BRINE DISPOSAL LAKES OF SOUTHWESTERN OKLAHOMA

AND NORTHCENTRAL TEXAS: POTENTIAL FOR

SELENIUM-RELATED IMPACTS ON WILDLIFE

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CHAPTER I

INTRODUCTION

Since the discovery of deformities and reduced reproductive capacity of aquatic birds in the San Joaquin Valley, California, during the mid-1980s, national attention has focused on the implications of elevated selenium (Se) concentrations in aquatic systems. Selenium was identified as the primary cause of the disappearance of fish species, the decrease in aquatic bird hatching success, and the high (64%) rate of deformed and dead bird embryos at Kesterson National Wildlife Refuge (KNWR) within the San Joaquin Valley (U.S. Fish and Wildlife Service 1992). These findings have generated a considerable amount of Se-related research and have prompted recent order-of-magnitude reductions in recommended waterborne selenium criteria, reevaluation of agricultural drainwater disposal practices, and an increased awareness of Se issues in water resources planning throughout the western United States.

In a letter dated 20 December 1991, the U.S. Fish and Wildlife Service (USFWS) expressed concerns related to potential Se impacts associated with proposed portions of the Tulsa District (TD), Corps of Engineers (COE) Red River Chloride Control Project, Oklahoma and Texas. Recent experiences at KNWR, naturally-elevated Se in soils and surface waters of Chloride Control project areas, and the proposed use of total evaporation brine disposal lakes (somewhat similar to those employed at KNWR) were the basis for these concerns.

Objectives of this study were to evaluate the potential for selenium accumulation in proposed Chloride Control brine disposal lakes and to estimate resulting impacts on resident or migratory wildlife (in particular endangered bird species). As evaporation lakes associated with the project are designed solely for disposal of naturally-occurring brine waters, primary environmental concerns are associated with impacts on semi-

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aquatic or terrestrial insectivorous or piscivorous organisms (primarily birds) and not with maintenance of diverse communities of exclusively aquatic species (i.e., plankton, invertebrates, fishes).

This study consisted of four principal activities: (1) a review of Se-related scientific literature addressing selenium chemistry, biogeochemical cycling in aquatic systems, and impacts on wildlife; (2) collection of water quality data from project areas; (3) predictive water quality modeling aimed at developing estimates of Se concentrations in water and sediments of proposed brine disposal lakes over the life of the project; and (4) evaluation of predicted Se concentrations with regard to impacts on wildlife. Methodology, assumptions, results, and conclusions for all activities are provided in this report.

CHAPTER II

PROJECT DESCRIPTION

General

The Red River Chloride Control Project, under control of the Tulsa District COE, consists of varied existing and proposed project elements in southwestern Oklahoma and northcentral Texas. The project was authorized by the Flood Control Act of 1966, Public Law 89-789, and has been the subject of considerable subsequent amending legislation. The overall objective of the project is to reduce natural chloride pollution in the Red River Basin by control of low flow emissions from naturally-occurring salt sources (seeps, springs, and salt flats). These sources currently contribute to chloride levels frequently prohibiting feasible municipal, industrial, and agricultural use of Red River waters above Lake Texoma. Detailed descriptions of specific Chloride Control project areas and site-specific features are provided in project design documents (U.S. Army Corps of Engineers 1976a,b; 1982a,b). Locations of all project areas are shown in Figure 1.

While the overall project includes varying chloride control elements, including ring dikes around salt source areas and deep-well injection of collected brines, project areas of concern to this study are those employing low flow collection of brine waters from source areas and transport of these waters to brine disposal lakes. These systems are designed for collection of tributary flows during low flow periods (when chloride levels are highest), passage of flow during high discharge periods, transport of collected brines via pipelines and pump stations, and permanent disposal of brines in surface impoundments. Brine disposal lakes are designed solely for total evaporative reduction in brine water volume and do not include outlet works for discharge from these systems.

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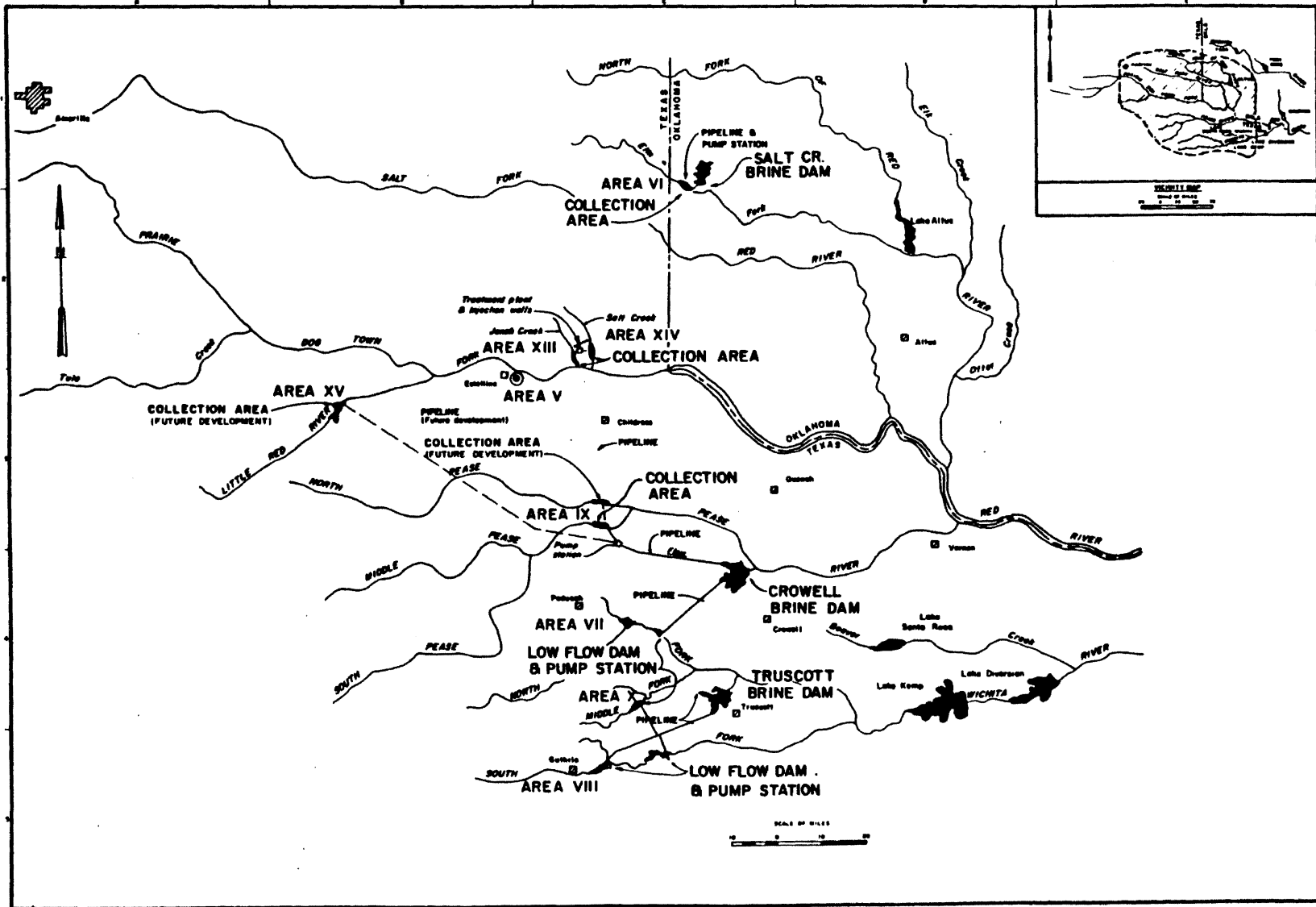
Figure 1. Red River Chloride Control Project Areas (U.S. Army Corps of Engineers)

Hydrology of these lakes is dominated by gradually increasing pool volumes over an anticipated 100-year economic project life.

The Red River Chloride Control project plan includes provisions for three brine disposal lakes: Truscott Brine Lake, Crowell Brine Lake, and Salt Creek Brine Lake (Area VI). Truscott Brine Dam was completed in December 1982 and began receiving brine inputs in May 1987. The remaining two lakes are proposed for construction. Locations, descriptions, and operational characteristics for each lake are described separately below.

Truscott Brine Lake

Truscott Brine Dam is located at river mile 3.6 on Bluff Creek, a tributary of the North Fork of the Wichita River, approximately 3 miles northwest of Truscott, Texas (Figure 1). The embankment, an earth-filled structure 15,500 feet long, was completed in December 1982, and the lake began receiving brines in May 1987. The lake drains a 26.2-square-mile area (primarily undeveloped and agricultural lands), receives brine input from collection facilities at Area VIII, and will receive future input from Area X (Figure 1). At the top of the brine storage pool (representing 100 years accumulation of brine and sediment), the lake is anticipated to have a surface area of 2,980 acres, a capacity of 107,000 acre-feet, and an average depth of 36 feet. Chloride levels are projected to reach a maximum of approximately 65,000 mg/l over the life of the project.

Brine inputs to Truscott Lake are currently transported via pipeline from collection facilities at Area VIII at river mile 74.9 of the South Fork of the Wichita River, about 5 miles east of Guthrie, Texas (Figure 1). Collection facilities consist of a deflatable fabric weir extending across the existing stream channel. The weir is 5 feet high, 49 feet long, and impounds a 31-acre area with a capacity of 83 acre-feet. Waters are pumped from this impounded pool, transported via pipeline, and discharged to Bluff Creek at the upper end of Truscott Lake.

Crowell Brine Lake

Crowell Brine Dam would be located about 5 miles northwest of Crowell, Texas, at mile 1.6 on Canal Creek, a south bank tributary to the Pease River. The lake would drain a 46-square-mile area of undeveloped and agricultural lands and would serve as the disposal facility for brines collected at source Areas VII and IX (Figure 1). Crowell Brine Dam would be an earth-filled embankment with a maximum height of 118 feet and a crest width of 32 feet. At the top of the brine storage pool, Crowell Brine Lake would have a surface area of 3,820 acres, a storage capacity of 110,700 acre-feet, and mean and maximum depths of 29 and 102 feet, respectively. Chloride levels are projected to reach a maximum of 80,000 mg/l over the life of the project.

Collection facilities at Area VII would be located at river mile 213.0 on the North Fork of the Wichita River, about 8 miles southeast of Paducah in Cottle County, Texas (Figure 1). A deflatable fabric weir 5 feet high with a base length of 80 feet extending across the existing river channel would impound a pool covering approximately 14 acres with a capacity of 22 acre-feet. Collection facilities would be very similar in design to those currently existing at Area VIII. Brines collected from this pool would be pumped 12 miles to Crowell Lake via pipeline at an average pumping rate of 8.2 cfs.

Brine collection facilities at Area IX would be located on the Middle Pease River approximately 6 miles upstream of its confluence with the North Pease in Cottle County, Texas (Figure 1). A collection facility design differing from those at other source areas was selected in an effort to minimize the potential for sediment problems in the sump pump and to reduce sediment storage requirements for the associated temporary storage lagoon. Collection facilities would basically consist of a 20-foot-long overflow weir, a settling basin designed to remove fine sand, and a secondary weir leading to a sump.

Brines collected at Area IX would be transferred to a temporary storage lagoon with a capacity of approximately 200 acre-feet, a surface area of 33 acres, and a normal maximum depth of approximately 10.5 feet. Local runoff would be diverted away from the storage lagoon to the Middle Pease River. Temporarily stored brines would

ultimately be transported 24.2 miles to Crowell Brine Lake via pipeline at an average pumping rate of 5.2 cfs.

Salt Creek Brine Lake (Area VI)

Salt Creek Brine Lake would serve as the disposal site for brines collected at Area VI on the Elm Fork, a tributary of the North Fork of the Red River in Harmon County, Oklahoma (Figure 1). Salt Creek Dam would be located on Salt Creek east of State Highway 30 and would consist of a 4,500-foot earthen embankment impounding 735 acres at the top of the 100-year brine storage pool. Storage capacity for collected brine and sediment would be 31,630 acre-feet. Maximum chloride levels approaching 195,000 mg/l are projected over the life of the project.

Salt sources (springs) are located in three box canyons (Salton, Robinson, and Kiser) along the south bank of the Elm Fork at Area VI. They extend from approximately one mile west of Oklahoma State Highway 30 to 3 miles east of the Texas-Oklahoma State line. Collection of brine at Area VI would be accomplished by constructing a closure dam along the existing Elm Fork channel at the upstream and downstream limits of the emission area to create a temporary 115-acre brine detention reservoir. A 200-foot-bottom-width channel would be excavated to divert Elm Fork waters around the emission area. Brines collected from emission areas would be transferred from the temporary detention reservoir to Salt Creek Brine Lake by a pumping station and 4 miles of pipeline.

CHAPTER III

ENVIRONMENTAL CONCERNS AND LITERATURE REVIEW

General

Selenium is a rather unique element owing to a narrow difference between nutritionally essential and toxic concentrations (National Academy of Sciences 1971). While Se-induced toxicity to domestic animals and wildlife is well-documented, trace Se levels (0.05 to 0.3 ppm) are believed to be essential as a dietary supplement for humans and other animals (USFWS 1992). For many organisms, Se deficiency may be manifested in periodontal disease, infertility, and growth inhibition and may actually pose a greater threat than toxicity (Eisler 1985). Selenium has been shown to prevent several forms of chemically-induced cancer in animals and has been implicated in reduced human cancer and heart disease death rates in high selenium areas (Shamberger 1981).

Industrial uses for Se include photoelectric cell production, xerography, ceramics, rubber, glass pigmentation, and flame-proofing of electric cable (Shamberger 1981). Eisler (1985) reported an annual release of approximately 4.6 million kg of selenium to the environment: 33% from combustion of fossil fuels, 59% from industrial losses, and 8% from municipal wastes. Of this total, approximately 25% is in the form of atmospheric emissions.

With the exception of highly localized areas of contamination associated with specific activities, anthropogenic releases of selenium are relatively insignificant relative to contributions from natural sources (Eisler 1985). While soil Se concentrations rarely exceed 2 ppm dry weight, soils produced by weathering of sedimentary rock may possess much higher levels. Such soils are widespread across the western United

States (Lemly and Smith 1987). Activities promoting release of Se from these soils (i.e., intensive irrigation and collection of return flows) may result in toxic concentrations of Se in receiving waters. Selenium concentrations in most fresh and salt waters are considerably lower than those in terrestrial materials and usually range from 0.05 to 4 ug/l (Doran 1982).

<div align="center">Aquatic Chemistry and Cycling of Selenium</div>

General Chemistry

Selenium is a semimetallic element characterized by an atomic weight of 78.96, an atomic number of 34, a melting point of 217 °C, a boiling point of 685 °C, and a density of 4.26 to 4.79. Elemental Se is very insoluble and therefore of limited availability to the environment, although it is capable of satisfying nutritional requirements (Eisler 1985).

Chemical Speciation

Selenium chemistry is highly complex due to the existence of multiple oxidation states, numerous Se-containing organic compounds, and biogeochemical interactions among these forms. Valence states of Se occurring in the natural environment include -2 (selenide), 0 (elemental Se), +4 (selenite), and +6 (selenate). Organic forms include such compounds as seleno-amino acids, seleno-amino acid derivatives, methyl selenides, methyl selenic esters, methyl selenones, and methyl-selonium ions (Thompson-Eagle and Frankenberger 1990). Cooke and Bruland (1987) identified a number of dissolved Se species including inorganic selenate and selenite, nonvolatile organic selenides, seleno-amino acids, a dimethylselenonium ion, and the volatile methylated forms dimethyl selenide (DMSe) and dimethyl diselenide (DMDSe) in surface waters from the San Joaquin and Imperial Valleys of California.

Dissolved inorganic Se may exist in natural waters as Se(-II), primarily as biselenide (HSe^-); Se(0), as colloidal elemental selenium; Se(IV), as the selenite oxyanion ($HSeO_3^-$ and SeO_3^{-2}); and Se(VI), as the selenate oxyanion (SeO_4^{-2})

(Cooke and Bruland 1987). At equilibrium, moderately to strongly oxidizing waters favor Se(VI) or Se(IV) as predominant inorganic forms of dissolved Se, while moderately to strongly reducing conditions favor the predominance of Se(-II) or Se(0) (Elrashidi et al. 1989).

Masscheleyn et al. (1990) incubated Se-contaminated Kesterson Reservoir sediments under controlled redox and pH conditions and reported maximum Se solubility under oxidized conditions (450 mV). Selenate was the predominant dissolved species present, constituting 95 and 75% of total soluble selenium at 450 mV for higher (8.9, 9.0) and lower (7.5, 6.5) pH values, respectively. Similar results were obtained with Hyco Reservoir (North Carolina) sediments (Masscheleyn et al. 1991). Selenium solubility reached a maximum under highly oxidized (500 mV) conditions with Se(VI) the predominant dissolved species. Cooke and Bruland (1987) identified selenate as the major dissolved selenium species (56 to 71% of total Se) in the San Joaquin River, while Saiki (1986) reported that most selenium in tile drainage from the San Joaquin Valley is in the Se(VI) form. Because of its stability under alkaline pH and oxidizing conditions, its solubility, and its availability to plants, the National Academy of Sciences (1976) warned that Se(VI) may be the most dangerous form of Se relative to environmental pollution.

Despite thermodynamic predictions of selenate as the exclusive inorganic Se species in oxidized environments, several investigators have reported significant concentrations of selenite in oxic waters (Measures and Burton 1978, Cutter 1982, Cooke and Bruland 1987). Cooke and Bruland (1987) reported Se(IV) concentrations comprising 33% of total selenium in oxic surface waters of the Salton Sea, California, with selenate below analytical detection limits. These authors suggested that these findings might be due to Se(VI) reductive incorporation by organisms in waters entering the Salton Sea. Measures and Burton (1978) reported the consistent presence of selenite in river and estuarine waters, but found that Se(IV) accounted for less than 10% of total dissolved selenium in these systems.

Similarly, selenium speciation contrary to thermodynamic predictions has been reported in deep, reducing waters of some systems. While Se(-II) and Se(0) should be exclusive species under such conditions, other forms may persist. Measures and Burton (1980) reported the presence of Se(IV) in deep waters of the Atlantic Ocean. Data collected from the Saanich Inlet, an intermittently anoxic fjord along the southeastern portion of Vancouver Island, by Cutter (1982) indicate the near absence of hydrogen selenide (the thermodynamically-predicted form). In contrast, data from anoxic waters of the Salton Sea (Cook and Bruland 1987) support thermodynamic predictions, revealing the dominance of the Se(-II, +0) fraction and virtual absence of Se(IV) and Se(VI).

While numerous examples of both adherence and deviation from thermodynamic predictions of Se speciation are present in the literature, many investigators agree that exceptions may be at least partially explained by kinetic stability of thermodynamically unstable forms (Measures and Burton 1980, Cutter 1982, Cooke and Bruland 1982, Cutter and Bruland 1984). The kinetically slow process of the oxidation of Se(IV) to Se(VI) has been proposed as an explanation for persistence of the former in oxidized waters (Cooke and Bruland 1987). Another example of kinetic stability might include persistence of organic selenide in oxic waters due to rapid production (through regeneration from biogenic particles) or slow removal (oxidation or biological uptake) rates (Cutter and Bruland 1984).

Runnells and Lindberg (1990) observed that Se speciation predictions based on equilibrium Eh-pH diagrams or equilibrium computer codes involve at least three important assumptions: (1) that all reactions are at equilibrium and fully reversible; (2) that the Eh and pH of the aqueous system can be measured reliably; and (3) that the sensing electrode itself is inert and does not participate in the reaction. These authors cite violations of all three assumptions but emphasize the inability to obtain meaningful Eh measurements with standard platinum electrodes as a major drawback in predicting Se speciation. They propose chemical analysis as the only true means of determining Se species of interest.

The complexity of Se chemistry in aquatic systems is enhanced by the existence of a wide variety of organic selenide compounds. While mechanisms for biological synthesis of organoselenium compounds from inorganic forms are currently poorly understood, a substantial portion of the total Se in aquatic systems may be in the organic form (Maier et al. 1987). Cutter and Bruland (1984) reported that organic selenide constitutes approximately 80% of the total dissolved selenium in surface waters of the North and South Pacific Oceans. These authors reported that the organic selenide maximum is closely tied to maxima of primary productivity, pigments, bioluminescence, and dissolved free amino acids.

From a quantitative standpoint, organic Se compounds of major interest include two seleno-amino acids (selenocysteine and selenomethionine) and two methylated compounds (dimethyl selenide and dimethyl diselenide) (Maier et al. 1987). Uptake of selenites and selenates by organisms and reductive incorporation in amino acid synthesis have been described as a biochemical pathway for seleno-amino acids production (Eisler 1985, Kiffney and Knight 1990). Methylated compounds are of particular importance to the Se cycle due to their volatility and resulting ability to mobilize Se from aquatic environments. Data collected during May 1986 indicate that DMSe comprised 12% of the total selenium in Kesterson Reservoir ponds (Cooke and Bruland 1987).

In aquatic systems, the overall Se cycle involves interconversions between organic and inorganic Se species predominantly through biological pathways (Maier et al. 1987). Major aspects of this cycle, seemingly applicable to both marine and freshwater systems, have been proposed by Cutter and Bruland (1984) and Cooke and Bruland (1987). The cycle involves reductive assimilation of selenate and selenite by organisms to organically bound selenide, release of dissolved organic selenide upon death of these organisms, and multistep oxidation of organic selenide to selenite and ultimately selenate. These authors stress the importance of kinetic effects to persistence of thermodynamically unstable organic selenides and selenite resulting from the multistep regeneration cycle.

SedimentWater Interactions

Biogeochemical cycling and distribution of Se between water and sediment phases are important factors in determining Se available for uptake by organisms in aquatic systems. Immobilization processes contributing to Se accumulation in sediments include bacterial dissimilatory selenate reduction to insoluble Se(0) (Oremland et al. 1990), formation of Se-iron complexes with limited solubilities (Geering et al. 1968), adsorption to particulate matter, and active biological uptake by microbes. Incorporation into settling detritus or excretion by organisms may result in accumulation of organoselenium compounds in sediments (Pease et al. 1992). Se sediment accumulation is particularly pronounced in shallow, highly productive, standing or slow-moving waters with low flushing rates and may result in accumulation of up to 90% of the total Se in these systems (Lemly and Smith 1987). Saiki and Lowe (1987) reported Se concentrations in Kesterson Reservoir sediments of up to 100 ug/g (approximately 200 times more than nearby systems unaffected by agricultural drain waters).

Once in the sediments, Se compounds may undergo further biotic reduction and immobilization or may be reintroduced to the water column by mobilization processes. Mobilization processes include oxidation and methylation by plants and microorganisms, mixing by physical processes or biological activity, and reintroduction to the system via the detrital food pathway (Lemly and Smith 1987). Sediment/water interactions appear to be highly dependent upon sediment type and composition with accelerated rates of Se accumulation in fine-grained, organically-enriched sediments (Nassos et al. 1980, Besser et al. 1989, USFWS 1990a). Experimental evidence seems to indicate that selenium cycling processes are confined to the upper few (0 to 8) cm of aquatic sediments (Rudd et al. 1980, Oremland et al. 1989, Oremland et al. 1990).

A number of researchers have investigated Se sediment/water interactions via experimental microcosm/enclosure studies (Nassos et al. 1980, Rudd et al. 1980, Turner and Rudd 1983, Besser et al. 1989, USFWS 1990a). In a microcosm study comparing Se dynamics of systems possessing pure silica sand versus sand mixed with 10% soil

(silty clay loam), Nassos et al. (1980) measured significantly higher substrate accumulation of selenium in the sand/soil system. Ecological magnification values, defined as the ratio of radiolabelled Se (as selenite) concentration in a system component (in this case sediment) to Se concentration in water were reported as 1.7 and 14 for sand and sand/soil systems, respectively.

Similarly, results of microcosm studies comparing Se-dynamics for San Joaquin River and Volta Wildlife Area sediments (both from California) were reported by Besser et al. (1989) and USFWS (1990a). In these studies, [75]Se (mixture of selenite, selenate, and selenomethionine) was sorbed more rapidly to fine-textured, highly organic Volta pond sediments relative to sandy San Joaquin River substrate. After 28 days of exposure, approximately 60% of microcosm radiolabelled Se was measured in Volta sediments compared to approximately 30% for San Joaquin substrate. In Se species-specific tests, loss rates of dissolved Se from water increased in the order: selenate < selenite < selenomethionine with half-lives of 33, 20, and 7 days for these species, respectively. These authors cautioned that while their findings suggest that sediment/water interactions influence the fate of dissolved Se in shallow systems with high sediment surface area/volume ratios, these interactions may be much more pronounced in microcosms than in larger test systems.

Rudd et al. (1980) and Turner and Rudd (1983) monitored Se and Hg dynamics in 10-m-diameter enclosures in Hg-contaminated Clay Lake, northwest Ontario. Sediments of this system were described as fine grey clay overlain with a thin layer of organic floc. While the major sink for added [75]Se (sodium selenite) in enclosures was sediment, stable partitioning of Se between water and sediments was not apparent after 6 weeks in these enclosures (Turner and Rudd 1983). Reported average half lives of ^{75}Se in the water column of all tubes exposed to sediments was 52 days (Rudd et al. 1980). Importance of sediment/ water interactions in Se removal from the water column was evident in bottom-sealed tubes (excluded from sediments) where ^{75}Se concentrations remained stable throughout the experiments.

Fates of metal radiotracers (including ^{75}Se as sodium selenite) added to a whole lake (Lake 224 of the Experimental Lakes Area, northwestern Ontario) were investigated by Hesslein et al. (1980). This oligotrophic lake has an area of 26 ha, a maximum depth of 27 m, and a mean depth of 12 m. Lake sediments are mostly sand and boulders overlain with a thin (<5 mm) covering of loose organic material. The major sink for isotopes lost from the water column in this study was reported to be sediments with both settling of particulate material and direct adsorption to sediments cited as important removal mechanisms. A half time for added ^{75}Se loss from the epilimnion was reported as 52.0 days. Surprisingly, this rate was identical to that reported by Rudd et al. (1980) in Clay Lake enclosures (described above) despite distinct differences in sediment types. Mass balance calculations 350 days after isotope addition to Lake 224 indicated that 54% of added ^{75}Se remained in the water column.

Results obtained by Masscheleyn et al. (1989 and 1991) regarding the influence of sediment redox potential and pH on Se speciation and solubility (discussed under speciation section) are important in consideration of sediment/water interactions and associated mobility of Se in thermally stratified reservoirs. Changes in the sediment environment (anaerobic to aerobic or vice versa) may result in changes in speciation, resulting solubilities, and seasonal differences in environmental behavior of Se. Based on results of these studies, it would seem that total Se concentrations would be highest in these systems during periods of complete mixing when more soluble oxidized species could potentially be released from sediments. Masscheleyn et al. (1991) reported the release of 13% of total Se present in sediments from Hyco Reservoir, North Carolina, at high redox levels (500 mV).

Sorption/Partitioning

A topic closely related to Se sediment/water interactions is the sorption of this element to suspended materials in aquatic systems. Significant amounts of both organic and inorganic Se may persist in the water column adsorbed onto suspended colloidal material (Maier et al. 1987). Approximately 20% of [75]Se (selenite) added to Experi-

mental Lake 224 was found to be associated with particulate matter (Hesslein et al. 1980) while this proportion was 15% in Clay Lake enclosure studies (Rudd et al. 1980). Takayanagi and Wong (1985; cited in Maier et al. 1987) reported that colloidal inorganic Se constituted 77, 40, and 0% of the total dissolved inorganic fraction, while colloidal organic Se comprised 70, 64, and 35% of the total dissolved organic fraction for fresh, estuarine, and marine waters, respectively.

Selenium sorption by kaolinite and montmorillonite clays over a range of pH values commonly observed in nature was studied by Bar-Yosef and Meek (1987). These authors reported that Se solubility in study suspensions was governed by adsorption which decreased with increasing pH and became negligible above pH 8. Above pH 8, approximately 85% of the total Se was found in solution, while this fraction was 33% at pH 5. Selenite sorption by Ca-kaolinite was described as a rapid process which was completed in approximately 35 hours, with approximately 95% of the total sorption occurring after 720 hours of equilibration. Following this rapid uptake, a much slower process which gradually depleted Se from the solution was observed. While desorption kinetics are poorly understood, Alemi et al. (1988) reported that desorption of Se is relatively slow and suggested that this process may therefore control Se transport at low concentrations.

Adsorption and desorption of Se(IV) and Se(VI) in a variety of soil solutions was reported by Singh et al. (1981). These authors reported that all soils sorbed variable amounts of both Se(IV) and Se(VI) in the following order: high organic carbon soil > calcareous soil > normal soil > saline soil > alkali soil. Organic carbon, clay content, $CaCO_3$, and cation exchange capacity reportedly contributed to adsorption, while high salt content, alkalinity, and increasing pH had negative effects on adsorption. While selenate was always sorbed in higher amounts than selenite in these experiments, other studies have reported that Se(VI) adsorption is minimal under most pH conditions (Masscheleyn et al. 1991). It has been shown that selenite adsorption generally decreases with increasing pH in the range of 4 to 9 (Neal et al. 1987, Masscheleyn et al. 1991). In addition to uncertainties regarding adsorption/desorption mechanics, selenium

partitioning in natural waters may be further complicated by concentration effects of adsorbing solids (O'Connor and Connolly 1980, Voice et al. 1983).

Volatilization

Factors affecting volatilization of methylated Se compounds have received considerable attention due to the ability of this process to remove Se from aquatic systems and the potential use of volatilization in remediation of Se-contaminated areas. Biomethylation of Se in oceanic surface waters may be a major source of vapor-phase selenium in the atmosphere and may therefore be important on a global scale (Cooke and Bruland 1987). Methylation may serve as a detoxification process for organisms as the toxicity of DMSe is orders of magnitude less than that of inorganic Se species (Franke and Moxon 1936, McConnell and Portman 1952; cited in Thompson-Eagle and Frankenberger 1990).

While Se methylation has largely been described as a fungal transformation (Doran 1982, Thompson-Eagle et al. 1989, Karlson and Frankenberger 1989), other organisms contributing to this process might include bacteria (Chau et al. 1976, Doran 1982) and algae (Maier et al. 1987). It is also suspected that aquatic macrophytes might be able to methylate Se due to their physiological similarity to terrestrial plants (Maier et al. 1987). The most active methylating fungus isolated from California evaporation pond waters was identified as Alternaria alternata by Thompson-Eagle et al. (1989). Regardless of the organisms involved, the production of volatile Se compounds appears to be a widespread, general process not restricted to any one group of organisms and is probably affected as much by chemical, physical, and biological characteristics of specific ecosystems as by differences in methylating species (Doran 1982). Se volatilization does not appear to be limited to high Se environments, and minimum threshold Se concentrations below which volatilization does not occur have not been detected (Karlson and Frankenberger 1989, Thompson-Eagle et al. 1990).

Three forms of methylated Se are synthesized by microorganisms: dimethyl selenide, dimethyl diselenide, and dimethyl selenone (Maier et al. 1987). Proposed

mechanisms for Se methylation are described by Reamer and Zoller (1980) and Doran (1982). Cooke and Bruland (1987) identified both DMSe and DMDSe as well as a dimethylselenonium ion (DMSe$^+$-R) in surface waters from the San Joaquin and Imperial Valleys of California. DMSe was the major volatile Se species present, constituting greater than 99.8% of the total volatile selenium. These authors suggested that the production of DMSe in aqueous systems might involve hydrolysis of DMSe$^+$-R to DMSe at neutral pH.

A number of researchers have investigated the influence of varying Se species as substrate for biomethylation. Karlson and Frankenberger (1989) reported volatilization rates in soils up to an order of magnitude higher with selenite as the Se source as compared to selenate. Similarly, Doran and Alexander (1976) reported conversion of inorganic Se(0), Se(IV), and Se(VI) to volatile products in soils with volatilization most rapid with selenite and slowest with elemental Se. In the same study, Se in certain organic forms (particularly selenomethionine) was reportedly more readily transformed to volatile products than inorganic Se. These findings were supported by microcosm data reported by the USFWS (1990a) in which volatilization accounted for 24% of ^{75}Se added as selenomethionine, compared to 1% or less of that added as Se(IV) and Se(VI).

Studies aimed at defining optimum environmental conditions for Se biomethylation and volatilization have been conducted by a number of investigators. These authors have reported a general increase in Se volatilization with increasing temperature, circumneutral pH, and significant increases in biomethylation rates associated with addition of various soil amendments (Doran and Alexander 1976, Frankenberger and Karlson 1989, Karlson and Frankenberger 1989, 1990).

In one of the few studies attempting to determine Se volatilization rate coefficients, Calderone et al. (1990) evaluated effects of environmental conditions and organic soil amendments on Se volatilization from sediments of Kesterson Reservoir and the San Luis Drain, California. Volatilization of selenium from sediments in this study was best described by an irreversible first-order rate expression with volatilization rate coefficients

(k values) in unamended controls ranging from 0.003 to 0.053 day^{-1}. Experimental increases in temperature accelerated Se volatilization (calculated Q_{10} = 1.96) as did organic soil amendments (1.7 to 3.2-fold increases over controls).

Apparent discrepancies exist in the literature regarding Se biomethylation under oxic versus anoxic conditions in aquatic systems. Masscheleyn et al. (1990) reported biomethylation of selenium only under oxidized conditions (200 and 450 mV) and found no evidence of volatilization under reduced conditions in experiments with Kesterson Reservoir sediments. Similar results were reported by Masscheleyn et al. (1991). In contrast, Doran and Alexander (1976) and Chau et al. (1976) reported DMSe production under anoxic conditions. Maier et al. (1987) suggested that even if methylation does occur in association with anoxic sediments, rates of Se methylation are most likely not high enough to be of ecological importance.

Reported overall significance of biomethylation and volatilization to Se inventories in aquatic systems has varied in a number of studies. This variation probably reflects the importance of complex environmental variables affecting this process. Reamer and Zoller (1980) reported minimal formation of volatile selenium compounds in unamended soils and sewage sludge. In closed system microcosm studies employing sediments from the San Joaquin River and Volta Wildlife Area, California, volatile Se compounds were found to comprise 3.0 to 7.9% of the total Se inventory (Besser et al. 1989). In similar studies with Kesterson Reservoir and Peck Pond sediments, Karlson and Frankenberger (1990) reported cumulative Se volatilization (273 days incubation time) of 6.1 and 14.0% of initial Se inventory for Kesterson and Peck sediments, respectively.

Cooke and Bruland (1987) reported that outgassing of Se may have been substantial in biologically active Kesterson Reservoir during the mid-1980s. These authors calculated an estimate of the DMSe evasion flux from this system and, based on mass balance calculations, concluded that roughly 30% of Se introduced to the reservoir via the San Luis Drain was volatilized to the atmosphere. Similarly, Thompson-Eagle and Frankenberger (1990) reported a 35% loss of the Se inventory in unamended pond water from Kesterson Reservoir after 43 days incubation. These

findings may emphasize the importance of substantial biological productivity to Se volatilization in aquatic systems.

Metal Complexes

The ability of Se to form complexes with a number of metals in the aquatic environment may affect Se solubility (Geering et al. 1968, Elrashidi et al. 1987) or expression of biological effects (Lemly and Smith 1987). Of particular interest to environmental cycling of Se is the extremely low solubility of the ferric selenites (National Academy of Sciences 1976). In theoretical development of Se equilibria in soils, Elrashidi et al. (1987) predicted that metal-selenate and selenite minerals are generally too soluble to persist in well-aerated alkaline soils, but that at low redox, elemental Se or metal-selenide minerals might control Se solubility. Cutter (1982) suggested that formation of metal selenides might be an important mechanism in removing Se(IV) and Se(VI) from anoxic zones of stratified waters.

Metallic selenides may be of biological significance due to their ability to sequester both Se and toxic metals in forms of limited availability for biological uptake (Eisler 1985). Turner and Rudd (1983) examined effects of Se additions on mercury uptake by organisms in experimental ecosystems. These authors reported reduced accumulation of mercury with increasing Se concentrations. The National Academy of Sciences (1976) cited studies indicating that formation of insoluble mercuric selenide may be a mechanism involved in dietary selenite reductions of methyl mercury toxicity.

Bioconcentration

Bioconcentration is defined as the direct biological uptake of a chemical from the water column or associated sediments to levels in organisms exceeding those in environmental media (water and sediments). This uptake may be the result of diffusion, facilitated transport, or active transport across epithelial or respiratory surfaces (Maier et al. 1987). Bioconcentration of selenium has been documented for a number of aquatic organisms and may be one of the most critical processes affecting expression of Se

effects in aquatic ecosystems. Extensive bioconcentration of Se may be due to chemical similarities with sulphur (Lemly and Smith 1987) and is influenced by water temperature, age and condition of organisms, organ or tissue specificity, and other complex environmental factors (Eisler 1985).

Algae exhibit a tremendous and varying capacity for Se bioconcentration with some species possibly capable of regulating intracellular selenium concentrations (Foe and Knight 1986). Selenium enters aquatic food chains primarily through direct uptake by primary producers (Pease et al. 1992), and high bioconcentration factors at this level are most likely a critical link in expression of biological effects at higher trophic levels. Algal bioconcentration factors (BCFs) reported in the literature have been summarized by Pease et al. (1992) with values ranging from 500 to 33,000 for marine systems and from 30 to 2,000 for fresh waters. Bioconcentration experiments with marine phytoplankton (Vandermeulen and Foda 1988) illustrate the species-specific nature of Se bioconcentration in algae.

While algae have been the subject of a great deal of the Se bioconcentration research, bioconcentration of Se in aquatic invertebrates has also been demonstrated. Sandholm et al. (1973) reported direct uptake of radio-labelled selenite in zooplankton in culture experiments. Similar results were obtained by Besser et al. (1989) where daphnids actually accumulated higher Se concentrations than periphyton. For organisms exposed to 1 ug/l ^{75}Se as selenite, Nassos et al. (1980) measured Se uptake by invertebrates in the following order: daphnia > mosquito larvae > snails.

Maier et al. (1987) suggested that a major factor affecting direct uptake of Se by invertebrates might be the nature of their exoskeleton/epithelium and also alluded to the importance of ecological roles of these organisms. These authors cited possible greater rates of accumulation in benthic organisms due to greater exposure to Se in sediments as an example of the importance of these roles.

While Se accumulation in aquatic plants has not been thoroughly researched, several studies have indicated that uptake rates may be low (Sandholm et al. 1973; Besser et al. 1989). Studies also show that while fish may accumulate Se directly from

the water (Nassos et al. 1973), dietary uptake of Se serves as the major mode of selenium accumulation in fish and higher organisms (Sandholm et al. 1973, Rudd et al. 1980, Lemly 1985).

Several studies have examined the importance of Se chemical speciation relative to bioconcentration in the aquatic environment. In experiments with marine phytoplankton, Vandermeulen and Foda (1988) reported preferential uptake of selenite over selenate at natural seawater concentrations (10^{-10} to 10^{-9} M Se), with increased selenate uptake at much higher concentrations (10^{-8} to 10^{-6} M). Overloading of the uptake mechanism was reported as the reason for Se(VI) uptake at high Se concentrations. These authors claimed that their findings suggest that selenite is not only taken up preferentially from water over selenate, but that cells actively exclude Se(VI) from uptake.

In uptake studies including organoselenium species, selenomethionine has been shown to be preferentially bioconcentrated over inorganic forms. Sandholm et al. (1973) reported low uptake of selenite, but tremendous uptake of selenomethione by phytoplankton in experimental systems. In microcosm studies, Besser et al. (1989) measured greater periphyton and zooplankton accumulation of Se from selenomethionine than from selenite or selenate despite higher concentrations of the inorganic species. Bioconcentration factors ranging from 1,520 to 12,193 were recorded for selenomethionine in uptake studies with the cyanobacterium Anabaena flos-aquae (Kiffney and Knight 1990), with BCFs ranging from 267 to 1,004 and 30 to 115 for selenite and selenate, respectively. Collectively, these high BCFs for organoselenium species reveal the probable importance of these forms in Se-related food chain dynamics and justify further research into the occurrence and toxicological significance of these compounds (Besser et al. 1989).

Biomagnification

Biomagnification (progressive increase in chemical concentration with successively higher food chain trophic levels) of Se following bioconcentration by primary producers

is a process potentially leading to expression of toxic effects in upper trophic levels of aquatic systems (Kiffney and Knight 1990). Upon review of a number of studies examining possible biomagnification of Se, Maier et al. (1987) reported that uncertainty exists as to whether Se is biomagnified in aquatic food chains. Where reported, biomagnification factors for selenium usually range from 2 to 6 between producers and lower consumers (invertebrates and forage fish) (Lemly and Smith 1987). Failure to account for potential biomagnification effects in aquatic ecosystems has been cited as a possible deficiency in existing selenium water quality criteria (Pease et al. 1992).

Selenium biomagnification has been reported in both laboratory and field studies. Increasing Se concentrations from water to algae to zooplankton (daphnids), but not to fishes, were reported for model ecosystems monitored by Nassos et al. (1980). Field data collected by Saiki (1986) and Saiki and Lowe (1987) from Kesterson Reservoir and the San Luis Drain reveal a general increase in Se concentration from water to plants to aquatic animals.

Biological Effects

Acute Toxicity

Toxic effects of selenium may be expressed in two general ways: (1) mortality of juvenile and adult organisms, and (2) reproductive impairment (Lemly and Smith 1987). While reproductive failure may be the first obvious sign of selenium contamination problems in aquatic systems (Lemly and Smith 1987), high enough Se concentrations can lead to acute toxicity. The mode of toxicity is believed to be the substitution of Se for sulfur in amino acid synthesis, with resulting metabolic impairment (Eisler 1985, Kiffney and Knight 1990).

Extensive lists of LC_{50} values for aquatic organisms are compiled in Nassos et al. (1980), Eisler (1985), Maier et al. (1987), and Moore at al. (1990). While these values vary considerably with species, life stage, exposure interval, and Se form, death has

been observed at waterborne Se concentrations as low as 60 to 600 ug/l in early life stages of sensitive organisms (Eisler 1985). In general, LC_{50} values for most organisms greatly exceed Se concentrations found in natural systems. Among inorganic Se forms, several studies have confirmed greater toxicity of selenite relative to selenate (Saiki 1986).

Chronic Toxicity

With the exception of reproductive abnormalities in avian species, sublethal effects of selenium toxicity in aquatic ecosystems are not extensively documented. Nevertheless, several studies have examined these effects. Studies reviewed by Eisler (1985) reported chromosomal aberrations, intestinal lesions, shifts in algal species composition, swimming impairment in protozoans, and behavioral modifications as possible symptoms of chronic Se toxicity. In a similar review of sublethal effects associated with agricultural drainwater constituents (predominantly selenium), the USFWS (1992) reported effects associated with reproduction, growth, internal structure, behavior, physiology, and biochemistry of fish and wildlife resources. Similar effects were noted for several fish species in experiments conducted by Hermanutz (1992) and Hermanutz et al. (1992). Reading and Buikema (1980) reported impacts on filtering rates for Daphnia pulex at selenium concentrations of 800 ug/l.

Effects on Aquatic Birds

While a number of studies have documented effects of elevated Se concentrations on varying classes of biota, major research efforts have been devoted to analyzing impacts on aquatic birds. While these studies have documented varying effects of selenium exposure in birds, results of a number of laboratory and field studies indicate that impacts on avian species are manifested primarily through decreased reproductive success (USFWS 1992). Careful evaluation of environmental factors contributing to impaired avian reproduction and embryonic development is critical to environmental

protection, as these conditions may be the first obvious biological indication of selenium contamination problems in an aquatic system (Lemly and Smith 1987).

Some of the first documented evidence of toxic effects of environmental Se to avian embryos was reported by Ohlendorf et al. (1986) for irrigation drainwater ponds in San Joaquin Valley, California. Of 347 nests of various species of aquatic birds studied by these authors, 40.6% contained at least one dead embryo and 19.6% had at least one chick or embryo with visible external deformities, including missing or abnormal eyes, legs, wings, feet and beaks. Abnormalities associated with brain, heart, liver, and skeletal systems were also noted. Embryonic mortality was highest at 31.7 and 14.6% among eared grebes (Podiceps nigricollis) and American coots (Fulica americana), respectively. Since this report, reproductive impairment in birds inhabiting Se-enriched environments has been reported at other locations, indicating that these effects are widespread, numerous, and not restricted to the San Joaquin Valley of California (see review in USFWS 1990b).

Reproductive impairment in aquatic birds is believed to result from the transfer of bioaccumulated Se to avian eggs where toxicologically significant concentrations may be only slightly higher than background levels (Skorupa and Ohlendorf 1991, Skorupa 1992). Accumulation of significant Se levels in eggs of varying bird species inhabiting environments relatively low in waterborne selenium have been reported in a number of studies (see citations in Skorupa 1992). Direct evidence of the detrimental effects of dietary Se exposure on avian reproduction has been largely obtained in feeding experiments with mallards (Anas platyrhynchos) conducted by Heinz et al. (1987 and 1989). These authors reported decreased reproductive capacity, lowered duckling survival rates, decreased duckling weights, and increased incidence of teratogenic effects with increasing dietary Se levels.

Selenium uptake, transfer efficiency to bird eggs, and resulting effects on avian embryos have been shown to be highly dependent upon the Se chemical species available to birds (Heinz et al. 1987, Skorupa 1992). In feeding experiments with mallards, Heinz et al. (1987) reported that dietary selenomethionine was much more

readily taken up and transferred to eggs relative to sodium selenite. In a comparison of feeding studies employing similar dietary levels of inorganic Se (Heinz et al. 1987) and organic forms (Heinz et al. 1989), selenomethionine exhibited greater effects on avian reproduction. This is particularly significant due to the predominance of forms functionally similar to selenomethionine in aquatic food chains (USFWS 1990b). Based on these findings, the dietary threshold for Se as selenomethionine resulting in avian reproductive impairment has been proposed as approximately 4 to 7 ppm (Heinz et al. 1989, Moore et al. 1990, USFWS 1990b).

Regression equations relating total recoverable waterborne Se, food chain Se, and Se bioaccumulation potential in bird eggs were developed by Skorupa and Ohlendorf (1991). For the San Joaquin Valley, the equation: Log (Mean Egg Se) = 3.66 + 0.57 Log (Waterborne Se) was found to be a reliable predictor of the maximum potential for Se accumulation in bird eggs. These authors stressed the important distinction between "potential" and "realized" selenium in bird eggs and cited various aspects of avian behavior (i.e., food preferences, home range size, habitat preferences, degree of residency) as possible factors affecting observed differences between the two. The eared grebe (a sedentary species) was cited as the best indicator species for egg Se bioaccumulation potential.

In developing recommended waterborne Se concentrations for protection of avian species, Skorupa and Ohlendorf (1991) also differentiated between "avian contamination" (mean selenium in eggs above normal or background concentrations) and "avian toxicity" (mean egg selenium above embryotoxic thresholds). They cited total waterborne Se concentrations of < 2.3 ug/l as necessary for minimizing avian contamination and concentrations of < 10 ug/l as a reasonable goal for prevention of most avian toxicity.

In addition to studies examining reproductive effects of selenium, unpublished results of several studies aimed at determining lethal and sublethal effects on birds were cited by USFWS (1990b). In one study, adult mallards were fed 0, 10, 20, 40, and 80 ppm Se as selenomethionine for 16 weeks over winter with resulting mortalities of 0, 0,

25, 95, and 100%, respectively. In a similar study conducted during spring and summer, lower rates of mortality were observed for 20 and 40 ppm dietary exposures, suggesting that adult mallards may be more sensitive to selenomethionine exposure during cold weather. Based on these results, the USFWS (1990b) recommended a maximum dietary exposure of 10 ppm for protection of overwintering aquatic birds when avian reproduction is not a concern.

Two important considerations in determining effects of selenium on aquatic birds are rates of Se accumulation and elimination in individuals of these species. Feeding experiments with adult mallards (Heinz et al. 1990) indicated that both Se accumulation and elimination are rapid processes in waterfowl—results that these authors claim are consistent with findings in experiments with domestic chickens. In adult mallards, concentrations of Se in liver reached 95% equilibrium in only 7.8 days with half-lives of 18.7 and 30.1 days for liver and muscle concentrations, respectively. Results of their experiments led these authors to conclude that ducks would quickly lose Se upon leaving a Se-contaminated area.

Studies reporting similarly short half-lives for Se in organisms were reviewed by Eisler (1985). In addition, the USFWS (1992) cited evidence of the rapid loss of Se in over 2 million pintails (Anas acuta) wintering in the San Joaquin Valley upon departure from the area. These results collectively suggest that as long as migratory birds do not die on wintering areas, leave Se-contaminated areas approximately 2 weeks prior to egg laying, and arrive at breeding grounds physically fit for breeding, reproduction should not be adversely affected by winter exposure to selenium (USFWS 1990b).

While most of the research concerning Se-related avian reproductive impairment has focused on embryotoxicity and teratogenesis, unpublished data (D. Barnum, USFWS) suggest that selenium exposure may result in decreased body weight, condition indices, and other detrimental effects on overwintering adult birds. These effects may decrease reproductive fitness by influencing mortality prior to egg laying, pair formation, nesting success, predator avoidance, behavioral patterns, and fledgling survival. Experiments subjecting overwintering Se-exposed birds to natural environ-

mental stress conditions are warranted for population-based evaluation of selenium-related reproductive impacts.

Many authors have stressed the importance of avian behavioral ecology in determining Se impacts on bird species (Lemly and Smith 1987, DuBowy 1989, Skorupa and Ohlendorf 1991). Differences in residence times, dietary habits, migration patterns, and local feeding sites result in varying exposures and subsequent manifestation of Se effects on bird species (Ohlendorf et al. 1986). The USFWS (1990b) also stressed the importance of "landscape mosaics" in influencing impacts of contaminants on highly mobile species such as waterfowl. Impoundments situated within a mosaic of relatively clean aquatic systems ("wet mosaics") were cited as significantly less dangerous than impoundments in water-limited "dry mosaics."

CHAPTER IV

LEVELS OF ENVIRONMENTAL CONCERN

Due to substantial Se-related research and subsequent greater understanding of impacts of selenium on aquatic species, recommended Se criteria have decreased significantly over the past decade (Table 1). Selenium concentrations adversely affecting wildlife (particularly in terms of impairment of avian reproduction) are extremely low and frequently only slightly above background levels. This has prompted a heightened awareness of the need to carefully evaluate selenium loading to aquatic systems and to anticipate related impacts on organisms associated with these environments.

For purposes of this study, it was necessary to select threshold selenium levels which, based on current information, would be expected to result in detrimental impacts on wildlife species in the project area. As evaporation lakes associated with the project would be constructed solely for disposal of brine waters, fish and wildlife concerns are limited to impacts on organisms tied to these systems via food chain dynamics. Due to a demonstrated sensitivity of aquatic birds to waterborne selenium and substantial information regarding impacts on these species, birds (particularly endangered species) became the major focus of the study.

Due to two distinct categories of Se-related impacts on aquatic birds, it was necessary to distinguish between Se criteria for: (1) potential reproductive impairment of birds nesting in the project area, and (2) potential detrimental impacts on adult and juvenile birds nesting at sites removed from the project. Since rapid loss of Se from birds has been demonstrated (see above discussion), reproductive impairment (at least in terms of embryotoxicity) would not be anticipated for aquatic birds using distant nesting sites. While impacts on these and other organisms undoubtedly vary with

Table 1. Published Selenium Levels of Concern to Fish and Wildlife Resources. (Concentrations are ug/l [water] and ug/g [food and sediments].)

Year	Environmental Media	Concentration	Protected Resource	Source
1980	Freshwater	35 (as Se^{+4})[a]	Aquatic Life	USEPA 1980
1980	Freshwater	760 (as Se^{+6})	Aquatic Life	USEPA 1980
1980	Salt Water	54 (as Se^{+4})[b]	Aquatic Life	USEPA 1980
1987	Freshwater	5	Aquatic Life	USEPA 1987
1987	Marine Waters	71	Aquatic Life	USEPA 1987
1987	Water	2-5	Fish, Waterfowl	Lemly & Smith 1987
1987	Sediment	4	Fish, Waterfowl	Lemly & Smith 1987
1990	Food Items	4	Bird Reproduction	USFWS 1990b
1990	Food Items	10	Bird Survival[c]	USFWS 1990b
1991	Water	10	Bird Embryos	Skorupa and Ohlendorf 1991
1991	Water	2.3	Avian Contamination[d]	Skorupa and Ohlendorf 1991
1992	Estuary Waters[e]	0.1-0.8 (Se^{+4})	Wildlife	Pease et al. 1992

[a]24-hour average, not to exceed 260 ug/l at any time.

[b]24-hour average, not to exceed 410 ug/l at any time.

[c]Young and adult birds when avian reproduction not a concern.

[d]Defined as mean egg selenium above background concentrations.

[e]San Francisco Bay.

chemical Se species, current criteria are generally proposed in terms of total selenium. Threshold values for this study were selected accordingly.

In studies relating selenium concentrations in water to bioaccumulation of Se in bird eggs, Skorupa and Ohlendorf (1991) proposed 10 ug/l waterborne selenium as protective of avian embryotoxicity under most conditions. This concentration was therefore adopted as the critical level potentially impacting avian reproduction in birds nesting at project evaporation lakes. While lower values have been proposed, it will be demonstrated that selection of this threshold is not critical to this study due to projected values exceeding all recommended threshold concentrations early in the life of the project.

Based on results of waterfowl feeding studies, the USFWS currently recommends a maximum dietary exposure of 10 ppm (dry weight) for protection of young and adult birds where reproductive impacts are not a concern (USFWS 1990b). Use of this dietary value necessitates estimation of waterborne Se levels resulting in 10 ppm in food organisms commonly used by aquatic birds. While a number of complex environmental factors affect the uptake and accumulation of Se in food organisms, empirically derived regression equations developed by Shelton et al. for evaporation ponds in the Tulare Basin of California (unpublished data cited by Skorupa and Ohlendorf 1991) have shown promise in estimating dietary Se on the basis of water-borne Se in egg bioaccumulation studies (Skorupa and Ohlendorf 1991). Other bioaccumulation regression equations have been proposed by Lillebo et al. (1988) for more freshwater environments, but these systems do not approach ionic strengths anticipated for Red River Chloride Control impoundments.

Skorupa and Ohlendorf (1991) estimated food chain Se concentrations using:

$$\text{Log (BSS)} = 3.25 + 0.49 \text{ Log (WS)}$$

where BSS are Se levels (ppb, dry weight) in brine shrimp, and WS is waterborne selenium (ppb, total recoverable).

These authors reported good performance of this equation in estimating the potential for Se accumulation in bird eggs in a number of environments, including those where brine shrimp do not occur. Lack of variation in bioavailable organoselenium concentrations among macroinvertebrate species in a given environment, the lack of a well developed chitinous exoskeleton which might possibly externally adsorb inorganic Se, or good representation of the type of aquatic invertebrate preferred by aquatic birds were cited as possible explanations for adequate performance of this equation in a wide variety of environments.

In an attempt to evaluate the appropriateness of the above brine shrimp equation in estimating Se uptake by food chain organisms for this study, the equation was applied to several field data sets for comparison among predicted and observed concentrations in biota. Using data collected from seven sites in the San Joaquin River system (USFWS 1990a), the equation generally overpredicted Se concentrations in aquatic invertebrates and fish species. Among invertebrates, overpredictions occurred in 64, 57, and 79% of seasonal mean values (spring and fall data at seven sites) for amphipods, chironomids, and crayfish, respectively. For fish species, overpredictions occurred in 42, 64, and 57% for bluegill, largemouth bass, and mosquitofish, respectively. Overall ratios of predicted to observed mean values were as follows: amphipods (1.42), chironomids (1.34), crayfish (1.73), net plankton (1.15), bluegill (1.07), largemouth bass (1.21), and mosquitofish (1.10). It should be emphasized that differences in productivity levels associated with flowing versus impounded waters (evaporation ponds) may account for these differences. Reported total waterborne Se concentrations ranged from <0.3 to 30 ug/l at these sites.

In contrast, the brine shrimp food chain equation grossly underpredicted biotic Se concentrations when applied to data collected for the San Luis Drain and Kesterson Reservoir (data from Saiki 1986, Saiki and Lowe 1987) where total Se concentrations of 36 to 330 ug/l were reported. This may reflect inaccuracy of this equation in estimating Se in food chain organisms of highly productive systems with excessively high

waterborne Se levels (a large portion of which may be present in highly bioavailable organic forms). Much better agreement was obtained with data from the Volta Wildlife Area (Saiki 1986, Saiki and Lowe 1987) where reported total Se concentrations were orders of magnitude lower.

Due to documented adequate performance of the brine shrimp equation in evaluation of food chain impacts on Se accumulation in bird eggs, reasonable agreement with field data under conditions similar to those expected in project evaporation ponds (moderate Se and productivity levels), observed high densities of aquatic invertebrates in saline evaporation ponds (Parker and Knight 1992), and probable conservative (overpredictive) nature of food chain Se estimations, this equation was deemed reasonable for use in this study. Use of this equation and the recommended 10 ppm dietary criteria yields a total waterborne Se concentration of 34 ug/l. This value was therefore used in this study as the threshold concentration for impacts on adult and juvenile birds in the absence of avian reproduction concerns.

CHAPTER V

STUDY METHODOLOGY

General

Prior to initiation of field activities, a search was conducted for existing water quality data from Red River Chloride source areas. This search included such resources as EPA's computerized STORET water quality database and files of other agencies involved in water quality data collection. As this search failed to identify any existing selenium data from source areas, initial phases of the study involved collection of water quality data required as input to predictive modeling exercises.

Water quality data collection was not possible at source areas proposed for input to Salt Creek Brine Lake (Area VI). Box canyons comprising these source areas are currently under private ownership with no government access to these locations. Due to anticipated exclusive collection of waters emitted from these areas (with diversion of the Elm Fork around temporarily stored brines), Se load estimates for modeling purposes could not be obtained. It was therefore determined that proposed Crowell Brine Lake should become the focus of the study, with findings from this system used in general evaluation of potential impacts at Area VI. While results obtained by this approach can be applied to Salt Creek Brine Lake in a general sense, site-specific investigations should be conducted for this system once access to Area VI source areas is obtained.

Limited data were obtained from Truscott Brine Lake for evaluation of operational and general limnological features associated with brine disposal lakes in the project area. With the exception of Truscott Lake, no similar systems exist in the region, and little information is available concerning the limnology of these lakes. Since proposed Crowell Brine Lake and Truscott share similar operational, morphometric, geologic, and

watershed characteristics, data obtained from Truscott were used in estimating future conditions in Crowell Lake for modeling purposes.

Due to operational and design characteristics of Red River Chloride Control project areas, the greatest potential for Se accumulation is anticipated to be associated with brine disposal lakes. While temporary pools at collection facilities would most likely attract waterfowl and other bird species, frequent flushing during high flow periods and selenium removal via pumping will greatly reduce the potential magnitude for selenium accumulation at these areas. Due to anticipated higher Se concentrations in brine disposal lakes, water quality modeling efforts were directed toward these systems and do not include collection facility pools.

Field Data Collection

Collection of field data was scheduled to begin during late spring/early summer 1992. However, unseasonably heavy rainfall during this period resulted in high flows at source areas and necessitated postponement of sampling activities until late June. As selenium concentrations were anticipated to be highest during low flow periods, it was the intent of the study to base water quality predictions on conservatively high selenium loading estimations derived from data collected primarily during periods of low stream discharge. Data were therefore collected approximately biweekly from the end of June to early November 1992, when streamflows at source areas were at a minimum.

Field activities at Crowell Lake source areas (Areas VII and IX) included collection of water samples and measurements of stream flow and field water quality parameters. Water samples were collected from midstream at a depth just below the surface in polyethylene containers precleaned to EPA specifications. Samples were preserved with nitric acid, immediately placed on ice, and transported to the Corps of Engineers Southwestern Division Laboratory, Dallas, Texas, for analysis by a COE-approved contract lab. Analytical parameters included total and dissolved selenium (EPA SW-846 Method 7740), total suspended solids, and major anions and cations. Quality assurance/quality control (QA/QC) measures included collection of duplicate samples at

an approximate 10% frequency, as well as laboratory method blank, reagent spike, matrix spike, and duplicate analyses.

Field measurements of water temperature, pH, dissolved oxygen (DO), conductivity, and redox potential were obtained at each sampling location with a Hydrolab Surveyor II data instrument. This instrument was calibrated according to the manufacturer's instructions prior to each sampling trip. Streamflows were calculated from measured cross-sectional areas and average velocities obtained with a Marsh-McBirney Model 201 current meter.

Water quality data from Truscott Lake and Area VIII were obtained on 22 July, 19 August, and 21 October 1992. Lake data were collected at sampling sites located near Truscott Brine dam, at approximately mid-lake, and near the upper end of the impoundment (Sites 1 through 3, respectively). Vertical profiles of field water quality parameters were collected at 1 m intervals at all sites, and water samples were collected from surface and near-bottom depths. Water samples from Truscott Lake as well as from Area VIII were analyzed for parameters identical to those employed at other locations. Undisturbed sediment cores (0 to 8 cm depth) were likewise obtained with a core sampler at selected Truscott Lake sampling sites and analyzed for total Se, grain size (ASTM hydrometer method), solids content (EPA 160.3), and total organic carbon (EPA 9060).

Water Quality Modeling

Water quality modeling was employed as a means of obtaining reasonable estimates of temporal changes in Se concentrations in water and sediments of proposed Crowell Brine Lake over the life of the project. Due to the complexity of selenium chemistry; uncertainty regarding the relative importance of complex physical, chemical, and biological interactions associated with Se cycling; and the virtual absence of Se fate and transport modeling studies in the scientific literature, modeling output should be viewed as a reasonable approximation based on currently available scientific

information. In an effort to partially mitigate inherent uncertainties associated with Se predictions, reasonably conservative assumptions, estimations, and input data were applied throughout this study where possible. This approach was based on a desire to use all available means of providing reasonable water quality estimates while providing maximum environmental protection.

Preliminary "worst case scenario" estimates of waterborne selenium concentrations in Crowell Brine Lake were derived by initially evaluating Se as a totally conservative substance. This approach ignored the influence of factors resulting in reduced water column Se concentrations (i.e., sorption, settling, volatilization, sediment burial) and was based on simple dilution of Se mass loads by lake water column volumes. While this approach most likely results in gross overestimation of water column Se concentrations, results of this analysis provided absolute worst case estimates and were useful in evaluating the relative significance of factors controlling Se distribution in modeling simulations.

Following development of initial conservative substance estimates, "best estimate" predictions of Se concentrations were obtained by applying mathematical simulations of physical, chemical, and biological kinetics of Se accumulation and distribution in aquatic systems. This approach employed the use of a computer code adaptable to simulation of Se dynamics in Chloride Control brine lakes. Input information for these analyses were derived from project area field data, field and laboratory studies described in the scientific literature, and professional judgment.

Following evaluation of a variety of water quality models, the Simplified Lake and Stream Analysis (SLSA) model developed for the Chemical Manufacturers Association Aquatic Research Task Group (Hydroqual, Inc. 1981, 1982) was deemed most appropriate for use in this study. The model is a relatively simple yet powerful screening tool incorporating mass balance calculations in evaluating effects of point source chemical inputs on lake or stream receiving waters. Available lake simulations include water column and sediment bed chemical accumulation in response to either

continuous or pulsed chemical loads, or chemical depuration following cessation of chemical inputs. Upon calculation of total chemical concentrations in both water column and bed sediments, the model internally calculates dissolved and particulate fractions in each layer (Hydroqual, Inc. 1982). Receiving water volume segmentation and transfer mechanisms are depicted in Appendix A (Figure 4).

Simplifying assumptions associated with SLSA include a completely mixed water column, uniform bed sediments considered as interactive with overlying waters, and a stable pool level. As a screening level model, SLSA does not simulate chemical concentrations with great temporal (i.e., seasonal) or spatial detail. Model output is generally based on overall lake water column and bed conditions over extended time periods (days/years). A complete discussion of the development and application of SLSA is presented in Hydroqual, Inc. (1981, 1982). Theoretical and site-specific applications can be found in Di Toro et al. (1981, 1983).

Water quality modeling for Chloride Control brine disposal lakes was conducted on the basis of total waterborne and sediment selenium. Attempts at modeling distribution of distinct chemical Se forms using output from chemical speciation models (i.e., EPA's MINTEQ model) were not conducted. While chemical speciation undoubtedly affects distribution of Se in aquatic environments and availability for biological uptake, published levels of concern with respect to wildlife species have generally been developed on the basis of total Se. The need to directly compare simulation results and levels of concern, combined with the increased complexity of speciation modeling, resulted in predicted concentrations for total Se only.

SLSA input parameters for Crowell Brine Lake Se simulations are presented in Table 2. Many input parameters are based on anticipated "average" conditions over the life of the project. Uncertainty associated with input parameter values not based on actual field or literature data resulted in selection of conservative estimates where possible. Estimation methods for a number of selected input parameters are described below.

Table 2. SLSA Model Input Parameters, Crowell Brine Lake Selenium Simulations.

Parameter	Units	Value	Source/Justification
Volumetric Flow Rate	m^3 sec^{-1}	0.001	Maximizes residence time
Water Volume	m^3	1.39E07-1.37E08	Varies with pool level
Contaminant Loading	kg day^{-1}	0.211	Source area field data
Water Column Depth	m	4.8-8.8	Varies with pool level
Sediment Layer Depth	m	0.08	Rudd et al. 1980; Oremland et al. 1989, 1990
Water Column Suspended Solids	mg/l	25	Truscott Lake field data
Sediment Suspended Solids	mg/l	1E06	Truscott Lake field data
Diffusive Exchange Coefficient	cm day^{-1}	50	Estimated
Resuspension Velocity	mm yr^{-1}	0	Minimal for deep lake
Sediment Settling Velocity	mm yr^{-1}	4.7-6.2	Varies with pool surface area. Calculated from sedimentation data (USACE 1982b)
Water Column Partition Coefficient	l/kg	100	Estimated Coefficient
Sediment Partition Coefficient	l/kg	20	Estimated from Bar-Yosef & Meek 1987 and Singh et al. 1981 isotherm data
Oxidation Rate*	day^{-1}	0	Not applicable
Biolysis Rate*	day^{-1}	0	Not applicable
Photolysis Rate*	day^{-1}	0	Not applicable
Hydrolysis Rate*	day^{-1}	0	Not applicable
Volatility Rate (water)	day^{-1}	2E-06	Estimated
Volatility Rate (sediment)	day^{-1}	2E-06	Estimated

*Water and sediment.

Establishment of volumetric flow rate (m^3/sec) provides for contaminant flushing from systems in SLSA lake simulations. Outflows possess contaminant concentrations corresponding to simulated water column levels and therefore result in loss of contaminant mass from the system. As Red River Chloride Control brine lakes possess no capacity for outflow, it was necessary to maximize contaminant residence time in simulations involving these systems in order to minimize unrealistic selenium loss. While the model will not permit volumetric flows of zero, the selected rate (0.001 m^3/sec) results in less than 1% loss of selenium mass associated with outflow in Crowell Lake simulations.

An obviously important parameter to water quality simulations is the rate of Se loading to proposed Crowell Brine Lake. Loading estimates were derived from field data collected at Crowell Lake source areas as part of this study. As noted, these data were collected during low flow periods in order to provide conservatively high loading estimates for model simulations. Loading estimates were based on average anticipated flow rates from source areas (0.232 and 0.147 m^3/sec for Areas VII and IX, respectively) and average Se concentrations (7.7 and 3.8 ug/l for Areas VII and IX, respectively) over the data collection period.

Nonpoint source (watershed input) Se loading rates to Crowell Lake were estimated based on predicted average daily runoff inflows of 0.108 m^3/sec (USACE 1976a) and an assumed total selenium concentration of 1 ug/l in inflow waters. While data are not available for Se concentrations in runoff waters from the Crowell Lake watershed, these concentrations are assumed to be low due to frequently observed absence of soluble selenium in surface soils (Doran and Alexander 1976) due to volatilization or rapid leaching of soluble forms from soils high in gypsum (Tanji et al. 1986).

Based on the above calculations, total selenium loading to Crowell Brine Lake was estimated at 0.211 Kg/day. Source areas VII and IX and watershed inflows account for 73, 23, and 4% of this total, respectively.

Active sediment layer depth was estimated at 0.08 m for Crowell Brine Lake SLSA selenium simulations. Several investigators have reported active Se processes at

sediment depths ranging from 3 to 10 cm in a variety of lakes (Rudd et al. 1980; Oremland et al. 1989, 1990). Input water column and sediment bed suspended solids concentrations (25 and 1,000,000 mg/l, respectively) were based on field data collected from Truscott Brine Lake and anticipated similarity in these parameters at Crowell Lake.

Suspended material settling velocities are internally calculated by SLSA via solids balance computations. An important input parameter in these calculations is the sediment settling (burial) velocity (mm/yr). Sedimentation estimates for Crowell Lake indicate that approximately 71,550 m^3/yr of sediment would be delivered to the impoundment (USACE 1982b) resulting in sedimentation rates ranging from 4.7 (full pool) to 6.2 (5-year pool) mm/yr. Use of these sediment settling velocities yields SLSA-calculated suspended material settling velocities (0.52 to 0.68 m/day) well within the general range of 0.15 to 2.0 m/day predicted by Stoke's Law calculations for fine silts and clays (predominant grain sizes in samples from Truscott Lake). These sedimentation rates were therefore considered adequate for use in Crowell Lake simulations. The potential for significant lake-wide sediment resuspension was considered low for Crowell Lake due to extreme water depths. Resuspension velocities were therefore input as 0 mm/yr in SLSA modeling exercises.

Required SLSA input also includes estimates of contaminant partition coefficients (l/Kg) for water and sediment layers. While estimation (or direct measurement) of these coefficients are difficult due to confounding influences of varying organic and inorganic chemical species, solids types, contaminant and solids concentrations, and other environmental variables, Se adsorption isotherm data presented by Singh et al. (1981) and Bar-Yosef and Meek (1987) were used in calculating a general range of sediment layer partition coefficients deemed reasonably applicable to this study.

Singh et al. (1981) evaluated selenium adsorption and desorption on a variety of soils, all of which were characterized by grain sizes dominated by sands. In contrast, Bar-Yosef and Meek (1987) measured selenium sorption on kaolinite and montmorillonite clays under varying pH conditions. It should be emphasized that all experiments in both studies involved inorganic selenium species (Se IV and VI) only. While partition

coefficients calculated from these data vary considerably with pH, Se concentration, and inorganic Se species, calculated values for conditions most reasonably resembling that expected for Chloride Control impoundments range from approximately 10 to 70 l/Kg. Accordingly, an initial conservative estimate of 20 l/Kg was adopted for the sediment partition coefficient. Due to reasonable performance of this coefficient in modeling exercises with limited Truscott Lake data (see results section), this value was retained for use in Crowell Brine Lake simulations.

Partition coefficients for water column suspended materials are typically higher relative to sediment values due to the influence of adsorbing solids concentrations (O'Connor and Connolly 1980, Voice et al. 1983). Estimates of Se partition coefficients for low suspended solids concentrations could not be calculated as field data sets reporting total and dissolved selenium, and suspended solids concentrations could not be found in the literature. While very limited USGS data from several Red River tributaries in Texas (retrieved from the STORET system) indicate that water column partition coefficients may range from 7,500 to 11,000 l/Kg, a conservative estimated value of 100 l/Kg was adopted for use in this study. Despite these uncertainties, low suspended solids concentrations result in unimportance of this parameter to Crowell Lake Se simulations (see sensitivity analysis results).

A final input parameter involved estimation of water column and sediment volatilization rate coefficients (1/day) for Crowell Lake Se simulations. As biomethylation and volatilization of selenium have been shown to vary considerably with Se species, concentrations, and overall aquatic productivity, estimation of these coefficients proved difficult. In an attempt to evaluate the potential significance of volatilization to Crowell Lake, literature reports of Se volatilization for different systems were reviewed.

Cooke and Bruland (1987) reported that outgassing of Se may have been substantial in biologically active Kesterson Reservoir and estimated that roughly 30% of Se introduced to this system via the San Luis Drain was volatilized to the atmosphere. Similarly, Thompson-Eagle and Frankenberger (1990) reported a 35% loss of the total

Se inventory in unamended pond water from Kesterson Reservoir after 43 days of incubation. Due to the highly productive nature of the Kesterson system and anticipated lower levels of productivity in Crowell Lake, diminished significance of volatilization would be anticipated for the latter.

In closed system microcosm studies employing sediments from the San Joaquin River, Volta Wildlife Area, Peck Pond, and Kesterson Reservoir (all California sites), volatile Se compounds were found to comprise 3 to 14% of total Se inventories (Besser et al. 1989, Karlson and Frankenberger 1990). Based partially on these results, conservative volatilization coefficients of 2E-06 day^{-1} were adopted for water and sediments in Crowell Lake simulations. These rate coefficients correspond to an approximate 3.5% loss of the total Crowell Lake Se inventory and are several orders of magnitude less than values reported in the literature (0.003 to 0.053 day^{-1}; Calderone et al. 1990).

A simplifying assumption of major importance to SLSA lake simulations is a completely mixed water column. Accordingly, model predictions do not address horizontal variation or effects due to vertical thermal/chemical stratification in receiving waters. While Truscott Lake data indicate that the complete horizontal mixing assumption would probably be reasonably valid for Crowell Lake, seasonal vertical stratification was observed in Truscott Lake and would most likely develop in Crowell Brine Lake. Relative contributions of thermal and chemical density differences to stratification in Truscott Lake are unknown, but lake turnover and complete mixing was observed in the fall of 1992 (see results section). Due to temporally increasing chloride levels and resulting density gradients, development of permanent meromixis with increasing project life and pool depths is a possibility for Chloride Control brine disposal lakes.

It is important to note that model predictions associated with this study should be considered as applicable during periods of complete mixing (such as might be experienced upon lake turnover). As selenium is generally immobilized under reduced conditions (see discussion in literature review section), highest Se concentrations would

be expected during periods of mixing with sediments serving as a Se "sink" during stratified periods. Model predictions can therefore be considered as representative of maximum Se level conditions with actual concentrations most likely considerably reduced during summertime stratification. Should meromictic conditions persist during later stages of Crowell Lake project life, model projections will most likely overestimate Se concentrations. The possibility of development of these conditions further adds to conservatism associated with model predictions.

Selenium loading estimates for Crowell Lake simulations are based on the assumption that measured total Se concentrations in source waters delivered to the impoundment are unchanged by collection/transport processes. While appreciable Se concentration changes associated with collection methods at Area VII (temporary ponding by inflatable dam) would not be anticipated, the use of settling basins and a temporary storage impoundment at Area IX could conceivably result in reduced total selenium concentrations in source waters from this location due to settling or sediment adsorption effects.

Upon selection of input parameter values deemed reasonable for use in Crowell Lake predictions, these values were applied in Se simulations for Truscott Lake. While limited field data and short operational life of this project precluded what could reasonably be considered either "calibration" or "verification" of the model, predicted Se concentrations were compared to observed field values as a general measure of the reasonableness of model predictions. Adequate performance of the model (see results section) resulted in reasonable confidence in adequacy of input parameter values.

Significance of individual input parameters in Crowell Lake SLSA water quality predictions were evaluated by sensitivity analysis procedures. Sensitivity analyses involved repeated model simulations with incremental changes in a single parameter value (with all others held constant) and evaluation of simulation results associated with these changes. Close scrutiny was given to input variables which had no site-specific or transferable data to support their selection.

SLSA selenium simulations were conducted for separate 5-year intervals over a total time span of 125 years. Discrete simulations were conducted in order to mitigate the influence of significantly increasing pool volumes and surface areas during the initial 20 to 30 years of the proposed project life. Input parameters dependent upon pool morphometry (water volume, sedimentation rates, and water depth) were varied to match anticipated conditions for each simulation period.

CHAPTER VI

RESULTS

Field Data

Results of all field measurements and water sample analyses for Crowell Brine Lake source areas (Areas VII and IX) are contained in Appendix B. Problems with excessively high analytical detection limits (10 to 20 ug/l) attributable to sample matrix interference (excessive chloride levels) were experienced in Se analyses for the first two sampling trips (29 June and 14 July). Due to these high detection limits, data from these dates were not used in Se load estimate calculations. Subsequent analyses incorporated preanalysis sample preparation and improved detection limits (1 ug/l).

Total selenium concentrations ranged from 5.4 to 9 ug/l at Area VII with a mean concentration of 7.7 ug/l. Mean total selenium at Area IX was 3.8 ug/l with a concentration range of <1 to 6.9 ug/l. Agreement between results of duplicate analyses was generally good. Little difference in total and dissolved Se concentrations was noted at both areas on most sampling dates. Waters at both areas were well-oxygenated with slightly alkaline pH values recorded on all sampling trips.

Results of all water quality analyses for Truscott Lake and Area VIII are contained in Appendix C. Total selenium concentrations of 6.6 and 4 ug/l were measured at Area VIII on 18 August and 20 October 1992, respectively. High analytical detection limits for Se analyses were reported for both Area VIII and Truscott Lake samples collected 21-22 July, but were lower for subsequent sampling dates.

Well-defined vertical stratification was observed in Truscott Lake during July and August (see field profiles, Appendix C). On 22 July, a water temperature reduction of approximately 7 °C was recorded between 6 and 7 m depth near Truscott Brine Dam,

with an accompanying drop in dissolved oxygen from approximately 7 to <0.2 mg/l. Significant reductions in redox potential and increases in specific conductance were also observed at this depth. Similar conditions were noted during a mid-August sampling trip. By 21 October, vertical stratification was no longer present in Truscott Brine Lake with nearly identical values of water temperature, redox potential, and conductivity at all water depths. While total selenium concentrations were below analytical detection limits (1 ug/l) in all Truscott Lake samples during periods of stratification, concentrations of 2 ug/l were reported for all samples following lake turnover (Appendix C).

Selenium concentrations in Truscott Lake sediment samples ranged from <0.3 to 0.7 mg/kg dry weight (Appendix C). Total organic carbon concentrations ranged from 1,400 to 9,600 mg/kg, while particle size was dominated by silts (57 to 65%) and clays (11 to 37%).

Modeling Results

Upon establishment of SLSA input parameter values deemed appropriate for this study, these values were applied to Se simulations in Truscott Brine Lake for the approximate 5-year operational period of this existing impoundment. While this application was based on limited data, the objective of the exercise was to test the general reasonableness of model output with respect to Se predictions in Chloride Control lakes. Site-specific parameter values (morphometric data, Se loading, and sedimentation rates) were changed to reflect Truscott Lake conditions, but all other input parameters proposed for use in Crowell Lake simulations (Table 2) were retained.

Predicted 5-year water column total Se concentration for Truscott Lake was 2.9 ug/l. This was in reasonably good agreement with observed concentrations of 2 ug/l in all Truscott lake water samples collected after lake turnover (Appendix C). Slight overprediction of waterborne Se may reflect overestimated loading rates resulting from low-flow data collection. SLSA-simulated sediment Se concentration (0.06 mg/kg dry weight) was considerably lower than 1992 observed values in Truscott Lake sediments (mean of 0.467 mg/kg). Preimpoundment existence of naturally-occurring Se in lake bed

soils could conceivably account for these differences. While based on limited data, overall performance of the model in Truscott simulations resulted in reasonable confidence in use of the model for Crowell Lake Se predictions.

Predicted total selenium concentrations for Crowell Lake are presented in Figure 2. When evaluated as a totally conservative substance, estimated Se concentrations exceed the avian reproductive impacts threshold (10 ug/l) within approximately 10 to 15 years of operational project life. For the same scenario, waterborne Se concentrations would be expected to exceed the young and adult bird effects threshold (34 ug/l) approximately 55 to 60 years after impoundment. Based on this totally conservative substance approach, the 100-year (economic project life) Se concentration in Crowell Brine Lake would be expected to be approximately 56 ug/l.

Best estimate total Se concentrations based on SLSA model projections are likewise presented in Figure 2. Sample SLSA model output (corresponding to the 100-year pool simulation) is contained in Appendix D. As previously noted, these predictions account for the anticipated influence of sedimentation, sediment sorption and burial, and volatilization in reducing waterborne selenium concentrations over the life of the project. Based on all available information and study methodology, these predictions are believed to be both reasonable and somewhat conservative in nature.

According to model projections, total selenium concentrations in Crowell Brine Lake would reach levels considered deleterious to successful avian reproduction within approximately 20 years of project operation (Figure 2). As the 100-year predicted concentration is approximately 30 ug/l, deleterious impacts on young and adult birds would not be expected during the anticipated project life. According to further projection, total selenium concentrations in excess of 34 ug/l (young and adult bird threshold) would be anticipated approximately 125 years after impoundment with development of a steady-state total Se concentration of approximately 46 ug/l after 350 years of project operation.
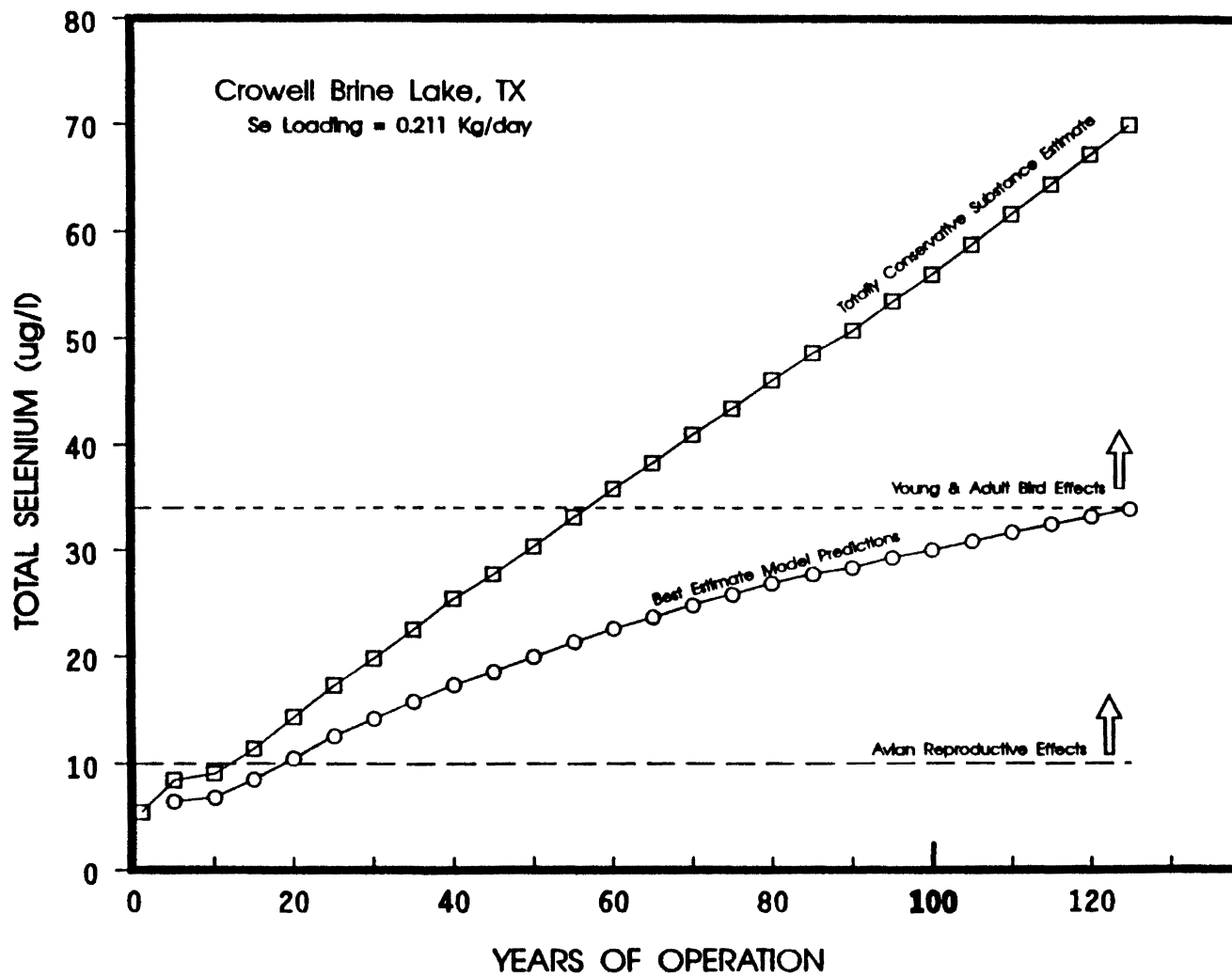
Figure 2. Predicted Total Selenium Concentrations, Crowell Brine Lake, TX

Predicted temporal changes in selenium levels in Crowell Lake sediments are presented in Figure 3. According to model projections, sediment Se concentrations in the impoundment would be approximately 0.629 mg/kg (dry weight) at the end of the 100-year project life. As these predictions assume no initial Se in preimpoundment lake bed soils, addition of estimated "background" levels of approximately 0.4 mg/kg (based on Truscott Lake sediment analyses) would yield predicted Se concentrations approaching 1 mg/kg 100 years after impoundment. In either case, predicted Se sediment concentrations in Crowell Lake are considerably lower than the 4 mg/kg concern threshold level proposed by Lemly and Smith (1987).

While Truscott Lake was not the major focus of this study, long-term Se simulations based on limited data collected during 1992 were also conducted for this impoundment. With source waters from Area VIII only, 100-year estimates for Truscott lake were 11.5 ug/l total waterborne selenium with sediment levels of approximately 0.640 mg/kg. The avian reproductive risk threshold would be exceeded in approximately 85 years under this scenario with no anticipated impacts on young and adult birds. With the addition of source waters from Area X (assuming Se concentrations equal to those at Area VIII), predicted 100-year water concentration is approximately 24 ug/l with sediment levels of 0.900 mg/kg. Assuming inputs from both source areas, the avian reproductive risk threshold would be exceeded after approximately 35 years of operation. As these projections are based on very limited data, resulting predicted concentrations for Truscott Lake should be viewed as very preliminary estimates only.

Sensitivity Analyses

Results of sensitivity analyses for Crowell Lake simulations are presented in Table 3. Substantial variation in input parameters resulted in predicted total Se concentrations ranging from 22.4 to 43.6 ug/l. The only simulations resulting in predicted Se concentrations exceeding the 34 ug/l threshold included those employing 50% reductions in either sediment suspended solids (predicted total Se concentration of 38.8
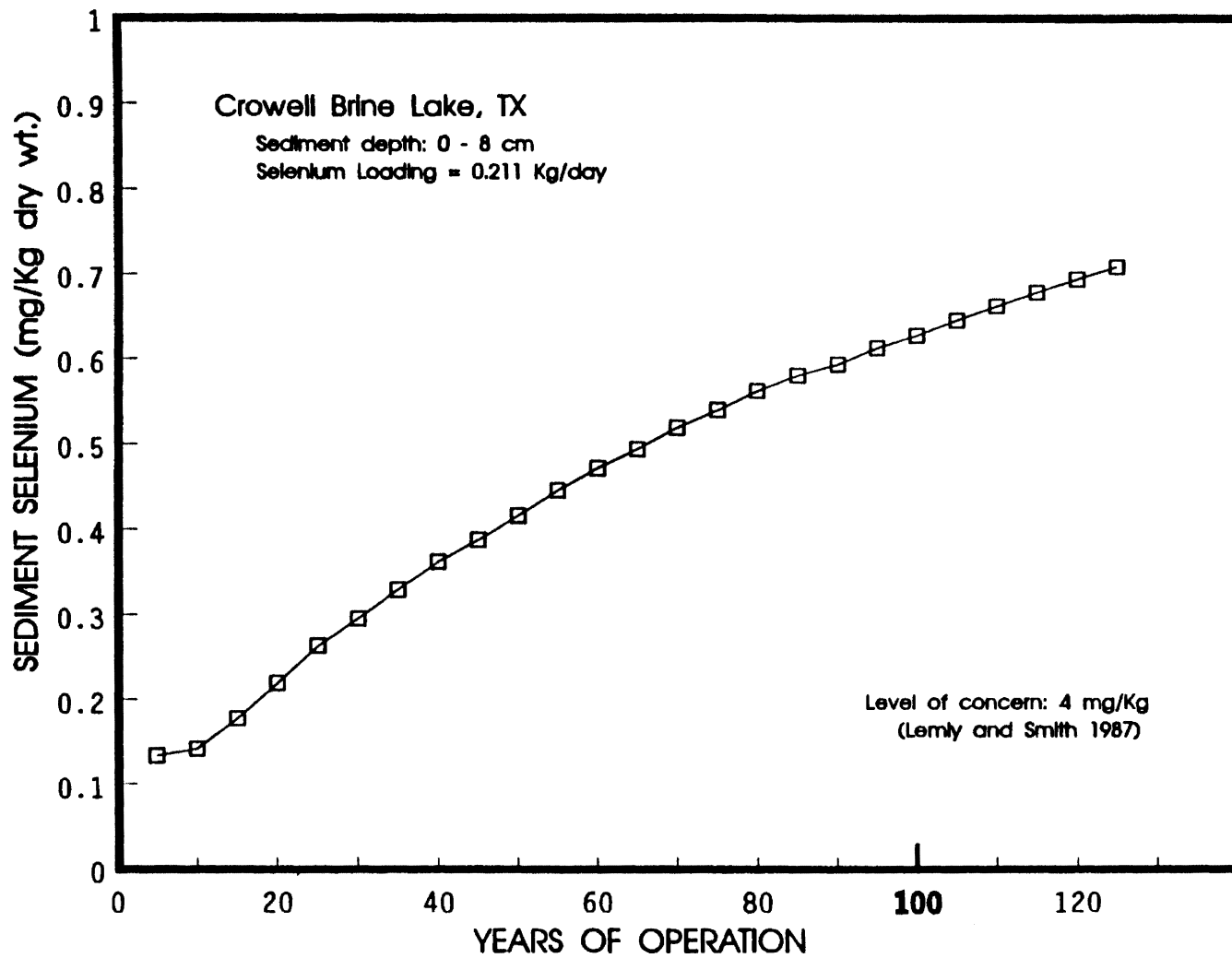
Figure 3. Predicted Sediment Selenium Concentrations, Crowell Brine Lake, TX

Table 3. Results of Sensitivity Analyses, Crowell Brine Lake Selenium Simulations.

Parameter	Variation (± Percent)	Value	Simulated 100-Year Se Conc. (ug/l)	Difference From Baseline (ug/l)	(Percent)
Baseline Simulation	0	—	30.0	—	—
Sediment Layer Depth (m)	-25	0.06	30.7	0.7	2.3
	+25	0.10	29.3	0.7	-2.3
	-50	0.04	31.5	1.5	+5.0
	+50	0.12	28.6	1.4	-4.7
Suspended Solids (water) (mg/l)	-25	18.80	30.0	0	0
	+25	31.25	30.0	0	0
	-50	12.50	30.0	0	0
	+50	37.50	30.0	0	0
Suspended Solids (bed) (mg/l)	-25	7.50E05	33.9	3.9	+13.0
	+25	1.25E06	26.8	3.2	-10.7
	-50	5.00E05	38.8	8.8	+29.3
	+50	1.50E06	24.1	5.9	-19.7
Diffusive Exchange Coeff. (cm day^{-1})	-25	37.50	30.0	0	0
	+25	62.50	30.0	0	0
	-50	25.00	30.0	0	0
	+50	75.00	30.0	0	0
Sediment Settling Velocity (mm yr^{-1})	-25	3.53	33.0	3.0	+10.0
	+25	5.88	27.3	2.7	-9.0
	-50	2.35	36.5	6.5	+21.7
	+50	7.05	25.0	5.0	-16.7
Water Partition Coeff. (l/kg)	-25	75	30.0	0	0
	+25	125	30.0	0	0
	-90	10	30.0	0	0
	+90	190	30.0	0	0
Sediment Partition Coeff. (l/kg)	-25	15	33.9	3.9	+13.0
	+25	25	26.8	3.2	-10.7
	-70	6	43.6	13.6	+45.3
	+70	34	22.4	7.6	-25.3
Volatility Rate (water) (day^{-1})	-25	1.5E-06	30.2	0.2	+0.7
	+25	2.5E-06	29.8	0.2	-0.7
	-90	2.0E-07	30.7	0.7	+2.3
	+90	3.8E-06	29.3	0.7	-2.3
Volatility Rate (sediment) (day^{-1})	-25	1.5E-06	30.0	0	0
	+25	2.5E-06	29.9	0.1	-0.3
	-90	2.0E-07	30.1	0.1	+0.3
	+90	3.8E-06	29.9	0.1	-0.3

ug/l) or sediment settling velocity (36.5 ug/l), or a 70% reduction in the sediment partition coefficient (43.6 ug/l).

Since parameters exerting the most significant influence on Crowell Lake Se simulations include sediment suspended solids, sediment settling velocity, and the sediment partition coefficient, careful evaluation of input values for these parameters was necessary. Bed suspended solids estimates were derived from observed characteristics of Truscott Lake sediments and are therefore considered adequate for Crowell Lake simulations. Sediment settling velocities are based on site-specific calculations of sediment transport from the Crowell Lake watershed and are therefore likewise considered appropriate for use in water quality simulations for this impoundment. Finally, sediment partition coefficients, while estimated from ranges calculated from literature data, are considered conservative and therefore appropriate for Se modeling predictions. In general, results of sensitivity analyses indicate that minor uncertainties associated with model input parameters not based on actual site-specific data should have minimal influence on Crowell Lake Se predictions.

Comparison With Other Studies

Model predictions concerning Se distribution in Crowell Lake yielded results similar to observed findings in other systems. SLSA simulation results predict an approximate 50% reduction in water column total selenium relative to totally conservative substance estimates over the life of the project. This corresponds to water column retention of approximately 50% of total Se mass delivered to the lake. Several investigators have reported similar ratios for experimental ecosystems (Nassos et al. 1980) and microcosm studies (USFWS 1990a). Similarly, Hesslein et al. 1980 reported water column retention of 54% of [75]Se 350 days after isotope addition. Similarities in these comparisons further support the reasonableness of model predictions associated with this study.

Study Uncertainties

Due to the complex nature of physical, chemical, and biological processes affecting the distribution and biological effects of selenium in the aquatic environment, several areas of uncertainty exist regarding results of this study. While not quantifiable with existing scientific information, these areas of uncertainty are identified and presented along with study results.

Chemical interactions have been shown to markedly affect selenium speciation, solubility, bioavailability, and distribution. Due to anticipated high ionic strengths in proposed Chloride Control brine disposal lakes, these interactions may be of significance. Of particular importance might be the influence of high sulfate levels on selenium adsorption/desorption and biological uptake. While sulfur has been shown to be effective in desorption of selenium from soils under certain conditions (Singh et al. 1981), elevated concentrations of Se in Truscott Lake sediments relative to those measured in the water column suggest that this may not be of significance in this system. Several investigators have also reported that some selenium forms may be absorbed by algae in direct competition with sulfur (Shrift 1954) thus limiting the bioavailability of Se (Maier et al. 1987) or providing significant protection against Se toxicity (Kumar and Prakash 1971; cited by Eisler 1985).

An important consideration in predictions concerning Se distribution in proposed Crowell Lake is the influence of vertical stratification (see discussion in modeling section). Results of this study most likely overestimate water column Se concentrations during periods of seasonal stratification and probably significantly overestimate these concentrations if permanent meromixis were to develop in the impoundment.

Final uncertainties exist regarding anticipated biological expression of Se impacts in aquatic systems. In particular, more research is needed concerning nonembryotoxic effects of selenium on avian reproductive fitness. While levels of concern used in this study are based on published experimental and field data for given species, variation in

species susceptibility to selenium may impact study conclusions. Despite uncertainties, results of this study are believed to represent best estimates of Se-related impacts available given current scientific information.

CHAPTER VII

CONCLUSIONS

Based on results of this study, it appears that the most significant anticipated selenium-related impacts on wildlife associated with Red River Chloride Control brine disposal lakes would be impaired reproduction of semi-aquatic or terrestrial insectivorous or piscivorous birds nesting in project areas. When applied to current design criteria, water quality modeling estimates indicate that total waterborne selenium concentrations considered deleterious to successful avian reproduction would be realized in proposed Crowell Brine Lake after approximately 20 years of project operation. Reproductive impacts would be most significant to sedentary species closely tied to brine disposal lakes via food chain dynamics.

Water quality simulations, combined with information from the scientific literature, do not indicate significant anticipated selenium-related impacts on young and adult birds temporarily residing at Crowell Brine Lake. Predicted total selenium concentrations over the anticipated 100-year project life are below estimated thresholds for impacts on young and adult birds in the absence of reproductive concerns. Due to the documented ability of birds to rapidly lose selenium upon leaving contaminated areas, embryotoxicity for birds overwintering at Crowell Brine Lake but breeding at remote sites is not anticipated.

While Crowell Brine Lake was the major focus of this investigation, study results can be applied to other Chloride Control brine lakes in a general sense. However, caution should be used in rigorously applying results of this study to other proposed impoundments in the absence of site-specific investigations. In particular, data collection is required at Area VI once access to source canyons is obtained prior to conclusions regarding Se levels in proposed Salt Creek Brine Lake.

Finally, it should be emphasized that results of this study are based on current design features of Crowell Brine Lake. Future changes in design criteria, operational characteristics, or relative contributions from brine source areas will require reevaluation of anticipated Se-related impacts.

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APPENDIX A

SIMPLIFIED LAKE AND STREAM ANALYSIS (SLSA)

WATER VOLUME SEGMENTATION

AND TRANSFER MECHANISMS

MECHANISMS

INFLOW   LOADING   OUTFLOW

Q_1 W_T Q_1

WATER COLUMN REACTIONS K_1

ADSORPTION-DESORPTION $m_1 \ \pi_1$

V_1 H_1

SETTLING   RESUSPENSION   DIFFUSION

          W_a W_{rs} K_L

SEDIMENT REACTIONS K_2

ADSORPTION-DESORPTION $m_2 \ \pi_2$

V_2 H_2

SEDIMENTATION

                                     W_s

LAKES

Q_1 W_T Q_1

             C_{T1} r_1

W_a W_{rs} K_L

     r_2 W_s

STREAMS

W_T

Q_1 C_{T1} r_1 Q_1

U_1 W_a W_{rs} K_L U_1

                 r_2

           W_s
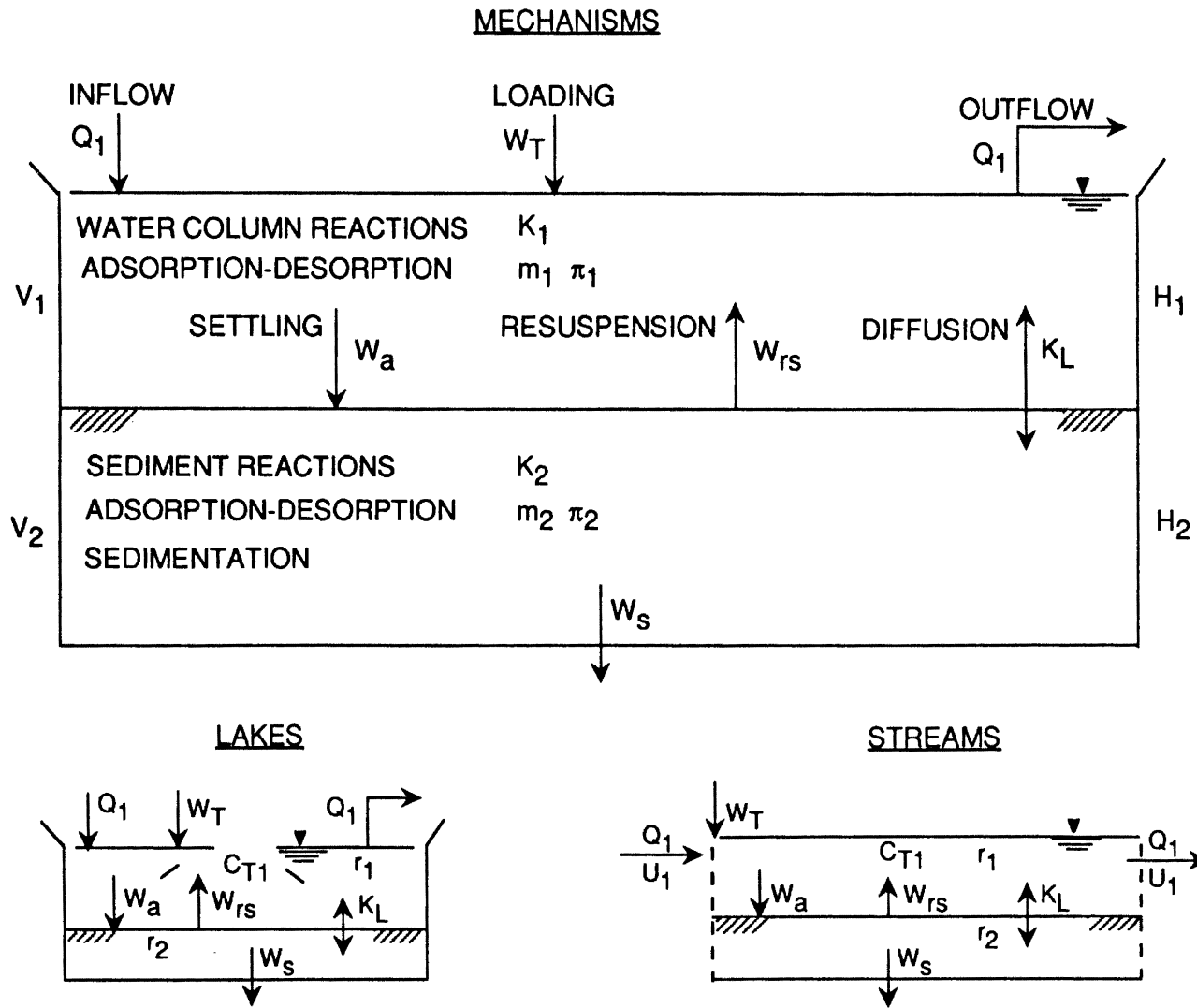
Figure 4. Simplified Lake and Stream Analysis (SLSA) Water Volume Segmentation and Transfer Mechanisms (Hydroqual, Inc., 1982)

APPENDIX B

WATER QUALITY DATA—CROWELL

BRINE LAKE SOURCE AREAS

Table 4. Water Quality Data, Red River Chloride Control Area VII, 1992.*

Parameter	29 Jun	14 Jul	29 Jul	19 Aug	16 Sep	30 Sep	21 Oct	4 Nov
Total Se	<0.010	<0.010	0.008/0.007	0.0054	0.0079	0.008	0.008	0.009
Dissolved Se	<0.010	<0.010	0.007/0.007	0.0066	0.0083	0.008	0.008	0.008
Total Suspended Solids	536	11	37	12	54	27	30	26
Calcium	135	397	627	322	804	697	701	729
Magnesium	39.5	126	139	132	153	196	148	144
Sodium	304	2,090	1,972	1,200	2,810	3,040	3,270	2,890
Potassium	12.0	7	11.9	11.6	11.7	25.9	12.300	12.800
Bicarbonate (as $CaCO_3$)	99.4	162	144/145	164	149	152	152	166/165
Carbonate (as $CaCO_3$)	<0.1	<0.1	—	<5.0	<5.0	<5.0	<5.000	<5.0/<5.0
Chloride	452	4,090	6,400	4,770	4,830	5,670	4,530	5,050
Nitrate	0.31	4.0	0.50	3.4	1.33	0.81	1.230	2.650
Sulfate	520	1,900	2,020	1,820	—	2,150	2,140	2,155
Temp (°C)	27.84	31.70	32.03	22.26	29.42	24.08	19.34	12.43
pH	7.65	7.96	8.03	8.01	7.64	8.37	7.45	7.61
Dissolved Oxygen	6.38	9.31	8.68	7.95	6.18	9.40	9.19	14.57
Conductivity (uS/cm)	2,370	14,530	15,700	16,600	17,400	17,200	17,400	17,700
Redox (mV)	0.169	0.120	0.357	0.354	0.129	—	0.284	0.243
Flow (m^3/sec)	4.99	0.67	0.52	0.53	0.52	0.59	0.56	0.66

*All values are mg/l unless otherwise noted.

Table 5. Water Quality Data, Red River Chloride Control Area IX, 1992.*

Parameter	29 Jun	14 Jul	29 Jul	19 Aug	16 Sep	30 Sept	21 Oct	4 Nov
Total Se	<0.010	<0.010/<0.010	0.004	<0.001/<0.001	0.0069/0.0067	0.005/0.005	0.002	0.003/0.004
Dissolved Se	<0.010	<0.020/<0.020	0.002	0.0012/<0.001	0.0051	0.005	0.004	0.004
Total Suspended Solids	143/145	5/15	45	5.0	60/59	62/59	44	51/59
Calcium	163/163	403/1,050	950	1,080	1,360	1,140	1,100	1,260
Magnesium	44.9/51.4	145/140	176	173	221	149	182	181
Sodium	510/528	3,870/3,910	7,140	7,620	8,140	8,420	9,090	8,650
Potassium	8.9/8.8	11/11	24.7	24.6	<300	12.7	26.3	24.8
Bicarbonate (as $CaCO_3$)	140/140	111/111	97.9	132.0	82	74	124	90.7
Carbonate (as $CaCO_3$)	<0.1/<0.1	<0.1/<0.1	---	<5.0	<5.0	<5.0	<5.0	<5.0
Chloride	877/824	6,560/5,990	12,300	13,000	15,300	14,800	13,800	13,400
Nitrate	0.08/<0.01	0.23/0.43	0.03	<0.1	<0.02	<0.02	0.03	<0.02
Sulfate	510/680	2,000/2,300	3,240	3,370	---	3,480	3,340	3,375
Temp (°C)	27.05	36.57	35.97	20.37	30.20	27.85	15.77	14.12
pH	7.39	7.83	7.79	7.44	7.60	8.60	7.20	7.63
Dissolved Oxygen	7.03	5.96	6.20	6.78	4.86	8.34	9.38	11.25
Conductivity (uS/cm)	3,250	22,000	37,300	38,000	41,600	39,500	41,400	41,600
Redox (mV)	0.166	0.112	0.297	0.125	0.124	---	0.145	0.253
Flow (m^3/sec)	---	0.31	0.09	0.12	0.09	0.10	0.12	0.12

*All values are mg/l unless otherwise noted.

APPENDIX C

WATER QUALITY DATA—AREA VIII

AND TRUSCOTT LAKE

Table 6. Water Quality Data, Red River Chloride Control, Area VIII, 1992.*

Parameter	21 July	18 August	20 October
Total Se	<0.020	0.0066	0.004
Dissolved Se	<0.020	<0.001	0.003
Total Suspended Solids	<1.0	<5.0	39
Calcium	820	877	722
Magnesium	204	204	216
Sodium	5,230	5,450	6,820
Potassium	26	28.8	28.6
Bicarbonate (as $CaCO_3$)	95.9	92.0	104
Carbonate (as $CaCO_3$)	<0.1	<5.0	<5.0
Chloride	13,500	10,100	10,100
Nitrate	1.01	5.3	<0.02
Sulfate	3,300	2,770	2,920
Temp (°C)	29.54	24.21	20.08
pH	7.23	7.25	7.15
Dissolved Oxygen	12.01	11.68	8.30
Conductivity (uS/cm)	28,600	30,900	33,500
Redox (mV)	0.157	0.250	0.357

*All values are mg/l unless otherwise noted.

Table 7. Water Quality Data, Truscott Brine Lake Site 1 (at Dam), 1992.*

Parameter	22 July (Surface)	(Bottom)	19 August (Surface)	(Bottom)	21 October
Total Se	<0.010	<0.010	<0.001	<0.001	0.002
Dissolved Se	<0.020	<0.020	<0.001	<0.001	0.002
Total Suspended Solids	<1.0	<1.0	18	14	26
Calcium	650	605	723	780	687
Magnesium	179	163	172	181	180
Sodium	3,260	3,600	3,680	4,080	4,200
Potassium	19	21.1	22.1	23.5	22.2
Bicarbonate (as $CaCO_3$)	111	116	90.0	108.0	91.8
Carbonate (as $CaCO_3$)	<0.1	<0.1	<5.0	<5.0	<5.0
Chloride	8,860	9,930	6,140	6,870	7,880
Nitrate	0.34	0.58	4.1	4.0	<0.02
Sulfate	2,500	2,800	2,290	1,940	2,110
Sediments (mg/kg dry)					
Total Se		<1		0.421	<0.3
Total Organic Carbon					1400/1400
Particle Size					
Percent Sand					23.5
Percent Silt					65.3
Percent Clay					11.2

*All values are mg/l unless otherwise noted.

Table 8. Water Quality Data, Truscott Brine Lake Site 2 (mid-lake), 1992.*

Parameter	22 July (Surface)	(Bottom)	19 August (Surface)	(Bottom)	21 October
Total Se	<0.010	<0.020	<0.001	<0.001	0.002
Dissolved Se	<0.020	<0.020	<0.001	<0.001	0.002
Total Suspended Solids	<1.0	<1.0	18	5.0	26
Calcium	622	810	715	792	690
Magnesium	166	233	171	182	168
Sodium	3,200	4,290	3,650	4,130	4,220
Potassium	16	17	22.4	24.0	23.2
Bicarbonate (as $CaCO_3$)	101	126	90	116.0	88.7
Carbonate (as $CaCO_3$)	<0.1	<0.1	<5.0	<5.0	<5.0
Chloride	8,510	9,570	6,170	6,910	7,390
Nitrate	3.02	6.2	3.9	4.2	<0.02
Sulfate	2,400	2,700	2,180	2,290	2,090
Sediments (mg/kg dry)					
Total Se		<1.0	0.309		0.40
Total Organic Carbon					6,600
Particle Size					
Percent Sand					6.50
Percent Silt					57.00
Percent Clay					36.50

*All values are mg/l unless otherwise noted.

Table 9. Water Quality Data, Truscott Brine Lake Site 3 (Upper End), 1992.*

Parameter	22 July (Surface)	19 August (Surface)	21 October
Total Se	<0.020	<0.001	0.002/0.002
Dissolved Se	<0.050	<0.001	0.002
Total Suspended Solids	4.0	29	31
Calcium	517	724	716
Magnesium	174	172	183
Sodium	3,010	4,350	4,340
Potassium	23	22.8	23.7
Bicarbonate (as $CaCO_3$)	106	89.6	89.7
Carbonate (as $CaCO_3$)	<0.1	<5.0	<5.0
Chloride	8,690	5,190	6,800
Nitrate	8.7	4.1	<0.02
Sulfate	2,600	2,060	2,150
Sediments (mg/kg dry)			
Total Se	<0.8	0.474	0.7
Total Organic Carbon			9,600

*All values are mg/l unless otherwise noted.
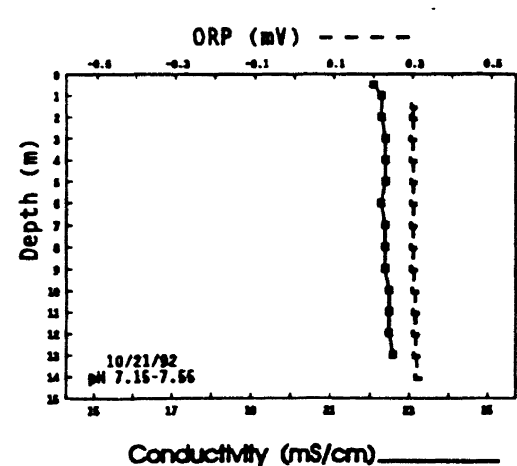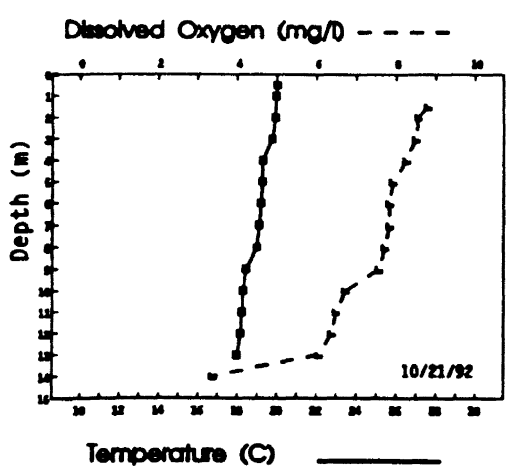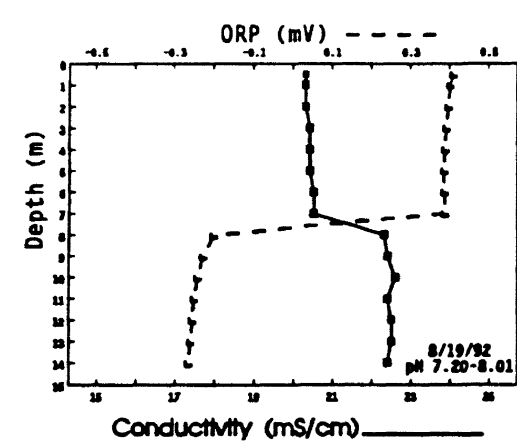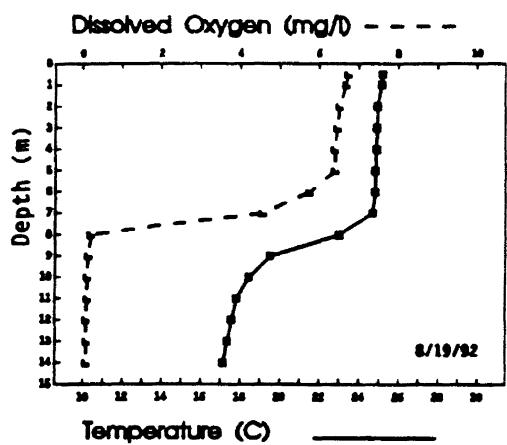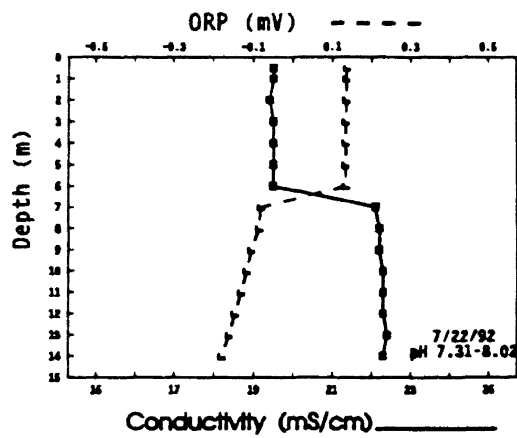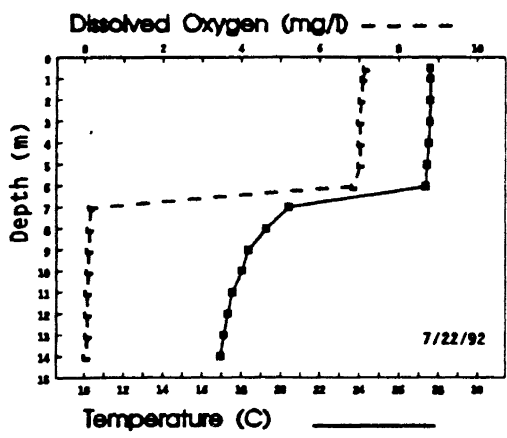
Figure 5. Vertical Profiles of Field Parameters, Truscott Brine Lake
Site 1 (Near Dam)
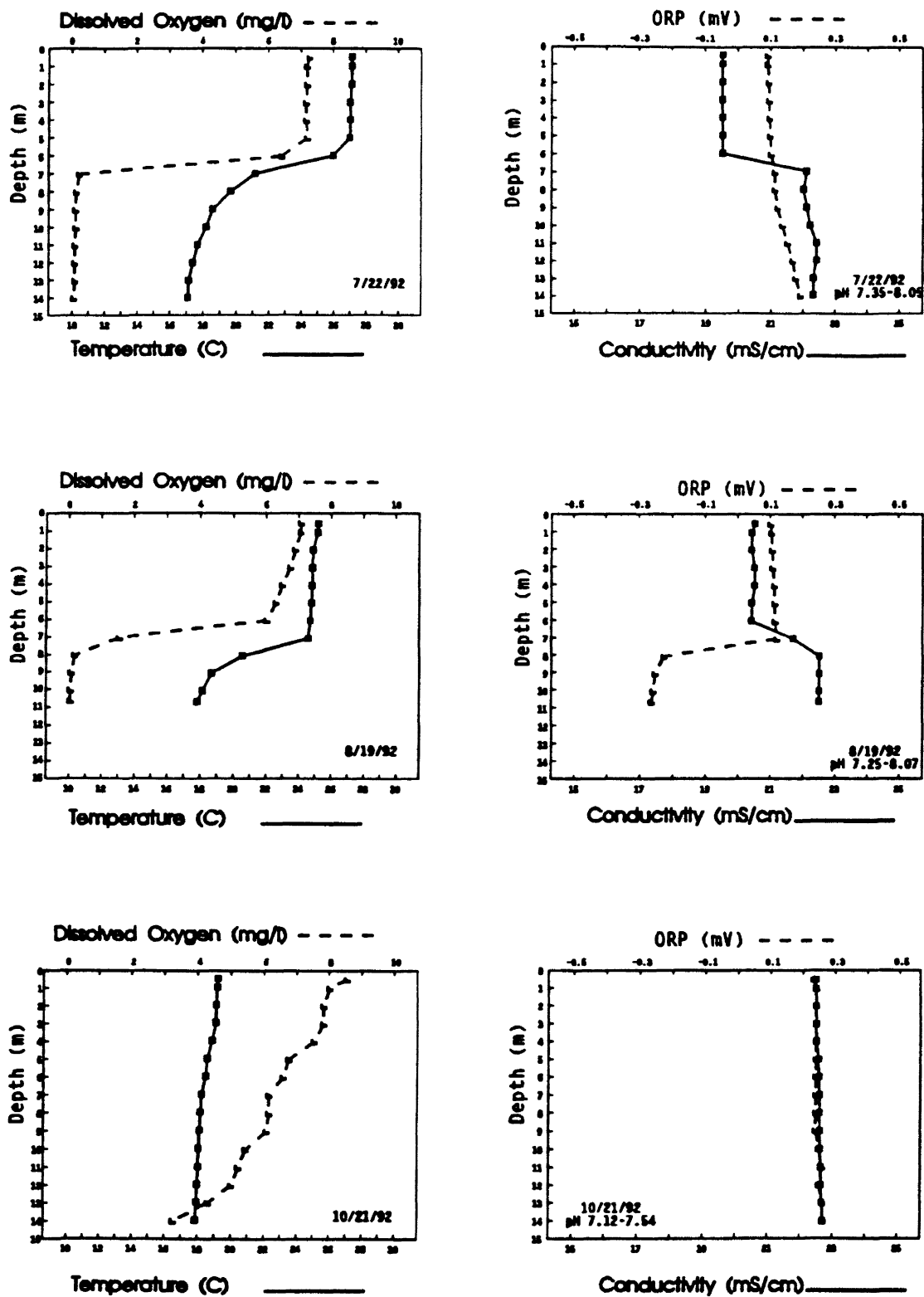
Figure 6. Vertical Profiles of Field Parameters, Truscott Brine Lake
Site 2 (Mid-Lake)
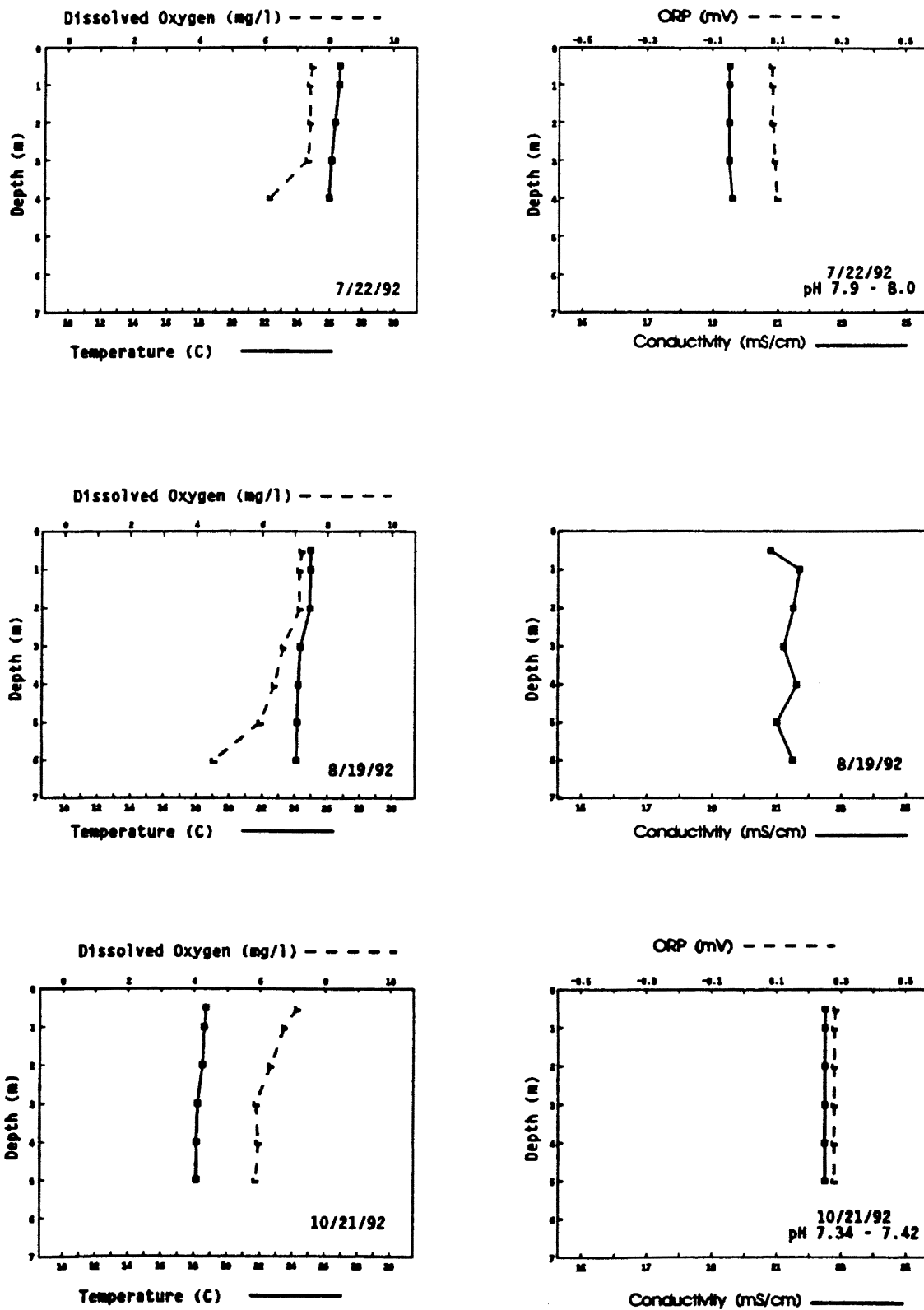
Figure 7. Vertical Profiles of Field Parameters, Truscott Brine Lake
Site 3 (Upper End of Lake)

APPENDIX D

SAMPLE SLSA MODEL OUTPUT

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    C M A   R E C E I V I N G   W A T E R   A N A L Y S I S
    ----------------------------------------------------------
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CROWELL BRINE LAKE SELENIUM ACCUMULATION ESTIMATE - 100 YEAR POOL

SIMPLE LAKE ANALYSIS

VOLUME........... 0.137E+09 M**3
DETENTION TIME... 0.159E+07 DAYS

WATER COLUMN   SEDIMENT LAYER
------------   --------------
DEPTH............ 0.880E+01 METERS   DEPTH............ 0.800E-01 METERS
SUSP SOLIDS...... 0.250E+02 MG/L   SUSP SOLIDS...... 0.100E+07 MG/L
SETTLING VEL..... 0.515E+00 M/DAY   SEDIMENT VEL..... 0.470E+01 MM/YR

RESUSP VEL....... 0.000E+00 MM/YR
DIFF EXCH COEFF.. 0.500E+02 CM/DAY

CHEMICAL/PHYSICAL PARAMETERS

FOR SELENIUM
WATER COLUMN   SEDIMENT LAYER
------------   --------------
PARTITION COEFF   PARTITION COEFF
(P1)............. 0.100E+03 L/KG   (P2)............. 0.200E+02 L/KG

PHASE FRACTIONS   PHASE FRACTIONS
PARTICULATE...... 0.249E-02   PARTICULATE...... 0.952E+00
DISSOLVED........ 0.998E+00   DISSOLVED........ 0.476E-01

HYDROLYSIS RATE.. 0.000E+00 /DAY   HYDROLYSIS RATE.. 0.000E+00 /DAY
OXIDATION RATE... 0.000E+00 /DAY   OXIDATION RATE... 0.000E+00 /DAY
BIOLYSIS RATE.... 0.000E+00 /DAY   BIOLYSIS RATE.... 0.000E+00 /DAY
PHOTOLYSIS RATE.. 0.000E+00 /DAY   PHOTOLYSIS RATE.. 0.000E+00 /DAY
VOLATILITY RATE.. 0.200E-05 /DAY   VOLATILITY RATE.. 0.200E-05 /DAY

TOTAL REMOVAL   TOTAL REMOVAL
RATE (K1)........ 0.200E-05 /DAY   RATE (K2)........ 0.200E-05 /DAY
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                      STEADY STATE SOLUTION
                      ---------------------


         CT1 = 0.477E+02 UG/L    CT2 = 0.100E+04 UG/L
         FD1 =  0.99751          FD2 =  0.04762
         FP1 =  0.00249          FP2 =  0.95238



                       DIAGNOSIS
                       ---------


                         VELOCITIES           RATES
                           MM/YR              /DAY
WATER COLUMN SETTLING......  (WA) 0.188E+06
SEDIMENTATION..............  (WS) 0.470E+01    (KS) 0.153E-03
RESUSPENSION...............  (WRS) 0.000E+00
DIFFUSIVE EXCH COEFF.......  (KL) 0.182E+06
WATER COLUMN REMOVAL.......                    (K1) 0.200E-05
SEDIMENT LAYER REMOVAL.....                    (K2) 0.200E-05



SEDIMENT CAPACITY FACTOR.....

               M2*H2*FP1
        BETA = ----------- = 0.952E+00
               M1*H1*FP2



RATIO OF PARTICULATE CONCENTRATIONS.....

        R2       (WRS+WS)*FP2 + KL*(P2/P1)*FD2
        ---- = -------------------------------
        R1       (WRS+WS)*FP2 + KL*FD2 + K2*H2

   R2      (   0.00 +   4.70 )*0.9524 +  50.00*(  0.20)*0.04762
   ---- = ------------------------------------------------------------
   R1     (   0.00 +   4.70 )*0.9524 +  50.00*0.04762 + 0.000*0.0800

               R2
               ---- =  0.2004
               R1



TOTAL APPARENT REMOVAL RATE.....

         KT = K1 + BETA*R2/R1*(K2+KS)    /DAY

   0.316E-04 =  0.00000 + 0.9522*0.200*(  0.00000 + 0.00015)
```

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TIME VARIABLE BEHAVIOR
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    TIME    CT1(T)/CT1(SS)   CT2(T)/CT2(SS)
   (DAYS)        (%)              (%)
  10613.04      25.00            24.99
  25575.88      50.00            49.99
  59389.66      80.00            80.00
  84968.83      90.00            90.00



                    DIAGNOSIS
                    ---------


MAGNITUDES: WATER COLUMN REACTION AND TRANSPORT    (/DAY)
     K1 =      0.200E-05     WA*FP1/H1 =  0.146E-03
     KL*FD1/H1 =  0.567E-01
----    S1 = K1 + WA*FP1/H1 + KL*FD1/H1 = 0.568E-01



MAGNITUDES: SEDIMENT LAYER REACTION AND TRANSPORT    (/DAY)
     K2 =      0.200E-05     WS*FP2/H2 =  0.153E-03
     KL*FD2/H2 =  0.29762     WRS*FP2/H2 =  0.000E+00
----    S2 = K2 + WS*FP2/H2 + KL*FD2/H2 + WRS*FP2/H2 = 0.29777


ST = S1 + S2 = 0.355E+00   ST + 1/TO = 0.355E+00 + 0.631E-06 = 0.355E+00



EXPONENTS:     (/DAY)
     G1 (EXACT) = 0.355E+00
     G1 (APPROX) = ST + 1/TO = 0.355E+00
     G2 (EXACT) = 0.271E-04
     G2 (APPROX) = S2/(ST + 1/TO) * (KT + 1/TO) = 0.271E-04
```

TIME	---W A T E R C O L U M N- - - - - -			- - S E D I M E N T L A Y E R- - -		
(DAYS)			(UG/L)			
	TOTAL	DISSOLVED	PARTICULATE	TOTAL	DISSOLVED	PARTICULATE
1.0	0.1502E-02	0.1498E-02	0.3746E-05	0.4314E-02	0.2054E-03	0.4108E-02
2.0	0.2940E-02	0.2932E-02	0.7331E-05	0.1539E-01	0.7329E-03	0.1466E-01
3.0	0.4336E-02	0.4325E-02	0.1081E-04	0.3132E-01	0.1491E-02	0.2983E-01
4.0	0.5700E-02	0.5685E-02	0.1421E-04	0.5054E-01	0.2407E-02	0.4813E-01
5.0	0.7044E-02	0.7027E-02	0.1757E-04	0.7218E-01	0.3437E-02	0.6874E-01
6.0	0.8374E-02	0.8353E-02	0.2088E-04	0.9547E-01	0.4546E-02	0.9093E-01
7.0	0.9690E-02	0.9666E-02	0.2417E-04	0.1199E+00	0.5708E-02	0.1142E+00
8.0	0.1100E-01	0.1097E-01	0.2744E-04	0.1451E+00	0.6911E-02	0.1382E+00
9.0	0.1231E-01	0.1228E-01	0.3069E-04	0.1709E+00	0.8138E-02	0.1628E+00
10.0	0.1361E-01	0.1358E-01	0.3394E-04	0.1971E+00	0.9387E-02	0.1877E+00
11.0	0.1491E-01	0.1487E-01	0.3717E-04	0.2236E+00	0.1065E-01	0.2129E+00
12.0	0.1621E-01	0.1616E-01	0.4041E-04	0.2503E+00	0.1192E-01	0.2384E+00
10001.0	0.1133E+02	0.1130E+02	0.2826E-01	0.2378E+03	0.1132E+02	0.2265E+03
20001.0	0.1997E+02	0.1992E+02	0.4980E-01	0.4192E+03	0.1996E+02	0.3992E+03
30001.0	0.2656E+02	0.2649E+02	0.6624E-01	0.5575E+03	0.2655E+02	0.5309E+03
40001.0	0.3159E+02	0.3151E+02	0.7877E-01	0.6630E+03	0.3157E+02	0.6314E+03
50001.0	0.3542E+02	0.3533E+02	0.8833E-01	0.7434E+03	0.3540E+02	0.7080E+03
60001.0	0.3834E+02	0.3825E+02	0.9561E-01	0.8048E+03	0.3832E+02	0.7665E+03
70001.0	0.4057E+02	0.4047E+02	0.1012E+00	0.8516E+03	0.4055E+02	0.8110E+03
80001.0	0.4227E+02	0.4216E+02	0.1054E+00	0.8873E+03	0.4225E+02	0.8450E+03
90001.0	0.4357E+02	0.4346E+02	0.1086E+00	0.9145E+03	0.4355E+02	0.8709E+03
100001.0	0.4456E+02	0.4444E+02	0.1111E+00	0.9352E+03	0.4453E+02	0.8907E+03
110001.0	0.4531E+02	0.4520E+02	0.1130E+00	0.9511E+03	0.4529E+02	0.9058E+03
120001.0	0.4588E+02	0.4577E+02	0.1144E+00	0.9631E+03	0.4586E+02	0.9173E+03
130001.0	0.4632E+02	0.4621E+02	0.1155E+00	0.9723E+03	0.4630E+02	0.9260E+03
140001.0	0.4666E+02	0.4654E+02	0.1164E+00	0.9794E+03	0.4664E+02	0.9327E+03

TIME (DAYS)	---WATER COLUMN------ (UG/L)			---SEDIMENT LAYER---		
	TOTAL	DISSOLVED	PARTICULATE	TOTAL	DISSOLVED	PARTICULATE
1.0	0.1502E-02	0.1498E-02	0.3746E-05	0.4314E-02	0.2054E-03	0.4108E-02
1826.0	0.2305E+01	0.2299E+01	0.5748E-02	0.4830E+02	0.2300E+01	0.4600E+02
3651.0	0.4497E+01	0.4486E+01	0.1121E-01	0.9431E+02	0.4491E+01	0.8982E+02
5476.0	0.6583E+01	0.6567E+01	0.1642E-01	0.1381E+03	0.6576E+01	0.1315E+03
7301.0	0.8568E+01	0.8547E+01	0.2137E-01	0.1798E+03	0.8561E+01	0.1712E+03
9126.0	0.1046E+02	0.1043E+02	0.2608E-01	0.2195E+03	0.1045E+02	0.2090E+03
10951.0	0.1226E+02	0.1223E+02	0.3057E-01	0.2572E+03	0.1225E+02	0.2450E+03
12776.0	0.1397E+02	0.1393E+02	0.3483E-01	0.2931E+03	0.1396E+02	0.2792E+03
14601.0	0.1560E+02	0.1556E+02	0.3890E-01	0.3273E+03	0.1559E+02	0.3118E+03
16426.0	0.1715E+02	0.1711E+02	0.4276E-01	0.3599E+03	0.1714E+02	0.3427E+03
18251.0	0.1862E+02	0.1858E+02	0.4644E-01	0.3909E+03	0.1861E+02	0.3723E+03
20076.0	0.2003E+02	0.1998E+02	0.4995E-01	0.4203E+03	0.2002E+02	0.4003E+03
21901.0	0.2136E+02	0.2131E+02	0.5328E-01	0.4484E+03	0.2135E+02	0.4271E+03
23726.0	0.2264E+02	0.2258E+02	0.5645E-01	0.4751E+03	0.2262E+02	0.4525E+03
25551.0	0.2385E+02	0.2379E+02	0.5947E-01	0.5005E+03	0.2384E+02	0.4767E+03
27376.0	0.2500E+02	0.2494E+02	0.6234E-01	0.5247E+03	0.2499E+02	0.4997E+03
29201.0	0.2610E+02	0.2603E+02	0.6508E-01	0.5478E+03	0.2608E+02	0.5217E+03
31026.0	0.2714E+02	0.2707E+02	0.6768E-01	0.5697E+03	0.2713E+02	0.5425E+03
32851.0	0.2813E+02	0.2806E+02	0.7016E-01	0.5905E+03	0.2812E+02	0.5624E+03
34676.0	0.2908E+02	0.2901E+02	0.7252E-01	0.6104E+03	0.2907E+02	0.5813E+03
36501.0	0.2998E+02	0.2991E+02	0.7476E-01	0.6293E+03	0.2997E+02	0.5993E+03
38326.0	0.3084E+02	0.3076E+02	0.7690E-01	0.6472E+03	0.3082E+02	0.6164E+03
40151.0	0.3165E+02	0.3157E+02	0.7893E-01	0.6644E+03	0.3164E+02	0.6327E+03
41976.0	0.3243E+02	0.3235E+02	0.8087E-01	0.6806E+03	0.3241E+02	0.6482E+03
43801.0	0.3317E+02	0.3308E+02	0.8271E-01	0.6961E+03	0.3315E+02	0.6630E+03
45626.0	0.3387E+02	0.3378E+02	0.8446E-01	0.7109E+03	0.3385E+02	0.6770E+03
47451.0	0.3454E+02	0.3445E+02	0.8613E-01	0.7249E+03	0.3452E+02	0.6904E+03
49276.0	0.3517E+02	0.3509E+02	0.8772E-01	0.7383E+03	0.3516E+02	0.7031E+03
51101.0	0.3578E+02	0.3569E+02	0.8923E-01	0.7510E+03	0.3576E+02	0.7153E+03
52926.0	0.3636E+02	0.3627E+02	0.9067E-01	0.7631E+03	0.3634E+02	0.7268E+03
54751.0	0.3691E+02	0.3681E+02	0.9203E-01	0.7747E+03	0.3689E+02	0.7378E+03
56576.0	0.3743E+02	0.3733E+02	0.9334E-01	0.7856E+03	0.3741E+02	0.7482E+03
58401.0	0.3793E+02	0.3783E+02	0.9458E-01	0.7961E+03	0.3791E+02	0.7581E+03
60226.0	0.3840E+02	0.3830E+02	0.9576E-01	0.8060E+03	0.3838E+02	0.7676E+03
62051.0	0.3885E+02	0.3875E+02	0.9688E-01	0.8154E+03	0.3883E+02	0.7766E+03
63876.0	0.3928E+02	0.3918E+02	0.9795E-01	0.8244E+03	0.3926E+02	0.7852E+03
65701.0	0.3969E+02	0.3959E+02	0.9897E-01	0.8330E+03	0.3967E+02	0.7933E+03
67526.0	0.4007E+02	0.3997E+02	0.9993E-01	0.8412E+03	0.4005E+02	0.8011E+03
69351.0	0.4044E+02	0.4034E+02	0.1009E+00	0.8489E+03	0.4042E+02	0.8085E+03
71176.0	0.4079E+02	0.4069E+02	0.1017E+00	0.8563E+03	0.4078E+02	0.8155E+03

VITA

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