, 1984).

A factor of 2-4 increased selenium burdens in eared grebes relative to other species at the Tulare Basin is observed despite equivalent diets for these birds (Dr. Joseph Skorupa, personal communication). This enhanced selenium concentration in eared grebes may reflect the effect of ingestion of feathers.

Avocets/stilts

Avocets and stilts were chosen on the basis that these birds breed on the Great Salt Lake, and their diets contain a high concentration of brine flies, brine shrimp, or corixids, thereby making them most at-risk relative to other over-wintering birds in terms of selenium burden. Furthermore, sufficient numbers of eggs can be obtained easily for this species, and their foraging area is restricted to relatively short distances.

A disadvantages of avocets is their relatively low sensitivity to Se.

Toxic endpoint

The most sensitive endpoint for the avocets/stilts is considered reproductive impairment (reduced egg hatchability) since these species breed at the Great Salt Lake.

Northern Shovelers

This species was chosen on the basis that it is an over-wintering species whose diet mostly comes from the GSL during the winter (probably cysts, but this not definitively determined). Mike Conover has a large sample of shovelers that were collected on the GSL on December 1 (n = 90) and on March 1 (n = 30) 2005. These samples are frozen and could be processed to determine their condition and Se concentrations. Dr. Conover also dragged duck nests along the GSL marshes for several years and is certain that shoveler nests can be found. Sampling for deformed or normal ducklings likely not possible since upon hatching, Shoveler ducklings are led by the hens deep into the marshes where it is impossible to find them.

An advantage of shovelers is that toxicity data from mallards may be transferable. A disadvantage of shovelers is that a portion of the population may be year round, but other portions may be transient. They may not rely heavily on the Great Salt Lake for diet since they nest at the interface between fresh and salt water.

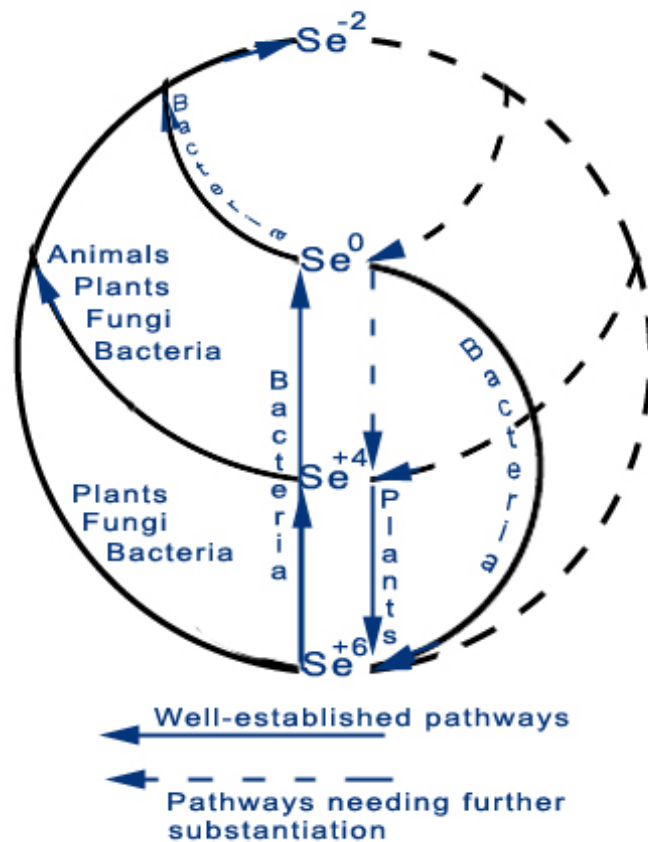
Toxic endpoint

The most sensitive endpoint is considered egg hatchability since these species breed at the Great Salt Lake.

Note: Dr. Clay Perschon (Utah Division of Wildlife Resources) does not agree with the choice of northern shoveler, since this species does not appear to use the lake extensively. Dr. Perschon suggests use of the common goldeneye, since they appear to use the lake extensively (brine shrimp and brine flies). However, a weakness of this approach is that common goldeneyes do not nest on the Great Salt Lake, so this would require designation of a different toxic endpoint relative to northern shovelers.

Biogeochemical cycling of selenium “below” the food chain

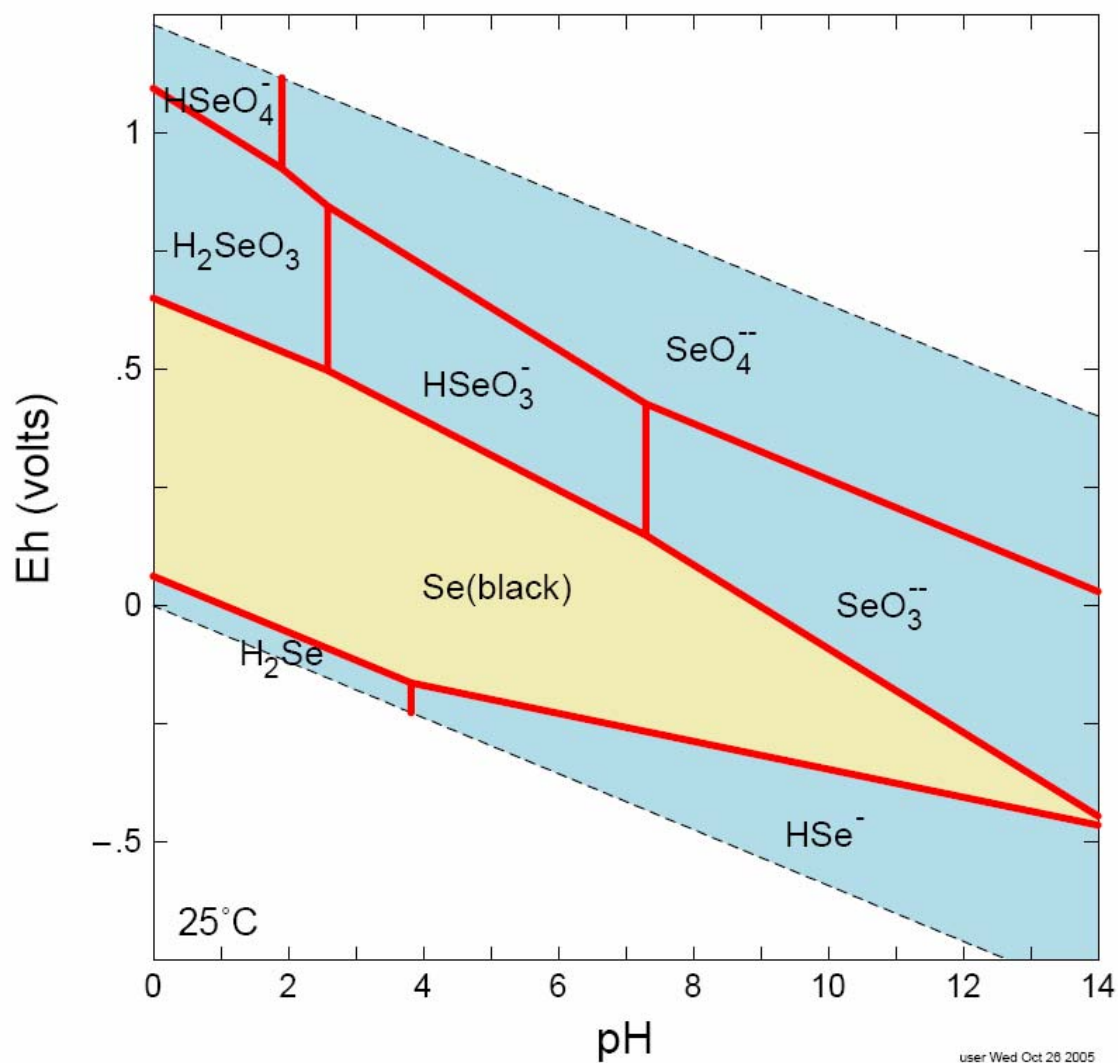
Expected selenium species in the Great Salt Lake fall into five categories: organic selenium Se(-II), selenide Se (-II), elemental selenium Se(0), selenite Se(+IV) (SeO_3^{2-}), and selenate Se(VI) (SeO_4^{2-}). If one lumps organic and volatile selenium, the pathways relating these species to one another can be generalized as shown below:



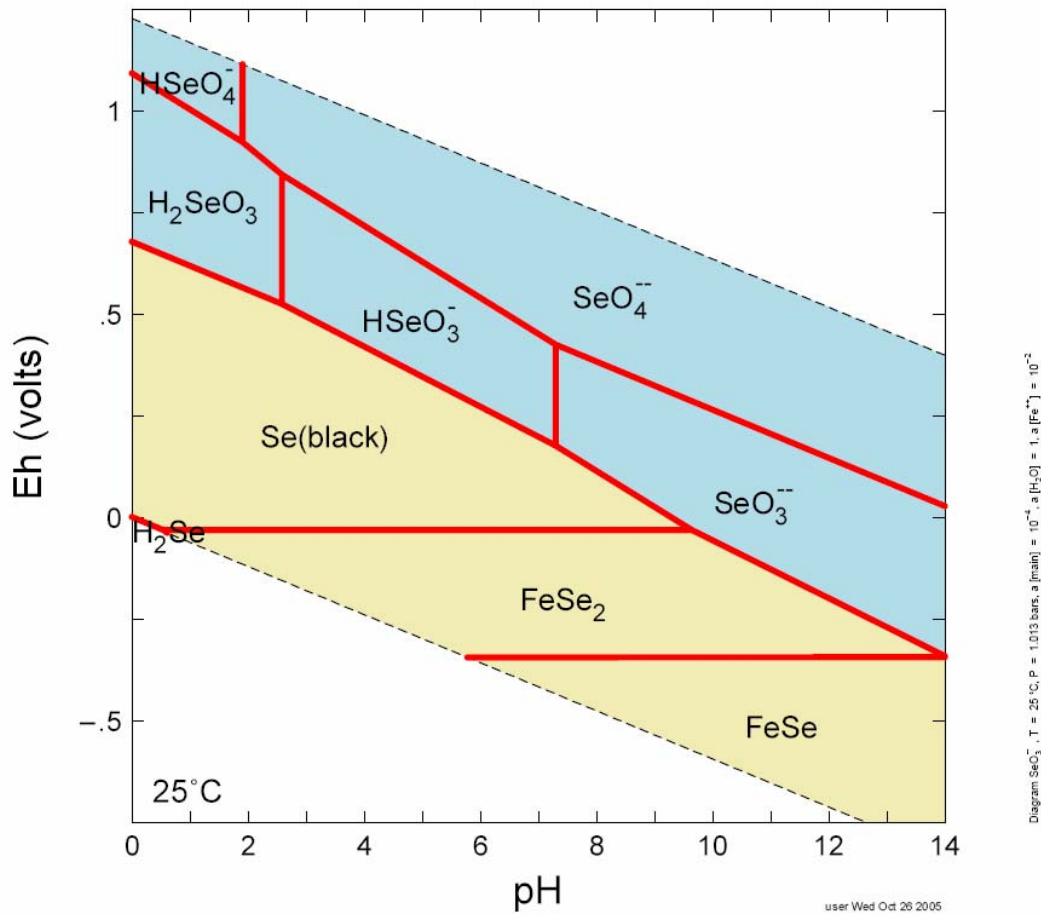
The figure above concisely describes the biologically mediated redox processes controlling Se behavior in the environment. Progress from the figure above toward a functioning semi-quantitative conceptual model requires identification of specific compartments in which the above processes occur, and also requires identification of processes governing physical mass transfer of Se between compartments.

Many of the simplifying assumptions below are derived from the expected speciation of selenium in water with salinities far below that of the Great Salt Lake. The expected speciation in the Great Salt Lake cannot be determined at this time via geochemical models due to the lack of information for activity coefficients under the hypersaline conditions of the Great Salt Lake.

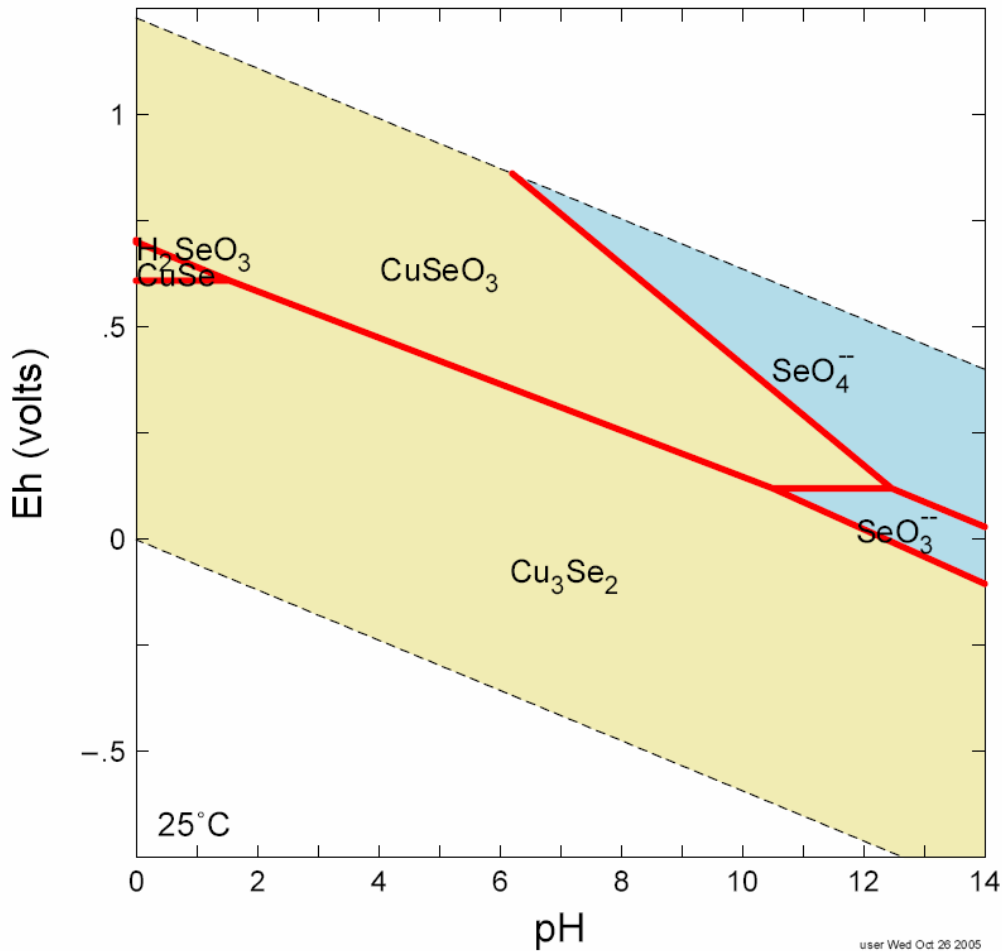
Equilibrium speciation diagrams using activity coefficients from less saline waters are used here as a tentative starting point. Equilibrium speciation of selenium is shown as a function of pH (negative log of proton activity) and p_e (negative log of electron activity) in the figure below developed using Geochemist's Workbench. The x-axis on this diagram demonstrates increasing pH from left to right. The y-axis on this diagram illustrates increasingly oxidizing conditions from bottom to top. The boundaries on the system represent the stability boundaries for water, which reacts to form oxygen at the top boundary, and forms hydrogen gas at the bottom boundary. The biogeochemical environment of the Great Salt Lake is therefore constrained within these boundaries.



It should also be noted that forms of particulate selenium other than elemental selenium are expected due to the presence of trace metals in the concentrated water of the Great Salt Lake. For example, addition of iron alters the particulates that should be formed, whereas the stability of the relatively oxidized aqueous species is largely unaffected.



However, addition of dissolved sulfate and copper to the water yields additional particulate phases and important decreases in the stability fields of the aqueous species (as shown below).



Important limitations & need for direct measurement

It is important to note that these stability fields depend on the aqueous activities of selenium and the trace metals. The activities used in these diagrams do not reflect hypersaline conditions, due to a lack of activity coefficients for selenium and trace metals in these systems. Hence, direct measurements to determine actual selenium speciation is crucial to understanding the mechanisms governing the aqueous selenium concentrations in the Great Salt Lake.

Furthermore, the stability diagrams reflect equilibrium conditions, whereas formation of particulate phases may entail kinetic processes that allow aqueous species to exist in a metastable state.

Simplifying assumptions

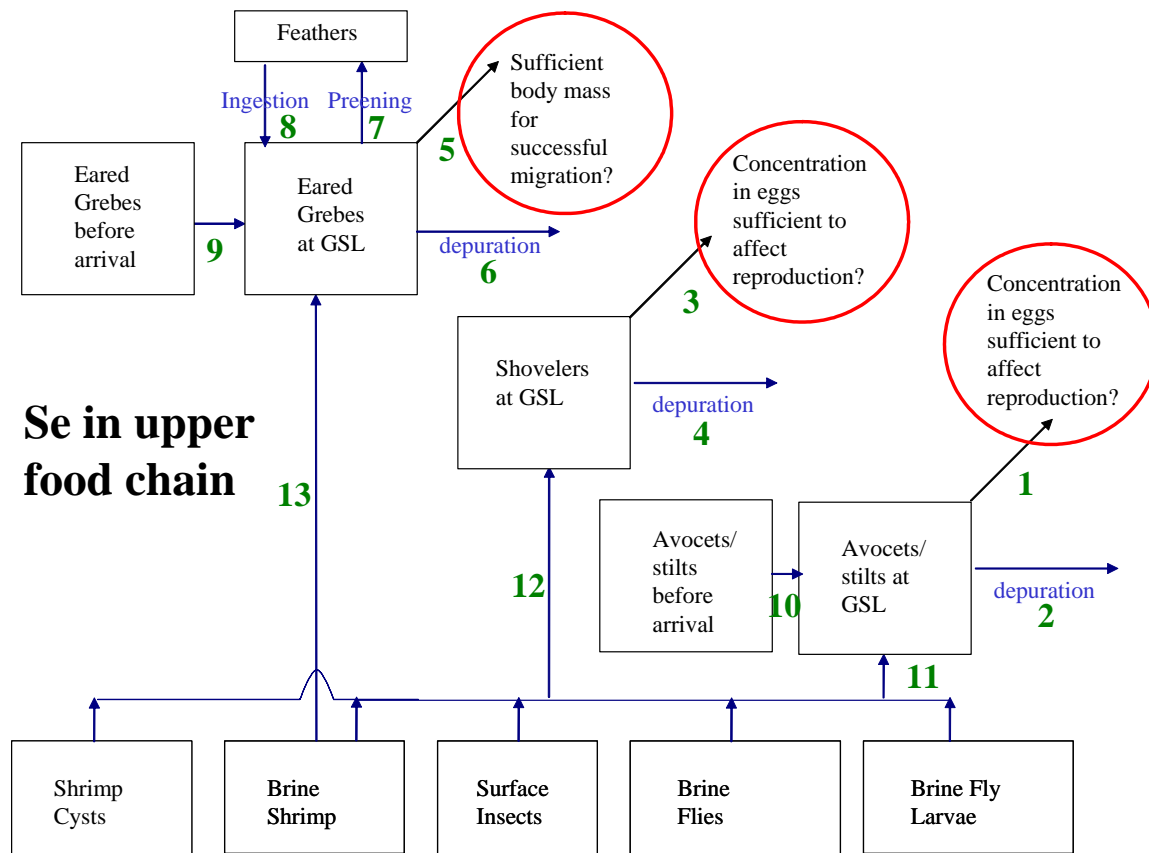
- 8) Selenium can be represented by five predominant lumped species:
 - a. non-volatile organic selenium (organic Se in figures below)
 - b. volatile organic and inorganic selenium (H₂Se in figures below)
 - c. elemental selenium (Se⁰)
 - d. selenite (SeO₃²⁻)
 - e. selenate (SeO₄²⁻)

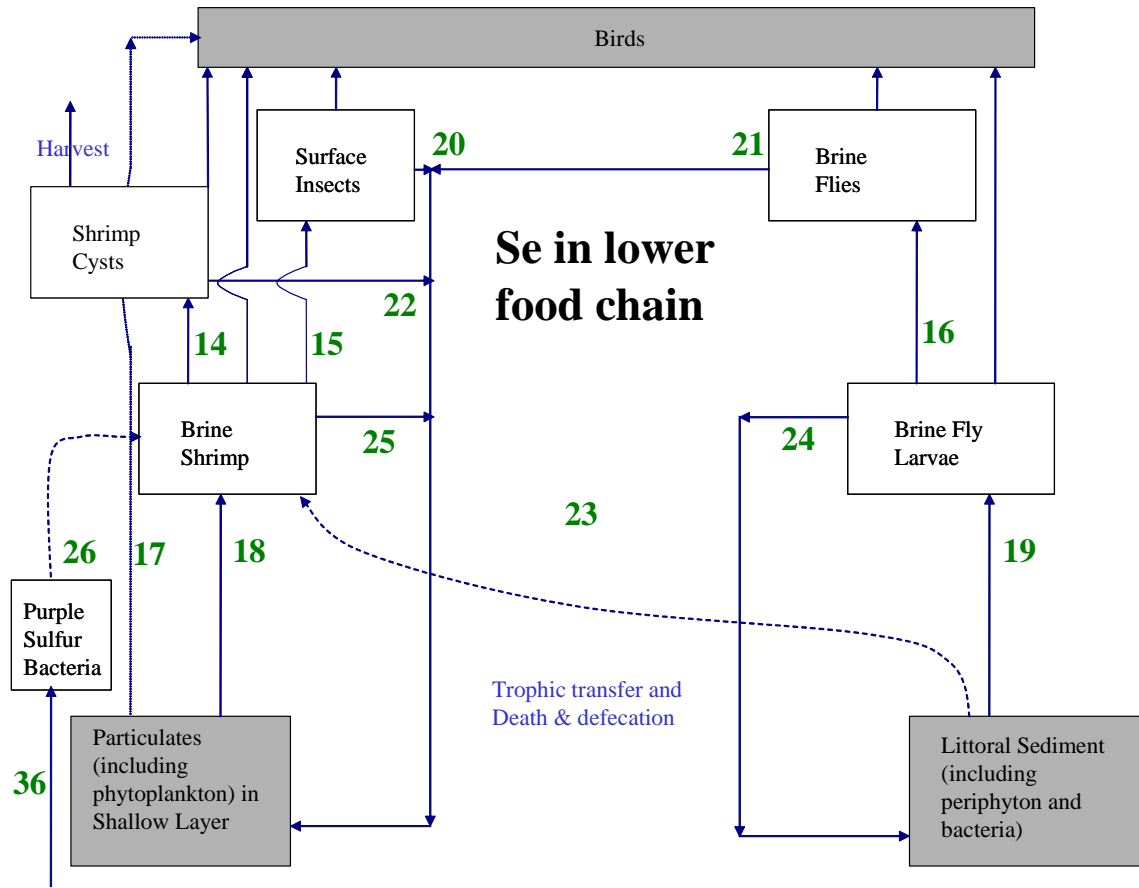
- 9) Physicochemical mass transfer processes (e.g. adsorption, desorption, precipitation, settling, volatilization, dissolution, and redox transformation) predominantly occur below the food chain, and these processes can be neglected within the food chain.
- 10) The cycling processes occurring in the oxidized layers (Shallow Layer, Littoral Sediment, and Exposed Sediment) are: 1) oxidation to selenate and selenite (from species with relatively-reduced Se); 2) reduction to selenite (from selenate); and 3) uptake of selenate, selenite, and organic selenium by phytoplankton, periphyton, and bacteria.
- 11) The cycling processes occurring in the reduced layers (Deep Brine Layer, Anoxic Sediment) are: 1) reduction to selenite, elemental selenium, volatile selenium (methyl and di-hydrogen selenides), and hydrogen selenide (from species with relatively oxidized Se); and 2) uptake of selenite, organic selenium, and hydrogen selenide by phytoplankton, periphyton, and bacteria.
- 12) Note that the hydrogen-selenide complex (HSe^-) is not volatile, and this complex is expected (rather than di-hydrogen selenide) for the pH range of the GSL (although no activity coefficients exist for Se^{in} hypersaline water, so we know this only approximately).
- 13) Atmospherically deposited selenium is assumed to be in the form of selenate, selenite, and elemental selenium.
- 14) The “particulate” phases include organic and mineral matter. The organic matter includes organisms and feces, which may settle or be re-suspended.
- 15) Se input from the North Arm is introduced only to the Deep Brine Layer as reduced species since the dense North Arm water becomes the deep brine layer in Gilbert Bay.
- 16) MagCorp, Inc. was not considered a significant contributor of selenium to Gilbert Bay.

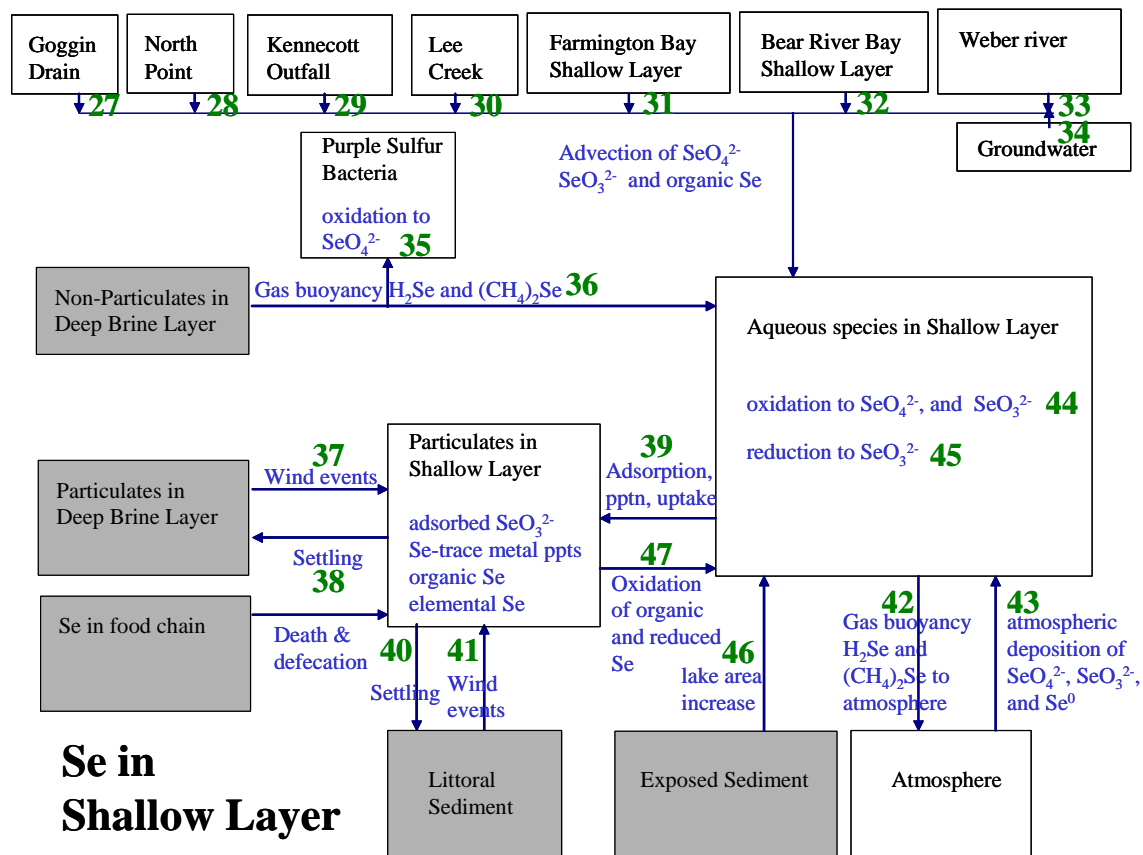
Note that influences on flows such as light, salinity, pH, dissolved oxygen, nutrients, etc. are NOT explicitly tracked in the model, but rather will be reflected in daily to seasonal variations in the flows depicted in the model.

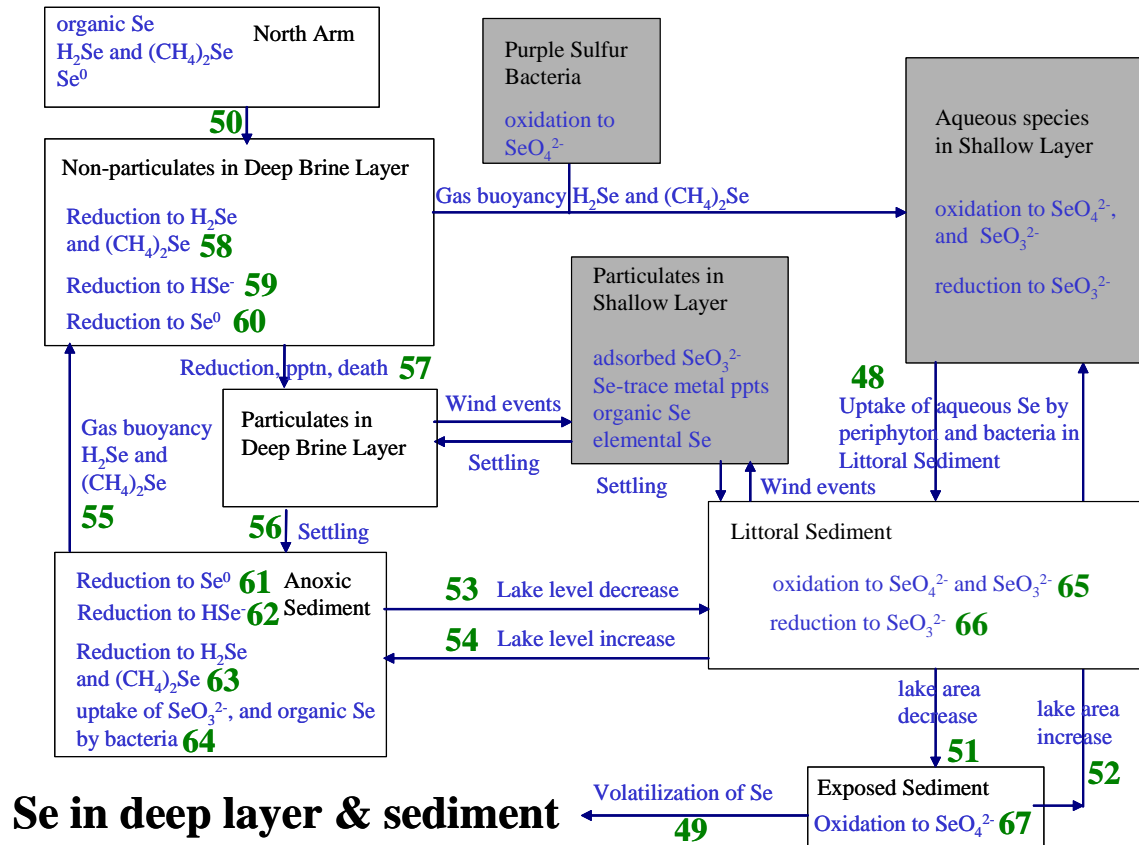
The final layer concerns the stocks and flows of water in order to track seasonal evaporative concentration and dilution of selenium species.

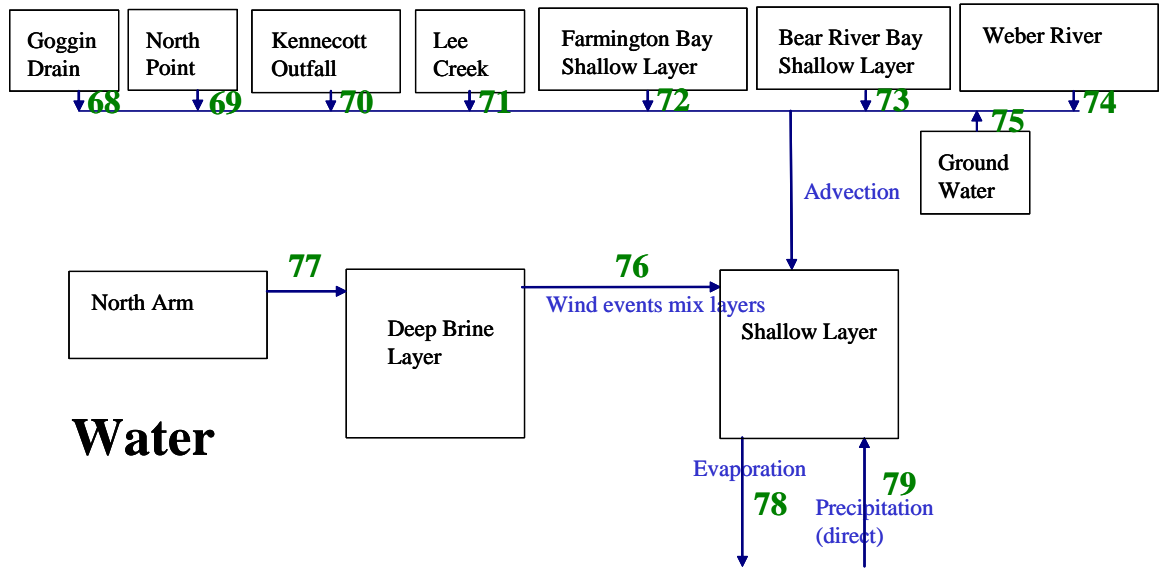
Visual depiction of conceptual model











Conceptual model supporting references

The supporting references are provided in the context of the corresponding process in the conceptual model, each number below refers to a labeled process in the conceptual model:

- 1) **Se transfer from adult avocets/stilts to eggs:** Anne Fairbrother indicates that development of a literature review on toxicological effects is unnecessary since the EPA is now developing a comprehensive review based on work at the San Francisco Bay. This will be available in the near future. The appropriate egg selenium threshold for toxicity to offspring is hotly debated (Fairbrother et al. 2000; Skorupa 1999; Fairbrother et al. 1999). Dr. Fairbrother et al. argue for a threshold of 16 ppm ww egg selenium as protective of chicks, whereas Dr. Skorupa argues for 6 ppm ww egg selenium as protective of embryo mortality effects.
- 2) **Selenium depuration from avocets/stilts:** This process would be subsumed into measured transfer of Se from avocet/stilt adults to their eggs (1 above). Depuration values are available from the literature for various birds. Selenium accumulation and depuration rates are rapid. Studies indicate that it would take about 2.5 months (71 days) for birds to return to background selenium levels once they leave a source, but they would be below effects levels of 10 ppm ww in about 8-10 days: (e.g. Heinz et al., 1990; Yamamoto et al., 1998; Heinz, 1996; Wilson et al., 1997).
- 3) **Se transfer from adult shovelers to eggs:** see (1).
- 4) **Selenium depuration from northern shovelers:** This process would be subsumed into measured transfer of Se from shoveler adults to their eggs (3 above). See also (2)
- 5) **Se influence on eared grebe mass loss:** The level of Se to impair adult health is higher than that required to impair reproduction. Heinz (1996) provides a summary of mallard work, and recommends a dietary value of 10 ppm, dw, to protect adult mallards from adverse effects. Ohlendorf (2003) reported that the dietary EC10 for reproductive impairment in mallards was 4.87 ppm, dw, with 95% confidence boundaries of 3.56 - 5.74 ppm, dw. Given that the value of 4.87 ppm is an EC10, not the expected LOAEL, and that one really should allow for inter-species variability in sensitivity. Dr. Skorupa advocates using the lower confidence boundary value of ca. 3.5 ppm. He suggests that this is consistent with Wilber's (1980) comprehensive review of selenium toxicology in *Clinical Toxicology*, 17:171-230, wherein he noted that the chronic toxic dose for "hens" ranged from 3.5 - 10 ppm. Presumably part of the variation in that range is due to different endpoints evaluated by different studies and also presumably the reproductive endpoints would have yielded the lower boundary of the range cited by Wilber (1980). Dr. Skorupa indicates that all parties agree now that the EC10 for mallard egg hatchability data is about 12 ppm (Adams et al., 2003; Ohlendorf, 2003). Furthermore, Ohlendorf (2003) reported that the 95% confidence boundary on that EC10 estimate was 6.4 - 16.5 ppm, dw. For the same reasons as outlined above, Dr. Skorupa advocates an EC10 of about 6 ppm. He suggests that the wisdom of this is further reinforced by a recent paper that reported about an EC15 control-adjusted effect in egg hatchability for spotted sandpipers at an average egg selenium concentration of 7.3 ppm, dw (Harding et al., 2005).
- 6) **Selenium depuration from eared grebes:** The relatively quick depuration of Se from eared grebes effectively resets Se concentrations within several weeks of migration, and

breeding occurs about 90 days following departure from the GSL. Hence, offspring would not reflect Se conditions at the GSL. See also (2)

- 7) **Se concentration in eared grebe preen oil:** Selenium accumulates to high levels in preen glands and does so fairly rapidly (e.g., from ca. 4 ppm ww to ca. 20 ppm ww in ca. 60 days in one study of small shore birds). The feathers concurrently also increase rapidly in Se content from preen gland (uropygial gland) secretions being applied to the feathers because the feathers were fully grown (i.e., hard panned) and therefore no longer had any vascular connection to pathways for metabolic (i.e., internal) deposition of Se (e.g. [Goede and De Bruin, 1986](#); [Goede and DeBruin, 1984](#)).
- 8) **Se ingestion via ingestion of feathers by eared grebes:** A factor of 2-4 increased selenium burdens in eared grebes relative to other species at the Tulare Basin is observed despite equivalent diets for these birds ([Dr. Joseph Skorupa, personal communication](#)). This enhanced selenium concentration in eared grebes may reflect the effect of ingestion of feathers.
- 9) **Se concentration in eared grebe upon arrival at GSL:** unknown. Joe Jehl has stored carcasses that may be helpful.
- 10) **Se concentration in avocets/stilts upon arrival at GSL:** unknown
- 11) **Avocet/stilt diet (mass consumption source and rate) while at GSL:** avocets and stilts on the GSL primarily consume brine shrimp and brine flies. However, the relative importance of each in their diets is unknown. The amount of each that is consumed daily is also unknown ([Dr. Michael Conover, personal communication](#)).
- 12) **Northern shoveler diet (mass consumption source and rate) while at GSL:** unknown. Dr. Conover has recently started conducting research on this topic for Utah Division of Wildlife Resources.
- 13) **Eared grebe diet (mass consumption source and rate) while at GSL:** Eared grebes eat brine shrimp (99.7% of diet). Feathers, corixids and brine flies each make up about 0.1% of their total diet according to research by Mike Conover, and work by Don Paul.
- 14) **Selenium transfer from brine shrimp to shrimp cysts:** Cyst production rate is a function of adult shrimp density, temperature and phytoplankton food level ([Wurtsbaugh 1995](#); [Gliwicz et al. 1995](#); [Wurtsbaugh & Gliwicz 2001](#)). Selenium deposition in cysts or eggs of Artemia is not know. Cysts have high lipid concentrations, and since selenium does not concentrate in lipids, selenium concentrations might be low in the cysts ([W. Wurtsbaugh comments](#)). Brad Marden knows of references to support. Brad Marden has archived cyst samples.
- 15) **Selenium transfer from brine shrimp to surface insects:** Corixid (surface insect) densities are low in Gilbert Bay, so this transfer is likely minimal ([W. Wurtsbaugh comment](#)). Brad Marden has not observed corixids in open water at salinities above 90 parts per thousand. High corixid densities are found in Farmington Bay and likely in Bear River Bay at moderate salinities ([W. Wurtsbaugh comment](#)). Corixid feeding on Artemia has been documented in [Marcarelli et al. \(2003\)](#). Laboratory predation experiments showed that corixids could eat 14-34 brine shrimp per day at temperatures of 20 °C, depending on the age and size of the shrimp. With the density of corixids found in Farmington Bay there was a potential to eat 20% of the adult and 60% of the juvenile brine shrimp ([W. Wurtsbaugh, personal communication](#)).
- 16) **Selenium transfer from brine fly larvae to brine flies:** Some selenium would remain in the cast of the metamorphosing and emerging brine flies, and thus would not transfer

- directly up the food chain to birds. Quantitative importance unknown (**W. Wurtsbaugh comment**). Harry Ohlendorf predicts a loss of ~30% based on damselfly samples.
- 17) **Se transfer from phytoplankton in shallow layer to birds:** According to Mike Conover, no GSL birds eat single-cell phytoplankton that dominate throughout the Great Salt Lake; they are just too small. Some algae species form dense colonies (floating mats, etc.), that are sufficiently large (several grams wet weight) for some ducks that are primarily herbivores (e.g., wigeon) and geese to pick up and eat. These algae species probably do not occur in the pelagic areas of the GSL. The algae can be significant at times in Farmington Bay. However, in most herbaceous birds, algae make up only a small part of their diet due to lack of nutritional value.
- 18) **Se transfer from Shallow Layer particulates (including phytoplankton) in shallow layer to brine shrimp:** Brine shrimp grazing is a function of shrimp size, temperature and phytoplankton density. Clearance rates (R , mL/individual shrimp/day) of the water column at 20 °C: $R = 5.45 L^{1.82}$, where L equals the shrimp length in mm (**Reeve 1963**). At an adult density of $4/L$, 100% of the water column can be cleared of algae each day (**W. Wurtsbaugh comment**). Uptake efficiency of selenium by brine shrimp is unknown, but efficiencies of 41-53% have been noted for other zooplankton feeding on phytoplankton (**Schlekat et al. 2004**). Selenium not taken up would be voided in feces and sedimented. **Schlekat et al. (2004)** found depuration rates of selenium by zooplankton of 12-25% per day. **Fisher et al. (2000)** provide a model of Se uptake by marine phytoplankton and incorporation into zooplankton. Brad Marden also knows of references to support. Brad Marden suggests that a weekly frequency of sampling is needed. Booms and crashes occur on weekly basis, based on secchi disk and algal cell count measurements. Given the large fetch and resuspension of sediments by wind action, there could be sizeable numbers of inorganic particles in the water column. The shrimp are not good at discriminating, so they would graze on these and it is possible that adsorbed Se could be stripped off.
- 19) **Se transfer from periphyton, detritus, and bacteria in littoral sediment to brine fly larvae:** Not known. Selenium transfer rates to benthic invertebrates in other systems have been analyzed several times (**Horne 1991; Alaimo et al. 1994; Besser et al. 1996; Lemly 1997; Wang et al. 1999; May et al. 2001; Schlekat et al. 2002; Peterson et al. 2002**) and benthic organisms can take up Se from algae, detritus and the sediments themselves. **Herbst (in Review)** found that brine flies in saline ponds did not contain Se, whereas brine shrimp and corixids did, whereas brine flies did contain Se at Kesterson (**Harry Ohlendorf, personal communication**). **Besser et al. (1996)** found that planktonic food webs bioconcentrated selenium more than benthic ones, but a model by **Baines et al. (2002)** indicated that Se would move up the food web more effectively via benthic organisms. Sulfate competitively inhibits uptake of selenium by organisms (**Forsythe et al. 1994; Bailey et al. 1995; Wu and Guo 2002; Brix et al. 2004**), and thus in high-sulfate systems like the Great Salt Lake, Se uptake may be less than in fresher systems.
- 20) **Flux of Se in dead surface insects to Particulates in Shallow Layer:** The residence time in the water column during settling is extremely short, such that this flux can be ignored (**W. Wurtsbaugh comment**).
- 21) **Flux of Se in dead brine flies to Particulates in Shallow Layer:** It is likely that the settling rate of brine flies would be sufficiently high to drive them directly to the sediments (**W. Wurtsbaugh comment**).

- 22) **Flux of Se in shrimp cysts to Particulates in Shallow Layer:** Unknown.
- 23) **Possible transfer from periphyton and bacteria in littoral sediment to brine shrimp:** Microbes capable of selenium reduction and accumulation either externally or internally could possibly transfer fairly large amounts of selenium, in the elemental form, to any organism that actively or passively consumes these microbes. Decaying plant matter provides sufficient glucose and glucose metabolic by-products to elicit selenium reduction in localized areas within the littoral sediment environment by diverse populations of microbes. Various microbes, including some algae, are capable of selenium reduction and accumulation or just selenium accumulation in diverse environments, including aerobic, micro-aerophilic, or anaerobic environments. The following references provide parameters important in selenium transfer and indicate the importance of potential selenium transfer to the brine shrimp (Saiki and Lowe, 1987; Sanders and Gilmore, 1994; Besser et al., 1989; Sherr et al., 1988; Wheeler et al., 1982; Riedel et al., 1991; Rassoulzadegan and Sheldon, 1986; Fenchel and Finlay; 1990).
- 24) **Flux of Se in dead brine fly larvae to Littoral Sediment:** unknown
- 25) Flux of Se in dead brine shrimp to Particulates in Shallow Layer: It is likely that the settling rate of brine shrimp would be sufficiently high to drive them directly to the sediments (W. Wurtsbaugh comment).
- 26) **Flux of Se from purple sulfur bacteria to brine shrimp:** Due to mixing that almost certainly occurs at regular intervals at the upper layer of the chemocline, brine shrimp would not necessarily have to venture into the anoxic environment to feed on substantial amounts of the purple sulfur bacteria. Purple sulfur bacteria move reduced sulfur and possibly some selenium from a reduced state to an oxidized state using CO₂ in an anaerobic environment. Purple sulfur bacteria (*Ectothiorhodospiraceae*) and green sulfur bacteria (*Chlorobiaceae*), mainly use sulfide and other inorganic sulfur compounds. In turn, *Desulfovibrio* reduces SO₄⁻² to H₂S, and provides H₂S for the green and purple sulfur bacteria. Since H₂S is volatile and has quite a high solubility coefficient, the H₂S produced by the anaerobic *Desulfovibrio* in the column can move up through the column where it can serve as an energy source for the sulfur oxidizing bacteria. Since sulfide and light occur in opposing gradients, the photrophic green and purple sulfur bacteria often grow only in a rather narrow zone of overlap, but can reach very high densities within this zone. The following references indicate the potential for selenium transport to the brine shrimp (Saiki and Lowe, 1987; Sanders and Gilmore, 1994; Besser et al., 1989; Sherr et al., 1988; Wheeler et al., 1982; Riedel et al., 1991; Rassoulzadegan and Sheldon, 1986; Fenchel and Finlay; 1990). It is not known if brine shrimp in the Great Salt Lake descend into the chemocline to feed on the purple sulfur bacteria. When food in the shallow layer is very low in summer, shrimp could go into the upper layer of the chemocline for short intervals (nearly anoxic) and feed on the bacteria (W. Wurtsbaugh comment).
- 27) **Transfer of selenate, selenite, and organic selenium from Goggin Drain:** Measurements of total selenium concentrations available from Kennecott.
- 28) **Transfer of selenate, selenite, and organic selenium from North Point Canal:** Measurements of total selenium concentrations available from Kennecott.
- 29) **Transfer of selenate, selenite, and organic selenium from Kennecott outfall:** Measurements of total selenium concentrations available from Kennecott.

- 30) **Transfer of selenate, selenite, and organic selenium from Lee Creek:** Measurements of total selenium concentrations available from Kennecott.
- 31) **Transfer of selenate, selenite, and organic selenium from Farmington Bay:** Samples downstream of wetlands have been accumulating at USGS; analyses needed.
- 32) **Transfer of selenate, selenite, and organic selenium from Bear River Bay:** Se could be moderately high in waters from Bear River watershed (Hamilton and Buhl, 2005). Samples downstream of wetlands have been accumulating at USGS; analyses needed.
- 33) **Transfer of selenate, selenite, and organic selenium from Weber River:** Samples downstream of wetlands have been accumulating at USGS, analyses needed.
- 34) **Transfer of selenate, selenite, and organic selenium from ground water:** Estimate required.
- 35) **Se transfer from Deep Brine Layer to purple sulfur bacteria: Purple sulfur bacteria (*Ectothiorhodospiraceae*) and green sulfur bacteria (*Chlorobiaceae*),** mainly use sulfide and other inorganic sulfur or selenium compounds. In an anaerobic environment, using CO₂ as a carbon source, the green and purple sulfur bacteria oxidize H₂S to SO₄⁻² or HSe to selenite and/or selenate during photosynthesis. *Desulfovibrio* sp. in this environment can reduce SO₄⁻² or oxidized selenium compounds to H₂S and HSe. No literature was found that quantifies this type of transfer.
- 36) **Vapor transfer of Se from Deep Brine Layer to Shallow Layer:** Oyamada et al., (1991); Neumann et al., (2003) provide references on production of gas phase selenium by bacteria. The generation of volatile selenium has been observed in a range of soils and sediments (Zhang and Frankenberger, 2002; Chau et al. 1976; Azaizeh et al. 1997; Frankenberger and Karlson, 1988; Frankenberger and Karlson, 1994; Pilon-Smits et al. 1999; Oremland et al., 1986, 1989, 1990, 1994; Steinberg et al., 1990; Zawislanski et al., 2001, Zawislanski, 1996). No references were found quantifying volatile selenium flux at the interface between anoxic brine and suboxic hypersaline waters.
- 37) **Re-suspension transfer of particulate Se species from Deep Brine Layer to Shallow Layer:** DYRSEM model of Imberger (URL) group can be implemented to predict these transports.
- 38) **Settling transfer of particulate Se species from Shallow Layer to Deep Brine Layer:** Here particulates are defined as any phase that settles. Settling rates of live and dead phytoplankton are highly variable, ranging from meters/day to mm/day (Reynolds 1984). Larger taxa, particularly diatoms, sink quickly whereas small bacterial-sized ones will not sink at all. The dominant phytoplankton in Gilbert Bay (*Dunelliella*) is flagellated and will not sink while alive. Most transport of organic particulate matter will be via fecal material of brine shrimp. Settling rates of these feces is unknown (W. Wurtsbaugh comments). According to sediment flux measurements conducted in sediments and wetland environments, particulate selenium in wetland and sediment systems range from <2.5% to 25% of the total selenium flux. Notably selenium deposits were generally highest in sediments and marsh layers in the upper 15 cm. The differentiation of various particulate forms of selenium: selenium bound to organic macromolecules, selenium bound to organic particulates, elemental particulate selenium, selenium adsorbed to mineral particles, etc. requires implementation of advanced size fractionation techniques such as field flow fractionation (Zhang et al., 2004; Johnson et al., 2000).
- 39) **Adsorption, precipitation, and uptake by phytoplankton of aqueous Se species to yield particulate Se species in the Shallow Layer:** Anne Fairbrother suggests Williams

et al. (1994) for uptake of selenate by algae. Fisher and Wentz (1993) describe mineralization rates of Se in marine phytoplankton. Baines et al. (2004) point out that Se uptake by phytoplankton is highly light dependent. See Doyle et al. (1995) for additional insights. Neumann et al. (2003) describe rapid metabolism of selenate to volatile dimethylselenide, but this process was inhibited by sulfate. Selenium is concentrated in the particle phase relative to the aqueous phase by factors ranging from ten to thousands. Theresa Presser suggests that these concentration factors are too variable to borrow from literature, and need to be measured. Wayne Wurtsbaugh notes: Fisher et al. (2000) provide a model of Se uptake by marine phytoplankton and subsequent incorporation into zooplankton. Baines et al. (2004) point out the light dependence of metals (including Se) by phytoplankton. Nishri et al. (1999) describe Se uptake by phytoplankton and its incorporation into dissolved organic matter. See also 54 (reduction of selenium in shallow layer) and 47 (adsorption, precipitation, and uptake by phytoplankton of aqueous Se species to yield particulate Se species in the Shallow Layer).

- 40) **Settling of Particulate Se in Shallow Layer to Littoral Sediment:** This process includes detrital material from sinking seston, and from periphyton that have died, as well as minerals. Settling rates of live and dead phytoplankton are highly variable, ranging from meters/day to mm/day (Reynolds 1984). Larger taxa, particularly diatoms, sink quickly whereas small bacterial-sized ones will not sink at all. The dominant phytoplankton in Gilbert Bay (*Dunelliella*) is flagellated and will not sink while alive. Most transport of organic particulate matter will be via fecal material of brine shrimp. Settling rates of these feces are unknown (W. Wurtsbaugh comments). See also 54 (reduction of selenium in shallow layer) and 47 (adsorption, precipitation, and uptake by phytoplankton of aqueous Se species to yield particulate Se species in the Shallow Layer).
- 41) **Re-suspension transfer of Particulate Se from Littoral Sediment to Shallow Layer:** Resuspension of particulate material and nutrients/Se in the interstitial water is thought to be important in the Salton Sea (G. Schladow-UC Davis, personal communication to W. Wurtsbaugh). The larger fetch of the GSL is likely to make re-suspension even more important.
- 42) **Vapor transfer of Se from Shallow Layer to atmosphere:** Volatilization of selenium from seawater and other high salinity aquatic settings is a well-observed phenomenon indicating significant potential for this process to be important in the selenium budget for the Great Salt Lake. Volatilization increases with the addition of organics, and increases with pH above 7. In many articles, selenite produced higher volatilization of selenium than did selenate, which emphasizes the importance of selenium species on selenium pathways and fluxes. Direct measurement of dissolved gas pressures would allow determination of the potential significance of selenium fluxes by this mechanism (Chau et al., 1976; Amouroux and Donard, 1996; Azaizeh et al., 1997; Atkinson et al., 1990; Barks and Fleming, 1974; de Souza et al., 1998; Fleming and Alexander, 1972; Frankenberger and Karlson, 1988; Frankenberger and Karlson, 1994; Oremland and Zehr, 1986; Pilon-Smits et al., 1999; Zhang and Frankenberger, 2002; Zieve and Peterson, 1985)
- 43) **Atmospheric transfer of selenium to Shallow Layer:** No references were found on this topic. We do not expect a substantial amount of selenium to be transferred from the atmosphere to the GSL environments modeled.

- 44) **Oxidation of various reduced Se species to selenate and selenite in the Shallow Layer:** Some inorganic forms of selenium have been reported to be oxidized by microorganisms. *Micrococcus selenicus* isolated from mud (Breed et al. 1957), a rod-shaped bacteria isolated from soil (Lipman and Waksman, 1923), and a purple bacterium (Sapozhnikov, 1937) have been reported to oxidize Se^0 to SeO_4^{2-} . Strains of *Bacillus megaterium* from top soil in river alluvium can oxidize elemental selenium to selenite and selenate; the red amorphous elemental selenium is more readily transformed than the grey elemental selenium. Additionally, *Thiobacillus ferroxidans* is able to oxidize copper selenide as a sole energy source and can also oxidize other selenium species to elemental selenium (Torma and Habashi, 1972). Reduced selenium species that are transported to the shallow layer will be oxidized according to oxidation-reduction equilibria. The significance of this process is uncertain. Since oxidized selenium species are soluble, this process potentially re-mobilizes selenium. The transport of reduced selenium species to the shallow layer may occur via re-suspension of sediment, lake area fluctuation, etc.. Determination of the significance of this process requires measurement of selenium fluxes in response to sediment re-suspension and lake area fluctuation.
- 45) **Reduction of selenate to selenite in shallow layer:** Selenium reduction can occur in all GSL environments including aerobic environments and reduction of selenate to selenite is a natural transformation by many bacteria that are able to reduce selenate to elemental selenium (Doran and Alexander, 1977; Oremland et al., 1989; Lortie et al., 1992; Steinberg et al., 1990; Zarate, 2001; Zawislanski and Zavarin, 1996). Quite a number of inorganic selenium compounds can be reduced by microorganisms. *Micrococcus* sp. have been demonstrated to reduce Se^0 to HSe^- and *Desulfovibrio* sp. can reduce selenite to Se^0 (Woolfolk and Whitney, 1962). A great variety of bacteria, actinomycetes, and fungi have been shown to reduce selenate and selenite to elemental selenium (Bautista and Alexander, 1972; Sarret et al. 2005; and Zalokar, 1953). Despite being in the same chemical family, selenite can be reduced directly to elemental selenium while sulfite cannot be reduced to S^0 , but is reduced to H_2S implying different enzymatic reduction mechanisms. *Desulfovibrio desulfuricans* has been shown to reduce selenate to selenide (Zehr and Oremland, 1987). With some microorganisms, sulfate can inhibit the reduction of selenate, suggesting that this mechanism in at least some microorganisms may be similar. In *Escherichia coli* and other microbes like some *Bacillus* sp. and *Pseudomonas* sp., reduction of selenate and selenite to elemental selenium via glucose metabolism results in elemental selenium being deposited on the cell surface rather than building up in the cytoplasm (Gerrard et al., 1974). Other microbial reductions of selenate and selenite can result in incorporation of selenide into organic compounds such as selenomethonine (Ahluwalia et al., 1968) or accumulation of elemental selenium internally. Other soil microbes reduce selenate or selenite to dimethylselenide (Fleming and Alexander, 1972; Doran and Alexander, 1977). Reduction of selenate and selenite by a wide variety of microbes represents a detoxifying mechanism in some and a form of respiration in others and is nutritionally required by a number of bacteria, plants, and animals.
- 46) **Transfer of oxidized Se from Exposed Sediment to Shallow Layer via lake area increase:** Naftz et al. (2005) provide flux rates of Se into water during re-flooding of wetlands.

- 47) **Oxidation of organic and reduced particulates to oxidized non-particulate species in the Shallow Layer:** Some inorganic forms of selenium have been reported to be oxidized by microorganisms. *Micrococcus selenicus* isolated for mud (Breed et al. 1957), a rod-shaped bacteria isolated from soil (Lipman and Waksman, 1923), and a purple bacterium (Sapozhnikov, 1937) have been reported to oxidize Se^0 to SeO_4^{2-} . Strains of *Bacillus megaterium* from top soil in river alluvium can oxidize elemental selenium to selenite and selenate; the red amorphous elemental selenium is more readily transformed than the grey elemental selenium. Additionally, *Thiobacillus ferrooxidans* is able to oxidize copper selenide as a sole energy source and can also oxidize other selenium species to elemental selenium (Torma and Habashi, 1972).
- 48) **Uptake of aqueous Se by periphyton and bacteria in Littoral Sediment:** Bacteria that reduce selenium and accumulate selenium on their exterior membranes produce submicron sized particles of selenium bound to their surface that could be released into the aqueous environment – it may be possible for these same microbes to bind particulate selenium from the littoral environment. In any event, microbes with bound selenium – internal and external – could be responsible for movement of selenium in this environment and to the next higher level in the food chain. The references provided indicate that a number of variables are important in the transfer of selenium from sediments to bacteria and that this transfer must be balanced with the production of dimethylselenide and concentration of selenium in the water column (Zarate, 2001; Doran and Alexander, 1977; Barks and Fleming, 1974).
- 49) **Volatilization of Se from Exposed Sediment:** see Frankenberger & Karlson (1995)
- 50) **Transfer of Se from North Arm to Deep Brine Layer:**
- 51) **Transfer of selenate, selenite, and organic Se from littoral sediment to Exposed Sediment via lake level decrease:** Estimation required.
- 52) **Transfer of selenate from Exposed Sediment to Shallow Layer via lake level increase:** Estimation required.
- 53) **Transfer of reduced Se from Anoxic Sediment to Littoral Sediment via lake level decrease:** Estimation required.
- 54) **Transfer of selenate, selenite, and organic Se from Littoral Sediment to Anoxic Sediment via lake level increase:** Estimation required.
- 55) **Vapor transfer of reduced selenium from Anoxic Sediment to Deep Brine Layer:** Blum et al. (1998) describe new halobacteria that reduce selenate to selenite and elemental Se.
- 56) **Settling transfer of particulate Se species from Deep Brine Layer to Anoxic Sediment:** Particulate matter in deep brine layer is very high, either because the high salt content “pickles” the material, thus slowing decomposition, and/or because the high density water is heavier than the settling particles, thus maintaining material in suspension (W. Wurtsbaugh comment).
- 57) **Transfer of Se from non-particulates in Deep Brine Layer to Particulates in Deep Brine Layer via reduction, precipitation:** Hockin and Gadd (2003) describe linked redox precipitation of sulfur and selenium under anaerobic conditions by sulfate-reducing bacteria.
- 58) **Reduction to vapor Se in Deep Brine Layer:** Quite a number of inorganic selenium compounds can be reduced by microorganisms. *Micrococcus* sp. have been demonstrated to reduce Se^0 to HSe^- and *Desulfovibrio* sp. can reduce selenite to Se^0

(Woolfolk and Whitney, 1962). A great variety of bacteria, actinomycetes, and fungi have been shown to reduce selenate and selenite to elemental selenium (Bautista and Alexander, 1972; Sarret et al., 2005, and Zalokar, 1953). Despite being in the same chemical family, selenite can be reduced directly to elemental selenium while sulfite cannot be reduced to S^0 , but is reduced to H_2S implying different enzymatic reduction mechanisms. *Desulfovibrio desulfuricans* has been shown to reduce selenate to selenide (Zehr and Oremland, 1987). With some microorganisms, sulfate can inhibit the reduction of selenate, suggesting that this mechanism in at least some microorganisms may be similar. In *Escherichia coli* and other microbes like some *Bacillus* sp. and *Pseudomonas* sp., reduction of selenate and selenite to elemental selenium via glucose metabolism results in elemental selenium being deposited on the cell surface rather than building up in the cytoplasm (Gerrard et al., 1974). Other microbial reductions of selenate and selenite can result in incorporation of selenide into organic compounds such as selenomethionine (Ahluwalia et al., 1968) or accumulation of elemental selenium internally. Other soil microbes reduce selenate or selenite to dimethylselenide (Fleming and Alexander, 1972; Doran and Alexander, 1977). Reduction of selenate and selenite by a wide variety of microbes represents a detoxifying mechanism in some and a form of respiration in others and is nutritionally required by a number of bacteria, plants, and animals.

- 59) **Reduction to HSe⁻ in Deep Brine Layer:** Blum et al. (2001) describe a novel bacterium growing in anoxic water that respire selenate to selenite and elemental Se. It is quite possible that the deep brine layer of the GSL would contain these organisms. See also (58).
- 60) **Reduction to elemental Se in Deep Brine Layer:** See (58).
- 61) **Reduction to elemental Se in Anoxic Sediment:** Most selenium reduction may occur before selenium reaches the anaerobic sediments. The anaerobic sediments may primarily act as a sink for accumulation of reduced forms of selenium (Doran and Alexander, 1977; Leatherbarrow et al., 2005; Oremland et al., 1990; Oremland, 1994; Oremland et al., 1989; Zawislanski and Zavarin, 1996; Steinberg and Oremland, 1990). See also (67).
- 62) **Reduction to HSe⁻ in Anoxic Sediment:** According to the references reviewed, this should be an important pathway for selenium transformation in the GSL. No transformation rates in the literature were available that could be directly related to the GSL environment. Environmental variables such as high amounts of excess sulfate and nitrate, for example, will in part determine selenium reduction pathways and the form and fate of the precipitated product(s). However, selenate reduction should be achievable under a broad range of environmental conditions (Zehr and Oremland, 1987; Zawislanski and Zavarin, 1996; Zawislanski et al., 2001). See also (59).
- 63) **Reduction to vapor Se in Anoxic Sediment:** See (58).
- 64) **Uptake of selenite, organic Se, and other reduced Se by bacteria in Anoxic Sediment:** According to the references reviewed, uptake of organic selenium and other reduced selenium forms is expected to be significant in the GSL anoxic sediments. Uptake of selenite may occur at higher rates in other GSL environments. As in most references that indicate rates of selenium transformations, no rates were available that were directly applicable to the GSL environment (Zehr, and Oremland, 1987; Sanders and Gilmore, 1994; Doran and Alexander, 1977). See also (58, 61).

- 65) **Oxidation to selenate and selenite in Littoral Sediment:** Some inorganic forms of selenium have been reported to be oxidized by microorganisms. *Micrococcus selenicus* isolated for mud (Breed et al. 1957), a rod-shaped bacteria isolated from soil (Lipman and Waksman, 1923), and a purple bacterium (Sapozhnikov, 1937) have been reported to oxidize Se^0 to SeO_4^{2-} . Strains of *Bacillus megaterium* from top soil in river alluvium can oxidize elemental selenium to selenite and selenate; the red amorphous elemental selenium is more readily transformed than the grey elemental selenium. Additionally, *Thiobacillus ferroxidans* is able to oxidize copper selenide as a sole energy source and can also oxidize other selenium species to elemental selenium (Torma and Habashi, 1972). Reduced selenium species that are transported to the Littoral Sediment will be oxidized. Since oxidized selenium species are soluble, this process potentially re-mobilizes selenium. The transport of reduced selenium species to the shallow layer may occur via re-suspension of sediment, lake area fluctuation, etc.. Determination of the significance of this process requires measurement of selenium fluxes in response to sediment re-suspension and lake area fluctuation.
- 66) **Reduction to selenite in Littoral Sediment:** See (45 and 48).
- 67) **Oxidation to selenite in Exposed Sediment:** See (47) and (65).
- 68) **Transfer of water from Goggin drain:** Data available from Kennecott.
- 69) **Transfer of water from North Point canal:** Data available from Kennecott.
- 70) **Transfer of water from Kennecott outfall:** Data available from Kennecott.
- 71) **Transfer of water from Lee Creek:** Data available from Kennecott.
- 72) **Transfer of water from Farmington Bay:** Data available from USGS.
- 73) **Transfer of water from Bear River Bay:** Data available from USGS.
- 74) **Transfer of water from Weber River:** Data available from USGS.
- 75) **Transfer of water from ground water:** Estimates required.
- 76) **Transfer of water from Deep Brine Layer:** Estimates required.
- 77) **Transfer of water from North Arm to Deep Brine Layer:** Estimates required.
- 78) **Evaporation:** Data available from variety of federal, state, and academic sources.
- 79) **Precipitation:** Data available from variety of federal, state, and academic sources.

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