Selenium Concentrations in Natural and Environmental Waters

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I. Introduction

Selenium (Se) is recognized as an essential micronutrient in most species, including man. It is an integral component of glutathione peroxidase (GSH-Px) and has a function in peroxide detoxification. Also, Se seems to exert some inhibitory effect on carcinogenesis. It is noteworthy that different health problems can arise from an excess as well as from a deficiency of Se, and the danger lies in the relatively narrow margin between its essential and toxic actions.

The role of Se in animal and human health has been reviewed.[1,2] Kwashiorkor, Keshan, and Kashin-Beck diseases are associated with low blood Se levels. Other effects due to Se deficiency are muscular dystrophy; reproductive disorders; dental caries; necrosis of liver, kidney and heart; and many types of cancer. In animals some diseases are also caused: liver necrosis, white muscle disease, multiple organ degenerations, exudative diathesis, cancer, retained placenta, cachexia; etc.

The Se concentration in water at which toxicity is observed varies with the organisms: algae, 0.01−80 mg of Se L^{-1}; invertebrates, 0.07−200 mg of Se L^{-1}, and vertebrates, 0.09−82 mg of Se L^{-1}.[3] The interactions of Se with Ag, As, Cd, Co, and Hg in organisms living in the aquatic environment were the subject of several investigations.[4]

Negative correlations were observed between the concentrations of Se in drinking waters (from well water, atmospheric precipitations, and river water) or in wheat (local staple diet) and the morbidity of the Kashin−Beck disease (KBD) in villages in loess plateau region of Shanxi, China.[5] The KBD clinical detection rate decreased from 41.89% in 1982 to 21.89% in 1990 in a Chinese village after a change in drinking water sources. The new source contained higher Se and lower humic acid concentrations.[6] In drinking water and soil from KBD areas in China there are higher humic acid and lower Se concentrations than in nondisease areas.[7,8] Humic acid is the main pool of Se in soil and affects the bioavailability of the element in soil−plant system.[9] An investigation of the organic degradation products of soil (humic acids) and Se in the pathogenesis of KBD was carried out. Their leading pathologic effect is on cells, possibly due to membrane injury due to peroxide.[10] Fulvic acid in soil could increase the Se level in

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plants,[8] but fulvic acid in drinking water inhibits the absorption of Se taken from diet.[9] The relationship between high content of organic matters in water and Se deficiency on the causes of KBD could be due to the limited synthesis of GSH-Px, which is generally stimulated by fulvic acid from drinking water.[9−11]

On the other hand, the populations receiving high Se levels in their drinking water were found to have Se in their urine at least 3−9 times the amount that occurs in the other populations.[12] Blood Se levels in the high-Se participants were not as high, but were 1.7 times higher than those of the low-Se group.[13]

Several official associations have imposed controls on the maximum concentrations of Se in waters destined for human consumption.[14−15] The National Interim Primary Drinking Water Regulations suggest a maximum total concentration of Se of 10 ppb.[14] The maximum permissible concentration of Se in water discharged into the public sewer system in most of the United States is 20 ppb. The maximum allowable level of Se in drinking waters is 10 μg L^{-1} in Finland,[16] Hungary,[17] E. E. C. countries,[18] and United States.[19] However, there are no specific recommendations on Se species levels.

Selenium occurrence in natural and environmental waters has received wide attention. A review of the literature on water pollution control, which includes a section on analytical methods and instrumentation is published annually by the Water Pollution Control Federation.[20−36] Other aspects, like biogeochemical cycling, toxicity, food chain bioaccumulation of Se in aquatic ecosystems were also reviewed.[37−43] The present review, of general character, emphasizes the speciation and levels of Se in natural and environmental waters, and covers the period 1975−1995. No references for works previous to 1975 are in this collection. Conference proceedings, obscure foreign journals, trade journals, and books are usually excluded.

A. Occurrence

In the environment, elemental Se is generally associated with sulfur and it is found in metal−sulfur deposits.[1,44] Total Se levels in environment range from 0.1−400 μg L^{-1} in natural waters,[45] to 0.06−1.8 ng g^{-1} in soils[46] and a few nanograms per cubic meter in the atmosphere. The levels in the atmosphere vary according to location; in urban and semirural locations they are 0.27[47] to 8.3 ng of Se m^{-3},[48] but in marine locations the variation is lower: 0.016[49] to 0.43 ng of Se m^{-3}.[50] The accumulation of total Se depends on the environmental matrix,[44] and it is affected by climatic factors and pH.

Worldwide emission of total Se into the atmosphere in 1983 was estimated at 6320 ton.[51] The main sources were industrial and domestic coal combustion, and pyrometallurgical Cu, Ni,[51−52] and Zn[52] production. Emission amounts in the United States are about 3600 ton of Se yr^{-1}.[44] The total Se emission into the atmosphere during 1989 in Finland was estimated at 27.9 tons, 72% of which came from nonferrous metal production, smelting, and refining, and 28% from primary energy consumption.[52] Also, fertilizer additions may be an important source of Se to the environment.[52] The total anthropogenic input of Se into the aquatic ecosystem was 41 $\times$ 10^6 kg Se yr^{-1}, and the same quantity into soil. There is significant contamination of freshwater resources and an accelerating accumulation of toxic metals in the human food chain. Also a survey of causes for high Se content in the environment of Hubei Province, China, was performed; Se content in waters ranged between 0.29−342.86 ppb, and the major sources of the pollution were due to anthracite and coal burning.[53]

Mosher et al.[54] have calculated a global ocean-to-atmosphere Se flux of (5−8) $\times$ 10^6 kg of Se yr^{-1}. The ecological classification scheme and geographical distribution of types of water from oceanic zones is given together with its area and partial Se flux. The total natural flux of Se to the atmosphere is in the range of (6−13) $\times$ 10^6 kg of Se yr^{-1}, and global estimates of anthropogenic and natural atmospheric Se emissions were 30−50% and 50−70%, respectively.[55] Lantzy et al.[56] estimated a global flux of 4.8 $\times$ 10^6 kg of Se yr^{-1}, by using preindustrial revolution ice sheet data from Greenland as an estimate of the Se content in rain, annual rainfall rates, and the assumptions that the ocean−atmosphere Se cycle was in a steady state and that two-thirds of the rainfall occurs over the ocean. The trace element composition of precipitation (rain and snow) provides a way of monitoring anthropogenic and natural emissions to the atmosphere. An inverse correlation between the Se concentration in rain water and the amount of rainfall was reported[57] which indicates that Se originates mainly from aerosols and dust in the rainfall areas. In Finland,[52] during 1989 the Se atmospheric precipitation was 18.4 tons, 65% from rain and 35% from snow; Se concentrations in rain were higher than those of lake water and groundwater. Selenium in atmospheric precipitation was of terrestrial origin, including fossil fuel combustion.[52] Cutter et al.[58] have examined data on concentration and oxidation state of Se in precipitation over coastal and midocean regions of the Western Atlantic Ocean. The wet depositional flux of Se in Bermuda is similar to the average total deposition estimated from aerosol measurements. In spite of the large reduction in Se flux between the coastal United States and Bermuda, this atmospheric input to the Central Atlantic is still significant (22% of that due to vertical upwelling).

II. Analytical Methods

A. Sampling and Storage

A geographic information system (GIS) provided information for a regression analysis that was used to help identify areas of potential sources of Se.[59] Physical and chemical characteristics of selected hydrologic subbasins were used as independent variables in the regression analysis. The physical characteristics of the study area were determined using GIS techniques, and chemical characteristics were determined from samples of soil, plants, and water. The area of irrigated land and length of irrigation canals within each subbasin are the most important factors in explaining the variability of median Se loads.[59] The geostatistical method of Kriging is applied in the determination of the optimal monitoring locations for sampling two groundwater quality

Table 1. Conditions for Sampling and Storage of Water Samples

material	sample volume, L	filter size, μm	pH	preservative	observations	ref(s)
polyethylene	1			HNO_3 5 mL	no filtration	75
polyethylene			unacidified		freezed with liquid N_2	76
polyethylene	10	0.45		HNO_3 10 mL/L		77
polyethylene		0.4	unacidified	UV irradiation	−26 °C	61
polyethylene	5	0.45	2	HNO_3	centrifugation 45000*g*, 4 °C in dark	78
polyethylene		0.4	1.5	HNO_3	filtration under vacuum, freezed	79
polyethylene	10				refrigeration	80
polyethylene	2	0.45	4	HNO_3 0.1 M		81
polyethylene		0.45	<2	HNO_3		82
polyethylene	5	0.45	1.5	HCl	go-flo sampler	83
polyethylene	1	0.45	1.5	HCl	pump sampler	84
polyethylene	5	0.45	4			85
polyethylene	25	0.45	2	HCl		86
polyethylene		0.45	2	NaClO 0.5 mg/L	for drinking water	87
polyethylene				HCl, refrigeration	for lake water	
polyethylene	1−2	0.45	2		deaerated with N_2, refrigeration	88
polyethylene		0.4		HNO_3		89, 90
polyethylene			unacidified		4 °C	72
polyethylene or pyrex	0.5		1.5	H_2SO_4 0.2%	125 days at 4 °C	
polyethylene or glass beaker	0.250	0.45	11	HNO_3	KOH for conversion of selenious acid into Se(IV)	92
polyethylene or quartz				HCl 3 M		93
polyethylene, polypropylene			1.6	HNO_3		94
polyethylene			1.5	H_2SO_4	125 days	40
glass			1			
polypropylene			2	HCl	4.5 months	
glass		0.45		HCl 1 mL/L		95, 96
borosilicate				HNO_3 1.0%		97
borosilicate		0.4	1.5	HCl	3 months	98
Teflon	0.250	0.45		1 mL HCl 30%		99
plastic	1	0.4		1 mL/HCl 32%		100
polythene	1				filtration or centrifugation	101
polyethene	1−2	0.45		HCl 5−10 mL		102
polythene	5	0.45	unacidified		freeze-drying, filtration under pressure	103
polythene	5	0.45		HCl		104
plastic, PVC, or glass			1.5	HNO_3	4 °C	105
PVC	1	0.45	unacidified		−20 °C	106
			1	HCl		107
	0.5		1−2	1 mL/L H_2SO_4 18 M		108
	1	0.45		HCl 10 mL/L		109
			<2	HNO_3	22 °C	110
	4		1−2	HCl		111
		0.4		4 mL/L HCl 6M		65
	2.5	0.4	1	HNO_3		112
	1			HCl 25 mL/L		113
	0.5−2	0.45		HCl		114

variables: The Se concentration and the subsurface soil salinity. To investigate the effect of the cross-correlation on the solution, the problem is solved for different degrees of cross-correlation between the two variables.[60]

Although there are specific reports on sampling methods,[61,62] standarized techniques are usually employed.[63−65] When sampling river water, the contribution due to tributary inputs and industrial effluents may cause inhomogeneities in analyte composition that are still appreciable for several miles downstream. In the case of lake water, stratification of cold and warm layers may lead to gradients in element concentrations.[66] For estuarine waters, mixing of fresh and salt waters follows a rather complex pattern, as the first tends to flow above the denser layers of the second[66−67] and changes in redox potential due to impurities in the water are produced. Some authors[68,69] describe several types of samplers used to take sample water for physical, chemical, and biological examinations. Mart[62,70] describes the collection of surface water samples in order to prevent contamination and other accuracy risks in the determination of trace metal concentrations. Several factors affect the sorption or loss of Se, or the interconversion among Se species: (a) characteristics of the solution (salinity, hardness, pH, suspended matter because of competition in the sorption process, complexing agents, microorganisms, and dissolved gases like O_2) which may influence the oxidation state; (b) properties of container (chemical composition, age, characteristics of the surface, cleaning method); and (c) external factors, such as contact time, agitation, temperature and access to light.[71−74]

A wide variety of sample sizes have been used (Table 1). It ranges from 250 to 60 L, but sample volume of several liters are normally used. The intimate contact that takes place between a liquid sample and the container facilitates any interactions between them, both in terms of release of elements from the bottle surface and chemisorption of analytes from the solution onto the walls themselves;[66] thus,

the smaller surface area per unit volume minimizes surface interactions.[72]

Polyethylene,[63,90,91,93,115−123] polypropylene,[102,124] polythene,[125] and glass bottles[116,126] are usually chosen for storing samples (Table 1). Pyrex, quartz, and borosilicate glass containers present advantages over polyethylene containers when used to store water samples for Se determinations.[71,72,74] But the selection of a specific material is also dictated by the instrumental technique to be employed for the analysis and its tolerance to the presence of possible interfering substances.[66] When poly(tetrafluoroethylene) (PTFE) containers were used,[127] Se(IV) and Se(VI) were stable at pH 2 (by adding H_2SO_4); however, at pH 6 (without acid addition) a great decrease of Se(IV) and an increase of Se(VI) was observed, which suggests that there was no loss of Se(VI), but perhaps, some transformation of Se(IV) into Se(VI). Samples stored at pH 2 in polyethylene containers completely lost Se(IV) at 10−50 μg L^{-1} levels in one year, with or without NaCl. The Se(IV) losses started after about 1 month of storage; Se(VI) is stable for a whole year. The stability of Se(IV) increased at pH 6 and its maximum storage time was 2 months without risk of Se(IV) losses. At 40 °C and pH 2 and 6, the stability of both species increased. Light had no significant effect on inorganic Se species stability. The maximum time of sample storage at room temperature and pH 6 is 2 months and 9 months in polyethylene and PTFE containers, respectively.[127] In polyethylene bottles,[74,91] tap, river, and snowmelt water samples (44.5−138 ng of Se L^{-1}) could be stored at 4 °C for up to 15 days without Se losses. In similar samples stored at room temperature, Se losses of 13−25% after 15 days were found, except for groundwater, which showed no Se losses during storage for 13 months at room temperature or at 4 °C. At room temperature, river water Se was stable for 7 days, but both snowmelt and tap water had Se losses after 3 days.[74,91] The Se(IV) and total Se concentrations of samples extracted at sea were compared with those extracted in the laboratory, both for various depths; for samples acidified to pH 2 with HCl and stored in either glass or linear polyethylene containers there was no significant change in concentration in their oxidation states over a period of 4−5 months. However, a decrease of approximately 30% in Se(IV) concentration after 3 months of storage was found.[88] The stability of different species of Se during storage followed the order selenate > selenomethionine > selenite.[74] Selenomethionine, representing organically bound Se, was lost to the same extent as selenite at room temperature. At 4 °C the initial loss rate was similar to that for selenite, 9.0% after 31 days, but slower thereafter.[71]

On the other hand, at pH 5.4−7.2 algal growth occurred in natural water; therefore Se(IV) is taken up by the algae.[71,72] Since algae cannot grow at pH 2 and partial transformation of Se(IV) into Se(VI) is not clearly observed, the Se(IV) losses in polyethylene containers might be attributed to adsorption onto the container wall.[127] The most commonly used preservation method (Table 1) is acidification with a strong acid, such as H_2SO_4, $HClO_4$, HCl, or HNO_3, which leads to a pH value between 1−2.[110] These preservatives can provide storing times of several months which can be improved when the samples are stored frozen. Without any preservation method the samples are only valid for a few hours.[124] However, some authors[76,103,128−130] have indicated that for speciation measurements, the water sample must not be acidified before storage, because this could change the speciation. It should also be kept in mind that, for general trace metal analysis, acidification of fresh water samples can cause the precipitation of humic material, which usually carries down some heavy metals. Thus, a Se(VI)-spiked sample stored at 4 M HCl for 7 days showed a 60% conversion to Se(IV). Sample storage at 1.0 M HCl preserves the Se(VI) as well as the Se(IV).[76] Storing at 4 °C limits possible losses at room temperature.[72] But the optimum temperature at which there is no significant risk of Se losses during one year of storing in polyethylene or PTFE containers is (−20 °C); these samples need not be acidified.[127] Only when the samples were quick-frozen in polyethylene bottles with liquid N_2 were the results satisfactory.[76]

Filtration must be done inmediately after sampling prior to analysis or storage to separate the particulates and to reduce the risk of biodegradation of the sample. With fresh water and some estuarine water samples, the suspended load will contribute significantly to the total metal concentration, and filtration is essential.[129] By convention, filtration is defined as separation by a 0.45 μm filter into a filter residue and a filtrate. The filtrate contains, of course, still the colloids and the fraction of very small particles of mineralogical and biological origin that have passed the pores of the 0.45 μm filter. This fraction is labeled as "soluble" or "dissolved" metal. The particulate fraction contains all phytoplankton and most bacteria and can be used for Se determination, directly, or after treatment.[66,70] This somewhat arbitrary delineation between particulate and dissolved matter is nevertheless a reasonable approach to evaluate, for example, the part of the total heavy metal load of a natural water that will eliminated by sedimentation.[70] Membrane filters need to be thoroughly washed with acid, distilled water, and sample water before use. Pressure filtration offers advantages in terms of speed. However, rupture of phytoplankton cells at pressures greater than 25 kPa is a serious disadvantage, because these cells will contribute soluble organic matter, nutrients, and heavy metals, which could significantly affect speciation studies.[129] Centrifugation has also been performed.[101]

The loss rate of Se from different natural water samples varies widely in the same storage conditions, because of the composition differences of Se species of the water.[74] However, some general conclusions may pointed out: (1) Filtration must be done inmediately after sampling.[129] (2) Thorough cleaning of filters and containers is mandatory before use.[66,70] (3) Selenium is more unstable in polyethylene than in quartz and borosilicate glass containers.[71,74] (4) Higher volume of containers minimizes surface interactions and influences positively the Se stability.[66,72] (5) Selenium is better preserved in waters stored at 4 °C or liophilized rather than at 20 °C.[72,74]

(6) Higher pH values proved unsatisfactory in all cases.[72] (7) Acidification must be avoided.[76,103,128−130] (8) It is recommended that unacidified water samples should be kept in polyethylene bottles at room temperature for no longer than 1 week, or stored at 4 °C for no longer than 2 weeks, before analysis for Se.[74]

B. Instrumental Determination

There are many available methods to determine Se. Five important methods stand out for the analysis of Se in waters: spectrofluorimetry (F), neutron activation analysis (NAA), atomic absorption spectrometry using the graphite furnace (EAAS) and the hydride generation (HG-AAS) techniques, gas chromatography (GC), and electrochemical methods (differential pulse polarography and voltammetry).

In general, preconcentration methods must be applied because the Se levels in waters are very low. These methods include elution through a chromatographic column, complexation, and coprecipitation. Lyophilization[61,81,103,131,132] or evaporation[81,133−135] have been applied in spectrophotometry (SP), EAAS, and some nuclear or atomic emission techniques. Liophilization as routine method gives reliable results for a great number of elements[132] because it reduces effects of contamination from the environment, losses by volatilization, and adsorption on the container walls.[103]

Acid digestion is the method of choice for most authors to minimize losses by volatilization, but the speciation is totally modified. These methods must be optimized according to the instrumental method used. Nitric acid, HNO_3-HClO_4, $HNO_3-HClO_4-H_2SO_4$, $HNO_3-H_2SO_4$ acid mixtures, with or without H_2O_2, or $KMnO_4$, $K_2S_2O_8$, or Br_2-HCl can be used for the total destruction of organic matter.[136]

On the other hand, to apply fluorimetric, electrochemical, or chromatographic techniques, digestion and reduction of Se(VI) to Se(IV) is needed. This reduction is usually carried out by heating with HCl 4−6 N, although HBr, or mixtures of HCl−KBr, Br_2−HBr, and HCl/NH_2OH HCl, humic acid, and UV irradiation were also used. After digestion and reduction, the sample must be treated with aromatic *o*-diamines to form piazselenols when fluorimetric or gas chromatographic techniques are used. The diamines more commonly employed are 4-nitro-*o*-phenylenediamine, 4-chloro-*o*-phenylenediamine, 1,2-diamino-3,5-dibromobenzene, and above all, 2,3-diaminonaphthalene (DAN). In order to eliminate interferences the Se complex is extracted into organic solvent and measured. The solvents more commonly used are toluene, and cyclohexane. Afterward, the fluorescence (λ_{ex} = 360 nm, λ_{em} = 520 nm) is measured in a fluorescence spectrometer. In biological materials and for concentrations of Se < 0.3 mg kg^{-1} fluorimetry has been selected as a reference method, because of its high precision, low detection limit, and complete recovery.[136]

Instrumental neutron activation analysis (INAA), if available, can be valuable as a reference for validating alternative analytical methods. In general, sensitivity and precision of INAA are lower than fluorimetric methods, and both are capable of producing unbiased results.[136] However, INAA has several advantages with respect to fluorimetric methods: it is a nondestructive method and the only losses of concern are those due to escape of volatile compounds. The sample treatment can be reduced to a minimum.

Selenium determination in a subnanogram range by AAS can be performed using the graphite furnace (EAAS) and the hydride-generation techniques (HG-AAS). Both techniques (HG-AAS and EAAS) have been correlated satisfactorily. The best absolute detection limit can be observed in a EAAS but HG-AAS is faster and cheaper. The relatively poor precision, losses, and interferences are the main problems of both methods. In order to stabilize or reduce the volatility of inorganic Se compounds of digested samples for direct determinations by EAAS, the addition of various metallic salts has been proposed. Nickel salts are commonly used.[110,118,137,138] Also, Cu alone[139] has a substantial equalizing effect on the atomization temperature.[136] In the HG-AAS techniques, it is necessary to use borohydride to reduce the selenate to selenite in the digested samples.

Inductively coupled plasma techniques by emission (ICP-AES) or by mass spectrometry (ICP-MS) present poor detection limits and low precision for Se. Recently, a powerful analytical method has been presented offering the possibility of rapid multielement analysis in combination with good detection limits. The technique uses a new type of magnetic sector field ICP-MS instrument and is applied to determine gold and other metals.[140,141] Also, advances in ICP-AES have been developed;[142] a comparison between axially viewed horizontal and conventional radial viewing ICP was made. An overall improvement factor of 5 in detection power was observed when using axial viewing compared with radial viewing. This approach can be further used for quality control and quality assurance of instrument performance.[142] These new methods are very promising but still are not applied to Se determination in natural waters.

In GC methods, digestion and reduction steps are necessary to determine Se, as in fluorimetric methods. After digestion and reduction, the sample is treated with aromatic *o*-diamines to form piazselenols. Selenium complex is extracted in organic solvent and measured by GC with the sensitive electron capture detector. However, the sensitivity of GC is not as good as in the AAS methods, although the reported precision is lower than the fluorimetric methods.[136]

Selenium(VI) cannot be reduced on a mercury electrode. However, Se(IV) is electroactive and is reduced in acidic solution in two steps, and its analysis by direct current polarography gives rise to two reduction waves at the dropping mercury electrode. In order to oxidize all species of Se to Se(IV) the sample must be subjected to UV irradiation with H_2O_2 as catalyst; if any Se(VI) is formed it must be subjected to reduction to Se(IV) and passed through a column.[143,144] The advantage of UV irradiation consists in eliminating the interference of natural organic surfactants and electroactive organic compounds. The polarographic technique offers little sensitivity and suffers from interference problems,

especially from elements that form insoluble selenides. The reaction $Se^{4+} + Hg + 4\ e^- \rightarrow (Hg)Se$ is irreversible, and the Se is deposited on the electrode surface in this way. The formation of the (Hg)Se on mercury electrodes has been used in determining Se by cathodic stripping voltammetry (CSV) and related techniques[145−149] by the reversible process $(Hg)Se + 2H^+ + 2\ e^- \rightleftharpoons Hg + H_2Se$.

III. Speciation of Selenium

Speciation of an element is the determination of its individual physicochemical forms which together make up its total concentration in a sample. Speciation measurements are necessary for the study of toxicity of metals, of its bioavailability, bioaccumulation, interactions with other substances, and transport in biological or environmental media. Therefore, it is important to emphasize that although the total concentration of a dissolved metal may be similar in two water systems, the chemical forms of the metal may be quite different. However, by convention, "dissolved" metal is defined as all metal species which pass through a 0.45 μm filter, although most colloidal particles may be included in this fraction.[130]

Trace-metal speciation has been based on the use of two different techniques: Computer (chemical) modeling and experimental measurement.[129,130] The computer modeling approach involves the use of published stability-constant data, together with known concentrations of various ions and suspended solids in the water, to compute the equilibrium concentrations of the various species. It is a powerful technique, but unfortunately, no reliable thermodynamic data are available for metal-ion interactions with many of the natural ligands, especially the colloidal particles present in natural waters. Moreover, the nature and concentration of these ligands are usually unknown, and there is disagreement about the values for many of the simple inorganic complexes in waters. The experimental measurement of trace-metal speciation is a very different task because of the very low concentrations of these metals. In contaminated waters, the analysis may be much easier. Since the operations involved in measurements or separations will generally alter the original equilibria to some extent, the speciation results will be method dependent, and it is important that full details of the analytical procedure be provided with any published speciation data. The separation of chemical species of elements can only be performed by techniques which do not destroy the chemical forms. There are three basic methods for separation: Chromatography (anion exchange, ion-pairing reversed-phase liquid chromatography, or capillary GC),[88,150] capillary zone electrophoresis (CZE),[151] and cold trapping.[76,87,88,152] Gas chromatographic techniques allow a better reproducibility and speciation.[96] The use of a capillary column facilitates the isolation of the piazselenol peak; the sensitivity is good.[150] Cold trapping requires a derivatization step and only volatile forms of elements can be separated. This technique presents both advantages to concentrate the species and to sequentially separate them according to their respective volatility.[153] The CZE method has the advantages of high speed and efficiency. It eliminates the complexing or derivatization steps often required in other separation techniques such as HPLC and GC and the efficiencies achieved are better than those of the other methods. However, CZE has a relatively lower concentration sensitivity than HPLC or GC because in CZE much smaller volumes of samples are used.[151]

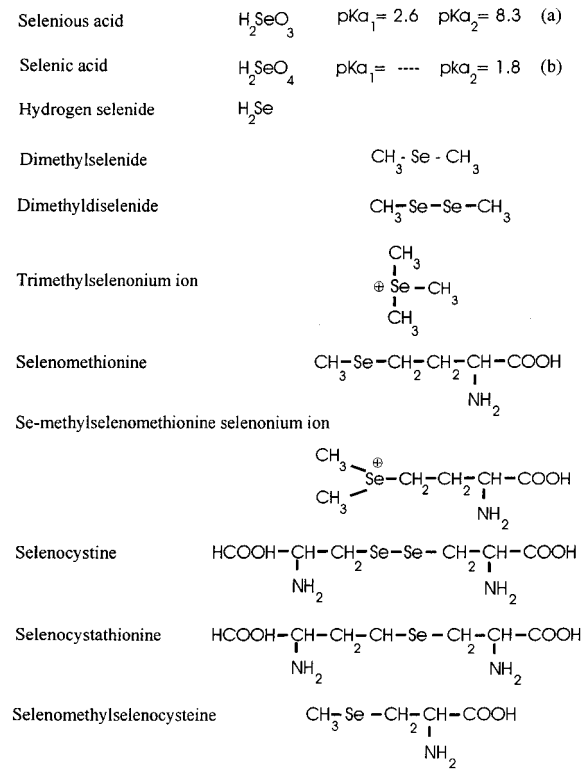

Figure 1. Chemical structures of the main selenocompounds found in natural waters: (a) From *Merck Index*, 10th ed.; Merck & Co. Inc.: Rahway, NJ, 1983. (b) From Perrin, A. A. *Ionization Constants of Inorganic Acids and Bases in Aqueous Solution*; IUPAC, Analytical Chemistry Division, Commision on Equilibrium Data; Pergamon Press: Oxford, 1982.

In water, selenium can exist in different oxidation states (−II, 0, +IV, +VI); Se(IV) and Se(VI) are the most common. The main organic species are dimethyl selenide, dimethyl diselenide (highly volatile), trimethylselenonium, and selenoamino acids (Figure 1). The speciation frequently applied in many investigations is based on the determination of selenite and total selenium concentrations. The selenate content is calculated by the difference of these data. However, by using this method, organoselenium compounds in the sample would cause higher selenate concentrations. Thus, some of the contradictory results may possibly be due to the fact that organic selenium compounds have not been taken into consideration in the analytical scheme. On the other hand, several methods are based on the determination of the inorganic Se content (sum of selenite and selenate), the total Se content, and the subsequent calculation of organoselenium by difference. In these cases, oxidizing or reducing agents are used to convert all inorganic species of selenium into the same oxidation state (+IV or +VI). However, in this process, organic selenium compounds may partly be converted into the inorganic form.[154] The number of determinations of chemical species in environmental

Table 2. Seawater

ocean or sea; depth	date; method	Se_{tot} (ng L^{-1}) (min−max)	Se(IV) (ng L^{-1}) (min−max)	Se(VI) (ng L^{-1}) (min−max)	Se(−II,0) (ng L^{-1})	Org-Se (ng L^{-1})	ref(s)
North Atlantic	1980; GLC						158
1 m		48	≤2	46			
60 m		28	≤2	26			
130 m		28	≤2	26			
468 m		50	6	44			
725 m		100	17	83			
1960 m		78	26	52			
2953 m		103	31	72			
3908 m		122	35	87			
4868 m		138	35	103			
North Atlantic (coastal); 50 m	1984; EAAS		20 ± 3 (16−25)				94
NE Atlantic, Bermuda; 1300 m	1984; EAAS		22 ± 3 (18−27)				94
NE Atlantic, Bermuda; 1300 m	1983; HG-AAS		24 ± 2 (21.4−27.3)				64
NE Atlantic, Bermuda; 1300 m	1983; GC-ECD		25.3 ± 1.4				63
North Atlantic, Iceland	1987; INAA	59 ± 25	16 ± 8.7				159
NE Atlantic	1980; GC		(27.0−152.2)				116
NE Atlantic	1980; GC						116
75 m			3.32−4.26				
400 m			24.9−26.5				
988 m			48.2−50.1				
1878 m		160−161.7					
4821 m		120.7−121.9					
NE Atlantic, Bedford Basin, Nova Scotia	1981; GLC					6.87−8.05	160
NE Atlantic, Chesapeake Bay, Maryland	1989; F	(29.2−82.9)	(11−46.6)	(11.8−36.3)			80
NW Atlantic, France, Landes	1992; DPCSV	<50	<50	<50			148
NW Atlantic, Spain, Canary Islands	1992; FI-HGAAS			10000 ± 1000			161
West Atlantic, Nigeria, Lagos	1983; INAA	145 ± 3[a]					81
Bering Sea (54° 30′ N, 177° 29′ W)	1988; F						162
0 m						1.03	
100 m						1.06	
500 m						2.16	
1000 m						0.95	
3800 m						2.96	
Cantabric Sea, Spain, Santander	1992; FI-HGAAS		<700	5000 ± 1000			161
Dead Sea	1988; INAA	2540 ± 340 (2250−3200)					85
East Indian Ocean	1989; GC-ECD	75	16	59			163
Indian Ocean; 1500 m	1990; Ads-CSV		37.1 ± 1.6 (16−158)				164
Indian-Pacific Oceans	1983; −						165
surface		44	4	39			
deep		170	62	110			
Japan Sea	1976; F	(40−110)					166
							167
Japan Sea	1977; F						168
surface			26	103			
25 m			55	96			
Japan Sea	1979; EAAS	<300					169
Japan Sea	1981; GC	(50−70)					157
Japan Sea	1990; F		(26.6−29.0)				170
Japan Sea	1978; GC-ECD						95
Aoya		33	12				
Shibukawa		47	32				
Ushimado		40	18				
Japan Sea	1979; GC						96
Aoya		52	9	40	2		
Katsurahama		51	6	41	4		
Muroto		51	<2	51	<2		
Naruto		48	12	31	5		
Shibukawa		55	31	18	6		
Ushimado		67	22	40	5		
Japan Sea, Shibukawa	1979; HG-FAAS	23 ± 5					109
Japan Sea, Osaka Bay, Sukematsu	1985; F	(31.2−32.4)	(11.7−12.2)	(19−20.7)		19.6	171
Japan Sea, Wakamatsu Beach	1992; INAA		(40−60)	(90−110)			114
Mediterranean Sea, Thessaloniki Gulf	1981; MECA	500[b]					172
Mediterranean Sea	1985; F						105
Greece		(100−250)					
Patras-Korinth		(250−400)					
Piraeus-Salonica		(400−650)					
Mediterranean Sea	1988; INAA	1140 ± 170 (880−1330)					85

Table 2 (Continued)

ocean or sea; depth	date; method	Se_{tot} (ng L^{-1}) (min−max)	Se(IV) (ng L^{-1}) (min−max)	Se(VI) (ng L^{-1}) (min−max)	Se(−II,0) (ng L^{-1})	Org-Se (ng L^{-1})	ref(s)
Mediterranean Sea, Gulf of Lions	1990; −						161
surface		39.5					
deep		71.1					
North Sea	1977−89; INAA	(45−78)					115,132
North Sea	1979; INAA	(70−120)					174
North Sea	1979−81; EDXES						100
surface		(110−1270)	(<40−140)	(<50−270)			
3−9 m		(<100−100)	<80	<100			
North Sea	1990; Asd-CSV		15.8				164
North Sea, Belgian coast	1987; DPCSV		(90−110)				175
North Sea, Kattegat Str., Laholm Bay, Sweden	1992; HGICP/MS	120 ± 5					176
North Sea, The Netherlands, Petten	1976; INAA	130 ± 30	100 ± 10	30 ± 30			101
North Sea, The Netherlands, Petten	1989; INAA		23.2 ± 9.4				86
Pacific Ocean	1976; F						167
surface		(60−120)	(40−80)	(10−60)			
deep		200					
Pacific Ocean; surface	1977; F	(70−80)				(19−36)	177
Pacific Ocean, California, La Jolla	1978; HG-AAS		<5	(58.4−80.2)			76
Santa Catalin Basin; surface			<5				
Santa Catalin Basin; 120 m			20.6				
Santa Catalin Basin; 250 m			33.1				
Santa Catalin Basin; 960 m			50.6				
Santa Catalin Basin; 1310 m (bottom)			70.2				
Pacific Ocean, California	1980; GLC						178
50 m		45	4	41			
130 m		54	5	49			
169 m		74	10	64			
199 m		79	13	66			
260 m		89	15	74			
326 m		104	20	84			
503 m		124	36	88			
703 m		143	46	97			
1001 m		152	53	99			
1400 m		164	60	104			
2062 m		178	64	114			
2994 m		184	65	119			
4089 m		175	62	113			
East tropical Pacific	1984; HG-AAS						179
15 m		83	6	11		65	
60 m		141	2	59		81	
125 m		144	24	101		19	
350 m		168	27	100		41	
500 m		156	37	111		8	
700 m		156	54	116		14	
1100 m		176	67	102		7	
1500 m		182	77	104		1	
2000 m		185	79	106			
3000 m		202	89	114			
3250 m		208	80	129			
NE Pacific Ocean, Gulf of Alaska (53°02′ N, 145°00′ W)	1985−88; F						180
0 m		61.9	21.0	30.0		10.9	
100 m		68.2	22.3	38.9		6.9	
299 m		115.9	49.8	10.7		55.4	
500 m		95.1	41.5	30.6		23.0	
750 m		117.2	49.5	20.4		47.2	
1000 m		110.3	53.3	31.2		25.8	
1500 m		130.7	40.0	58.2		32.4	
2000 m		125.8	56.5	39.0		30.2	
3001 m		117.8	51.3	42.3		24.2	
4000 m		117.8	38.3	51.2		28.3	
Central North Pacific Ocean, Loihi Seamount (19°01′ N, 154°55′ W)	1985−88; F						180
0 m		38.6	10.0	21.8		6.8	
10 m		39.5	5.5	26.8		7.2	
50 m		42.5	4.4	26.5		11.5	
99 m		41.6	4.3	22.3		15.0	
198 m		50.4	3.0	27.4		19.9	
298 m		47.1	8.2	27.6		11.4	
496 m		75.2	30.1	28.2		17.0	
694 m		58.7	33.7	17.8		7.1	
1091 m		100.3	56.4	22.6		21.2	
2018 m		130.8	48.7	50.2		31.8	
3007 m		131.5	53.6	60.4		17.5	

Table 2 (Continued)

ocean or sea; depth	date; method	Se_{tot} (ng L^{-1}) (min−max)	Se(IV) (ng L^{-1}) (min−max)	Se(VI) (ng L^{-1}) (min−max)	Se(−II,0) (ng L^{-1})	Org-Se (ng L^{-1})	ref(s)
3997 m		114.8	44.0	43.2		27.6	
4986 m		152.4	47.1	52.4		52.8	
Pacific Ocean, Hawaii, Oahu	1978; SP	400 ± 120					108
NW Pacific Ocean	1976; F						166, 181
surface		(60−120)	(40−80)	(10−60)			
4000 m	1976−77; F	(60−200)	(60−90)	(60−90)			
NW Pacific ocean, (40°00′ N, 170°03′ E)	1985−88; F						180
0 m		50.4	0.0	32.1		18.3	
50 m		85.9	11.7	23.1		51.1	
99 m		79.6	0.0	33.7		45.9	
198 m		69.2	3.0	22.3		44.0	
397 m		90.6	15.1	30.4		45.1	
496 m		110.5	11.7	9.6		89.2	
793 m		112.5	16.6	34.6		61.3	
992 m		113.2	33.6	17.0		62.6	
1946 m		133.2	36.9	42.2		54.1	
2014 m		157.8	23.1	50.5		84.2	
3892 m		149.2	32.4	26.5		90.2	
5007 m			38.5	20.4			
6274 m		171.8	30.2	28.3		113.4	
Sargasso Sea, 28°18′ N, 63°00′ W	F; 1981						182
0 m		0.0395[a]					
1200 m		0.0711[a]		0.0326[a]			
1500 m		0.0766[a]		0.0326[a]			
2000 m		0.0750[a]		0.0326[a]			
Waddenzee, The Netherlands	1979; INAA	240 ± 20					174
Orca Basin (oxic brine)	1985; −						183
0 m			0.0197[a]			0.0395[a]	
78 m						0.1097[a]	
0−250				0.0189[a]			
250−1230 m				0.0395[a]			
750 m			0.0363[a]				
750−1230 m			0.0308[a]				
Orca Basin (anoxic brine)			0.0197[a]			0.2053[a]	

[a] Units of μg kg^{-1} (ppb). [b] Units of ppm.

matrices carried out in routine and research laboratories has increased considerably in the last few years. However, the quality of results on speciation received less attention than reproducibility or accuracy of the instrumental determination. Speciation methods are prone to high risks of errors owing to the different analytical steps usually encountered (e.g., extraction, derivatization, separation, detection).[153] Thus, good quality control of speciation analyses has not yet been achieved.[153,155]

The predominant oxidation state in natural waters is not well established. Thus, the speciation of Se in the water of Urban Lake (China) shows that >70% of the total Se was in ionic form, mainly Se(IV).[156] In lake water samples from Finland,[90] more than half of the total Se was in the form of hydrophobic acidic organo-Se. Hydrophobic neutral organo-Se ranged from 3.7 to 7.5% of the total Se, and the hydrophobic basic organo-Se was a very small percentage.[90] In river waters the Se(VI) state may be important.[83,123,129,157] In snow, there was more selenate than selenite, and in rain, 60% of the total Se is in the form of selenite.[91] In groundwater, selenate is the major fraction of Se. Contents of different Se species in several natural and environmental waters are shown in Tables 2−10. Selenium is a growth factor for plankton algae in freshwaters and the bioavailability of Se for algae depends on the chemical forms of Se present in waters.[209] Selenium is rapidly accumulated in phytoplankton and then further enriched in herbivorous fishes and finally in predatory fishes.[43] The oxidation number of the prevailing present forms depends on salinity, redox potential, pH, kinetics, and other factors such as the manner in which Se is associated with the particular matter, and the water-sediment interface.

A. Salinity

Groundwater is being increasingly used to supplement drinking water supplies. In certain parts of the USSR, 62% of the drinking water supply is derived from alluvial deposits.[246] Selenium generally occurs in soils derived from crustaceous pyritic shales, especially in districts with a low rainfall. The natural concentrations of Fe, F, Be, Se, and Mn frequently exceed the permissible limits, and the use of these waters presents problems. However, under certain conditions, the Se levels are low because Se can be coprecipitated or adsorbed by Fe and Mn hydroxides.[186] Also, the Se concentrations in thermal and geothermal waters (Table 6) are low, because Se forms volatile compounds under reducing conditions, and these compounds are lost during sampling procedure. The groundwater composition is variable (Table 6) and depends on several factors: (1) mineralization of the areas; (2) migration of ions in the form of stable complexes with fulvic acids[246] and/or humic acids; (3) long- and short-term changes caused by vertical overflow induced by the abstraction of the groundwaters; (4) pollution, particularly in the upper horizons, by industrial and agricultural activities. Thus, the high Se levels found in wells from Kansas

Table 3. Selenium Species Concentrations in Estuarine Water

country; estuary	date	method	Se_{tot} (ng L^{-1}) (min-max)	Se(IV) (ng L^{-1}) (min-max)	Se(VI) (ng L^{-1}) (min-max)	Se(−II,0) (ng L^{-1}) (min-max)	Org-Se (ng L^{-1})	ref(s)
NE Atlantic	1980	GC-ECD	8.84	1.50				116
Belgium; Scheldt River	1979−81	EDXES	660	600				100
Canada; Hamilton Harbour	1979	EAAS	1120					72
Japan; Nagoya Harbour	1984	F	(79−430)	(10−150)	(13−28)			111
Japan; Nagoya Harbour	1987	AAS		(30−40)	55 ± 10			184
U.K.	1977	GC-ECD						67,124
Beaulieu River			(73−85)	<2				
Hamble River			390	31				
Itchen River			250	18				
Meon River			278	20				
Test River			(369−376)	(18−21)				
U.K.								
Tamar estuary (salinity 0.1%)	1990	Ads-CSV		189				164
Tamar estuary (salinity 34%)				9.5				
United States, California		EAAS						83
Golden Gate	Apr, 1986		96.3 ± 2.4	26.8 ± 4.7	69.5 ± 1.6	−		
	Sep, 1986		71.1 ± 0.8	26.8 ± 0.79	28.4 ± 0.79	15.8 ± 0.79		
Sacramento River	1984−87		(39.5−110.5)	(<0.79−34.7)	(11.8−74.2)	(<0.79−57.6)		
San Francisco Bay	Apr, 1986		(96.0−322.9)	(15.8−48.9)	(45.0−195.0)	(<0.79−195.8)		
	Sep, 1986		(48.2−358.5)	(18.9−104.2)	(16.6−190.3)	(<0.79−104.2)		
San Joaquín River	1984−87		(135.8−2866)	(15.0−152.4)	(97.1−1816)	(<0.79−1026)		
United States, California		EAAS						84
Sacramento River	1987−88		68.7 ± 23.7	9.47 ± 6.32	30.0 ± 19.7	30.0 ± 18.9		
San Francisco Bay	Oct−Dec, 1987		(116.9−287.4)	(30.8−124.8)	(<0.79−217.9)	(<0.79−92.4)		
	Mar−May, 1988		(75.8−280.3)	(22.9−132.6)	(39.5−171.3)	(<0.79−93.2)		
San Joaquín River	1987−88		1808 ± 805	118.4 ± 55.3	1295 ± 742	394.8 ± 315.8		
United States: New York Harbor	1980	EAAS	<5000					110
United States, Virginia; James River, Chesapeake Bay	1984	F	(71.1−150.8)[a]	(42.6−135.8)[a]	(15.0−28.4)[a]			185

[a] Units of ng kg^{-1}.

(United States) were likely to be due to naturally occurring soil and rock formations, such as exposed Cretaceous shales.[247] A significant correlation was found between Se concentrations in streamwaters of Finland and the Se in groundwater, from the nearby wells.[123] Also, during 1988 an extraordinarily high content of Se (up to 38 μg L^{-1}) was detected in the water of some wells in the Nazareth Mountains (Israel). This contamination may be due to the proximity of a chalky quarry and to infiltration of the waste into the groundwater by rainwater.[248] However, in Finland, Se from precipitation had no impact on groundwater Se.[91] The mean Se concentration of infiltration waters was significantly lower than the median Se concentration of snow and rain in Finland,[52,91] indicating that precipitation may be one source of soil Se. Therefore, soil has a high capacity of retaining Se and retains Se(IV) more effectively than Se(VI). The annual net Se deposition from precipitation into soils was estimated to be 0.49 and 0.33 g ha^{-1} in southern and northern Finland, respectively.[91]

Shallow groundwater of agricultural areas in the San Joaquín Valley, CA, has been extensively studied. Selenium, occurring naturally in alluvial soils of the arid western San Joaquín Valley, is leached by irrigation water and concentrated, with other salts, in the topsoil by evaporation. Selenium is mobilized when the soils are drained to remove all accumulated salts and is carried into the reservoir.[249] Aspects such as distribution and mobility of Se, salinity, availability of imported irrigation water, climate, geomorphology, and hydrology of the alluvial fans were discussed. An evaluation was conducted on the human health impacts of the elevated levels of Se in this area, but no adverse health effects in the local population were found,[250−255] although toxic levels of Se may be produced in the food chain.[256,257]

The possible pollution of natural waters by Se added via agricultural fertilizers was studied. Selenium concentrations were determined in lakes and groundwater from Finland,[106] where the enrichment of fertilizers by Se has continued for 8 years. Until 1984, the Se concentration in fertilizers was <1 mg kg^{-1}. During 1984−1990, the recommended addition of Se given per hectare was about 8 or 3 g for grain or grass fields, respectively. After 1990, the Se concentration in fertilizers was to be kept at the level of 6 mg kg^{-1}.[106] The amount of Se used in fertilizers in 1989 was 19.7 tons.[52] In lake water samples, from 13 lakes, no significant correlations were found between Se and pH, chlorophyll a, total nitrogen, or phosphorus; agriculturally affected and nonaffected lakes showed no differences in their Se concentrations. Only one lake close to a coal power plant had a higher water Se concentration.[106] In groundwater samples, there was a big variation in Se levels, which may partly be explained by different Se concentrations of bedrock and sediments. However, the simultaneous increase of total nitrogen, phosphorus, and Se levels indicates some leaching of Se from the fertilizers into lakes and groundwater in certain areas.[106] The sulfate and phosphate fertilizers decrease the adsorption of selenite and selenate on the

Table 4. Selenium Species Concentrations in River Water

country; river	date	method	Se_{tot} ($\mu g\ L^{-1}$) (min-max)	Se(IV) ($\mu g\ L^{-1}$) (min-max)	Se(VI) ($\mu g\ L^{-1}$) (min-max)	Se(−II,0) ($\mu g\ L^{-1}$) (min-max)	ref
Andorra, Andorra; Valira R.	1992	F	0.0612				123
Australia; Calcrete basin	1973	EAAS	(0.008−0.330)				186
Austria, Vienna; Donaukanal	1991	F	0.122				123
Belgium; Scheldt R.	1979−81	ICP-AES	(0.23−1.78)	(0.13−1.45)			100
Belgium; "unpolluted" river			(<0.05−0.58)	(<0.04−0.20)			
Belgium; Scheldt R.	1987	INAA	1.85 ± 0.15				174
		AAS	1.55				
China	1982	HG-AAS		0.10	<0.01		187
polluted river				0.28	0.37		
China; Bing R.	1989	INAA	0.26				188
		DPP	0.284 ± 0.017	0.009	0.275		
China; Songhua R.	1989	DPP	0.06 ± 0.002	0.037 ± 0.003	0.023		188
China; Songhua R.	1988	DPP	(0.07−0.19)[a]				189
China; Jia-Ling R.	1988	SF		(2.47−2.75)			113
China, Hainan Island	1991		(0.10−1.85)				190
Czechoslovakia, Prague; Vltava R.	1991	F	0.127				123
Finland	1993	F	0.125				74
Finland; Degerby R.	1990[b]	F	0.0867				123
	1991[b]		0.138				
	1992[b]		0.108				
Finland; Ingaskila R.	1990[b]	F	0.0872				123
	1991[b]		0.140				
	1992[b]		0.101				
	Jul, 1992		0.111	0.0114	0.0182		
Finland; Keravanjoki R.	1991[b]	F	0.129				123
	1992[b]		0.110				
	1991−92		(0.0917−0.185)				
Finland; Mätäpuro Brook	1991[b]	F	0.139				123
	1992[b]		0.121				
	1991−92		(0.0714−0.217)				
Finland; Mustio R.	1990[b]	F	0.0924				123
	1991[b]		0.0981				
	1992[b]		0.0948				
Finland; Svartbäck R.	1990[b]	F	0.122				123
	1991[b]		0.132				
	1992[b]		0.132				
Finland; Torp R.	1990[b]	F	0.0754				123
	1991[b]		0.142				
	1992[b]		0.104				
Finland; Vantaanjoki R.	1991[b]	F	0.132				123
	1992[b]		0.112				
	Jul, 1992		0.104	0.0139	0.0129		
	1991−92		(0.0818−0.188)				
Finland; Vejans R.	1990[b]	F	0.125				123
	1991[b]		0.150				
	1992[b]		0.125				
Finland; Viikinoja Brook	1991[b]	F	0.103				123
	1992[b]		0.105				
	1991−92		(0.0718−0.160)				
	Jul, 1992		0.115	0.0105	0.0602		
	Dec, 1992		0.110	0.00910	0.0478		
	Jan, 1993		0.126	0.00891	0.0680		
Finland	1993	F	(0.0997−0.115)	(0.0105−0.0139)	(0.013−0.0602)	(0.037−0.0416)	89
Finland, Helsinki; Brook Viikki R.			0.123 ± 0.001	0.0089 ± 0.0023	0.068 ± 0.0025	0.0328	
France	1981	GC-ECD	(<2−10)				191
France; Rhone R.	1987−89		0.182				173
			(0.107−0.327)				
France, Nice; Paillon R.	1992	F	0.198				123
France, Paris; Seine R.	1991		0.522				
France, Toulouse; Garonne R.	1992		0.0838				
France, Versailles; Grand Canal	1991		0.180				
Germany, Siegen; Main R.	1978	HPLC	0.8				192
Germany	1985	HG-AAS		6			193
Germany, Darmstadt; Main R.	1976	INAA	0.7[a]				131
Germany; Rhin R.	1987	INAA	0.14 ± 0.01				174
		AAS	0.13				
Germany, Berlin; Spree R.	1991	F	0.234				123
Germany, Hamburg; Elbe R.	1992		0.277				
Greece; Penios R.	1988	F	(0.120−0.190)				105
Hungary, Budapest; Danube R.	1992	F	0.108				123
India, Bombay; Vaitarana R.	1987	RNAA	25 ± 8				194
Italy		EAAS					186
Alessandria; Bormida R.	1977		0.17				
Chiavari; Entella R.			0.06				
confluence of Orcia R.; Orci R.	1973		0.01				

Table 4 (Continued)

country; river	date	method	Se_{tot} ($\mu g\ L^{-1}$) (min-max)	Se(IV) ($\mu g\ L^{-1}$) (min-max)	Se(VI) ($\mu g\ L^{-1}$) (min-max)	Se(−II,0) ($\mu g\ L^{-1}$) (min-max)	ref
Pavia; Po R.	1977		0.06				
Pavia; Ticino R.			0.02				
Pescara; Pescara R.			<0.002				
Pisa; Arno R.			0.09				
Prato d. Signora; Aniene R.	1978		<0.002				
Rome; Tiber R.			(<0.002−0.025)				
Viterbo; Marta R.			<0.002				
Italy	1982	INAA					117
Navigliaccio R.			76.5 ± 6.5	55.83 ± 6.0	40.65 ± 4.12		
Ticino R.				(25.2−26.3)	7.5 ± 0.6	(3.22−5.78)	
Italy, Alessandria district; Belbo R., Borbera R., Bormida R., Erro R., Grana R., Lemme R., Lovassina R., Orba R., Po R., Rotaldo R., Scrivia R., Stura R., Stura M. R., Tanaro R., Tiglione R.	1989−91	HG-AAS	0	0	0	0	195
Italy, Tuscany	1975	INAA	0.7				196
Italy, Florence; Arno R.	1992	F	0.243				123
Italy, Pisa; Arno R.			0.243				
Italy, Rome; Tiber R.			0.169				
Japan	1977	F	0.04	(0.006−0.017)	(0.084−0.171)		168
Japan	1979	EAAS	2				169
Japan	1981	GC-ECD	(0.016−0.230)				157
Japan; coastal rivers	1976	F	0.04				167
Japan; Arakawa R.	1984	HG-AAS	(0.10−0.12)[a]				121
Japan; Arakawa R.	1987	HG-AAS		(0.11−0.48)			197
Japan	1977	GC-ECD					95
Asahi R.			0.023	0.012			
Takahashi R.			0.022	0.008			
Japan	1979	GC-ECD					96
Asahi R.			(0.016−0.020)	(<0.002−0.002)	(0.003−0.009)	0.011	
Takahashi R.			0.016	0.004	0.007	0.005	
Yoshii R.			0.231	0.016	0.202	0.012	
Japan	1981	F					198
Chikup R.			0.082[a]	0.022[a]	0.060[a]	<0.0047[a]	
Ishikari R.			0.043[a]	0.019[a]	0.024[a]	<0.0047[a]	
Kiso R.			0.043[a]	0.026[a]	0.017[a]	<0.0047[a]	
Kitakami R.			0.064[a]	0.021[a]	0.043[a]	<0.0047[a]	
Mogami R.			0.031[a]	0.019[a]	0.011[a]	<0.0047[a]	
Shinano R.			0.039[a]	0.019[a]	0.019[a]	<0.0047[a]	
Yoshino R.			0.088[a]	0.025[a]	0.062[a]	<0.0047[a]	
Yudo R.			0.067[a]	0.019[a]	0.048[a]	<0.0047[a]	
Japan, Osaka; Yamato R.	1985	F		0.0102 (0.0074−0.0077)	0.0025 (0.0082−0.0085)	0.0044	171
Japan, Nagoya; Tempaku R.	1992	INAA		(0.15−0.19)	(0.12−0.16)		114
Japan, Yokohama; Tama R.	1992	HPLC		≤0.025	≤0.127		199
Luxemburg, Luxemburg; Petrusse R.	1991	F	0.244				123
New Zealand	1979−80	F					126
Puruki stream			0.05 (0.02−0.08)				
Purutaka stream			0.05 (0.02−0.08)				
Waikato R.			0.05				
Nigeria; Benin R.	1983	INAA	1060 ± 110[a]				81
Norway, Oslo; Akers R.	1991	F	0.0858				123
Norway; Skien R.	1974	INAA	<0.34				75
Poland	1980	PIXE	50−200000[a]				200
Poland, Warszawa; Wista R.	1991	F	0.255				123
Romania, Bucharest; Dimbovita R.	1992	F	0.126				123
Spain, Madrid; Manzanares R.	1992	F	0.111				123
Spain, Sevilla; Guadalquivir R.	1992	F	0.349				123
Sweden, Uppsala; Fyrisan R.	1991	F	(0.0864−0.129)				123
Switzerland	1978	INAA					77
Meiringen; Aare R.			0.10				
Thun; Aare R.			0.12				
Bern; Aare R.			0.11				
Hagneck; Aare R.			0.10				
Geneve; Arve R.			1.2				
Switzerland, Davos; Landwasser R.	1991	F	0.117				123
U.K.	1980	ICP-AES					102
Gannel R.			(0.2−0.42)				
Hayle R.			(0.3−0.9)				

Table 4 (Continued)

country; river	date	method	Se_{tot} (μg L^{-1}) (min-max)	Se(IV) (μg L^{-1}) (min-max)	Se(VI) (μg L^{-1}) (min-max)	Se(−II,0) (μg L^{-1}) (min-max)	ref
U.K.; Thames R.	1981	INAA	0.23 ± 0.08 (0.13−0.41)				103
United States	1978	XRFS		24			201
United States, Connecticut; Norfolk R.	1981	EAAS	<0.8				118
United States, New Mexico, Las Cruces; Río Grande	1992	CSV	0.16				149
United States, Washington, Richmond; Dambe R.	1990	IDMS	(0.20−0.35)[a]	(0.051−0.056)[a]	(0.118−0.280)[a]		92
USSR	1978	ND-AFS					202
Bermo R.			0.0685 ± 0.0021				
Biryusa R.			0.0851 ± 0.0030				
Kizir R.			0.0563 ± 0.0018				
USSR	1981	IC		0.11 ± 0.007	0.22 ± 0.007		203
USSR	1983	IC			0.3 ± 0.02		204
		INAA			0.2		
USSR (Moscow); Moskva R.	1991	F	0.0966				123
Venezuela; Orinoco R.		GC					65
Ciudad Bolívar	1982−83		(0.032−0.050)	0.0039			
Puerto Ordaz	1982		(0.034−0.042)	0.0079			
Musinacio	1982−83		(0.048−0.049)	0.0084			
Cabruta	1982		0.058	0.0129			
Capanaparo	1983		0.038				
Parguaza	1982		0.022	<0.0016			
Meta	1982		(0.014−0.019)				
Apure	1982		0.028				
Caura	1982		0.033	<0.0016			
Atabapo	1982		0.017				
Venezuela		GC					65
Caroni R.	1982−83		(0.016−0.020)	<0.0016			
Aro R.	1982−83		(0.020−0.022)				
Mapire R.	1982		0.022				
Cuchivero R.	1982−84		(0.019−0.023)	<0.0016			
Caura R.	1982−84		(0.016−0.023)				
Tortuga R.	1982		0.015				
Suapure R.	1982		(0.007−0.014)	<0.0016			
Parguaza R.	1982−84		(0.005−0.009)	<0.0016			
Cataniapo R.	1982		0.007				
Paria Grande R.	1982		0.013				
Samariapo R.	1982		0.012				
Sipapo R.	1982−83		(0.011−0.012)				
Cuao R.	1983		0.015				
Ventuari R.	1983		0.006				
Atabapo R.	1982−84		(0.013−0.020)	<0.0032			
Inirida R.	1982−83		(0.009−0.014)				
Guaviare R.	1982−83		(0.018−0.022)	<0.0016			
Meta R.	1982−84		(0.052−0.070)				
Cinaruco R.	1982		0.013				
Capanaparo R.	1982−83		(0.026−0.044)	<0.0016			
Arauca R.	1982		0.055	0.0027			
Apure R.	1982−85		(0.085−0.231)	(0.028−0.037)			
Bocono R.	1984		0.082	<0.016			
Guanare R.	1984		0.296	0.025			
Portuguesa R.	1984		0.206	<0.016			
Morador R.	1984		0.408	0.046			
Acarigua R.	1984		0.384	0.1334			
Domingo R.	1984		0.039				
Canagual R.	1984		0.018				
Suripa R.	1984		0.050				
Caparo R.	1984		0.031				
Dorados R.	1984		0.039				
Tururu R.	1984		0.026				
Uribante R.	1984		0.055				
Manapire R.	1982		0.075	0.016			
Cabruta R.	1982		0.034				
Yugoslavia, Belgrade; Sava R.	1992	F	0.123				123

[a] Units of μg kg^{-1}. [b] Annual mean.

surface of clay minerals and hydrous iron oxides by competing for the same ionic exchange sites, thus increasing the mobilization of Se.[258] Also, the observed decrease of river water Se concentration in 1992 compared with that of 1991 may be the result of the change in Se application.[123] The median Se concentration in wells, lakes, and natural groundwaters[90,91] suggests that the Se transported to surface runoff from soils is the main source of the increased Se in river water.[123]

Speciation of both the Se fluxes in San Francisco Bay, as well as the Se contribution from refinery

Table 5. Selenium Species Concentrations in Lake Water

country; lake	date	method	Se_{tot} ($\mu g\ L^{-1}$) (min-max)	Se(IV) ($\mu g\ L^{-1}$) (min-max)	Se(VI) ($\mu g\ L^{-1}$) (min-max)	ref
Australia	1973		0.2			186
Belgium	1979−81	EDXES	(<0.05−0.23)	(<0.04−0.15)	(<0.05−0.08)	100
Belgium	1983	XRF				205
Campus Lake			0.23[a]	0.15[a]	0.080[a]	
Het Broek Pond			0.14[a]	0.09[a]	0.050[a]	
Canada	1980	FAAS				97
Dufault L.			<0.1			
Duparquet L.			<0.1			
Canada	1982	AAS				206
Bass L.			0.1			
Horseshoe L.			0.1			
MacFarlane L.			0.2			
Nelson L.			0.2			
Ramsay L.			0.4			
Rankin L.			0.1			
Vermillion L.			0.1			
Wavy L.			0.2			
Windy L.			0.1			
Canada; Yssel L.	1979	INAA	0.45 ± 0.03			174
China	1988	HG-AAS	1.52 ± 0.02			93
			1.34 ± 0.04			
China	1988	DPP	(0.07−0.19)[a]			189
Finland		F				90
Artjärvi L.	1990		0.0887			
Degersjö L.			0.0932			
Enäjärvi L.			0.0882			
Humaljärvi L.			0.0689			
Iso-Hietajärvi L.	1987		0.0338	0.0044	0.0035	
Iso-Parikasjärvi L.			0.0674			
Kevätön L.;	1991					
0 m			(0.0314−0.0363)			
0−2 m			(0.0279−0.0348)			
2−4 m			(0.0294−0.0322)			
4−6 m			(0.0330−0.0357)			
6−8 m			(0.0301−0.0384)			
8−9.3 m			(0.0314−0.0382)			
Kolmperä L.			0.0510			
Korkjärvi L.			0.0653			
Köyliönjärvi L.	1987		0.0592			
Lapinlahti L.			0.0786			
Lounatlammet L.			0.0265			
Pääjärvi L.	1990		0.143	0.0095	0.0171	
Pesosjärvi L.	1991		0.0892	0.0067	0.0065	
Pyhäjärvi L.	1987		0.0807	0.0056	0.0047	
Pyhäselkä L.	1985		0.0545			
Rusutjärvi L.			0.0856			
Sääksjärvi L.			0.0867			
Salmijärvi L.			0.0752			
Syväsmäki L.			0.0643			
Tarpeinen L.			0.0449			
Tuusulanjärvi L.			0.0960			
Valkea-Kotinen L.	1992		0.0583	0.0038	0.0048	
Villikkalanjärvi L.	1991		0.113			
Vitträsk L.			0.0771			
Ylärieveli L.			0.0643			
agriculturally affected	1990		0.0640 ± 0.0149			
			(0.0254−0.0809)			
	1991		0.0768 ± 0.0179			
			(0.0445−0.121)			
forest lakes	1990		0.0603 ± 0.0196			
			(0.0287−0.115)			
	1991		0.0564 ± 0.0133			
			(0.0331−0.0857)			
Finland	1992	F				106
Hirvijärvi L.			0.0512			
Iso-Kisko L.			0.0821			
			(0.0720−0.0952)			
Kakskerranjärvi L.			0.0779			
			(0.0716−0.0829)			
Kirkkojärvi L.			0.0931			
			(0.076−0.109)			
Krailan Pitkäjärvi L.			0.110			
Leikkistenjärvi L.			0.0934			
			(0.0848−0.106)			

Table 5 (Continued)

country; lake	date	method	Se_{tot} (μg L^{-1}) (min-max)	Se(IV) (μg L^{-1}) (min-max)	Se(VI) (μg L^{-1}) (min-max)	ref
Littoistenjärvi L.			0.0841 (0.0674−0.121)			
Luolalanjärvi L. (coal power plant area)			0.272 (0.190−0.404)			
Naarjärvi L.			0.0839 (0.0723−0.0971)			
Pyhäjärvi L.			0.0834 (0.0772−0.0950)			
Taattistenjärvi L.			0.0780 (0.0740−0.0818)			
Tervakas L.			0.0684			
Ylttistenjärvi L.			0.0752 (0.0684−0.0855)			
Finland	1993	F	(0.0337−0.0894)	(0.0044−0.0067)	(0.0035−0.0065)	89
Finland; Valkea-Kotinenjärvi[b]	1992	F	0.0583 ± 0.0023	0.0038 ± 0.0006	0.0048 ± 0.0007	
Germany	1990	IDMS				92
artificial lake			0.19 ± 0.01[a]	0.030 ± 0.007[a]	0.171 ± 0.023[a]	
coal mining area			0.83 ± 0.03[a]	0.046 ± 0.006[a]	0.805 ± 0.007[a]	
Moorland L.			(0.21−0.24)[a]	(0.027−0.141)[a]	(0.035−0.047)[a]	
Germany; Constance L.	1977	HG-AAS	<0.05			99
Germany; Constance L.	1980	HG-AAS	0.1			207
Japan, Nanpo; Biwa L., 0−80 m	1984	ICP-AES	<0.8			112
Japan, Nanpo; Biwa L.	1985	F		0.0095		171
Sweden; Erken L.	1980	F	(0.065−0.20)[a]	(0.01−0.04)[a]	(0.03−0.16)[a]	208
Sweden; Kinneret L.	1983	F	0.102[a]			209
Sweden, Uppsala; Flottsund L.	1992	GC-ECD		(0.0026−0.0042)		88
		HG-AAS		(0.001−0.0045)		
Sweden, Uppsala; Lafssjön L.	1991	GC-ECD	(0.124−0.132)			150
Sweden, Uppsala; Lafssjön L.	1991	HG-AAS	(0.103−0.143)			87
Switzerland; Maggiore L.	1976	INAA	0.4[a]			131
United States, California; Arrowhead L.	1978	HG-AAS		0.0177	<0.005	76
United States, Michigan; Erie L.	1977	F	(1.003−4.998)[a]			210
USSR	1978	ND-AFS				202
Pyasino L.			0.860 ± 0.016			
Shira L.			0.385 ± 0.009			
Svatikovo L.			0.248 ± 0.006			
Uchum L.			0.420 ± 0.009			

[a] Units of μg kg^{-1}. [b] Organo selenium compounds concentration: 0.0374 μg L^{-1}.

effluents and municipal discharges were studied by Cutter et al. during 1984−1987[83] and 1987−1988.[84] Correlations between diverse species of Se and salinity were made. Generally, the higher concentrations of total dissolved Se are centered at ≈50 km from the Golden Gate, in the middle of the Carquinez Strait (salinity: 13.7−24.9‰). In addition to the concentration of total Se in the midestuary being higher than that in the Sacramento River, selenite is enriched within the midestuary; selenite increases on average to 48%, while selenate remains at 44% of the total dissolved Se. Compared with riverine Se, concentrations in the refinery effluents are up to three times higher, and selenite is the predominant form of dissolved Se (an average of 62% of the total for all refineries).[84] In general, total Se and Se(−II,0) concentrations correlated inversely with salinity.[83] Composition as a percentage of each Se species was given. Also, temporal variability of Se fluxes, with regard to anthropogenic and riverine contributions was studied. During winter months when river discharge is at a maximum, the Se flux from San Francisco Bay is ≈106 mol day^{-1}, of which 48% is riverine in origin. In contrast, during a period of low river discharge, <10% of the total Se flux of 99.8 mol day^{-1} is riverine.[84] The total Se concentration of waters is also related to the river discharge in other countries.[83,173] The seasons had only a minor effect on both wellwater and groundwater.[91] However, in some well water and groundwater samples large seasonal fluctuations were found, that indicate that irrigation water dilutes Se.[59] In river waters, the seasonal variation of the Se concentration is mainly controlled by the amount of precipitation and had a clear response to as little as 5 mm of rainfall.[123] However, the variation in Se speciation in the same river between summer and winter periods was small.[123]

Also, speciation of Se in the Gulf of Lyons (France) and the outlet of Rhone River was investigated.[173] The concentrations of different species decrease linearly with increasing salinity, without significant interconversion between Se species.[173] The relationships between salinity and the concentrations of total Se and Se(IV) were studied in samples of estuarine water from the Solent, in midsouthern England;[124] the regression of total dissolved Se on salinity with its extrapolation to zero salinity is shown; also, total Se and Se(IV) decrease when salinity increases. However, according to some authors,[80] salinity does not correlate well with total Se, selenite, or selenate.

B. Redox Potential and pH

In seawater Se occurs, predominantly, as Se(VI) (Table 2), but the presence of Se(IV) suggests that

Table 6. Selenium Species Concentrations in Groundwater, Well Water, and Thermal Water

geographical location	date	method	Se_{tot} ($\mu g\ L^{-1}$) (min-max)	Se(IV) ($\mu g\ L^{-1}$) (min-max)	Se(VI) ($\mu g\ L^{-1}$) (min-max)	refs
		a. Groundwater				
Australia	1978		(0.008−0.330)			186
Belgium	1979−81	EDXES	(<0.05−1.33)	(<0.04−0.21)	(<0.05−1.33)	100
Belgium	1980	EAAS	(0.125−0.175)	0.025		133
Finland		F				91
Ahvenisto	1990		0.838			
Joutsa	Jan, 1990		0.588			
	Nov, 1990		0.499			
Kylmälahti	May, 1990		0.840			
	Dec, 1992		0.814			
Oripää	1993		0.216	0.0020	0.194	
Finland	1992	F				106
Bläsnäsin lähde, Parainen			0.209			
Hossojan lähde			0.0484			
			(0.0335−0.0595)			
Kalliokaivo, Hinnerjoki Eura			0.0428			
Kultalähde, Kiikala			0.178			
Kuninkaanlähde, Köyliö			0.0371			
Lammin lähde			0.155			
			(0.115−0.189)			
Mäntykankare, Sauvo			0.167			
Oripään lähde, Oripää			0.245			
			(0.233−0.260)			
Finland	1993	F	0.069 ± 0.0023			74
Germany	1988	ID-MS				122
Donaustetten			<0.08[a]			
Rottenacker (1)			4.8 ± 0.2[a]	0.40 ± 0.02[a]	4.0 ± 0.2[a]	
Rottenacker (2)			17.36 ± 0.08[a]	0.19 ± 0.01[a]	15.64 ± 0.09[a]	
Germany	1988					120
Rottenacker		ID-MS	4.1 ± 0.2[a]			
		HG-AAS	4.2[a]			
1		ID-MS	13.3 ± 0.1[a]			
		HG-AAS	11.6[a]			
2		ID-MS	22.32 ± 0.07[a]			
		HG-AAS	29.4[a]			
Germany	1990	IDMS				92
Gravel aquifer			1.80 ± 0.06[a]	0.130 ± 0.009[a]	1.63 ± 0.02[a]	
Karst aquifer			(13.66−15.56)[a]	(0.59−1.29)[a]	(12.26−15.09)[a]	
Italy, Grosseto; Boccheggiano pyrite mine	1973	EAAS	0.003			186
Italy, Grosseto; Niccioleta			0.01			
Italy, Tavoliere	1975		(0.035−0.385)			
Italy, Val Rendena; uranium mine	1973		(0.01−1.94)			
Italy, Tuscany	1975	INAA	<0.7			196
United States, North Dakota; coal mine	1981	HG-AAS	(0.16−0.74)			152
		IC-HG-AAS	(0.48−0.70)	(0.04−0.20)	(0.40−0.47)	
United States, Washington, Hanford site, Richland	1992	CSV	0.09			149
United States, Wyoming	1988−89	CSV				59
Bates Creek subbasin			20.0			
Oregon Trail Drain subbasin			17.5			
Poison Spider Creek subbasin			50.0			
Poison Spring Creek subbasin			10.0			
Casper Creek subbasin			25.5			
United States, Wyoming	1994	HGAAS, IC	(22−151)	(1.3−54.4)	(7−98.1)	211
USSR; mine water	1978	Polarography	6.6 ± 0.318			212
		b. Well Water				
China	1982	HG-AAS		0.04	0.64	187
China	1989	HG-AAS		(0.062−0.082)		213
Denmark	1993	FI-HG-AAS		(0.023−0.038)		214
Finland		F				91
stone-lined in yard well	1990−91		0.263 ± 0.299			
			(0.0279−0.880)			
drilled in yard			0.154 ± 0.0497			
			(0.0048−0.646)			
concrete in yard			0.196 ± 0.320			
			(0.0041−2.720)			
concrete in field			0.120 ± 0.151			
			(0.0042−0.913)			
concrete in forest			0.0792 ± 0.0843			
			(0.0122−0.295)			
concrete on slope			0.0895 ± 0.0992			
			(0.0042−0.326)			
concrete on lowland			0.0566 ± 0.0335			
			(0.0392−0.132)			
	Sep−Oct, 1990		0.153 ± 0.250			
			(0.0041−2.720)			

Table 6 (Continued)

geographical location	date	method	Se_{tot} ($\mu g\ L^{-1}$) (min-max)	Se(IV) ($\mu g\ L^{-1}$) (min-max)	Se(VI) ($\mu g\ L^{-1}$) (min-max)	refs
	Mar−Apr, 1991		0.132 ± 0.244 (0.0038−1.920)			
	Jul−Aug, 1991		0.120 ± 0.195 (0.0050−1.470)			
Hämeenlinna	1993		0.270 (0.089−0.533)			
Joutsa	1993		0.504	0.0079	0.418	
India, Bombay	1987	RNAA	8			194
United States, New Mexico	1975	HG-AAS	537 ± 650 (26−1800)			215
United States, New Mexico, Milan	1980	HG-AAS	327.46 ± 549.1 (26−1800)			216
United States, New Mexico, Grants	1987	MTES	(700−1900)			82
USSR, Moscow	1978−79	F	(0.095−0.95)	(0.09−0.85)	(0.005−0.100)	217
		c. Thermal Water				
China	1988	SP		(1.33−1.38)		113
Germany	1988					120
Bad Buchau		ID-MS	<0.08[a]			
		HG-AAS	<2[a]			
Jordanbad		ID-MS	0.17 ± 0.06[a]			
		HG-AAS	<2[a]			
Saulgau		ID-MS	<0.08[a]			
		HG-AAS	<2[a]			
Hungary, Szarvas	1989	EAAS	<2			218
Italy		EAAS				186
Agnano; Fanghiera	1977		<0.002			
Agnano; Pisciarelli			<0.002			
Grosseto; Saturnia	1973		<0.002			
Napoli; Stufe di Nerone-Bacoli	1977		<0.002			
Pozzuoli; Terme Putuelane			0.055			
Pozzuoli; Terme Salute			0.110			
Rome; Stigliano	1978		<0.002			
Siena; Petriolo Terme	1973		<0.002			
Siena, Rapolano			0.003			
Viterbo; Bagnaccio	1973−78		<0.002			
Viterbo; Bullicame	1978		<0.002			
Viterbo; Tuscania			<0.002			
Larderello; geothermal water	1973−78		(0.002−0.015)			
Rome; geothermal water	1975		0.02			
Spain	1993	HG-FAAS				219
Barcelona, Caldas de Montbuy; Broquetas			<1			
Barcelona, Caldas de Montbuy; Solá			<1			
Barcelona, Caldas de Montbuy; Termas Salud			<1			
Barcelona, Caldas de Montbuy; Termas Victoria			<1			
Barcelona, La Garriga; Blancafort			<1			
Gerona, Caldas de Malavella; Prats			<1			
Spain, Gerona, Caldas de Malavella; San Narciso	1987	SP		<1		135
Spain	1993	HG-FAAS				219
Gerona, Caldas de Malavella; San Narciso			<1			
Gerona, Santa Coloma de Farnés; Termas Orión			<1			
Lérida, Caldas de Bohí; Avellaner			<1			
Lérida, Caldas de Bohí; Baños			<1			
Lérida, Caldas de Bohí; Boix			<1			
Lérida, Caldas de Bohí; Bon			<1			
Lérida, Caldas de Bohí; Canem			<1			
Lérida, Caldas de Bohí; Capellanes			<1			
Lérida, Caldas de Bohí; El Bosque			<1			
Lérida, Caldas de Bohí; Las Estufas			<1			
Lérida, Caldas de Bohí; La Tartera			620			
Lérida, Caldas de Bohí; Las Termas			<1			
Lérida, Caldas de Bohí; Pompeyo			<1			
Lérida, Caldas de Bohí; Salenca			<1			
Lérida, Caldas de Bohí; Santa Lucía			<1			
Lérida, Caldas de Bohí; Titus II			<1			
Tarragona, Vallfogona de Riucorp; Fuente Grande			<1			
Tarragona, Vallfogona de Riucorp; Fuente Pequeña			<1			

[a] Units of $\mu g\ kg^{-1}$.

Table 7. Selenium Species Concentrations in Natural and Drinking Waters

procedence; commercial name	date	method	Se_{tot} ($\mu g\ L^{-1}$) (min-max)	Se(IV) ($\mu g\ L^{-1}$) (min-max)	Se(VI) ($\mu g\ L^{-1}$) (min-max)	ref(s)
		a. Natural Waters				
Belgium	1975	EAAS				137
			(0.13−0.14)	0.05		
(Brussels)			(0.34−0.375)	0.02		
China	1989	HG-AAS		0.040		213
China, Taiwan, Kaohsiung County	1993	ICP-MS	0.38 ± 0.01			220
Finland, Äijälä	Nov, 1990	F	0.0505			91
	Jun, 1993		0.0253	0.0019	0.0069	
Germany, Franconia	1983−84	HG-AAS	(15−35)	(5−9)		119
Germany	1985	HG-AAS		500	1240	193
Germany; "Imnaver", "Überkinger", "Weissenberger"	1991	EAAS	≤3			221
Greece; Spa waters	1988	F	≤20			105
Hungary	1988	EAAS				218
"Hunyadi"			<5			
"Mira"			<5			
"Mohai"			<2			
"Salvus"			<2			
Hungary; "Paradi"	1991	EAAS	≤3			221
Iceland; "Icelandic"			≤3			
Italy, Cuneo; "Fonti San Bernardo"	1977	RNAA	0.043 ± 0.012[a]			222
Italy, Tuscany	1975	INAA	<0.7			196
Italy, Viterbo; Acqua Rossa spring	1978	EAAS	<0.002			186
Japan	1980	EAAS	<0.4			139
Romania; "Poljustrovo"	1991	EAAS	≤3			221
Singapore; "Amust"	1994	CZE		<12		151
Spain; "Fontvella"	1987	SP		1.6		135
Spain	1990	SP		<0.012		223
United States	1978	XRF		<2.4		201
Yugoslavia	1982	EAAS	<0.5			224
Yugoslavia; "Radmska"	1991	EAAS	≤3			221
		b. Drinking Water				
Belgium	1979−81	EDXES	(<0.05−0.84)	(<0.04−0.28)	(<0.05−0.84)	100
Belgium	1982	EDXRF	0.290[a]			225
			(<0.04−1.33)[a]			
Belgium, Brussels	1980	EAAS	(0.13−0.38)	(<0.02−0.05)		133
China	1981	F	(5−159)			226
China	1986	F	1.72			227
			(0.37−12.27)			
Denmark	1993	FI-HG-AAS		(0.018−0.028)		214
France	1981	GC-ECD	(<2−10)			191
France, Bordeaux	1988	PIXE	2[a]			228
Germany, Darmstadt	1976	INAA	1.1[a]			131
Germany, Siegen	1978	HPLC	<0.32			192
Germany	1978	EAAS	(<0.12−3)			229
Germany	1985	HG-AAS		321	67	193
Greece	1985	F	(0.205−0.214)			105
Italy, Pisa	1988	ND-AFS	0.203 ± 0.007			230
Singapore	1994	CZE		<12		151
Sweden, Uppsala	1991	HG-AAS	(0.203−0.222)			87
United States, New Mexico	1974	EAAS	5			138
United States, New York State	1980	EAAS	<5			110
United States	1988	HG-AAS				13
Nevada, Sun Valley			<3.1			
Wyoming, Casper			1.7 ± 0.4			
Wyoming, Jade Hills			189 ± 10.8			
Wyoming, Red Butte			496.1 ± 45.6			
USSR, Moscow	1977−79	F	0.125	0.05	0.075	217
USSR, Moscow	1983	IC	0.3 ± 0.02[a]			204
		INAA	0.2[a]			
Venezuela	1972	F				231
Caracas			0.186			
Villa Bruzual			0.204			

[a] Units of $\mu g\ kg^{-1}$.

the ratio of the two species can be used as an indicator of the redox potential of natural waters. Some investigators[80,158,259] have suggested that most of the Se in seawater should be present as the thermodynamically stable hexavalent state. The Se(IV), although thermodynamically not favored, is found in deep water where, probably due to kinetic stability, it persists as the product of the vertical transport and biological reduction of Se(VI).[158] However, Chau et al.,[260] because of the oxidation−reduction potential, concluded that the tetravalent state was the most probable.

Table 8. Selenium Species Concentrations in Tap Water, Freshwater, and Swimming Pool Water

procedence	date	method	Se_{tot} (μg L^{-1}) (min-max)	Se(IV) (μg L^{-1}) (min-max)	Se(VI) (μg L^{-1}) (min-max)	ref(s)
			a. Tap Water			
Belgium	1979−81	EDXES	(0.31−0.32)	(0.05−0.07)		100
Belgium	1982	EDXF	(<0.04−1.33)[a]			225
Canada, Halifax	1978	INAA	<2[a]			232
China	1989	HG-AAS		(0.048−0.082)		213
China, Changdun	1989	DPP	0.047 ± 0.004	0.014 ± 0.002	0.033	188
Denmark	1993	FI-HGAAS		(0.018−0.034)		214
Finland	1993	F	0.045			74
Finland	1993	F	0.0347	0.0109	0.0205	89
Germany, Darmstadt	1976	INAA	1.1[a]			131
Greece	1984−85	F				105
			(<0.100−0.200)			
Athens			(0.103−0.132)			
India, Bombay	1987	RNAA	11 ± 4			194
India, Bombay	1986	RNAA				134
Colaba				190 ± 10[a]		
Dadar				31 ± 2[a]		
Ghatkopar				73 ± 1[a]		
Malad				335 ± 5[a]		
India, Bombay	1990	RNAA				125
Borivali			23 ± 1			
Colaba			190 ± 10			
Dadar			31 ± 2			
Ghatkopar			73 ± 1			
Malad			35 ± 5			
The Netherlands, Petten	1976	INAA	0.16 ± 0.02	0.06 ± 0.01	0.10 ± 0.03	101
New Zealand	1980	F	0.0458			233
New Zealand, Hamilton	1980	F	(0.028−0.044)			126
Spain, Palma de Mallorca	1990	SP		1.3		135
United States, Kansas	1976	PIXE	<61[a]			234
United States, New Mexico	1978	HG-AAS	537 ± 650			215
			(26−1800)			
USSR, Krasnoyarsk	1980	ND-AFS	0.0835 ± 0.0024			202
USSR, Moscow	1981	IC		0.10 ± 0.01	0.21 ± 0.01	203
Venezuela, Mérida district	1988	HG-AAS	9.5 ± 0.7[a]			235
			b. Fresh Water			
Israel	1988	INAA	0.36 ± 0.08			85
			(0.26−0.48)			
The Netherlands, Petten	1976	INAA	0.20 ± 0.02	0.20 ± 0.01	0.00 ± 0.03	101
The Netherlands, Petten	1989	INAA		0.023 ± 0.004		86
United States, Utah	1976	HG-AAS	(0.4−22)			236
			c. Swimming Pool Water			
Belgium	1979−81	EDXES				100
chlorinated water			0.33	<0.04		
ozonized water			0.20	<0.04		
Italy, Pisa	1988	ND-AFS	0.095 ± 0.004	<0.006		230

[a] Units of μg kg^{-1}.

Eutrophic coastal ecosystems should prove to be useful models in which new methods of trace analysis can be applied to examine such fundamental biochemical processes. Thus, Cutter[98] presents data on Se species in reducing and anoxic waters from the Saanich Inlet, an intermittently anoxic fjord located on Vancouver Island (Canada), obtained in 1981 by HG-AAS method. The station (48°32.2′N, 123°32.7′ W) has a water depth of 196 m. The interface between H_2S and O_2 was *ca*. 175 m. A suboxic zone, characterized by low O_2 values and nitrate reduction, extended from approximately 110 to 170 m; waters above these depths were considered oxic. Speciation was made, which includes selenite, selenate, total dissolved selenium, hydrogen selenide (HSe^- + H_2Se), and dissolved organic selenide (dimethyl selenide and Se-containing amino acids), and were measured, and diagrams show the occurrence of these species with regard to the depth. In the anoxic region, no detectable selenate, selenite, hydrogen selenide, or dimethyl selenide was found, or only at levels which are almost below the limit of detection. This fact suggests that some removal mechanism could be operative but the presence in these reducing waters of about 1 nmol L^{-1} of dissolved organic selenide indicates that the regeneration of Se in the form of organic species may be the dominant process.

Takayanagi et al.[154,185] studied waters of Chesapeake Bay and the Atlantic Ocean off Cape Henry; about 60% of the total Se found was organically bound. A positive correlation was found[80] between nitrate reductase activity and the concentration of Se(IV) in seawater, suggesting that Se(IV) may be formed in coastal waters by the combination of NADPH or NADH, iodate/iodide, and nitrate reductase. Salinity did not correlate well with total Se, Se(IV), or Se(VI). Correlations of Se(IV), Se(VI), and organic selenium compounds with the apparent oxygen utilization and nutrients such as nitrate and

Table 9. Selenium Species Concentrations in Rainwater and Snow

geographical location	date	method	Se_{tot} ($\mu g\ L^{-1}$) (min-max)	Se(IV) ($\mu g\ L^{-1}$) (min-max)	Se(VI) ($\mu g\ L^{-1}$) (min-max)	Se(−II,0) ($\mu g\ L^{-1}$) (min-max)	ref(s)
			a. Rain Water				
Belgium	1979	EAAS	0.91				133,237
Belgium, Antwerp	1979−81	EDXES	(<0.05−0.25)	(<0.04−0.05)	(<0.05−0.20)		100
Belgium, Gent	1978	INAA	<3				61
Belgium, Mechelen	1986	DPSV	(<0.1−1.6)				104
Finland		F					52
	Spring, 1990		0.126 ± 0.0439 (0.0736−0.222)				
Helsinki	Oct, 1990		0.114 ± 0.0216 (0.0677−0.156)				
Finland, Helsinki	1992	F	0.0435	0.0263	0.0147		89
Germany	1985	HG-AAS		2			193
Greece	1988	F	(100−210)				105
Japan, Tokyo	1981	F	(0.0047−0.1176)	(0.0047−0.1042)			57
The Netherlands	1987	INAA					159
Lelyst			(0.054−0.212)				
Petten			(0.082−0.184)				
United States, California, La Jolla	1978	HG-AAS		0.0524	<0.005		76
United States, Bermuda	1986	HG-AAS	0.174				58
United States, Delaware, Lewes			0.030				
USSR	1975	inverse voltammetry	<0.001				238
USSR (Krasnoyarsk)	1978	ND-AFS					202
country			0.0475 ± 0.0016				
city			0.116 ± 0.004				
Venezuela	1982	GC	(<13400−56900)				65
			b. Acid Rain Water				
Canada	1981	INAA	0.14 (0.012−0.62)				79
			c. Snow Mantle				
Antartide	1975	INAA	0.17				239
Belgium, Antwerp	1979−81	EDXES	0.29	0.22			100
Finland	Apr, 1990	F	0.0303 ± 0.0173 (0.0131−0.0766)				52
	Feb−Mar, 1991		0.0729 ± 0.0246 (0.0180−0.142)				
Finland, Helsinki	Mar, 1990		0.0935 ± 0.0625 (0.0414−0.246)				
	Jan, 1991		0.0446 ± 0.0318 (0.0146−0.170)				
	Jan, 1992		0.0589 ± 0.0383 (0.0258−0.228)				
Finland	1993	F	0.138				74
Finland	1993	F					89
Helsinki			0.0509	0.0173	0.0285		
Viikki			0.0559	0.0166	0.0316		

phosphate in three zones of the North Pacific Ocean were determined.[180]

A temporal study of the response of Se levels and redox state to pulses of primary productivity in a fjord ecosystem (Bedford Basin, Nova Scotia, Canada) between January and April 1981 was performed.[160] The concentrations measured by GLC of Se(IV), Se(VI), and total Se were 10 pmol L^{-1} with RSD of ±4, ±10, and ±6% , respectively.

The regenerative and biogeochemical cycles of Se are quite complex. Experiments on the regeneration of Se from two types of marine particulate matter, zooplankton and source term material (fresh biogenic particles produced by these zooplankton), were made.[179,261] In suboxic waters of the tropical Northeast Pacific[179] organic selenide concentrations rise, and Se(IV) values decrease. Hydrogen selenide is believed to be an intermediate in the conversion of Se(IV) and Se(VI) to organic Se compounds by marine algae, plants, and animals.[262] The downward flux of particulate Se generally decreases with depth, and fluxing particulate Se is primarily in the (−II) oxidation state.[179] Selenium(−II,0) is correlated with indicators of biological activity such as chlorophyll-a, bioluminiscence, and primary productivity.[179] On the other hand, in surface waters biotic processes produce reduced species,[261] while in deep anoxic waters lateral advection and sinking detritus deliver oxidized species from surface waters. In both cases, slow rates of conversion allow unstable species to persist.[261] These data allow a reevaluation of the internal biogeochemical cycle of Se. This cycle includes selective uptake, reductive incorporation, particulate transport, a multistep regeneration, and kinetic stabilization of thermodynamically unstable species.[179] These aspects are also studied by others investigators.[183,263]

The biologically mediated flux of Se from surface water to deep water in seas is estimated to range from 7.4×10^6 to 10.0×10^6 kg Se yr^{-1}.[160] Selenium fluxes between the ocean interfaces are estimated.[3,180] About 75% of Se in the eutrophic layer is utilized by

Table 10. Selenium Species Concentrations in Wastewater

procedence	date	method	Se_{tot} (μg L^{-1}) (min-max)	Se(IV) (μg L^{-1}) (min-max)	Se(VI) (μg L^{-1}) (min-max)	ref(s)
Belgium	1975	XRF	(<30−1800)[a]			240
Belgium	1979−81	EDXES				100
influent water			(0.36−0.47)	(0.05−0.13)	(0.31−0.34)	
effluent water			(0.10−0.20)	(<0.04−0.18)		
China	1988	HG-AAS	3.44 ± 0.10			93
Germany, Pittsburg	1974	AAS	(1−105)			241
		colorimetry	(1−90)			
Germany, Siegen	1978	HPLC	2.1 ± 0.116			192
Germany	1980	INAA	(1.41−1.68)			78
Japan	1975	EAAS		(480−700)		242
Japan	1976	EAAS	(14−38)	(12−14)	(26−27)	107
Japan	1979	EAAS	(25−280)			169
Japan	1980	ND-AFS ($NaBH_4$ reduction)	(0.9−8.4)			243
		ND-AFS (Zn reduction)	(1.1−8.0)			
Poland	1989	SP	(51−236)			244
United States, Chicago	1975					245
metal industry		EAAS	(13−14)			
		HG-AAS	(11−16)			
power plant		EAAS	(11−15)			
		HG-AAS	(11−13)			
sewage plant		EAAS	(10−15)			
		HG-AAS	(12−13)			
United States	1978	EDXES		<2.4		201
United States	1978	EAAS	(0.4−9.3)			237
United States, California; San Francisco Bay[a]	1987−88	EAAS	(0.4422−156.18)	(<0.00079−128,07)	(<0.00079−60.96)	83
United States, California	1987−88	EAAS				84
reffinery effluents[b]			(5.46−202.14)	(0.054−141.34)	(<0.00079−57.40)	
municipal discharges[c]			(0.24−2.19)	(0.011−0.598)	(<0.00079−1.239)	
USSR, Moscow	1978−79	F	(0.182−0.268)	(0.071−0.115)	(0.111−0.153)	217

[a] Se(−II,0): (<0.00079−24.71) μg L^{-1} (ref 83). [b] Se(−II,0): (<0.00079−148.92) μg L^{-1} (ref 84). [c] Se(−II,0): (<0.00079−1.17) μg L^{-1} (ref 84).

phytoplankton proving that Se is a biointermediate element in the ocean.

The redox potential and pH are key factors in the biogeochemistry of Se.[264] Under natural supergene conditions, Se(IV) is stable and can pass into solution especially when the pH values are high, but it is easily adsorbed by solid phases, particularly by the clay minerals with which it comes into contact.[186] The fixation of total Se decreases at pH above 7,[65] and at pH > 11 it is not adsorbed at all.[186] If the weathering process takes place under acid conditions, Se will be mostly immobile. But if the weathering process takes place under basic conditions, the Se is more likely to enter into solution as a selenite ion[186] or may be oxidized to soluble selenate. Values of the redox potential (*E*h) can be used to estimate the upper boundary of the zone of possible pollution by Se since it cannot be present at concentrations higher than 1 ng L^{-1} at *E*h < 130 mV, pH 7, or at *E*h < 50 mV, pH 8.[265] Seasonal changes in soil moisture related to irrigation create changing reduction/oxidation conditions within the soil profile. These changing soil conditions affect the solubility of minerals containing Se and its transport.[59] Thus, the mean water Se concentration of lakes surrounded by cultivated fields was significantly higher than the Se concentration of forest lake waters collected in August, but not of samples collected in spring.[90]

Samples of waste water from the San Luis Drain and the Kesterson Reservoir contain very high Se levels (140 to 1400 μg L^{-1}).[266] The influence of redox potential and pH on Se solubility, speciation, and volatilization was studied in sediments of Kesterson Reservoir, CA.[264] Under reduced conditions, Se solubility was low and controlled by a selenide phase. Selenium(−II,0) comprised 80−100% of the total soluble Se. Selenium(VI) was the predominant dissolved species present, after oxidation, constituting 95% (at pH 8.5−9) to 75% (at pH 7.5−6.5) of the total soluble Se.[264]

Also, samples of water collected in the desert area of western Australia were studied.[186] In this area, the waters are very strongly oxidizing and the levels of organic matter are very low. These conditions should facilitate the solubilization of Se. Thus, the Se content is relatively high, although there is no increase in Se as the evaporitic processes continue.

C. Depth

Table 2 shows an increase of total Se and Se(VI) concentrations in seawater when depth increases. However, Kai et al.[163] found no variation of Se(VI) and total Se concentrations with depth (0−200 m) in the Indian Ocean; Se(IV) increased gradually with depth. Organic selenium concentrations were below detection limits. In the Pacific Ocean and Bay of Bengal[267,268] the Se(IV) and total Se concentrations increased gradually with depth (0−1000 m); therefore, Se(IV) level correlated with total Se concentration. Organic selenium concentration was very low and almost constant with depth. The Se(VI) concentration was predominant in the surface water at a depth below 200 m. Correlations between total selenium and Se(IV) with depth are shown in Figures 2 and 3; data are taken from refs 178 and 179, respectively. Concentrations of Se(VI) are calculated by difference and really represent the sum of Se(VI), Se(−II), and organoselenium compounds.

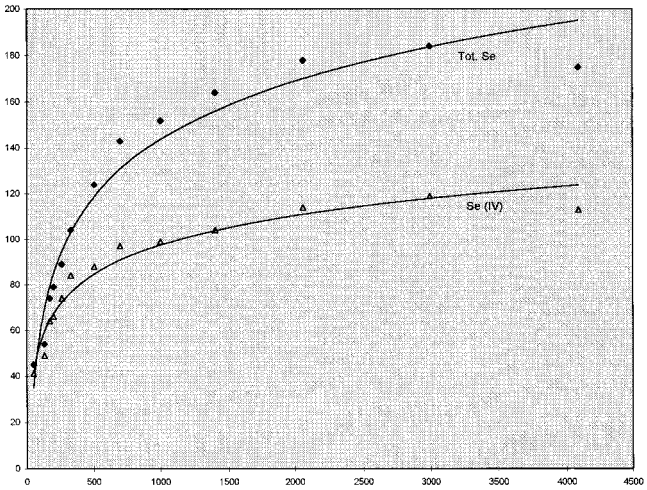

Figure 2. Correlations between total selenium and Se(IV) with depth according to ref 178. (Top) $y = 36.362 \ln(x) - 107.39$. $R^2 = 0.9583$. (Bottom) $y = 18.64 \ln(x) - 31.218$. $R^2 = 0.9548$.

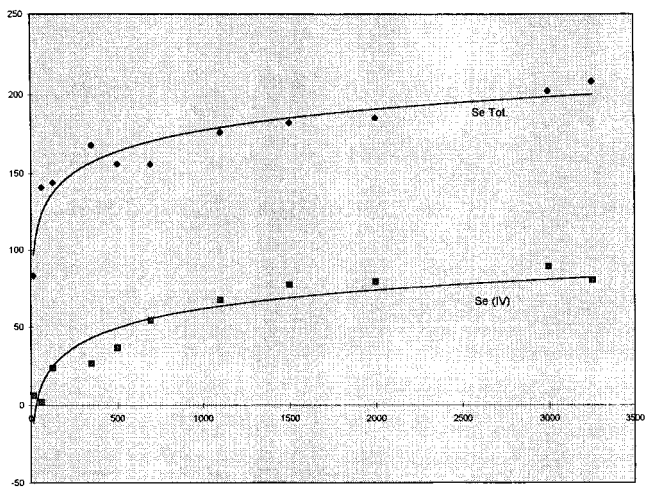

Figure 3. Correlations between total selenium and Se(IV) with depth according to ref 179. (Top) $y = 19.212 \ln(x) - 44.499$. $R^2 = 0.9108$. (Bottom) $y = 17.367 \ln(x) - 58.503$. $R^2 = 0.8958$.

The relationship of the distribution of dissolved Se(IV) and Se(VI) in three oceans was determined.[165] Pacific and Indian Oceans have Se(IV) concentrations of 50 pmol L^{-1} in surface waters, and 790 pmol L^{-1} in deep waters. With regard to Se(VI) contents, 500 pmol L^{-1} in surface waters and 1400 pmol L^{-1} in deep waters were measured. Atlantic Ocean concentrations are 30−40% lower. The low Se(VI) values found in certain zones are the result of advection of water masses from regions of intense oxygen minimum, but a corresponding selenite maximum was not observed.[165] In surface waters of the Pacific ocean,[179] organic selenide makes up ~80% of the total dissolved Se, and according to Sugimura et al.,[177] it only reaches a maximum of 45%; Se(IV) concentrations are uniformly low, and Se(VI) concentrations rise with increased vertical mixing. Deep ocean waters are enriched in Se(IV) and Se(VI), whereas organic selenide is nondetectable. The Se(IV) and Se(VI) that mix into the anoxic waters are probably reduced to HSe^- and precipitated as insoluble transition metal selenides; hence, no detectable dissolved H_2Se is observed in the anoxic waters. However, Aono et al.[180] found that the vertical profiles of organic selenium in the upper 1 km layer are similar to those of nutrients with some exceptional high values; in the bottom layer, the concentration of organic Se increases with depth.[180] Some authors[154,162,269] pointed out that seleno amino acid (known as selenomethionine) is the most likely organic selenium in sea water. The level of total dissolved Se[180] increases with depth from 0.5−1.0 nmol L^{-1} in the surface layer to 1.3−1.4 nmol L^{-1} at the depth of 1 km approximately, whereas it is almost constant or slightly increases with depth in the deeper layers. The content of Se(VI) is variable, but its mean concentration in waters below 2 km is higher than that in the upper 1 km layer.[180]

In the Mediterranean waters of Gulf of Lyons (France) the total dissolved Se increases from 500 pM in the surface waters to 900 pM in the deep waters; organic Se was observed in deep water, which differs from those of Atlantic and Pacific Oceans.[173] The distributions of total inorganic Se, Se(IV), and Se(VI) are strongly related to silicate and phosphate concentrations as in the major oceans.[159,173] Sugimura et al.[166,167,177] have determined fluorimetrically the chemical forms of Se in seawater at different depths. The ratio of Se(−II) to total Se was 0.5−0.8 in the surface water and 0.4−0.6 in the deeper water. In the Indian Ocean, the Se(VI) to total Se concentration ratio was 0.8, at a depth below 200 m.[163]

The vertical distribution of selenium in the humic acids, carbohydrates, organic acids, and amino acids fractions in the Bering Sea,[162] Lake Biwa (Japan), and ocean waters was studied.[270] In lake waters[90,208] the vertical distribution of dissolved Se was nearly uniform, except during blooms of algae. The Se levels increased with depth and on the shoreline when blooms of algae started. These changes in the Se concentration cannot be ascribed to thermal stratification or to the deoxygenation of the bottom waters.[90] A small increase in the selenite fraction, such as 5−20 ng L^{-1}, could contribute to algae blooms.[209]

On the other hand, an inverse correlation between Se concentrations and the depth of drilled wells indicates that the deeper wells were less influenced by Se from surface sources. Wells located outside household areas had the lowest Se concentrations.[91]

IV. Concluding Remarks

Selenium is an essential micronutrient for human and other species. Some diseases are associated with low Se intakes. Humic acids are the main reservoir of Se in soils. Fulvic acid, present in some drinking waters, inhibits the absorption of Se taken from diet, and can produce Se deficiency. Also, Se is a growth factor for phytoplankton and is rapidly accumulated; Se is further enriched along the food chain.

Speciation measurements of Se are necessary for a whole study of toxicity, bioavailability, bioaccumulation, interactions with other substances, and transport in biological or environmental media. Sampling and storage are fundamental steps that can change the Se speciation. The water samples must be filtrated but not acidified before storage. Only a few analytical methods allow speciation measurements. Thus, the speciation frequently applied in many

investigations is based on the determination of Se(IV) and total Se concentrations; Se(VI) is calculated by difference. In consequence, organo-Se compounds in the sample would cause higher and erroneous Se(VI) values. On the other hand, oxidizing or reducing agents may partly convert organo-Se compounds into the inorganic forms, or transform these inorganic forms into a single oxidation state.

Seasonal changes in soil moisture related to irrigation create changing redox conditions within the soil profile. These changing soil conditions affect the solubility of minerals containing Se and its transport. Under reduced conditions, and/or at low pH values, Se solubility is low and controlled by a selenide phase. The oxidizing conditions and the high values of pH facilitate the solubilization of Se.

In suboxic and anoxic waters, where reducing conditions are established, Se(IV) concentrations decrease and organoselenium compounds levels rise. Selenium(−II,0) correlate with indicators of biological activity. Hydrogen selenide is considered an intermediate in the conversion of Se(IV) and Se(VI) to organic Se compounds by marine organisms. Seleno amino acids are the most likely organic selenium species in seawater. The Se(IV) persists in deep waters as the product of the vertical transport and biological reduction of Se(VI); a positive correlation was found between nitrate reductase activity and Se(IV) concentration. In anoxic waters, lateral advection and sinking detritus deliver oxidized species from surface waters.

Soils retain more Se(IV) than Se(VI). Precipitation can be one source of soil Se, and seems to have no impact on groundwater Se. Selenium-enriched fertilizers cause an increase in the Se concentrations in rivers, lakes, and groundwaters. Thus, Se concentrations in natural waters are correlated with the Se content of soils. Furthermore, significant correlations were found between Se in streams or river waters, with Se in groundwater and well water. With regard to salinity in estuarine water or seawater, the lack of available data does not allow us to come to any firm conclusion.

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