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SELENIUM SPECIATION IN GROUND WATER

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MASTER

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SELENIUM SPECIATION IN GROUND WATER

INTRODUCTION

Lakin and Davidson (1973) reported that selenium toxicity diseases in animals may occur when the intake exceeds 4 mg/kg and selenium deficiency symptoms may occur when dietary intake is less than 0.04 mg/kg. Since the selenium dietary requirement is very close to toxic concentration, it is important to understand the distribution of selenium in the environment. With the discovery of toxic concentrations of selenium in the Kesterson National Wildlife Refuge (Masscheleyn, et al, 1989), there is increasing interest is the chemistry of selenium. Selenium occurs in four oxidation states (-II, 0, +IV, and +VI) as selenide, elemental selenium, selenite (SeO_3^{-2}) and selenate (SeO_4^{-2}). Of the selenium species occurring, selenate is reported (McNeal and Balistrieri, 1989) as more soluble and less adsorbed than selenite. Selenate is more easily leached from soils and is the most available form for plants.

Increased mobility of Se into the environment via anthropogenic activities, and the potential oxidation-reduction behavior of the element have made it imperetive to study the aquatic chemistry of Se. For this purpose, Se species are divided into two different categories: dissolved Se (in material that passes through filters with 0.45 um openings) and particulate Se (in material of particle size > 0.45 mm) typically suspended sediment and other suspended solids. Element and colloidal phase, not truly dissolved, but passing through the filter is deemed to consist of selenium (-2,0). In dissolved state selenium may exist in three of its four oxidation states; Se(-II), Se(+IV), and Se(+VI).

Particulate Se may exist in the same oxidation states as dissolved Se and can be found in different phases of the particulate matter. In sediments, Se may be within the organic material, iron and manganese oxides, carbonates or other mineral phases. The actual chemical forms of Se may be adsorbed to or co-precipitated with these phases (primarily selenite, SeO_3^{2-} and selenate, SeO_4^{2-}). Selenide, Se(-II), can be covalently bound in the organic portion of a sediment. In addition, Se may be found in anoxic sediments as insoluble metal selenide precipitates, an insoluble elemental Se or as ferroselite ($FeSe_2$) and Se containing pyrite (1).

Development of Oxidation Reduction Equations

Oxidation-reduction potential (redox) and pH are the prime factors in considering selenium transformations (Masscheleyn, et al. 1989). Eh-pH diagrams indicate that SeO_3^{-2} is the dominant Se species under reducing conditions (low pH, low O_2 concentration, high moisture content and low Eh), whereas SeO_4^{-2} is the dominant form under oxidizing conditions (high pH, high O_2 concentrations, low moisture content and high Eh). Since SeO_4^{-2} is the most mobile species and most readily absorbed by plants, the conditions under which transformations occur between SeO_3^{-2} and SeO_4^{-2} are important. Coal contains sulfur and selenium is often associated with sulfur. Selenium compounds could then be leached from the coal spoils and enter the ground water system.

The equilibrium redox reactions (Elrashidi, et al, 1987) reported for selenite/selenate are:

$$SeO_4^{-2} + 2e^- + 2H^+ = SeO_3^{-2} + H_2O \qquad (1)$$

$$SeO_4^{-8} + 6e^- + 8H^+ = Se\ (\text{hexagonal, black}) + 4\ H_2O \qquad (2)$$

$$SeO_4^{-2} + 8e^- + 8H^+ = Se^{-2} + 4\ H_2O \qquad (3)$$

$$SeO_3^{-2} + 4e^- + 6H^+ = 1/2\ Se_2\ (g) + 3H_2O \qquad (4)$$

$$SeO_3^{-2} + 6e^- + 6H^+ = Se^{--} + 3\ H_2O \qquad (5)$$

Oxidation-reduction reactions are common in the soil environment. Redox equilibria are generally expressed in terms of Eh which is a millivolt potential difference between a platinum electrode and a reference electrode (a standard hydrogen electrode). Redox reactions are expressed as half-reactions indicating a loss or gain in electrons. The chemical species gaining electrons is the oxidizing agent and subsequently undergoes reduction. The species losing electrons is the reducing agent and itself is oxidized. Since the half-reactions are balanced indicating a transfer of electrons, the number of electrons (e^-) can be considered as either a product or reactant.

The redox potentials can be expressed as pe (-log of the electron activity) rather than as Eh (millivolt measurements). A platinum electrode can be used to measure redox potential at the selected coal mine spoil sites. The reference electrode uses the standard hydrogen half-reaction such that Eh is defined as the potential of the cell: Pt, H_2/H^+// reduced, oxidized, Pt. Using appropriate substitution and numerical values Eh can be expressed in terms of pe.

Soil systems often consist of an aqueous environment where water dissociation into hydrogen gas (H_2) and oxygen gas (O_2) imposes limits on oxidation - reduction in soils. Equilibria reactions for water dissociation (Lindsay, 1979) are:

$$\begin{array}{ll} H_2O + e^- = 1/2\ H_2\ (g) + OH^- & (6) \\ H^+ + OH^- = H_2O & (7) \\ \hline H^+ + e^- = 1/2\ H_2\ (g) & (8) \end{array}$$

for the reduction reaction and,

$$H^+ + e^- + 1/4\ O_2\ (g) = 1/2\ H_2O \qquad (9)$$

for the oxidation reaction. The thermodynamic equilibrium expression, K°, for Eq. 8 is:

$$K^\circ = \{H_2\,(g)\}^{1/2} / \{e^-\}^2\,\{H^+\} \qquad (10)$$

and expressed as logarithms:

$$\log K^\circ = 1/2 \log \{H_2\,(g)\} - \log \{e^-\} - \log \{H^+\} \qquad (11)$$

such that

$$\log K^\circ = 1/2 \log \{H_2\,(g)\} + pe + pH \qquad (12)$$

By definition K° for the dissociation of water is defined as 1 (unity) when $[H^+]$ is 1 M and the H_2 (g) is measured as the partial pressure of H_2 (g) at 1 atmospheric pressure. When the partial pressure of H_2 (g) is 1 atm., pe + pH = 0. The value pe + pH = 0 represents the most reduced condition in a soil aqueous environment.

For the oxidized reaction (9), the K° expression is

$$K^\circ = [H_2O]^{1/2} / [H^+]\,[e^-]\,[O_2\,(g)]^{1/4} \qquad (13)$$

Since $\{H_2O\}$, the activity of water, is nearly unity in a very dilute system, the logarithm form is

$$\log K^\circ = -\log [H^+] - \log (e^-) - 1/4 \log [O_2(g)] \qquad (14)$$

and

$$\log K^{\circ} = pH + pe - 1/4 \log [O_2(g)] \quad (15)$$

where

$$pe + pH = \log K^{\circ} + 1/4 \log [O_2\ (g)] \quad (16)$$

When $[O_2\ (g)]$ equals 1 atm pressure (partial pressure of oxygen gas), then pe + pH = log K° . A measurement of the soil gases (O_2 and CO_2 in particular) helps determine oxidized or reduced conditions. Also, the pe + pH parameter provides a description of the redox environment in soil aqueous systems. The oxidation state of selenium affects both the mobility and solubility of Se species. The parameter, as described, not only addresses pe, but also pH, the - log of the activity of H^+ . Since Eh is measured, it is then useful to convert Eh into pe.

The Nernst equation,

$$E = E^{\circ} - (R\ T / n\ F)\ \ln Q \quad (17)$$

can then be used to obtain an expression for Eh related to pe. The relationship between Eh and pe is derived from the Nernst equation and the redox reactions which occur between the platinum electrode and the reference electrode used to measure Eh. The overall cell reaction (Lindsay, 1979) is:

$n/2\ H_2\ (g) + \text{oxidized species}\ \text{------}\ n\ H^+ + \text{reduced species.}$

With the reference electrode being the standard hydrogen electrode, $\{H^+\}$ and $\{H_2\ (g)\} = 1$ and E in the Nernst equation becomes Eh. Applying the Nernst equation to the described cell reaction gives

$$E = E' - (R\ T\ /\ n\ F)\ \ln\ \{H^+\}^n\ \{\text{reduced species}\}/\ \{H_2\ (g)\}^{n/2}\ \{\text{oxidized species}\} \qquad (18)$$

With $\{H^+\} = 1$ and $[H_2\ (g)] = 1$, Equation 17 reduces to

$$Eh = E^{\circ} - (RT\ /\ nF)\ \ln\ \{\text{reduced species}\}/\{\text{oxidized species}\} \qquad (19)$$

Combining Eq. 18 with the K° expression for a general half reaction gives

$$Eh = E^{\circ} - (RT\ /\ nF)\ (\log K^{\circ} - n\ pe) \qquad (20)$$

where ln is changed to log base 10. E° is the standard cell potential and K° described in Eq. 19 is the thermodynamic equilibrium, expression for a general half-reaction:

$$\text{oxidized species} + ne^- \qquad \text{reduced species} \qquad (21)$$

Since SeO_4^{-2} is the most mobile species and most readily absorbed by plants, the conditions under which transformations from SeO_3^{-2} to SeO^{4-2} are important.

Since $E^\circ = (2.303\ RT\ /nF)\ \ln K^\circ$ is derived from the G° expression and the standard cell potential, Equation 19 becomes

$$Eh = (2.303\ RT\ /\ F)\ pe \qquad (22)$$

At R, the gas constant, equals 1.987 cal/degree - mole, T, the absolute Kelvin temperature, at 25 °C equals 298.15 K and F, the Faraday constant, equals 23.061 kcal/volt - equivalent, Equation 21 becomes

$$Eh\ (\text{millivolts}) = 59.2\ pe \qquad (22)$$

Equation 22 shows how Eh and pe can both be used to express redox relationships. These equations are developed from Sposito (1989), Lindsay (1979), Sawyer and McCarty (1978) and Garrels and Christ (1965).

The roles of pH and Eh are very important in determing the rates of Se oxidation, even as it applies to Se oxidation in coal mine spoils. Preliminary investigations from surveying the 77 Oklahoma counties indicate the most abundant selenium species in ground water is the selenite (SeO_3^{-2}) ion rather than the selenate (SeO_4^{-2}) ion as generally reported. The redox equations (1-5) establish the importance of pH and Eh (or pe) as important parameters in the investigation of redox potential for Se transformation. It is worth noting that bacterial activity also is a parameter in speciation and form of Se.

SELENIUM AND FRESH WATER SYSTEMS

A. Rivers, Streams and Canals

While considering the recent available information, the overall speciation data shows SeO_3^{2-} to be the dominant form of selenium, with Se (-II) ans Se(0) having the lowest concentrations. Nevertheless, the data also indicated that every river is unique with respect to its speciation and concentration of Se, and broad generalizations are therefore, inappropriate. Cutter (1) has obtained speciation data for the largest river system of California, the San Joaquin and Sacremento rivers. The San Joaquin, which drains the southern portion of the agriculturaly important central valley of California, has total Se concentration an order of magnitude higher than those of the Sacremento draining the northern valley. In San Joaquin, SeO_4^{2-} is the dominant form, while SeO_3^{2-} and Se (-II) or Se(0) are primary species in Sacremento (1).

B. Selenium in Ground Water nad Drinking Water

The content and speciation of selenium in groundwater and drinking water is of the most direct concern to humans. Selenium occurs as a minor constituent in drinking water in a concentration range of less than 0.1 to 100 ug/l. Safe drinking water act of USEPA, has established an upper limit of 0.01 mg/L which is rarely exceeded. However, water derived from some of the Cretaceous zones may have high concentrations of both selenium and total soluble salts (2).

In a study by Donovan et al 1981, in central Montana, it was reported that water from wells drilled into any of the geologic formations, cretaceous Colorado group, contained as much as 1000 mg/L Se (2). An important source of drinking water, ground water, has total Se concentration ranging from less than 0.6 to 342 n-mole/kg. From these, a worldwide average of 30 n-mole/kg can be extrapolated. All of the available data shows that SeO_4^{2-} is the major selenium species in ground water. (1) Humic substances in ground water interfere with the ground water selenium speciation.

Selenium concentrations in surface water averages 2 ug/l or less. Drainage from irrigation and soil leaching are principal sources of Se in surface water. In the Colorado river basin, elevated Se concentrations in surface water have been attributed to drainage from seleniferous soils. High concentrations of Se also occurs in subsurface drainage waters from irrigated soils in much of the San Joaquin valley. However, the occurance of elevated selenium levels in grond water within this region is not uniform. Some areas having relatively low concentrations of Se occur among nearby surrounding areas with much higher selenium levels. (3)

Mechanism for Selenium to Enter Aquatic System

Selenium is continously cycled by natural processes. A general model explaining the cyclic process is shown in figure 1. Selenium is transported from the core to the surface of the earth through igneous extrusions and volcanic gases. Soils may obtain selenium from rocks, volcanic activities, industrial waste, irigation water and fertilizers. Selenium and other trace elements are released through coal combustion and enter aquatic systems either by direct discharge or indirect input. Irrigation drainage effluent may be discharged into water bodies or into wet lands that are important wild life habitats (3).

In aquatic system, Se is predominantly associated with the sediments, which act as both sink and reservoir, or with plants and animals living there; very small amounts are found dissolved in water. From the sediments and water, Se is accumulated by phytoplankton, algae, rooted vegetation and invertebrates.
Aquatic bacteria can concentrate Se to high levels and provide a link into the food chain. The ultimate fate of Se and other trace elements is their return to sediments or other translocation systems. Other routes of escape for Se from an aquatic system include volatalization (3).

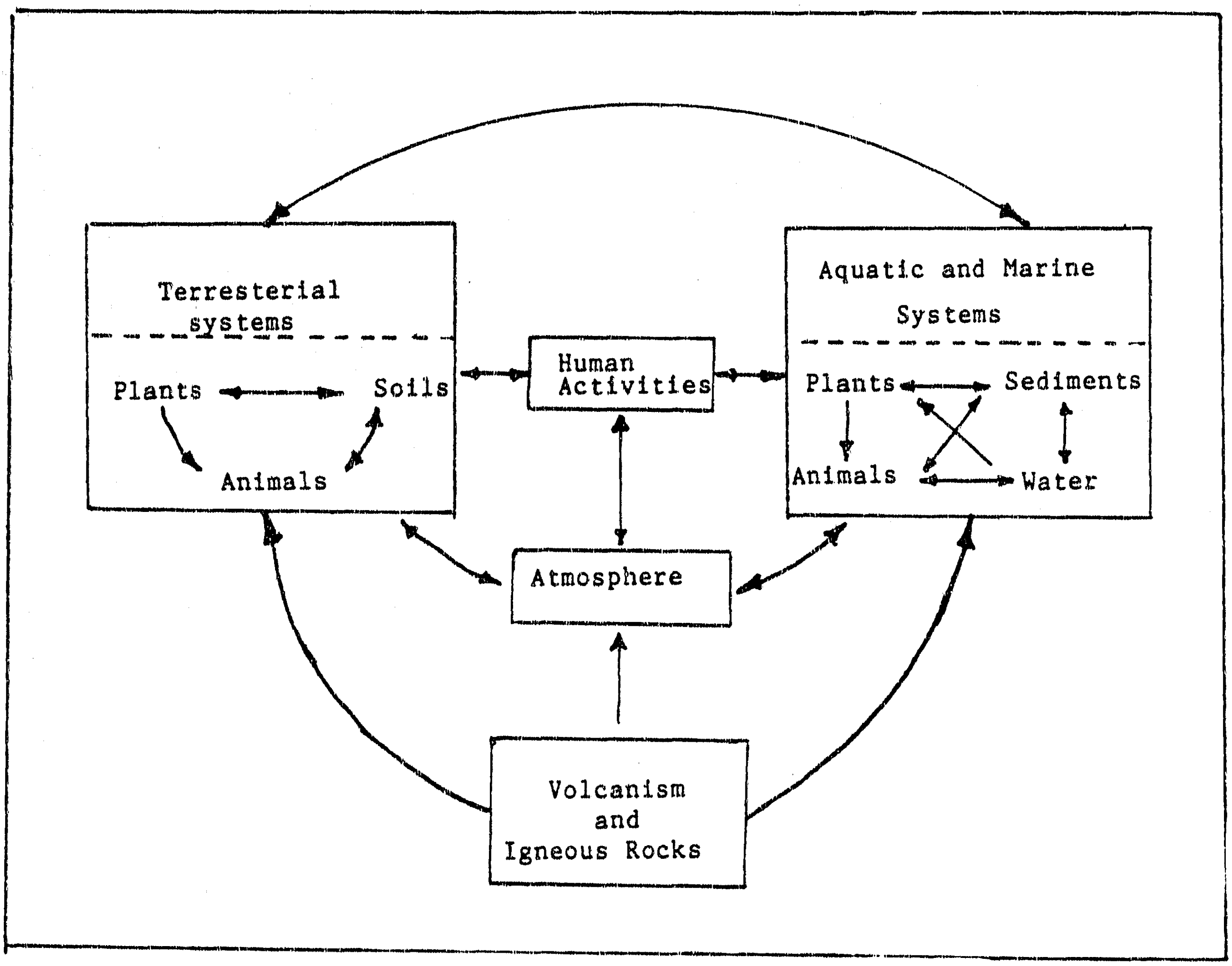


Figure 1. The cycling of Se in nature. For Simplicity, microorganisms are not included in the scheme, although they are important to many of the processes involved in the cycle (3).

Aquatic Chemistry of Selenium

Inorganic Se is found in the environment with an oxidation state of -II, 0, +IV, or +VI. Construction of an Eh-pH diagram from the approperiate redox and acid-base reactions provides a theoretical indication of which species might predominate under a given set of environmental conditions. The Eh-pH diagram for Se is shown in Figure 2 with the normal Eh-pH range of water indicated as the area contained within the two dotted lines. Based on the figure, the only soluble inorganic Se species expected in ground wters will be either Se(+IV) or Se(+VI). Since selenic acid (H_2SeO_4) is an exremely strong acid (pK = -3), Se(+VI) will occur as SeO_4^{2-}, and the protonated form ($HSeO_4^-$) does not occur above pH = 4. Selenious acid (H_2SeO_3) is a much waker acid (pK = 2.7), and Se(IV) will occur predominately as the monoprotic species ($HSeO_3^-$) in the pH ranges of 6 to 9 which is typical of most ground waters.

The aquatic chemistry of Se is complicated since it can exist in four different oxidation states and as a variety of inorganic and organic compounds (5). The chemistry of Se resembles that of sulfur. Selenium, like sulfur, can exist in the -II, 0, +IV, and +VI oxidation states. The concentration, speciation and association of Se in a given environment depend upon the pH and redox conditions, the solubility of its salts, the biological interactions and reaction kinetics.

Many reactions in aqeuous media involve transfer of electrons

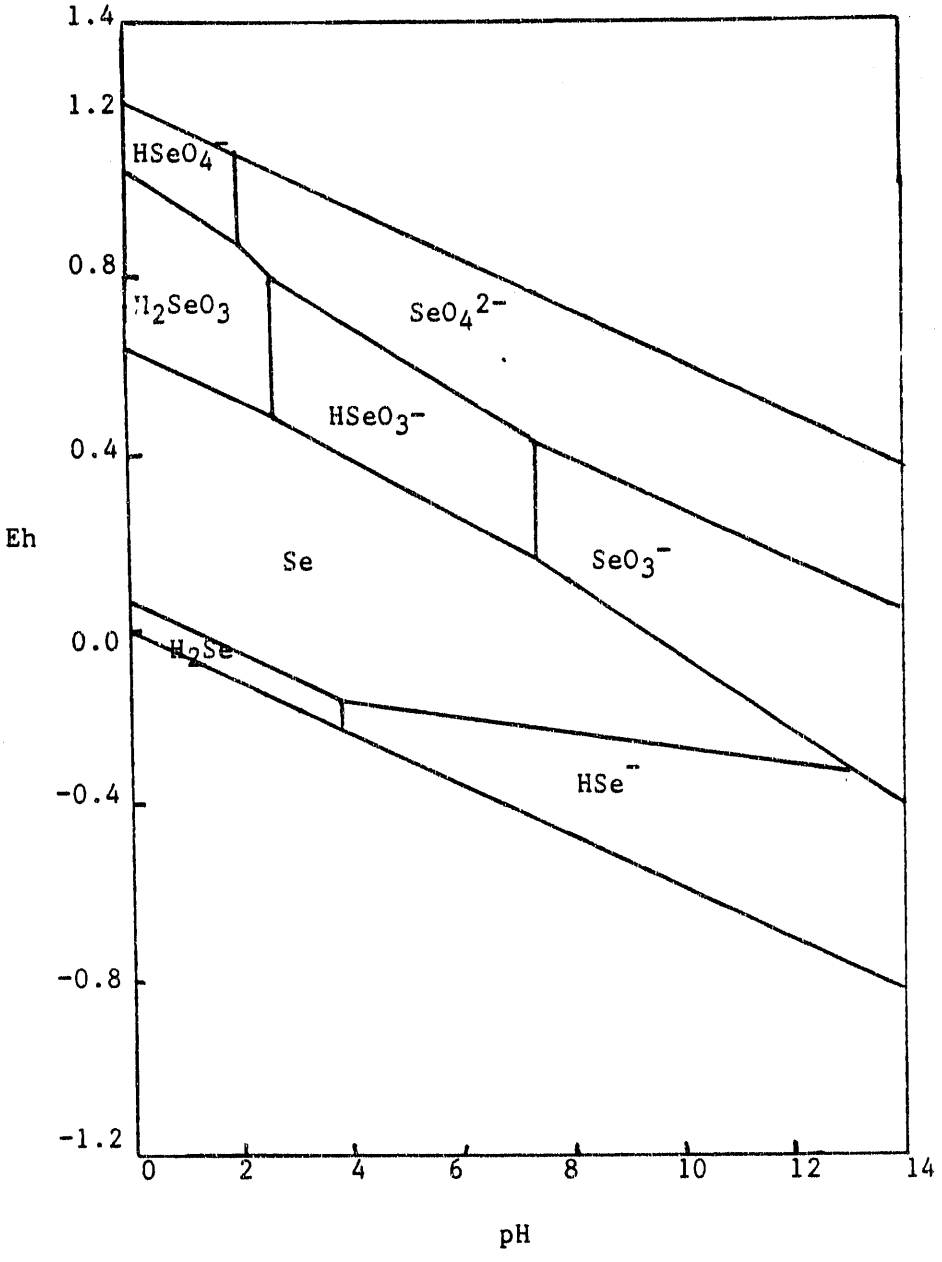


Figure 2. An Eh-pH diagram for the Se-H_2O system.

and protons. Such reactions can be represented in an Eh-pH diagram. The activity of the electrons is related to Eh in the same manner as pH is related to the activity of protons (H^+ ions) in solutions. Redox potential is a very useful parameter in describing and predicting the behavior of many important elements that occur in more than one oxidation states (4). Several species of Se exist in the aqueous environment (see Figure 2), however, the most dominant ones are those that are involved in oxidation reduction reactions. The main species involved are:

a) Selenide (Se^{2-}); which may be found in the dissolved states as H_2Se + HSe- (Hydrogen selenide) in anoxic waters or as organic selenides, primarily seleno-amino acids bound in soluble peptides, in oxic and anoxic waters. (1) Equilibrium constants and solubility products show that selenide must exist in reducing environment as hydrogen selenides. Selenide is a foul smelling, poisonous gas. It is a weak acid, and when dissolved in water it easily oxidises to elemental Se (6).

b) Elemental Se, Se(0); which is present in colloidal form and is presumed to result from decomposition of seleniferous minerals by bacteria, fungi and algae. The quantity of Se(0) is exceedingly small (7). The Eh-pH diagram indicates that elemental selenium is stable in reducing environments. All crystalline forms are insoluble in water. In a study by Sarath Chandra (6) 1981 it is reported that elemental Se can be oxidised to selenites and trace amounts of selenates by certain microorganisms.

c) Selenite (SeO_3^{2-}) which according to a study in fresh water by Turner and Dickson (1), exists as $HSeO_3^-$ at pH 6, and 31% $HSeO_3^-$ + 69% SeO_3^{2-} at pH 9. Other thermodynamic data shows that SeO_3^{2-} is favoured under mildly oxidising conditions. Selenious acid is a weak acid and is protonated when pH values are acidic to neutral. Most SeO_3^{2-} salts are less soluble than the corresponding selenate salts. Selenite is reduced to elemental Se by mildly reducing agents (6).

d) Selenate (SeO_4^{2-}), the (+IV) oxidation state of Se, is stable in well oxidised environments. Selenic acid, H_2SeO_4, is a strong acid and therefore not protonated over pH range of natural waters (6). Dissolved Se is found as selenate in fresh water from pH 6 to 9 (1). Selenate salts are very soluble and conversion of SeO_4^{2-} to SeO_3^{2-} is a very slow process (6).

Figure 3 shows the P^e-pH diagram for Selenium in an aqeous system under standard conditions. The redox range is considered to be bounded by the H_2O (1)/O_2(g) and H_2(g)/H_2O(1) couples.

The boundary is represented by the line:

$$P^e = 14.75 - 1.00pH \qquad (23)$$

This line corresponds to the Pe/pH conditions for which

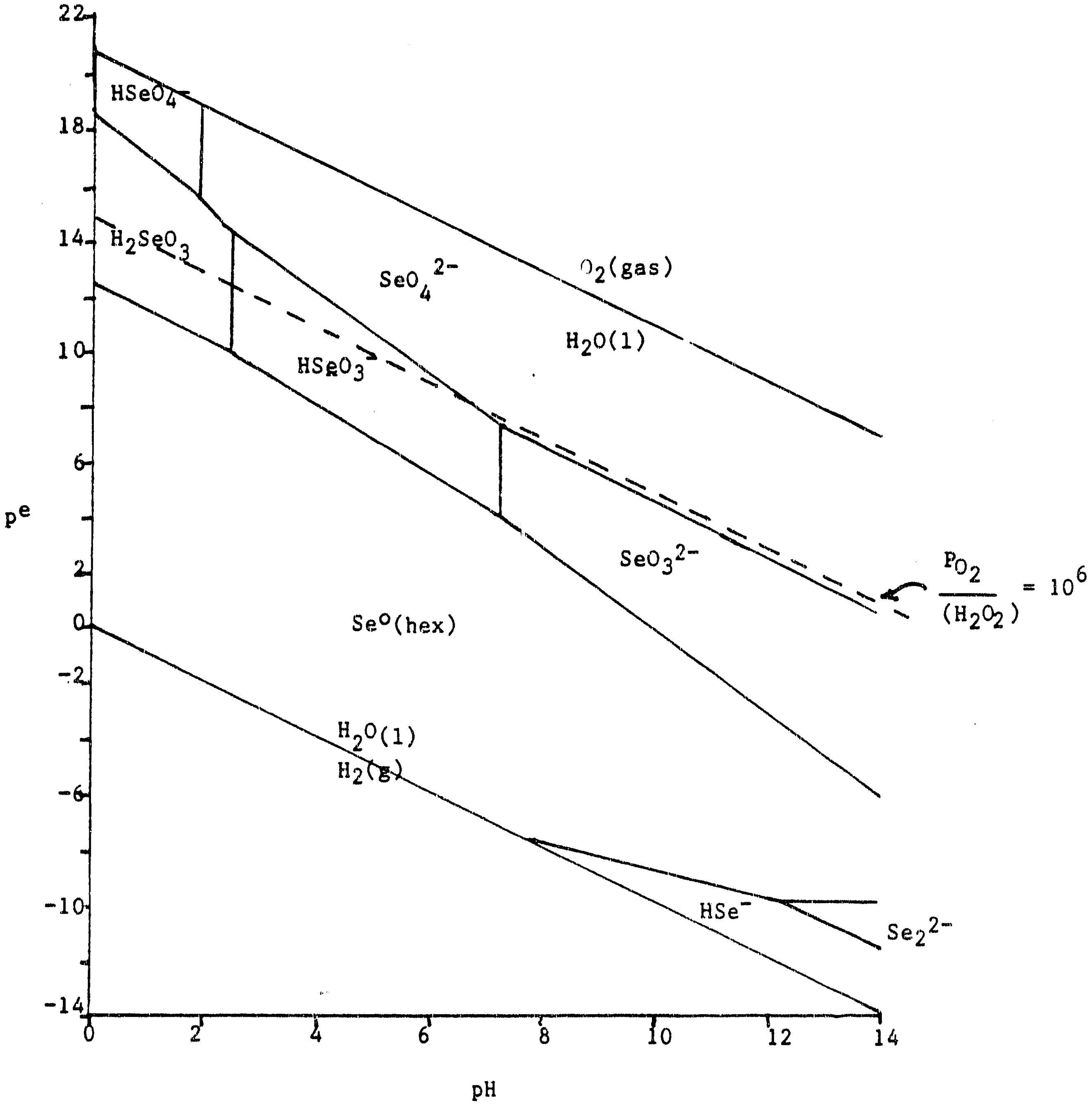


Figure 3. Predominance area diagram for selenium in an aqueous system under standard conditions (8).

$$\log PO_2/H_2O_2 = 6 \qquad (24)$$

It can be seen from the predominance area diagram that SeO_4^{2-}, $HSeO_3$-, SeO_3^{2-}, SeO and HSe- are each predominant for some Pe/pH range within the overall conditions set on the system. Selection of the predominant form in the system is also based on thermodynamic data.

To predict the behaviour of Se in the aquatic environment, the system can be divided into four broad catagories - bulk water, interstitial water, suspended solids and sediment solids. Various transformation occuring in the system can, thus, be predicted by making use of the above catagories.

At equilibrium, the relationship between the oxidation of the aqeous acidic form of the selenite (4) ion ($HSeO_3^-$) to the aqeous selenate ion (SeO_4^{2-}) is given by:

$$\log HSeO_3^-\ (aq)/\ SeO4^{2-}(aq) = 36.3 - 3\ pH - 2P^{e} \qquad (25)$$

The reduction of the aqeous selenate ion to the hexagonal form is given by:

$$\log Se(0)/SeO_4{}^{2-}(aq) = 88.9 - 8pH - 6Pe \qquad (26)$$

The reduction of the aqeous selenate ion to the aqeous HSe^- ion is given by:

$$\log HSe^{-}(aq)/SeO_4^{2-}(aq) = 81.19 - 9pH - 8P^{e} \qquad (27)$$

As can be sen from the predominance area diagram, the boundary between the selenate ion, $HSeO_3^-$, and SeO_3^{2-} ion falls below the boundary determined by the H_2O/O_2 couple. However, the oxidation potential in the natural aqeous system does not reach the boundary defined by the couple. Sato(8) proposed that the maximum oxidation potential in most aqeous systems may fall on or below a line defined by the H_2O/O_2 couple which is given by:

$$\log PO_2/H_2O = 6 \qquad (28)$$

If this boundary is accepted as the upper limit on the oxidation potential in most aqeous systems, selenate may be slightly predominant under neutral to alkaline conditions, if the oxidation potential reaches the maximum potential predicted.
Under acidic conditions, or under alkaline conditions with the oxdiation potentials falling below the maximum predicted, $HSeO_3^-$ or SeO_3^{2-} will be predominant. While predicting the relative amounts of selenates and selenites in natural waters, the kinetics for the reduction of the selenate ion to the selenite ion or to the elemental selenium is also to be considered.

In a study conducted by Deverel and Millard (9) on shallow ground water samples in San Joaquin valley, it is reported that Se is much more enriched in the coastal range alluvial-soil zone and is strongly related to salinity of the soil. The mobility and distribution of Se has been attributed to the geologic origin of the alluvial deposits.

Sampling and analysis for Se in the San Joaquin valley in California has provided some very important facts. Volatile methylated selenium compounds (methyl selenides) and dimethyl selenonium compounds (DMSE-R) were documented in a study by Cooke and Bruland (5).

SEPARATION OF SELENIUM SPECIES IN GROUND WATER

The total Se concentration in potable water is Federally regulated not to exceed 0.01 mg/L because of potential health effects. Many ground water supplies in seleniferous areas of the country such as South Dakota, Colorado, Oklahoma, Kansas, Wyoming, and southern California contain Se levels considerably above the Federal limit. An effective removal technology is required if these drinking water supplies are to meet the standard.

The predominant Se species in ground water supplies is not well characterized because the element is regulated as total Se, and the EPA-approved analysis method is atomic absorption spectroscopy, which cannot differentiate among Se species. Determination of the predominant Se species in Ground water supplies containing significant amounts of Se is needed to assess the feasibility of Se removal by activated charcoal or other technologies.

There are vast range of technologies for determining Se(+IV) such as fluorometery, electron capture gas chromatography, hydride generation atomic absorption, and X-ray fluorescence, but non of these procedures are straight foreward. Most of them require organic solvent extractions and preconcentration to lower the detection limit. An alternate technique is the use of ion chromatography with conductivity and variable weavelength detectors which can separate soluble Se species (SeO_3^{2-} and SeO_4^{2-}) and enables their quantitation. Refinement of the method is, however, required to achieve adequate sensitivity to detect Se species at the ug/L level and to elimnate interferences from other anions.

Ion chromatography is an accurate, rapid method for the analyis of Se species when the concentrations of nitrate and sulfate are low enough not to interfere. Figures 4 and 5 show the extent of interferences by 100 ppm nitrate on 10 ppm SeO_3^{2-}, and 100 ppm sulfate on 5 ppm SeO_4^{2-}, respectively. Ground water supplies specially those near agricultural areas normally contain high levels of sulfate and nitrate. Both of these anions come from applied fertilizers and are highly mobile in the soil environment. In typical ground waters, the level of these interfeering anions are too high to allow detection of selenite or selenate without chemical pretreatment.

Addition of $Ba(OH)_2$ on equivalent basis successfully reduced sulfate interference on SeO_4^{2-} by precipitating out the sulfate. At this equivalent level, SeO_4^{2-} did not co-precipitate with sulfate. Although the pH of the resulting solution had to be adjusted before

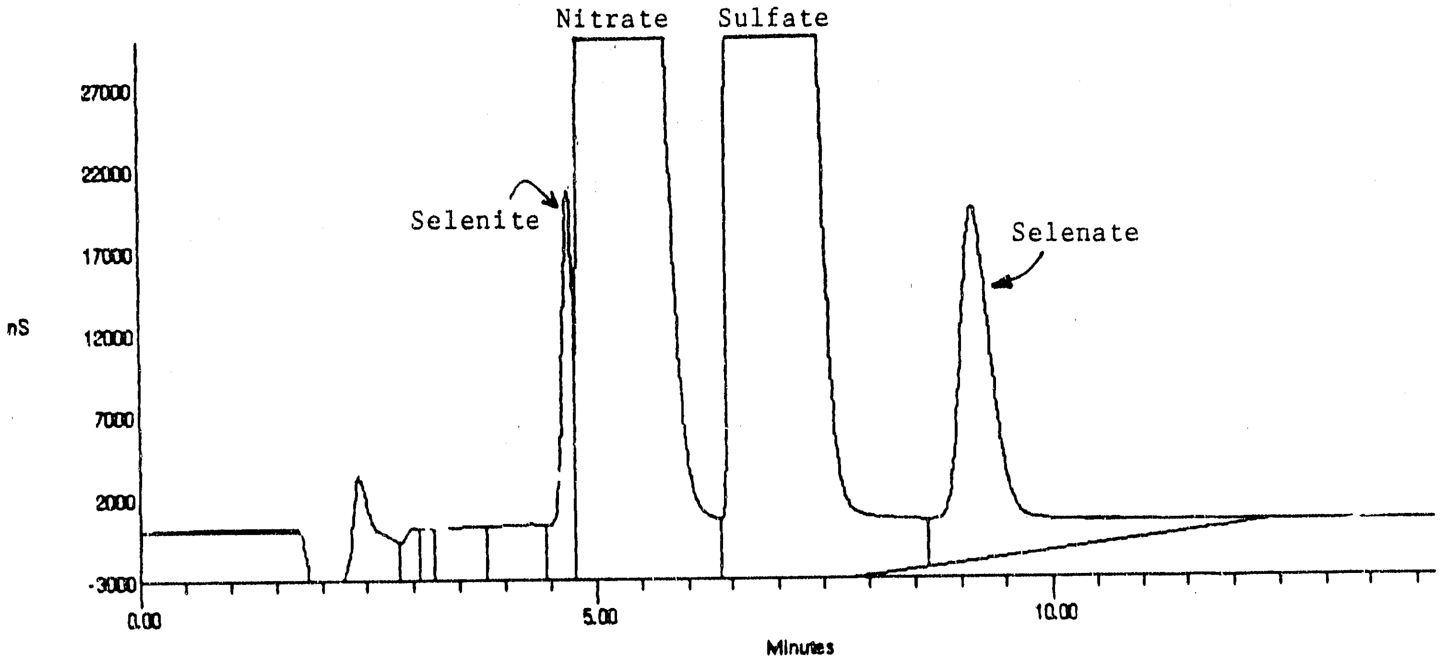


Figure 4. Ion chromatogram showing the effect of 100 ppm nitrate and 100 ppm sulfate on the separation of selenite and selenate species.

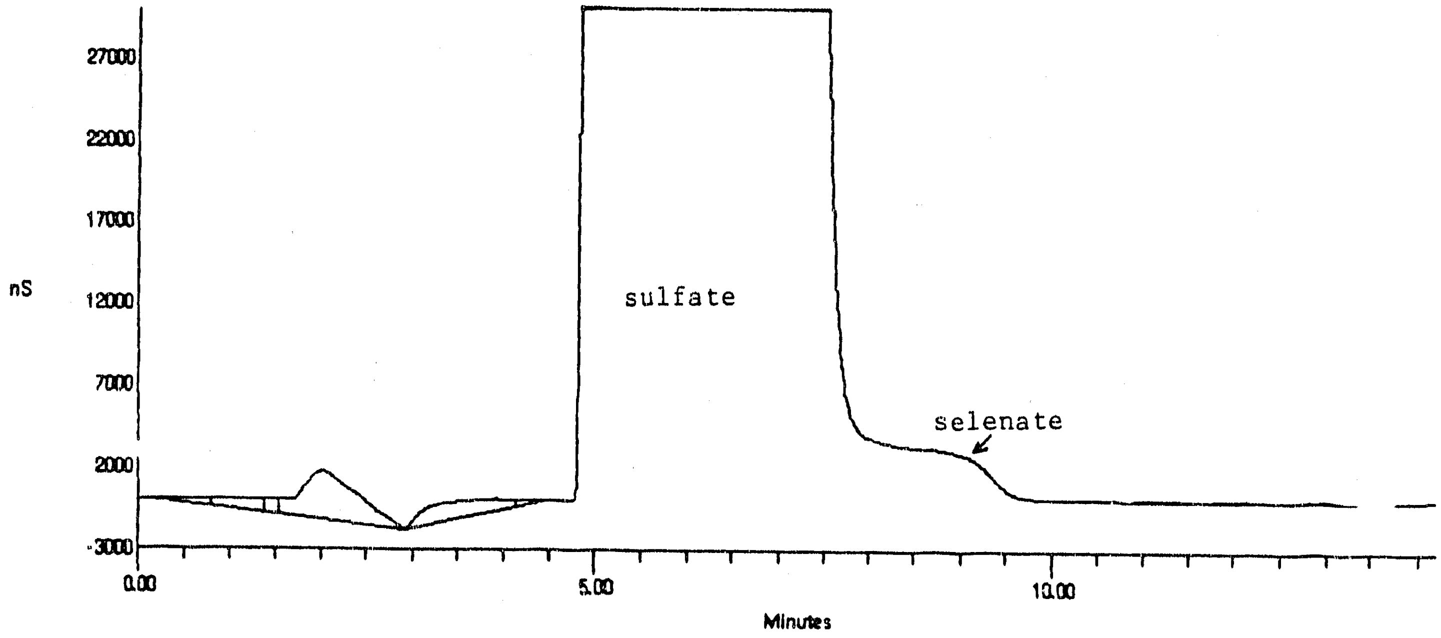


Figure 5. Ion chromatograph showing the effect of 1000 ppm sulfate on the resolution of 5 ppm selenate.

analysis with ion chromatography, it did not seem to affect the speciation of Se. An equilibration time of one hour before centrifugation was enough to precipitate out most of the sulfate. The use of $BaCO_3$ did not precipitate sulfate effectively. Another technique we used to solve sulfate interference was by applying variable wavelength detection. Sincs sulfate is not chromophoric, it does not absorb UV light, therfore it cannot be detected. Unfortunately there is no similar pretreatment technique that can be used to remove nitrate interference on SeO_3^{2-}. Selenite like nitrate is highly chromophoric and can be analyzed by UV detection with greater sensitivity than by conductivity detection.

Removal of Sulfate Interference on Selenite

Since adequate resolution between the selenate and sulfate peaks was not achieved by varying instrumental paramenters, the next step was investigation of chemical pretreatment to eliminate the sulfate interference. Addition of a barium salt to selenate - sulfate standards was investigated as a means of eliminating the sulfate interference through its precipitation as barium sulfate. This form of pretreatment should remove the sulfate without precipitating any selenate beacause the solubility product of $BaSO_4$ is approximately three orders of magnitude lower than that of $BaSeO_4$ and the selenate concentration in ground waters is typically three orders of magnitude lower than the concentration of sulfate. The solubility products and saturation solubilities of $BaSO_4$ and $BaSeO_4$

are 1.1 x 10^{-10}, 0.00233 mg/L, and 1.7 x 10^{-7}, 0.118 mg/L, respectively. Based on calculations using these solubility products, a 500 ug/L selenate concentration would not begin to precipitate upon addition of barium until the added barium was 7 g in excess of the quantity needed to stoichiometrically match the sulfate concentration in the sample. Although solubility calculations indicate that barium addition should not cause precipitation of selenate, there is still the possibility of selenate loss occuring with the precipitating $BaSO_4$ in a sweep floc effect.

To test the efficency of barium addition on removing the interference of sulfate on selenate, a serries of known concentrations of standard sulfate solutions in centrifuge tubes were dosed with various concentrations of $Ba(OH)_2$ soluttions. The results of this study are shown in Table 1. Initially a 25 ug/L selenate, 100 mg/L sulfate standard was made up with approximately 1 mM barium present as $Ba(OH)_2$. The standard sample was first centrifuged using a bench top centrifuge at 1000 x g then filtered via a 0.45 micron Gelman syringe filter. The pH of the solution was adjusted to near neutral, prior to analysis by ion chromatography, by adding drops of 1 M Na_2CO_3 solution. Addition of the barium salt to this standard increased the practical percentage resolution from 0 to 45%, and did not result in any selenate loss. This preliminary result indicated that barium addition can effectively eliminate sulfate interference and maintain the integrity of the selenate concentration when the quantity of added barium stoichiometrically

Table 1. The effect of adding 5 mM barium on selenate + sulfate standards.

	Before Dose			After Dose		
Standard	SeO_4^{2-} ppm	SO_4^{2-} ppm	Resolution %	SeO_4^{2-} ppm	SO_4^{2-} ppm	Resolution %
1	25	0	--	25	0	--
2	25	50	100	25	5	100
3	25	100	85	24	15	100
4	25	500	<5	19	90	44

matched the sulfate concentration.

Non-stoichiometric addition of barium to sulfate was also conducted to discern the effectiveness of barium addition to a sample of unknown concentration of sulfate and selenate. Results indicated that a 5 mM Barium dose could precipitate upto 500 mg/L sulfate, which in most cases is the maximum sulfate level in ground waters.

Effect of pH on Barium Hydroxide Dosing

Barium hydroxide was chosen for the barium dosing because it is one of the only barium compounds which is sufficiently soluble in water and does not introduce interfeering anions to the sample as in the case of barium nitrate or barium chloride. The use of barium carbonate was not investigated since the compond is not soluble in water. Pretreatment of a sample with barium hydroxide will, however, substantially increase the pH of the sample and possibly alter the selenium speciation. Addition of 5 mM barium as barium hydroxide raised the pH of the mixed selente + sulfate standard from 6 to 12. To investigate the effect of this pH change on speciation, 5 mM barium as barium hydroxide was added to a standard containing 100 ppm selenite, and 100 ppm selenate. An ion chromatographic scan of this standard before and after the barium addition indicated that no shift in speciation had occured due to the increased pH.

Although the pH increase due to addition of barium hydroxide does not appear to alter the selenium speciation in a mixed standard, it might influence speciation in the complex matrix of a real sample. To eliminate the change in sample pH up on addition of barium, the use of ion exchange resin (barium form) is currently being considered.

SELENIUM IN OKLAHOMA RURAL GROUND WATERS

As part of the contractual agreement for this project, water and surface soil samples were collected from each of the 77 counties in Oklahoma and screened for SeO_4^{2-}, SeO_3^{2-}, and total selenium levels. The results of this investigation indicate that Oklahoma's rural ground waters contain primarily SeO_3^{2-} with no detectible SeO_4^{2-} present. This was in contrast to what is being reported for ground water samples by most other investigators. Selenate is being considered as the predominant species of selenium in ground waters due to its suspected high mobility and less adsorptive characteristics.

Table 2 lists level of SeO_3^{2-} in ground water from each of the 77 counties in Oklahoma. It is apparent from this data that almost all county ground awater samples (over 90 percent of them) collected exceeded the allowable drinking water limit set for selenium. According to this data, the highest concentration of selenium (greater than 5 ppm Selenite) is found in the South Western portion of the state. However, most of the Eastern and

Table 2. Selenite levels, pH and depth to the ground water in rural Oklahoma. Samples were collected from each of the 77 counties in the state.

County	Well Depth (ft.)	pH	Selenite (ppm)
Adir	70.0	6.67	0.225
Alfalfa	90.0	7.87	0.212
Atoka	165.0	7.15	2.360
Beaver	100.0	8.01	0.177
Beckham	140.0	7.52	0.318
Blaine	200.0	7.90	0.590
Bryan	150.0	7.53	1.597
Caddo	unkn*	7.00	0.296
Canadian	unkn	7.57	2.160
Carter	30.0	7.25	0.333
Cherokee	3.0	7.42	0.016
Choctaw	50.0	5.78	0.064
Cimarron	280.0	8.06	1.720
Cleveland	100.0	8.07	1.717
Coal	75.0	5.85	0.889
Comanche	100.0	7.60	1.520
Cotton	30.0	7.53	0.856
Craig	117.0	7.18	0.162
Creek	unkn	7.18	0.967
Custer	160.0	7.66	0 077

Table 2. (continued)

County	Well Depth (ft.)	pH	Selenite (ppm)
Delaware	120.0	7.26	1.061
Dewey	28.0	7.55	0.460
Ellis	150.0	7.75	0.250
Garfield	50.0	7.35	1.880
Garvin	120.0	8.06	0.270
Grady	>100.0	7.79	0.799
Grant	100.0	8.17	4.033
Greer	654.0 ?	7.52	4.190
Harmon	200.0	7.78	11.280
Harper	80.0	8.03	0.096
Haskell	25.0	7.45	5.310
Hughes	90.0	7.66	0.203
Jackson	54.0	7.47	1.860
Jefferson	16.0	7.28	0.884
Johnston	125.0	6.94	0.225
Kay	25.0	7.86	3.000
Kingfisher	48.0	7.46	1.228
Kiowa	18.0	7.60	10.730
Latimer	unkn	7.22	0.688
LeFlore	135.0	6.95	0.645
Lincoln	unkn	7.14	0.280

Table 2. (Continued)

County	Well Depth (ft.)	pH	Selenite (ppm)
Logan	75.0	7.18	2.040
Love	110.0	6.56	0.492
Major	58.0	7.65	0.447
Marshall	100.0	6.23	0.243
Mayes	100.0	7.26	0.120
McClain	48.0	7.75	0.092
McCurtain	80.0	6.02	0.092
McIntosh	unkn	6.75	1.092
Murray	100.0	7.42	3.404
Muskogee	10.0	6.73	0.048
Noble	90.0	7.28	0.373
Nowata	40.0	7.83	0.403
Okfuskee	unkn	7.65	0.580
Oklahoma	57.0	7.90	2.260
Okmulgee	unkn	7.41	0.850
Osage	80.0	6.93	0.230
Ottawa	unkn	7.41	0.206
Pawnee	unkn	7.39	1.940
Payne	30.0	7.34	1.116
Pittsburgh	70.0	7.07	0.426
Pontotoc	150.0	6.10	0.152

Table 2. (Continued)

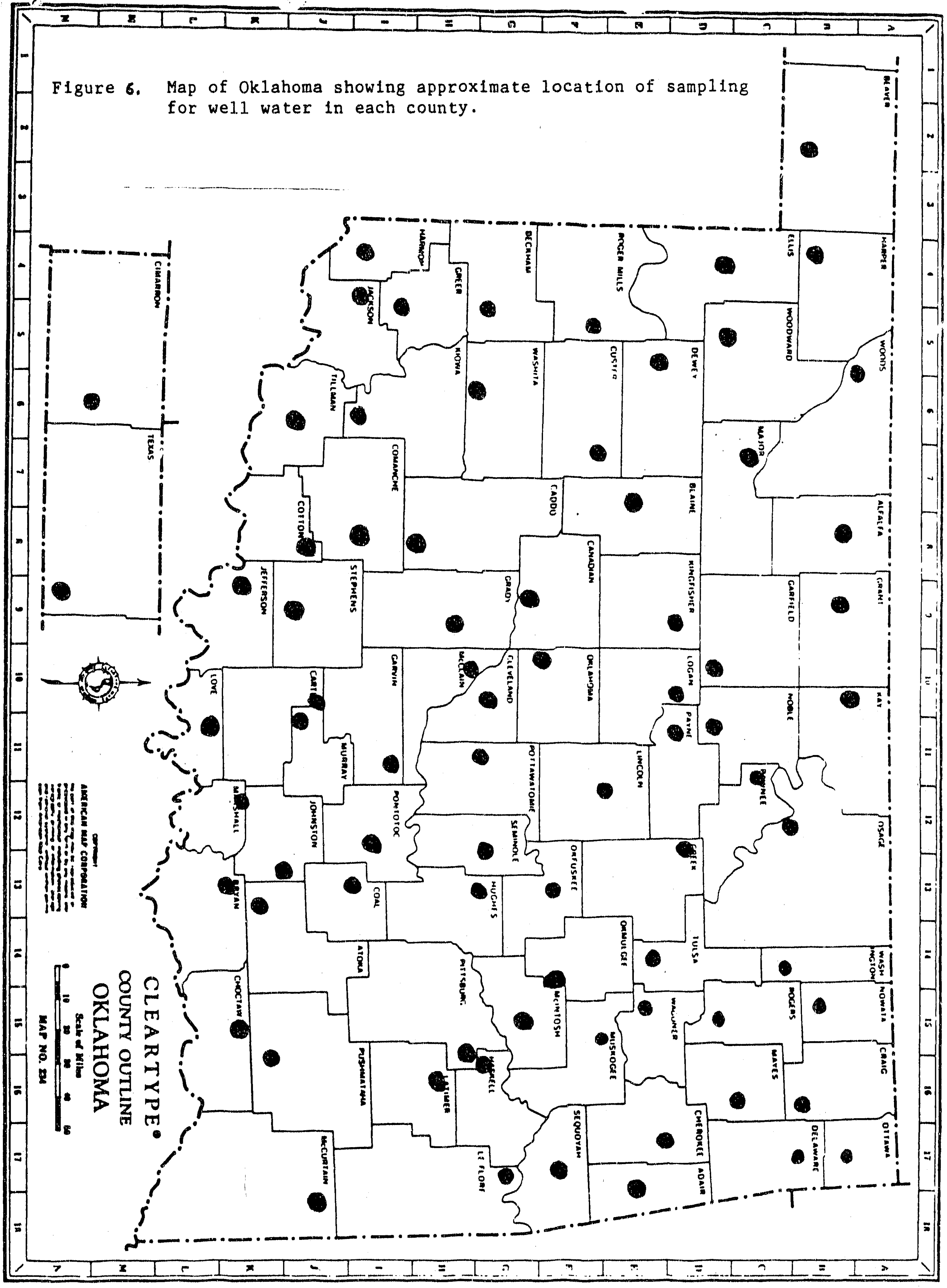
County	Well Depth (ft.)	pH	Selenite (ppm)
Pottawatomie	90.0	7.30	0.426
Pushmataha	unkn	7.20	1.141
Roger Mills	150.0	7.75	0.161
Rogers	84.0	1.485	1.485
Seminole	180.0	6.76	9.490
Sequoyah	unkn	7.19	1.151
Stephens	95.0	7.48	6.210
Texas	400.0	8.09	0.728
Tillman	30.0	7.62	3.363
Tulsa	4.0	7.02	1.034
Wagoner	23.0	7.12	0.947
Washington	25.0	6.81	0.796
Washita	120.0	7.72	1.460
Woods	150.0	7.73	0.192
Woodward	46.0	8.08	0.298

'unkn = depth of that well is unknown

South-Eastern portions of the state, where there has been or still is coal mininga ctivity, did not indicate higher level of selenium.

Figure 6 is a sampling distribution map for the state of Oklahoma. All dotted markings are approximate locations in each county where samples of ground water have been collected. All effort has been devoted to get a well-distributed sampling scheme.

Figure 6. Map of Oklahoma showing approximate location of sampling for well water in each county.



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