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GEOLOGICAL SURVEY

Total and water extractable selenium in soils  
and stream sediments, and total selenium in alfalfa  
from the Marty II study area, South Dakota

by

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## CONTENTS

	Page
Introduction .....	1
Geologic background .....	1
Previous selenium studies .....	3
Sample Collection .....	6
Water samples .....	6
Soil and sediment samples .....	7
Alfalfa samples .....	7
Sample Preparation .....	7
Soil and sediment samples .....	7
Water extractable selenium in soils .....	7
Alfalfa samples .....	8
Analytical techniques .....	8
Total selenium in solid samples.....	8
Total selenium in aqueous samples .....	9
Total selenium in alfalfa samples .....	9
Results and Discussion .....	9
Total selenium in soils .....	9
Water extractable selenium .....	11
Percent water extractable selenium .....	13
Total versus water extractable selenium .....	18
Alfalfa samples.....	18
Stream sediment samples .....	20
Ground water samples .....	20
Quality control data.....	21
Summary .....	21
References .....	23

## TABLES

Table 1.	Water quality standards for selenium in selected water systems .....	26
Table 2.	Total selenium concentrations in soils from selected studies in the western United States .....	27
Table 3.	Water extractable selenium concentrations in soils from selected sites in the western United States .....	28

Table 4.	Dry weight selenium concentrations in alfalfa samples collected in the Marty II study area .....	29
Table 5.	Analysis of replicates and standards for the Marty II study .....	30

## APPENDICES

Appendix A	Total selenium in soils from the Marty II study area .....	31
Appendix B	Water extractable and percent extractable selenium in soils from the Marty II study area .....	32
Appendix C	Total selenium concentrations in alfalfa plants from the Marty II study area .....	35
Appendix D	Total selenium concentrations in Mosquito Creek sediment samples from the Marty II study area .....	36
Appendix E	Total selenium concentrations in ground water from the Marty II study area .....	37

## ILLUSTRATIONS

Figure 1.	Location of the Marty II study area .....	2
Figure 2.	Relation of selenium concentrations in ground water to drain locations for 1, 6, and 15 year fields from the San Joaquin Valley studies .....	4
Figure 3.	Ground water flow patterns in soils of the San Joaquin Valley .....	5
Figure 4.	Distribution of total selenium concentrations in soils from the Marty II study area .....	10
Figure 5.	Total selenium concentrations in soils versus collection depth for Marty II study area .....	12
Figure 6.	Water extractable selenium distribution in soils from the Marty II study area .....	14

Figure 7.	Water extractable selenium concentration in soils versus sample collection depth for the Marty II study area .....	15
Figure 8.	Water extractable selenium concentration versus sample collection depth for sites 1A, 6, and 12, Marty II study area .....	16
Figure 9.	Percent water extractable selenium versus collection depth for the Marty II study .....	17
Figure 10.	Total versus water extractable selenium in soils, from the Marty II study area .....	19

## INTRODUCTION

In September of 1989 the Bureau of Reclamation (BOR) and the U.S. Geological Survey (USGS) entered into a cooperative agreement to evaluate selenium levels in soils associated with the proposed Marty II irrigation project. The Marty II project is designed to bring irrigation waters to the Marty, South Dakota region as part of a cooperative agreement between the Bureau of Reclamation and landowners in that area. The study area consists of approximately 3,500 acres composed primarily of glacial till and loessial soil types (Hedges, 1975, Reber, 1982). Project plans include the installation of subsurface drains spaced between 50 and 200 feet apart. The drains are designed to remove excess ground and irrigation waters from the Marty II area and transport them to Mosquito Creek, which flows into Slaughter Creek and finally into the Missouri river.

### Geologic background

The study area, located in southeastern South Dakota (Figure 1) has bedrock material containing several geologic units. The two principal formations are Cretaceous age, Niobrara Marl and Pierre Shale (Hedges, 1975), (Tourtelot, H.A., 1962). Other geologic units identified in the study area include Pleistocene till and outwash terrace deposits, loess of the late Wisconsin to Recent age, and alluvium and colluvium of late Wisconsin to Recent age.

The occurrence of selenium is well documented in the Cretaceous bedrock of South Dakota (Pugsley and Cox, 1937; Moxon, and others, 1950; Anderson and others, 1961). It also appears that the soils derived from Pierre Shale, in particular the Mobridge, Sharon Springs, and Virgin Creek members, may be the principal sources of selenium often found in this area (Pugsley and Cox, 1937). In an extensive soil survey (Moxon and others, 1939) over 500 samples, derived primarily from Niobrara and Pierre Shale formations, were analyzed. Examination of the results indicate a mean and maximum selenium concentrations of 5.8 ppm and 113 ppm respectively. It was suspected that these soils had given rise to seleniferous vegetation in the area.

Based on these early studies, questions arose over the distribution of selenium in the Marty, South Dakota area and the potential for selenium mobilization under irrigation/drainage conditions. Three of the major concerns at the outset of this study were: 1) the degree of selenium migration under proposed irrigation conditions, 2) the expected selenium concentrations in receiving waters during the initial irrigation period, and 3) the long term impact of selenium on local water systems. Due to lack of information on selenium mobility in terrain similar to Marty II, other studies were consulted to see if they could provide insight to these problems.

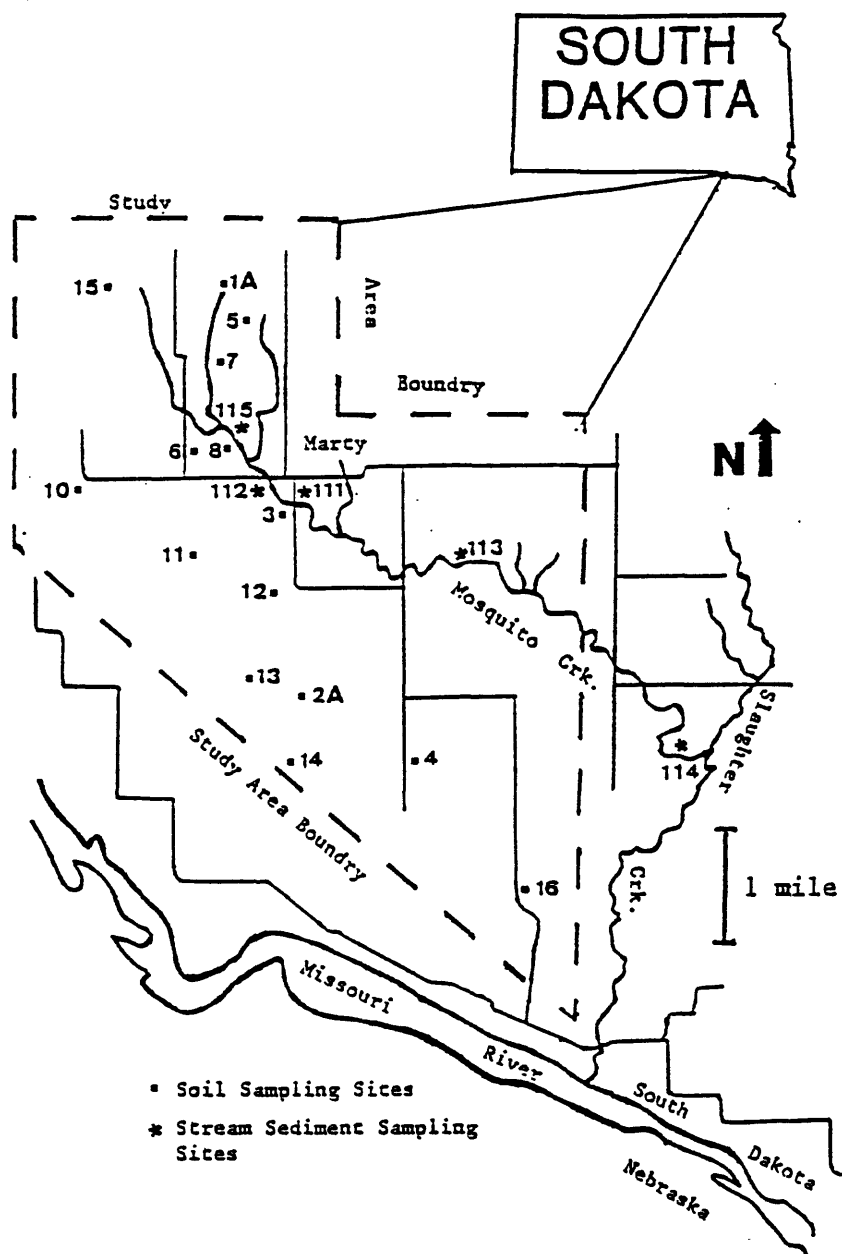


Figure 1. Location of the Marty II study area

### Previous selenium studies

The western side of the San Joaquin Valley (SJV) of central California has received a great deal of attention due to problems encountered with the mobilization of selenium from soils under irrigation. Several investigators have examined mobilization and transport processes at work in the valley and have developed models that explain the mechanisms governing the transport of selenium. Even though Marty II and SJV study areas are composed of different geologic formations and soil types, it is believed that models developed in the SJV studies could be useful in explaining the processes that govern selenium mobilization in the Marty II study area. While helpful in explaining the processes at work, the models can not be expected to predict the absolute quantities of mobilized selenium in the Marty II area.

USGS studies (Fujii and others, 1982; Deveral and others, 1984; Deveral and Millard, 1986) in the SJV of California have detailed the short- and long-term effects of irrigation on the mobility of selenium in irrigated lands. Studies (Deveral and Fujii, 1988) done in the SJV indicate that a mean (geometric, GM) selenium concentration 2800 ppb was observed in return flow waters during the first year of drainage. This high-selenium flux was followed by a decrease in selenium concentrations (2800 ppb to 109 ppb) over the next 15 years. Selenium removal from the field over time is illustrated in Figure 2 for the 1, 6, and 15 year fields.

Figure 2 demonstrates that fields using subsurface drainage for the first year show constant and elevated selenium levels across the study area (GM = 2800 ppb). In subsequent years as selenium deficient irrigation waters are applied to the fields, mobile selenium is displaced towards the drain. This results in lower selenium levels between the drains but persistently high levels at inlets to the drain.

Due the importance of surface and ground water interaction, additional studies examined the entire hydrologic system in order to determine how the various parameters interact. These studies are schematically represented in Figure 3 (Deveral, and Fujii, 1988).

One of the principal questions in the SJV studies was, under what time frame does the system respond to change? To answer this question, tritium data was used as an indicator of water age. It is apparent in Figure 3, that irrigation waters added close to a drain have a residence time in the soil of approximately 8 years. Water added away from the drain, or to soils that are less porous, will have longer residence times in the soil. Closer examination of Figure 3 also reveals that ground water originating in the sand or silt layers below the water table may have a shorter residence time than water added to soils above the water table. This shorter residence time is due

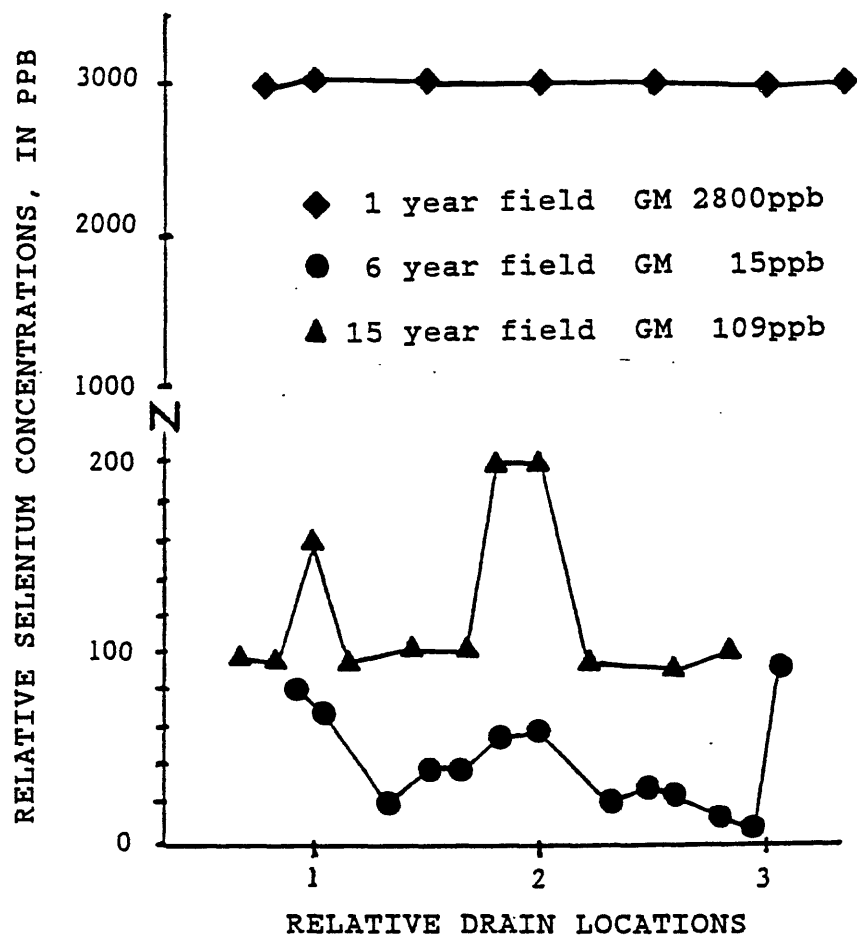


Figure 2 Relation of selenium concentrations in ground water to drain locations for 1, 6, and 15 year fields from the San Joaquin Valley studies (adapted from Deveral and Fujii, 1988)



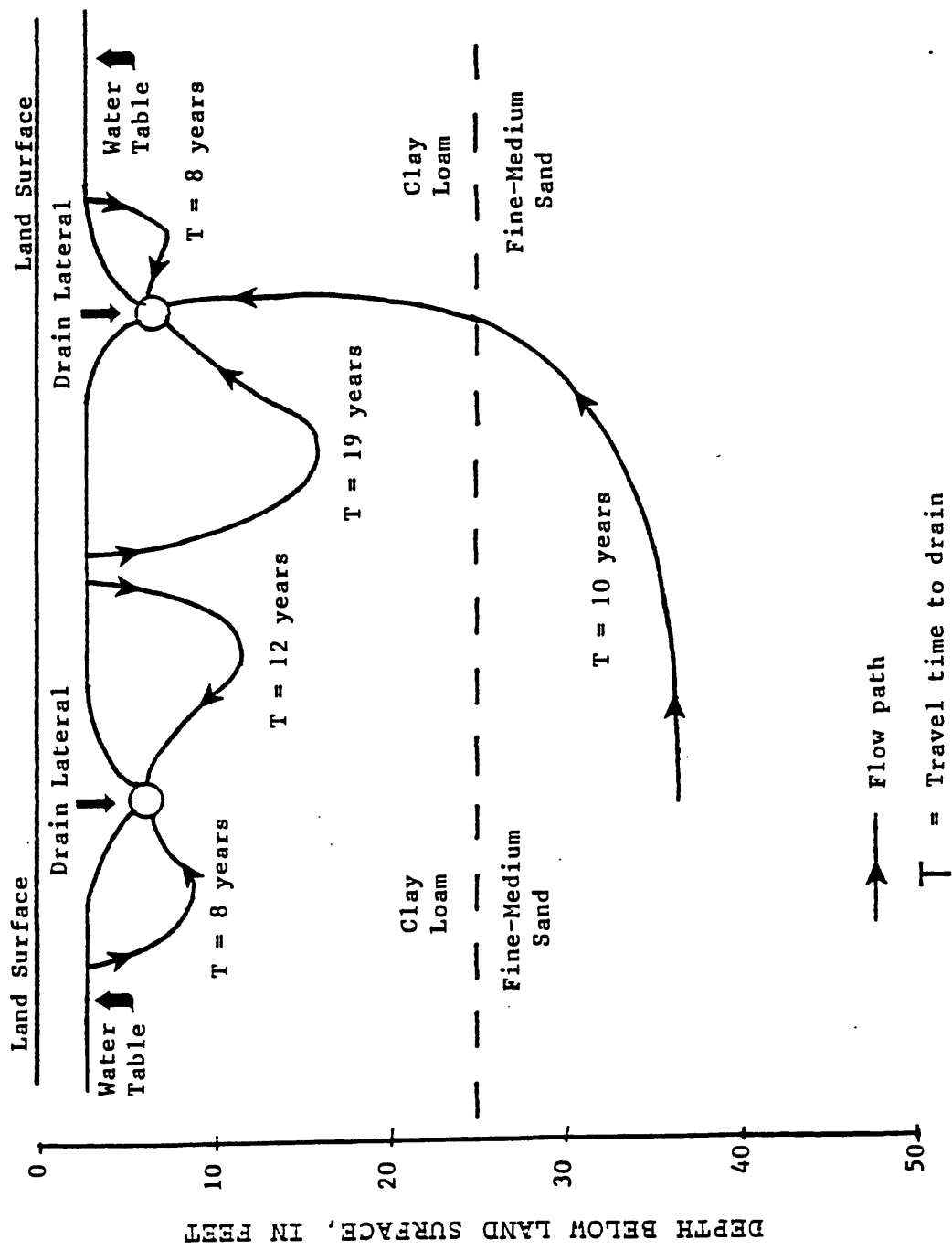


Figure 3 Ground water flow patterns in soils of the San Joaquin Valley (adapted from Deverall and Fujii, 1988)

to the greater permeability of the sand or silt material. The decrease in residence time for these waters may be significant for the Marty II study area especially if the sand layer is shallower than that observed in the San Joaquin Valley.

The San Joaquin drainage problem was compounded by the creation of twelve storage ponds which were designed to receive drainage waters. These ponds were eventually incorporated into the Kesterson National Wildlife Refuge (KNWR). Under the intensive evaporation conditions occurring in the SJV, selenium and other salts reached elevated concentrations at the KNWR. Studies done at KNWR and the adjacent Volta NWR (operated using a different water source) found 300 ppb and 1 ppb selenium respectively in receiving waters (Ohlendorf and Hothem, 1986). Analysis of algae samples at KNWR revealed selenium concentrations between 12 and 330 ppm (Ohlendorf, 1989). In addition, selected aquatic plants (e.g. widgeon grass) typically eaten by ducks contained selenium concentrations between 18 and 390 ppm (GM = 73 ppm) (Ohlendorf, 1989). These elevated levels of selenium in algae and plant material were considered pathways for the bioaccumulation of selenium in nesting waterfowl. These concerns were verified in the analysis of coot livers at KNWR, which showed an average selenium concentration of 43 ppm compared to baseline values of 4.4 ppm (Ohlendorf, 1989). These elevated levels of selenium were considered important factors in the significant number of waterfowl deaths and deformities seen at KNWR. The situation at KNWR may represent an extreme, but it still serves as a measure of how significant selenium contamination can be.

In light of SJV and other studies, water quality standards have evolved to limit the amount of selenium that can be tolerated in different water systems. Table 1 lists some of the more important criteria. Based on these water quality criteria and the important environmental impact of selenium, studies were undertaken in the Marty, South Dakota area to evaluate the potential for selenium mobilization due to irrigation/drainage programs.

## SAMPLE COLLECTION

### Water samples

During the summer of 1989 (May through July) the South Dakota Geological Survey (SDGS) and the Bureau of Reclamation collected water samples in the Marty II study area. During the initial field studies four observation wells were installed for the purpose of measuring water table depth and collecting ground water samples for selenium analysis. The wells were drilled to approximately 15 feet below the water table and a 2-inch PVC casing installed. Sampling of the wells occurred on June 1, 1989. Ground water was obtained from each well (sites 3, 5, 6, 13) Figure 1. Well water samples from sites 3, 5, and 6 had

electrical conductivity measurements greater than 5,000 microsiemens. At sites 13 the electrical conductivity was 3,490 microsiemens. A water sample was also taken from a spring located near the town of Marty, South Dakota.

#### Soil and sediment samples

Soil samples were collected from 16 sites across the study area (Figure 1). A six-inch hollow-stem auger was used and core segments separated based on specific soil characteristics. Each core segment (approx. 2 feet) was mixed in the field and an aliquot obtained for chemical analysis. Sample collection depth varied at the 16 sites but never exceeded 120 inches.

Sediment samples were collected at five locations along Mosquito Creek above and below the town of Marty, South Dakota (Figure 1). The sediment material was collected at the surface down to a maximum depth of 3 inches. The samples were allowed to sit for one hour, after which the excess water was decanted and the container sealed. The container was then placed in a plastic bag and tagged with the sample ID.

#### Alfalfa samples

Alfalfa samples were collected in order to observe any relationships between the selenium content of soils and plants. A total of 13 samples were collected at three sites at variable distances from the soil collection site. Each sample was the composite of approximately five plants. Only that portion of the plant greater than three inches above the soil was collected to minimize any significant soil contamination.

### SAMPLE PREPARATION

#### Soil and sediment samples

Soil and sediment samples were dried at room temperature for a period of three days. The samples were then disaggregated, a representative split obtained and the split material ground to pass a 100 mesh sieve. The ground samples (<100 mesh) were placed in three-ounce containers and mixed for a minimum of one hour. The samples were then submitted to the laboratory for analysis.

#### Water extractable selenium in soils

Extractable selenium investigations used a saturation-paste procedure to obtain the water soluble selenium fraction. In the saturation procedure performed by BOR, air-dried soil is disaggregated to pass through a 2 mm sieve. The sieved material is added to an 800 mL plastic beaker, filling it approximately

two-thirds full and the weight recorded. Distilled water is added to the soils until the surface of the mixture glistens, flows slightly when the cup is tipped, and slides cleanly off the mixing spatula. The beaker is then covered with a watch glass and allowed to sit overnight. The next day an eight-inch diameter porcelain buchner funnel equipped with a Whatman #42 filter paper is prepared and the sample transferred. Vacuum is applied to the filtration system and allowed to operate until a minimum of 10 mL of solution is obtained. The aqueous sample is transferred to a disposable plastic container, sealed and stored for analysis. Percent saturation is calculated by weighing a 10 gram aliquot of saturated material, drying it in an oven overnight and reweighing. The weight of the water lost is divided by the dry weight and a percent saturation calculated.

#### Alfalfa samples

Alfalfa samples received in the laboratory were immediately washed three time with deionized water in a teflon beaker. The plants were then placed in an aluminum colander and rinsed with a final aliquot of deionized water. The cleaned plant material was then dried at room temperature for 48 hours. The dried material was finally processed through a Thomas Willey Mill, Model No. 4, until all the material passed a 2mm screen. The ground material was placed in a half pint container and tumble mixed for one hour.

### ANALYTICAL TECHNIQUES

#### Total selenium in solid samples

Total selenium was determined using Hydride Generation Atomic Absorption Spectroscopy (HG-AAS) (Briggs and Crock, 1986; Crock and Lichte 1982). In this procedure an aliquot (0.2500 g) of sample is placed in a 30 mL teflon bomb and predigested for one hour at room temperature using a 2 mL aliquot of saturated potassium persulfate solution. The sample is then digested using a combination of concentrated nitric, perchloric, and hydrofluoric acids. After the digestion is complete the sample is transferred to a 2 ounce polyethylene bottle, diluted to 50 mL (55 g) with 6 M hydrochloric acid and allowed to sit overnight. The 6 M hydrochloric acid assures the conversion of Se(VI) to Se(IV), an important prerequisite to reliable selenium analyses by HG-AAS.

In the HG-AAS procedure the sample is reacted with 0.1 M sodium borohydride solution, and the hydride gas separated from the aqueous phase using a specially designed phase separator. The hydride gas is passed into a quartz atomization cell, positioned in the light path of an atomic absorption spectrometer. Selenium is quantified using a series of external standards, and a linear

regression analysis. The relative standard deviation (RSD) for the procedure is 10 %, with a detection limit of 0.1 ppm in sample.

#### Total selenium in aqueous samples

The preparation of aqueous samples for hydride analysis starts with a persulfate digestion of the solution. In this digestion 10 mL of sample is transferred to a 30 mL teflon bomb. A 1 mL aliquot of a saturated potassium persulfate solution is added, the teflon bomb covered with a watch glass and allowed to sit for one hour at room temperature. A 1 mL aliquot of concentrated hydrochloric acid is then added and the bomb heated for one hour at 110 C. After this heating interval, the bomb is uncovered and heated until the volume is reduced to approximately 5 mL. Two milliliters of concentrated hydrochloric acid are then added, the bomb covered and the solution heated for an additional hour. The solution is then transferred to a two ounce polyethylene bottle and brought to a final mass of 20 g with deionized water. The RSD for this procedure is 10% with a detection limit of 1 ppb.

#### Total selenium in alfalfa samples

A 1.000 g sample of dried plant material is placed in a 250-mL Erlenmeyer flask and 20 mL of concentrated nitric acid added. The flask, equipped with a specially designed reflux adapter is allowed to sit overnight. The next day the flask is heated (120 - 130 C) for one hour or until the generation of nitric acid fumes ceases. A 5-mL aliquot of hydrogen peroxide is then added at a rate of 1-mL per 5 minutes). When the addition is complete the reflux head is removed and the container heated for two hours, or until the volume is reduced to 5 mL. A 2-mL spike of concentrated perchloric acid is added and the container heated to fumes of perchloric. After the solution is cooled, 25 mL of 6M hydrochloric acid is added, the contents transferred to a 2-ounce container, and the final mass adjusted to 55 g with deionized water.

### RESULTS AND DISCUSSION

#### Total selenium in soils

Eleven of the fifteen soil profiles collected had at least one sample analyzed for total selenium, results are seen in Appendix A. Total selenium concentrations in the soil for the 23 samples analyzed ranged between 300 and 4200 ppb, with a mean (geometric) concentration of 854 ppb. The distribution of total selenium by concentration range is seen in Figure 4.

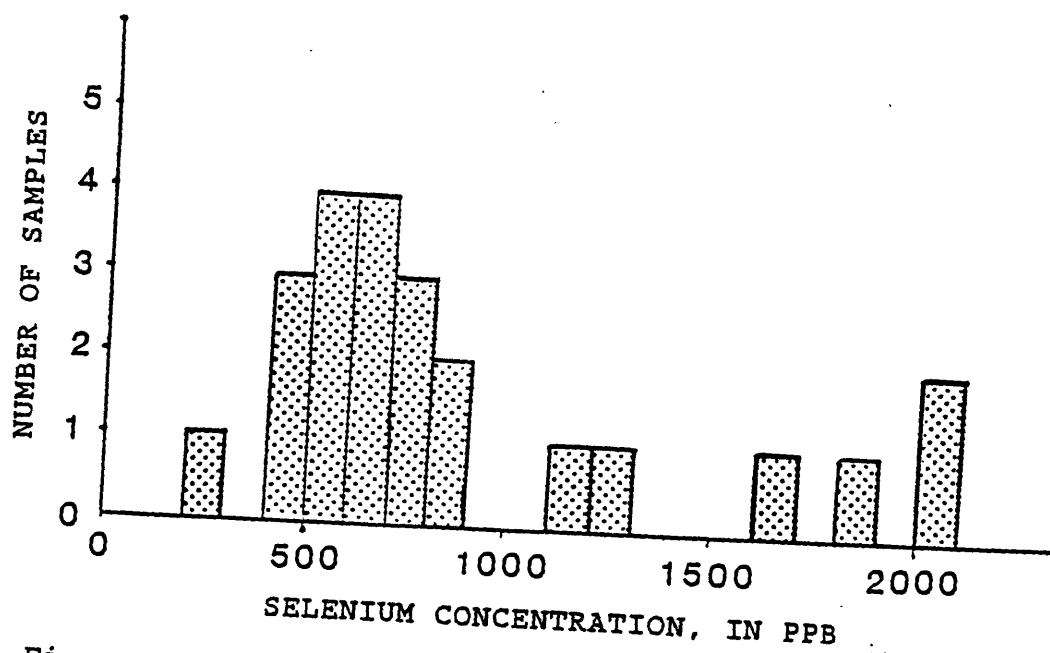


Figure 4 Distribution of total selenium concentrations in soils, from the Marty II study area

It is apparent that there is a skewed distribution of total selenium concentrations in the study area. The majority of samples (16) are distributed within the 400-900 ppb concentration range. Examination of selenium concentrations in Appendix A and sample collection sites in Figure 1 reveals no definitive selenium distribution pattern across the study area. It does appear however, that generally lower selenium concentrations are located in the southeast corner of the study area, which may reflect the deeper mantle of loess material along the Missouri breaks. The lack of a clearly defined selenium distribution pattern is probably governed by two factors, 1) the low sample density used in this part of the study and 2) the large local variability of the area.

In order to evaluate the total selenium distribution in the Marty II study, results from previous USGS investigations in the western United States were collected and compiled in Table 2. The total selenium concentrations presented in Table 2, are from previous U.S. Geological Survey investigations in California, North Dakota, and Wyoming. The data in Table 2 show that the mean concentration of total selenium in soils from the Marty II study area is the highest of any area studied to date. This is important when comparing the Panoche Fan and the Kendrick studies, due to problems encountered in these areas with wildlife deformities and death attributed to selenium contamination of irrigation drainage waters.

A final comparison was made between total selenium and sample collection depth, to examine the possibility of greater total selenium concentrations with increasing depth (Figure 5). A regression analysis, comparing average sample collection depth and total selenium concentration showed a poor correlation ( $r = <0.002$ ) between the two parameters. This indicates an inconsistent distribution of selenium with depth.

#### Water extractable selenium

In order to evaluate the mobility of selenium in the Marty II study area, water extraction tests were performed on all samples collected. Water soluble selenium concentrations are presented in Appendix B. Also present in Appendix B are percent extractable selenium values for the 23 sites where total selenium data are available. Percent extractable values were calculated using equation 1.

$$\frac{(\text{Water extractable Selenium conc.})}{(\text{Total Selenium conc.})} \times 100 \quad (1)$$

Examination of the data reveals that extractable selenium concentrations ranged from 2.6 to 8,800 ppb, with a mean

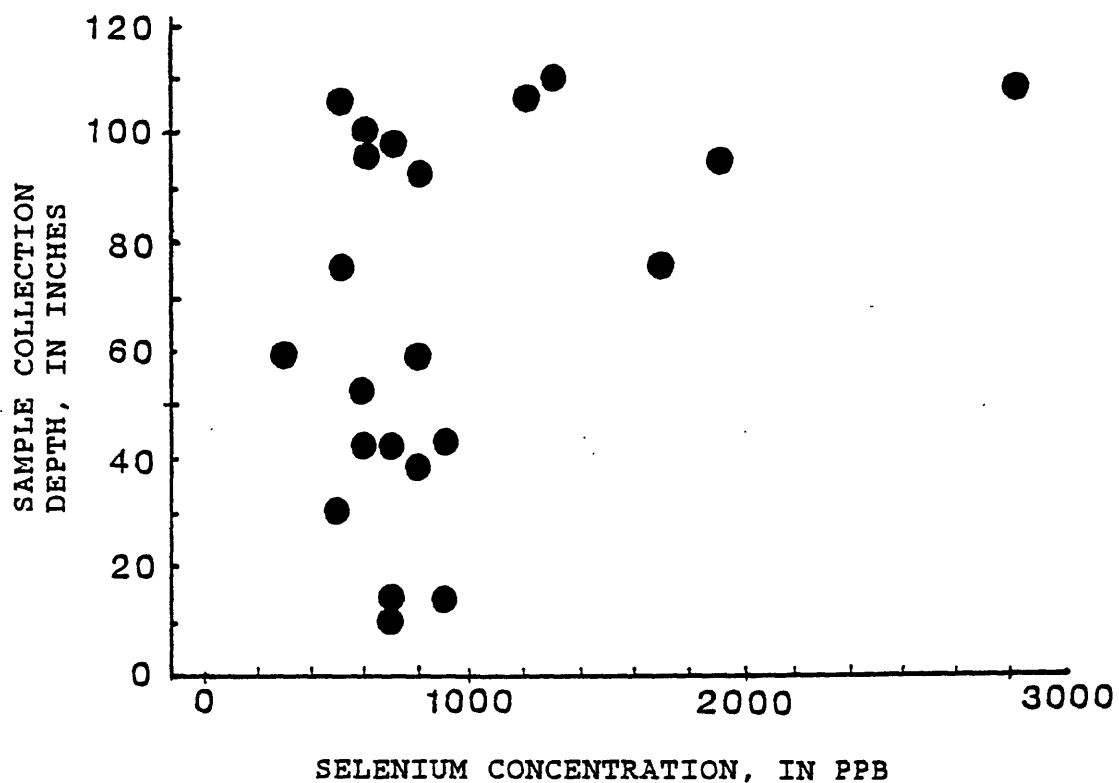


Figure 5 Total selenium concentrations in soils versus sample collection depth for Marty II study area



(geometric) selenium concentration of 21 ppb. A histogram of the extractable selenium results by concentration range is presented in Figure 6.

A skewed distribution is once again observed with over 90% of the samples containing less than 300 ppb. For comparison purposes, water soluble selenium results from the Marty II study and other USGS investigations are presented in Table 3. Levels of water soluble selenium in the Marty II study approximate those found in the Lake Andes-Wagner and Kendrick studies, but are about half of those seen in the San Joaquin investigations. The similarity in extractable selenium values for the Lake Andes-Wagner, and the Marty II studies is expected, based on the similar geology encountered in both areas. Contrary to results observed for the total selenium data, the water extractable values at Marty II were generally lower (except for Oakes site) than previous USGS studies. This indicates that, based on the samples collected, a smaller fraction of the total selenium is water soluble under the test conditions used.

In this comparison, extractable selenium concentration versus average sample collection depth was examined to see if a relationship existed between these parameters (Figure 7). A regression analysis of these parameters produced a correlation coefficient of 0.1. This low correlation coefficient indicates that for the entire data set, no significant relationship exists between these two variables, a condition previously observed in total selenium versus depth data. Closer examination of data for each location reveals that selected sites (6, 1A, and 12) do show a significant increase in extractable selenium with depth (Figure 8).

#### Percent water extractable selenium

Examination of the data in Appendix B reveals a wide range of percent extractable values. Values ranged from 0.4% to 57% with a mean (geometric) value of 4.1 %. Regression analysis of percent extractable selenium versus average sample collection depth (Figure 9) for the 23 samples results in a correlation coefficient of 0.07. This low correlation probably reflects the lack of a significant trend between these parameters, but may misrepresent the situation due to the limited number of core samples analyzed for total selenium. In the one core (site 7) where the entire profile has total selenium data, the percent extractable selenium increased slightly from 0.5 % to 2.8 % with depth. This increase may not be significant however, due to the low extractable selenium concentrations and the analytical precision at this concentration range.

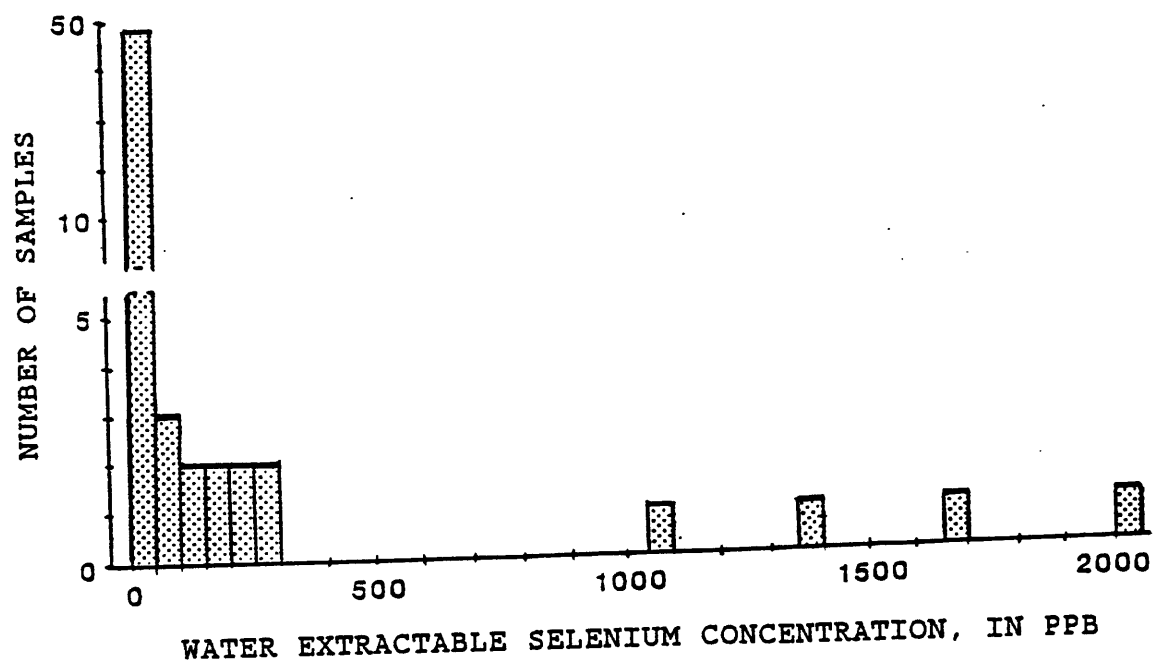


Figure 6 Water extractable selenium distribution in soils from the Marty II study area

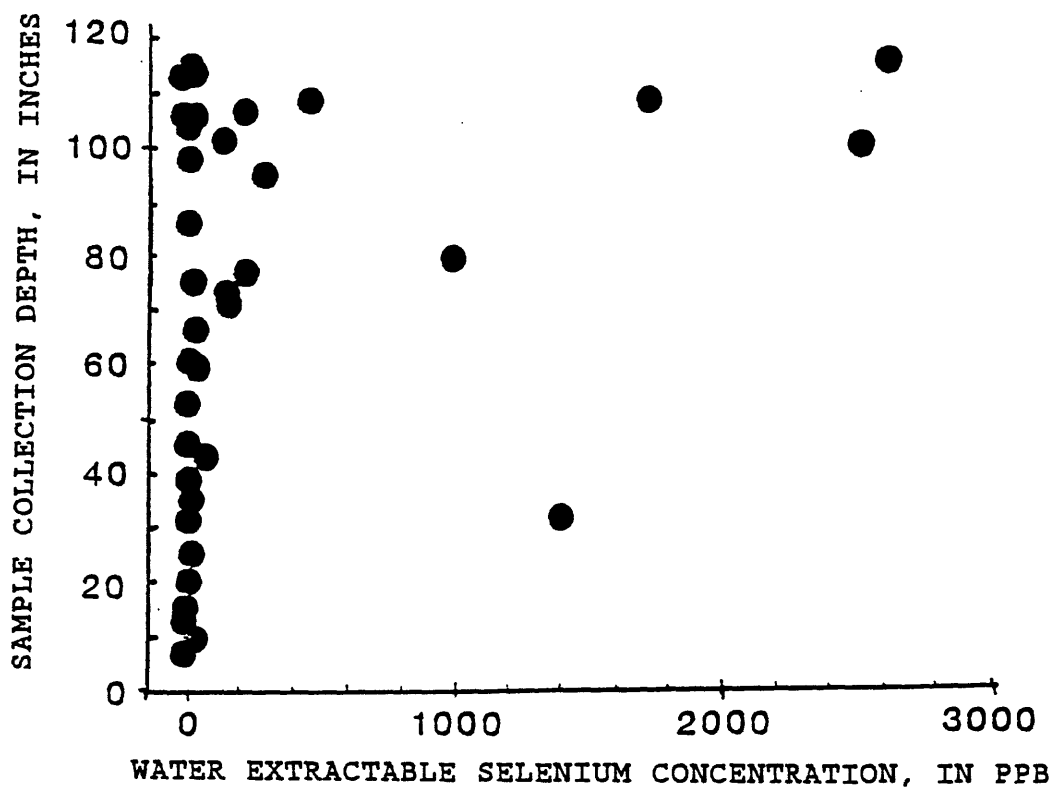


Figure 7 Water extractable selenium concentrations in soils versus sample collection depth for Marty II study

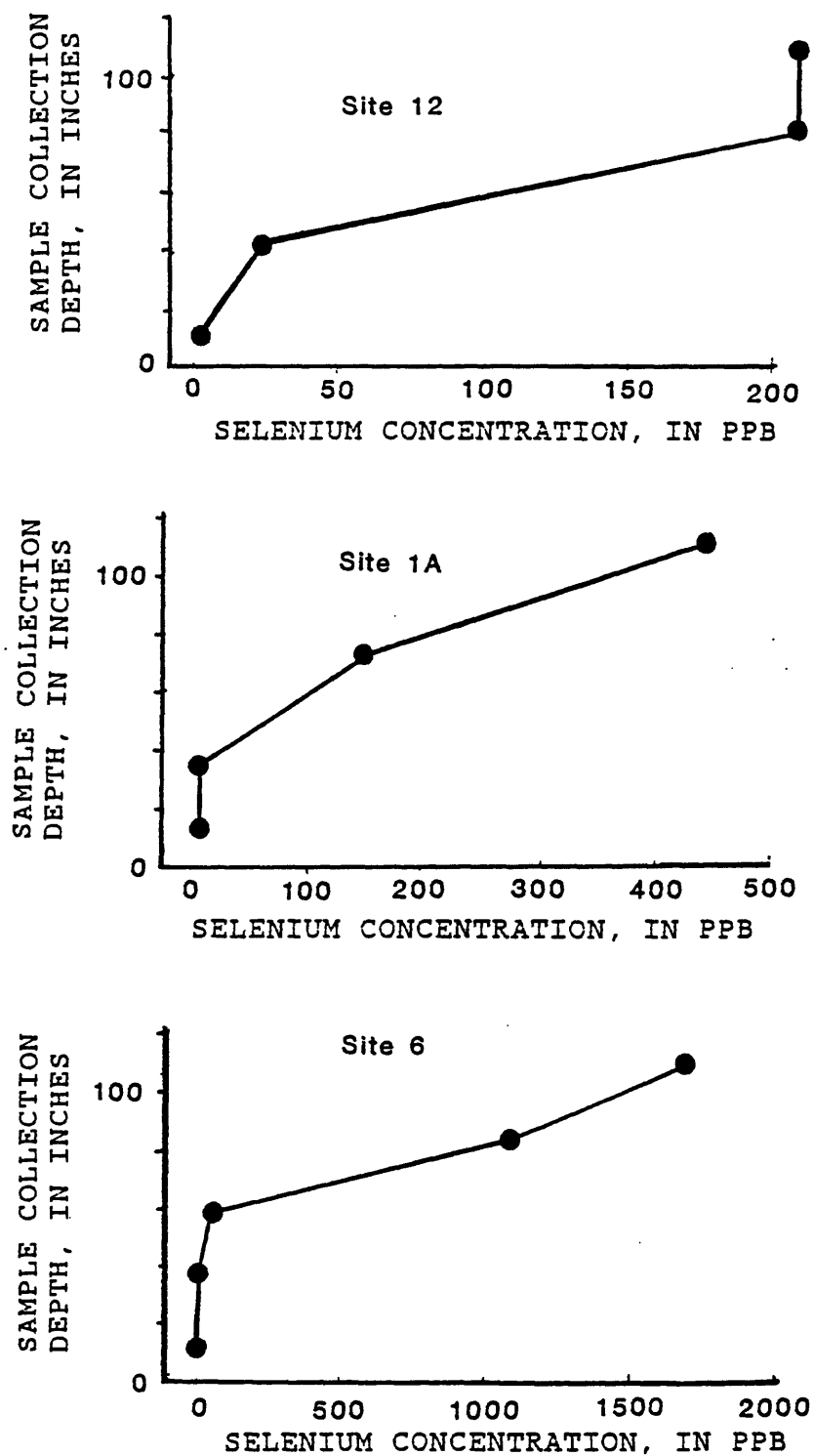


Figure 8 Water extractable selenium concentration versus sample collection depth for sites 1A, 6, and 12, Marty II study area

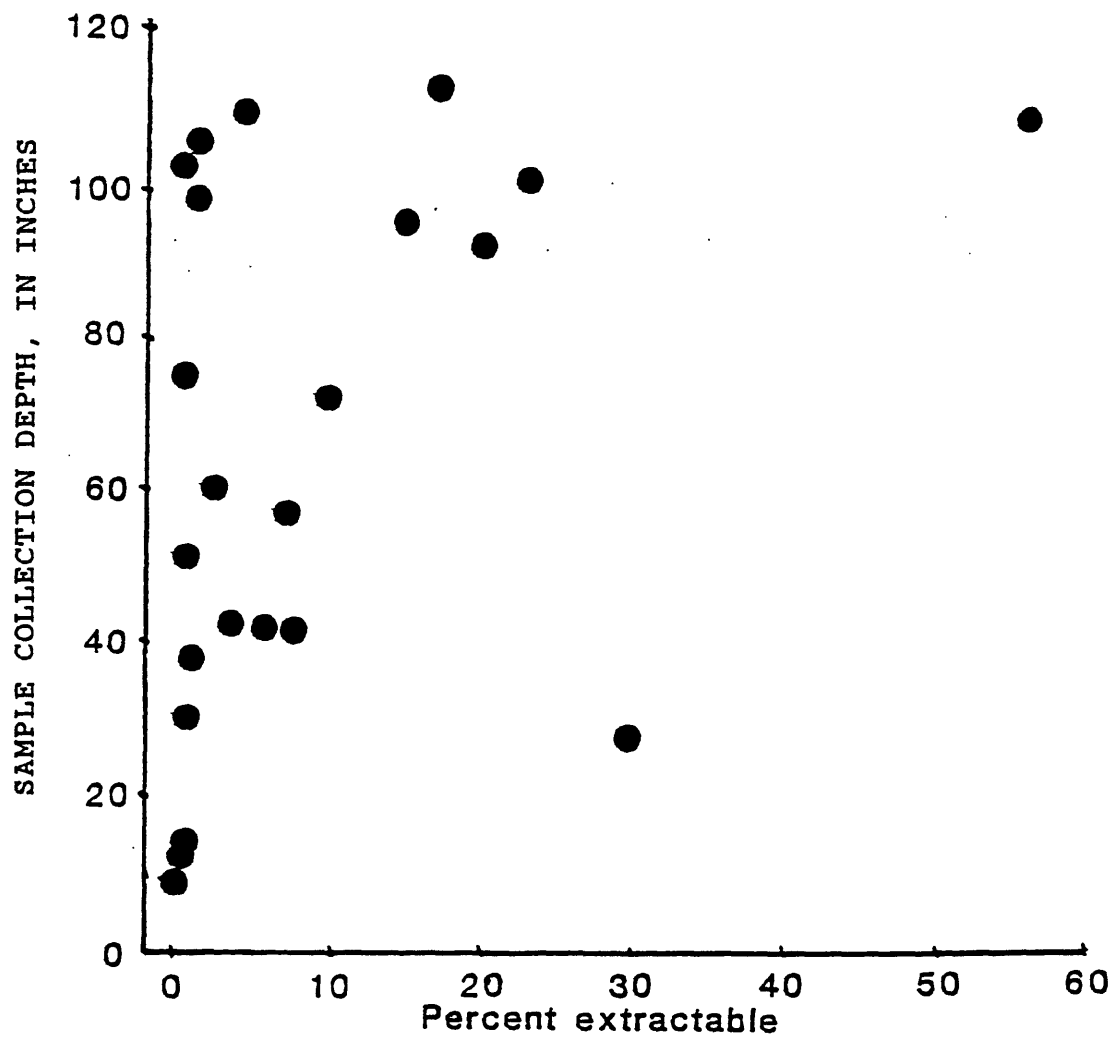


Figure 9 Percent water extractable selenium versus collection depth for Marty II study area

From the examination of water and percent extractable selenium results, we speculate that several forms of selenium exist in the Marty II soil environment. These forms may include selenate, selenite, organo-selenides and selenide. Based on earlier studies, selenate is the form which is most important due to its greater solubility and its ability to be incorporated into the food chain. It is apparent that at specific locations selenate is the dominant form of selenium and will be mobilized under irrigation/drainage conditions. At the present time it is impossible to quantify the amount of selenium that will be mobilized, due to several factors. Conditions such as established water table, surface terrain, soil permeability, agricultural protocols, amount of irrigation water used and forms of selenium will all influence the effect irrigation will have on the mobilization of selenium from irrigated lands.

#### Total versus water extractable selenium

A final comparison was made between total and extractable selenium concentrations (Figure 10). Regression analysis performed on the entire data set (23 values) reveals a correlation coefficient of 0.86, a slope of 1.8 and an intercept of 730 ppb (total Se). Regression analysis on a subset (21 values) of the data with total selenium concentrations below 2500 ppb reveals a correlation coefficient of 0.73 a slope of 3.7 and an intercept of 620 ppb (total Se). The high correlation coefficient for both sets of data indicates that samples containing higher total selenium values are expected to have greater amounts of extractable selenium.

#### Alfalfa samples

Thirteen alfalfa samples were collected from three sites in the study area, and analyzed for total selenium content. The results are presented in Table 4. The wide variation of selenium concentration in alfalfa plants is typical of plants grown in the western United States (Rosenfeld, I. and Beath, O, 1964). Studies at the Kendrick Wyoming site displayed even greater variation (250 to 15,000 ppb) over similar distances (Erdman, and others, 1989). Other studies have examined potentially toxic levels of selenium in alfalfa in southern Colorado (Byers and others, 1938), and in Israel (Ravikovitch and Margolin, 1957) where 7000 ppb and 44,000 ppb were detected respectively.

The impact of soil selenium concentrations on plant uptake for the Marty II study is difficult to assess. Factors such as the few samples collected, the complex plant biogeochemistry of selenium and the lack of reliable data from areas with geology similar to the Marty II site, make short or long term projections impossible. It is anticipated however, that the uptake of

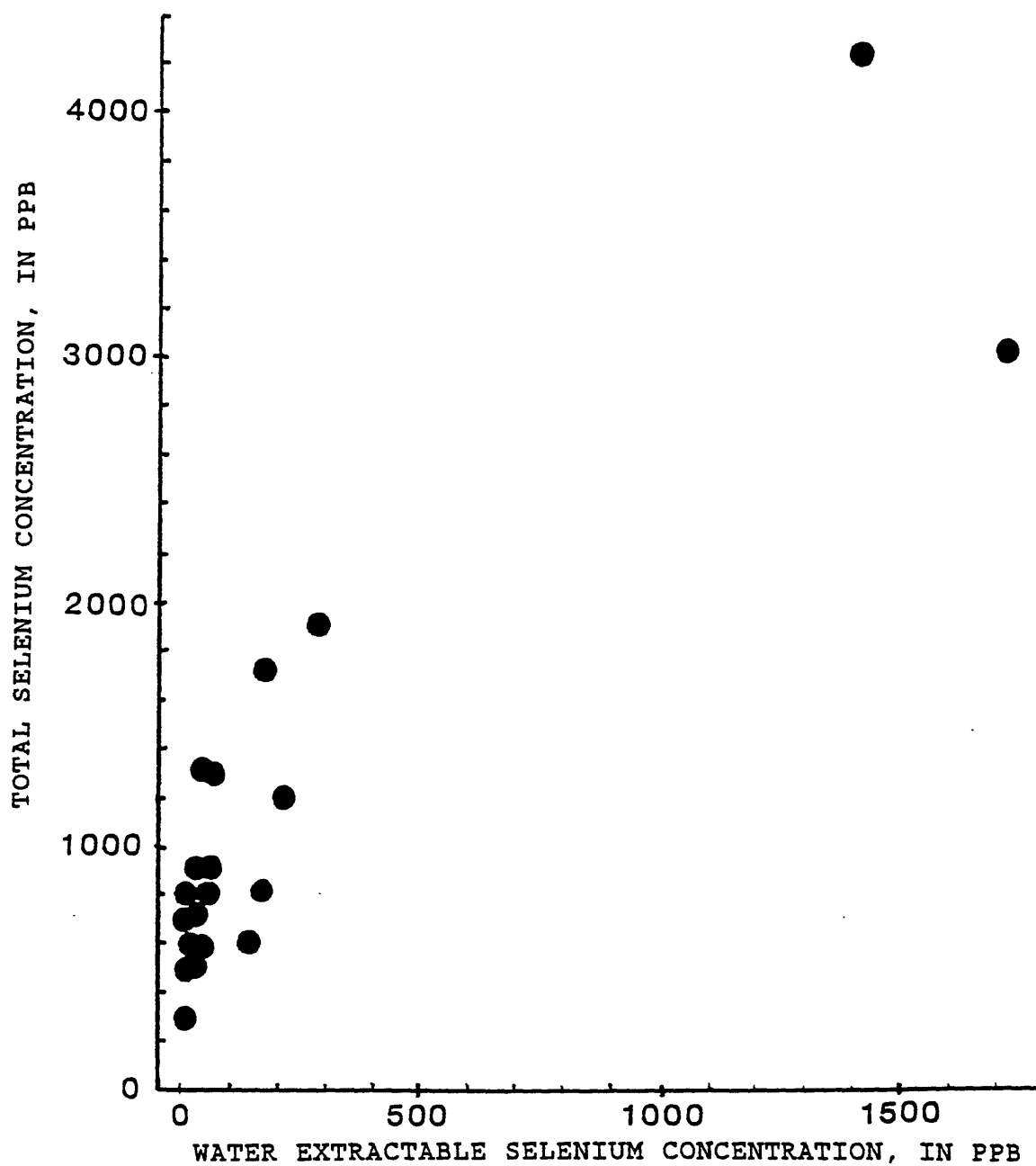


Figure 10 Total versus water extractable selenium in soils from the Marty II study area

selenium by alfalfa and other plants will be influenced primarily by management practices such as time and duration of irrigation. The levels observed in this study will not constitute a significant risk especially if harvested material is mixed with material from selenium deficient areas.

#### Stream sediments samples

Five samples were collected along Mosquito Creek and its tributaries from the top 3 inches of sediment material. This sediment depth is generally subjected to the greatest variability in redox conditions as well as periods of flooding and drying. Results are presented in Appendix D. As expected, the water extractable selenium fraction was extremely low, as far down stream as site 114, the confluence of Mosquito and Slaughter Creek. This low level of water extractable selenium was anticipated because water soluble forms of selenium would be mobilized during periods of stream flow.

Evaluation of the total selenium levels in stream sediments is difficult because only one sample (No. 113) was analyzed for total selenium (1700 ppb). If this sample is indicative of sediment material along Mosquito Creek then there are significant quantities of selenium contained within the sediment material. It is also evident that selenium in the sediment material is in an immobile form. This form could include selenide, selenite, or an organo-selenium compound. The environmental impact of selenium in the stream should remain minimal, as long as the stream conditions continue to maintain selenium in this immobile (reduced) form. If sediment material is transported (during flooding) to a more oxidizing environment or redox conditions change along Mosquito Creek, then selenium may be converted to the selenate form. The conversion to the selenate form would be significant because in this form selenium can be accumulated by water plants along the creek.

#### Ground water samples

The concentration of selenium in collected ground water samples are seen in Appendix E. Four (sites 3, 5, 8, 13) of the five samples contained selenium concentrations in excess of the irrigation criteria (0.1 mg Se/L) for alfalfa production (Albasel and others, 1989) as well as the drinking (0.01 mg Se/L) water and domestic-livestock water standards (0.05 mg Se/L) established by the Environmental Protection Agency (U.S. Environmental Protection Agency, 1977). These elevated levels of selenium in the ground water will require careful evaluation with regards to their use in crop or livestock production. Further examination of the ground water and water extractable selenium results indicate no correlation between the two data sets at the sites



selected. One possible explanation is that selenium in the ground water is derived from deeper shale formation and not the result of surface water percolation. A second possibility is that the high selenium ground water is imported from some other location. The elevated levels of selenium in the ground water systems is especially significant if subsurface drainage is installed in the Marty II area. As was pointed out by Deveral (Deveral and Fujii, 1988) the installation of subsurface drains will continually remove selenium containing ground water, until irrigation waters have displaced all ground water in the drainage zone. In the SJV studies, the displacement process contributed significant levels of dissolved selenium to return water for at least ten years. Unlike the SJV study however, the lower salt content of the Marty II soils and the different climatic conditions will require less irrigation water and could delay the upward movement of the water table. This will have a significant impact on the migration of selenium out of the soils.

#### Quality control data

Several duplicates and soil standards were included in the samples analyzed to monitor the quality of the data. Table 5 outlines the results of these analyses. The maximum relative standard deviation (RSD) for the soil duplicates analyzed in the study was 9 %. Replicate analyses of water and soil reference materials produced RSD of <1% and 8 % respectively. These results fall within established laboratory guidelines.

#### SUMMARY

The geology of the Marty II area suggests that there should be formations containing low to moderate levels of total selenium. Examination of eleven test sites for total selenium reveal an average concentration of 850 ppb (Geometric Mean). Similar concentrations have been observed in the San Joaquin Valley of central California (GM = 680 ppb), and Kendrick Wyoming (GM = 370 ppb). At both the San Joaquin and Kendrick sites selenium contamination problems have been observed and correlated with irrigation/drainage programs. In the Marty II study the average extractable selenium level was lower (GM = 21 ppb) than most previous studies but may still represent a significant problem if mitigation planning is not carried out. It is apparent that under irrigation/drainage conditions selenium will be mobilized. The uncertainty at this time is the magnitude and duration of this mobilization. In order to evaluate the final environmental impact at the Marty II site specific areas need to be studied. They include: 1) what processes govern selenium speciation and transport, 2) what is the time frame over which selenium mobilization occurs, 3) what impact will selenium have on surface and subsurface water systems especially as it relates to food

chain uptake, 4) does the local geology permit the removal of selected areas (elevated selenium) from irrigation in order to lessen the impact of mobilized selenium on the environment. These questions can only be addressed through a detailed study in the Marty II test area.

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Table 1. Water quality standards for  
selenium in selected water systems

<u>Material</u>	<u>Water Quality Standard</u>	<u>Reference*</u>
Freshwater Aquatic Life	5 ppb (chronic) 20 ppb (acute)	1 1
Livestock	50 ppb	2
Agricultural Crops	20 ppb	3
North Dakota Class I Streams	10 ppb	4
EPA Drinking Water Std.	10 ppb	5
National Acad. of Sci. Irrigation Criteria	20 ppb	6

1 Federal Register January 5, 1988

2 U.S. Fish and Wildlife report 85(1.4)

3 Canada water quality standard, 1979

4 Standards of water quality for North Dakota, rule 33-16-02, April 1, 1985

5 EPA Office of Water Quality USEPA report 57019-76-003 1986

6 National Academy of Science, National Academy of Engineering, 1973

\* For complete reference see bibliography

Table 2 Total selenium concentrations in soils from  
selected studies in the western United States

<u>Location</u>	Min. Se Content <u>ppb</u>	Max. Se Content <u>ppb</u>	Avg. Se Content* <u>ppb</u>	<u>Reference</u>
San Joaquin Valley, Ca.	<100	2800	240	Wilson and others 1990
Panoche Fan Ca.	<100	4500	820	Ryder, and others 1989
Oakes Irrig. Area, N.D.	<100	2100	130	Goolsby and others 1989
Kendrick Wyo	<100	3800	450	Severson, and others 1989
Marty II S.D.	300	4200	850	This study

\* Geometric Mean

Table 3 Water extractable selenium concentrations  
in soils from selected sites in the  
western United States

<u>Study Area</u>	<u>Max. ppb</u>	<u>Min. ppb</u>	<u>Mean* ppb</u>	<u>Reference</u>
Oakes, N.D.	0.16	<0.02	0.02	Goolsby and others, 1989
San Joaquin Valley, Ca.	2800	3	60	Deveral and others, 1984
Kendrick** Wy.	2700	<0.02	31	Crock, 1989
Lake Andes Wagner, S.D.	2600	<0.6	27	Wilson and others, 1990
Marty II	8800	2.6	21	This study

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\* Geometric Mean

\*\* 1:5 (Soil/water) extractions



Table 4. Dry-weight selenium concentrations in alfalfa samples collected in the Marty II study area

Sample Collection Site	Number of Samples	Min. Se conc. ppb	Max. Se conc ppb	Mean Se conc. ppb
13	5	800	8300	2400
7	5	600	2800	1400
15	3	300	4800	950

Table 5      Analysis of replicates and standards  
for the Marty II study

Sample I.D.	Total Se ppb		Water Extractable Se ppb	
	Analysis #1	Analysis #2	Analysis #1	Analysis #2
M-1	1200	1100		
M-7	600	500	<0.6	<0.1
M-14	500	600		
M-37	200	200		
M-40	1200	1200		
USGS Soil Standard*	1000	1000		
USGS Water Standard**	11	13		
<hr/>				
* In-house standard determined value			1000 ppb	
** WRD Reference standard 81 certified value (Long, K., 1989)			12 ppb	

# Appendix A Total selenium in soils from the Marty II study area

Site No.	Field I.D.	Site Location		Collection interval inches	Average Depth inches	Total Se ppb
		Lat.	Long.			
2A	M-50	42 57' 58"	98 25' 21"	26-58	42	600
	M-52	" "	" "	84-120	102	600
3	M-53	42 59' 14"	98 25' 34"	0-29	15	900
5	M-65	43 00' 28"	98 25' 40"	36-68	52	600
	M-66	" "	" "	68-120	94	1900
6	M-69	42 59' 48"	98 26' 56"	48-68	58	800
	M-71	" "	" "	96-120	108	3000
7	M-72	43 00' 32"	98 26' 02"	0-18	9	700
	M-73	" "	" "	18-24	21	500
	M-74	" "	" "	42-76	59	300
	M-75	" "	" "	76-120	98	700
9	M-80	42 59' 46"	98 24' 48"	20-36	28	4200
	M-81	" "	" "	36-108	72	1700
10	M-84	42 59' 32"	98 27' 49"	29-46	38	800
	M-87	" "	" "	81-120	100	600
12	M-93	42 58' 33"	98 25' 37"	23-60	42	700
	M-95	" "	" "	92-120	106	1200
13	M-97	42 58' 02"	98 25' 56"	20-64	42	900
	M-98	" "	" "	64-120	92	800
14	M-99	42 57' 23"	98 25' 28"	0-29	15	700
	M-102	" "	" "	92-120	106	500
15	M-105	43 01' 18"	98 27' 24"	50-99	74	500
	M-106	" "	" "	99-120	110	1300

# Appendix B Water extractable and percent extractable selenium in soils from the Marty II study area

Site No.	Field I.D.	Site Location		Collection interval inches	Average Depth inches	Water Soluble Se, ppb	Percent Extractable Se
		Lat.	Long.				
1A	M-45	43 12' 00"	98 26' 15"	0-25	12	3.0	
	M-46	" "	" "	25-44	20	3.6	
	M-47	" "	" "	44-96	75	150	
	M-48	" "	" "	96-120	108	450	
2A	M-49	42 58' 05"	98 25' 27"	0-26	13	3.2	
	M-50	" "	" "	26-58	42	47.	7.8
	M-51	" "	" "	58-84	71	12.	
	M-52	" "	" "	84-120	102	7.7	1.3
3	M-53	42 59' 19"	98 25' 34"	0-29	15	3.7	0.4
	M-54	" "	" "	23-48	40	3200	
	M-55	" "	" "	48-90	69	8800	
	M-56	" "	" "	90-108	99	2500	
	M-57	" "	" "	108-120	114	2600	
	M-58	42 57' 26"	98 24' 10"	0-18	9	5.2	
	M-59	" "	" "	18-45	32	2.6	
4A	M-60	" "	" "	45-68	56	9.9	
	M-61	" "	" "	68-104	86	3.9	
	M-62	" "	" "	104-120	112	6.2	
	M-63	43 00' 28"	98 25' 40"	0-13	7	5.7	
	M-64	" "	" "	13-36	24	4.8	
5	M-65	" "	" "	36-68	52	5.8	1.0
	M-66	" "	" "	68-120	94	290	15.
	M-67	42 59' 48"	98 26' 56"	0-22	11	3.6	
	M-68	" "	" "	22-48	35	9.1	
6	M-69	" "	" "	48-68	58	59.	7.4
	M-70	" "	" "	68-96	82	1100	
	M-71	" "	" "	96-120	108	1700	57.

# Appendix B Continued

Site No.	Field I.D.	Lat.	Site Location	Long.	Collection interval inches	Average Depth inches	Water Soluble Se, ppb	Percent Extractable Se
7	M-72	43 00' 32"	98	26' 05"	0-18	9	3.7	0.5
	M-73	" "	"	"	18-42	30	4.8	1.0
	M-74	" "	"	"	42-76	59	8.6	2.9
	M-75	" "	"	"	76-120	98	10.0	1.4
8	M-76	42 59' 53"	98	26' 10"	0-40	20	7.5	
	M-77	" "	"	"	40-92	66	18.	
	M-78	" "	"	"	92-120	106	7.	
9	M-79	42 59' 46"	98	24' 48"	0-20	10	3.4	
	M-80	" "	"	"	20-36	28	1400	33
	M-81	" "	"	"	36-108	72	170	10
	M-82	" "	"	"	108-120	114	5.8	
10	M-83	42 59' 33"	98	27' 50"	0-29	14	3.7	
	M-84	" "	"	"	29-46	38	9.1	1.1
	M-85	" "	"	"	46-67	56	22	
	M-86	" "	"	"	67-81	74	34	
	M-87	" "	"	"	81-120	100	140	23
11	M-88	42 59' 01"	98	26' 35"	0-36	18	9.1	
	M-89	" "	"	"	36-51	44	7.5	
	M-90	" "	"	"	51-92	72	8.0	
	M-91	" "	"	"	92-120	106	33	
12	M-92	42 58' 43"	98	25' 38"	0-23	12	<4	
	M-93	" "	"	"	23-60	28	24	3.4
	M-94	" "	"	"	60-92	76	210	
	M-95	" "	"	"	92-120	106	210	18

Appendix B Continued

<u>Site No.</u>	<u>Field I.D.</u>	<u>Site Location</u>		<u>Long.</u>	<u>Collection interval inches</u>	<u>Average Depth inches</u>	<u>Water Soluble Se, ppb</u>	<u>Percent Extractable Se</u>
		<u>Lat.</u>	<u>Long.</u>					
13	M-96	42 58' 02"	98 25' 56"		0-20	10	5.5	
	M-97	" "	" "		20-64	42	53	5.9
	M-98	" "	" "		64-120	92	170	21.
14	M-99	42 57' 23"	98 25' 28"		0-29	15	3.7	0.5
	M-100	" "	" "		29-52	40	5.0	
	M-101	" "	" "		52-92	72	4.4	
	M-102	" "	" "		92-120	106	7.4	1.5
15	M-103	43 01' 18"	98 27' 24"		0-18	9	3.7	
	M-104	" "	" "		18-50	34	3.2	
	M-105	" "	" "		50-99	75	4.6	0.9
	M-106	" "	" "		99-120	110	59.0	4.5
16	M-107	42 56' 25"	98 23' 03"		0-21	11	8.4	
	M-108	" "	" "		21-46	34	9.4	
	M-109	" "	" "		46-76	61	9.1	
	M-110	" "	" "		76-120	98	11.0	

Appendix C Total selenium concentrations in alfalfa plants  
from the Marty II study area

Site No.	Field I.D.	Site Location		Total Se ppb
		<u>Lat.</u>	<u>Long.</u>	
13	1	42 58' 02"	98 25' 56"	8300
	2	" "	" "	1600
	3	" "	" "	7000
	4	" "	" "	1000
	5	" "	" "	800
7	6	43 00' 32"	98 26' 05"	600
	7	" "	" "	1400
	8	" "	" "	1400
	9	" "	" "	1500
	10	" "	" "	
15	11	43 01' 18"	98 27' 24"	2800
	12	" "	" "	600
	13	" "	" "	300

Appendix D Total selenium concentrations in Mosquito Creek  
sediment samples from the Marty II study area

<u>Site No.</u>	<u>Field I.D.</u>	<u>Site Location</u>		<u>Extractable Se ppb</u>	<u>Total Se ppb</u>
		<u>Lat.</u>	<u>Long.</u>		
1	M-111	42 59' 28"	98 25' 32"	4.1	
2	M-112	42 59' 38"	98 25' 50"	4.0	
3	M-113	42 58' 57"	98 23' 47"	3.6	1700
4	M-114	42 57' 24"	98 21' 16"	6.6	
5	M-115	42 59' 53"	98 26' 10"	4.5	



Appendix E    Total selenium concentrations  
                 in ground water from the  
                 Marty II study area

<u>Collection Site*</u>	<u>Selenium conc. ppb</u>
3	1200
5	4600
8	140
13	6200
Spring	8

\* ground water collection sites  
correspond to soil collection  
sites.