



Review Paper

# A review on environmental selenium issues

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## Abstract

Selenium is an essential element since it is necessary for metabolism and is also toxic to the living things if it is consumed above the desirable limit. For instance, up to 40 µg per d of dietary selenium is essential for human health; however, consumption of a little over 400 µg per d could result in adverse physiological problems. In the environment, selenium occurs in different species; of which selenate and selenite are its most toxic forms accounting for 95% of selenium toxicity. Though, selenium fortification is important for normal human physiology in selenium deficient environments, it needs to be minimized or removed from selenium rich environmental media. Thus, its quantification is significantly important to control per limit. Currently there is advancement in the detection and quantification of selenium in environmental including the use of a Hydride Generating Atomic Absorption Spectroscopy. Due to the excess occurrences of selenium in different locations the removal techniques from geogenic or anthropogenic sources include microbial metabolism, phytoremediation, sorption, membrane separation, coagulation, ion exchange and catalytic reduction. Most of all, the microbial removal is applied in drinking water supply and in selenium recovery from wastewater sludge. Though current selenium removal from sorption studies reported better efficiency, phytoremediation appears attractive due to its field scale application advantage. However, the fate of selenium following phytoremediation remains unaddressed.

**Keywords** Selenium · Toxicity · Occurrence · Environment

## 1 Introduction

Both geogenic and anthropogenic activities govern selenium in the environment. Environmental biogeochemical conditions control the bioavailability and the nature of selenium species [1–5]. Geogenic pollution of groundwater is referred to as the natural occurrence of elevated concentration of certain elements in groundwater having negative health effects [6]. In fact, selenium is listed among the minor constituents in geogenic water pollution (0.1–100 µg/l). Moreover, the narrow tolerance limit of selenium brings serious concerns through deficiency as well as toxicity in the biological and environmental systems. Toxicity generally results when certain ions are taken up with the soil–water and accumulate in some organs of plants and animals. Though geogenic selenium

contamination is a concern for toxicity from drinking water, plants are the main source of dietary selenium [7].

By elemental category, selenium is nonmetal and sometimes it is considered as trace element. Geographically, it is widely distributed throughout the world, but only in small quantities. It is more commonly found together with the sulfides as the selenides in the ores of such metals as iron, lead, silver, and copper [8]. Selenium salts are toxic in large amounts, but trace amounts are necessary for cellular function in many organisms, including all animals [9, 10].

Fortified selenium is an ingredient in many multivitamins and other dietary supplements, including infant formula in many countries. In human, low dietary selenium intakes are associated with health disorders including oxidative stress-related conditions, reduced fertility and immune functions and an increased risk of cancers. For

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that purpose the daily intake in the diets differ worldwide, for UK adult female and male 60 and 75  $\mu\text{gSe/d}$  respectively are expected while for the World Health Organization (WHO), it is 10  $\mu\text{g/l}$  in water [11, 12]. Contrasting the former, a study in Burundi of Africa that reported risk in deficiency with average intake of 17  $\mu\text{gSe/d}$  from diet [13]. In fact, intake depends on age and sex [14]. However, selenium turns out to be toxic in low margin beyond limit causing hair and nail loss, cancer and even death as detailed later in the toxicity section of this article.

Until recently a lot of research have been done on selenium either as toxic or as nutrient. As of the middle of the 1990s approximately 100,000 research papers had been published on the topic of selenium since it was discovered by the Swedish chemist Jons Jakob Berzelius in 1817 [5]. However, it is only recently that its geogenic contamination and bioremediation, selenium recovery as resource, selenium detection methods, and occurrence as well as distribution especially in the African continent have begun to be discovered.

Therefore, the objective of this mini review is to comprehensively present the nature, geochemistry, toxicity, biochemistry, detection and quantification methods reported on selenium in the past researches. Further it systematically reports the remediation techniques applied to selenium at various scales and shows fillable gaps for further research.

## 2 Selenium property and toxicity

### 2.1 Physicochemical properties of selenium

The physical, atomic properties and periodic table position of selenium is shown in figure one. Selenium appears

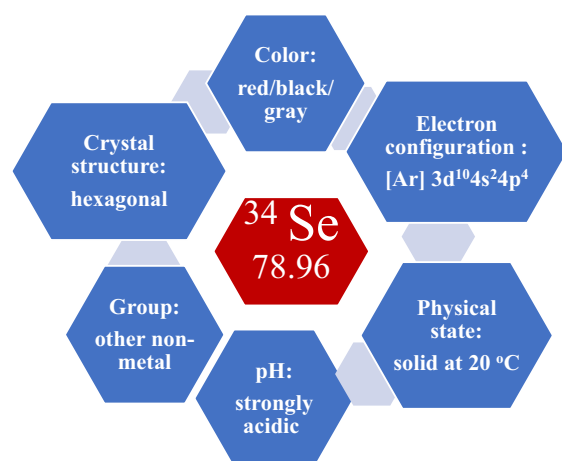


Fig. 1 Appearance and properties of selenium

as black and red allotropes (Fig. 1). It was found out long ago that its electrical resistance is greater in the light than in the dark [15, 16]. Analogous to the behavior of other chalcogens, selenium forms hydrogen selenide,  $\text{H}_2\text{Se}$ . It is a strongly odiferous, toxic, and colorless gas. It is more acidic than  $\text{H}_2\text{S}$ . In solution it ionizes into  $\text{HSe}^-$  [17].

Chemically, selenium is reactive towards many reagents allowing their incorporation into organic compounds. Further, symmetric or non-symmetric diselenides are often used as starting materials for the preparation of more complex chalcogen-containing derivatives [8]. Selenium also forms complexes with heavy metals including cadmium, sparing its biological effects as reported earlier [18].

Although the element selenium itself is not toxic, many of its compounds are extremely toxic. For instance,  $\text{H}_2\text{Se}$  is a colorless, foul-smelling gas that is poisonous. It also forms selenides with most metals (for example, aluminum selenide, cadmium selenide, and sodium selenide). In groundwater, selenium exists in the dissolved forms of Se (+VI), Se (+IV), and Se (-II). Selenium (+IV) is more toxic due to its higher bioavailability.

### 2.2 Selenium in plants: toxic dose, symptoms and distribution

Though debatable, it has been reported that selenium is not an essential element to plants but it can be toxic to them [19]. Generally, the plant toxicity of inorganic selenium, namely selenate and selenite anions, is higher than the organic forms of selenium depending on three major factors. Absorption of the anions by the roots and the subsequent translocation into other parts of the plant is the first factor. Secondly, the metabolism of the anions into organic forms in the cell and thirdly the interference of cellular biochemical reaction in plants due to selenium metabolite of which replacing the role of sulfur [20] and protein functions are worth to mention.

The distribution of selenium in plants is all over it, from the root to its aerial parts. However, there is dissimilarity between selenate and selenite in distribution. Furthermore, the toxicity and tolerance character vary among plants [21]. The later mainly depends on their ability to divert selenium away from the accumulation of selenocysteine and selenomethionine that ranges from 2 mg/kg in non-accumulators, such as rice, and 330 mg/kg in white clover, to several thousands of mg/kg in the accumulator *Astragalus bisulcatus*. For instance, in non-accumulator's selenium toxicity occurs under about 10–100 mg Se/kg of dry weight (DW). Toxicity occurs mostly due to the accumulation of selenium in the plant tissues. The characteristic symptoms due to selenium toxicity includes stunting, chlorosis, and fading of leaves, interfering with chlorophyll combination and nitrate accumulation that is generally

assumed to occur from selenium levels higher than 1 mg/kg [22–25].

### 2.3 Selenium in animals: toxic dose and health symptoms

Earlier, selenium is identified as micronutrient for bacteria, mammals and birds earlier; however, it is now recognized as a problem if it is consumed in excess. A case in point is the alkali disease in livestock that was observed in the American great plains since then concern on chronic and acute selenosis raised [26]. Based on testes on laboratory animals, the minimum lethal dose of selenium as acute toxicity in rabbits, rats, and cats was between 1.5 and 3.0 mg/kg body weight as sodium selenite or selenate and irrespective of the mode of entry of the compound into their body. During acute toxicity, laboratory animals showed garlicky breath odor, vomiting, dyspnea, tetanic spasms, and death from respiratory failure accompanied by pathological changes. Chronically, a selenium dietary dose of 4–5 parts per million (ppm) proved to cause growth inhibition [27].

In farm animal's selenium acute toxicity occurs due to the ingestion of seleniferous accumulator plants or due to excess supplements with following signs of severe distress that include labored breathing, abnormal movement and posture, and prostration and diarrhea, and even death in few hours [27, 28]. The chronic selenosis also known as alkali disease occurs in animals consuming grains containing 5–40 mg Se/kg over a period of several weeks or months with signs and symptoms that include liver cirrhosis, lameness, hoof malformations, loss of hair, and emaciation [29].

The determination of selenium level in animal tissues and organ has been investigated along with its metabolism in sheep. Findings revealed that the accumulation of selenium varies among the different organs, the liver being the highest accumulator. Further the share of selenium through enzymatic extracted in the form of amino acid compounds was 40% [30]. In a related earlier study in Burundi of Africa, kidney of goats and cows is found to be the accumulator organ for selenium ranging 994–1852 ng/g wet weight for goats and 1056–1801 ng/g wet weight for cows. This finding has relevance to note the safety and adequacy of nutrients for people in developing countries; however South Africa is the only African state on the list of seleniferous areas which rather mentioned Africa in relation to selenium deficiencies in crops and livestock as reported in a recent study [31, 32].

Selenium toxicity in animals or plants edible to human is a primary concern since bio-magnification of selenium starts when animals consume plant biomass that has impounded large amounts of selenium and get magnified

in food chains that can involve aquatic selenium pollution [33, 34]. Besides, due to irrigation run-off concentrations of selenium tend to be very high in aquatic organisms in many areas. Thus, the bioaccumulation potential of selenium can further cause toxicity to the natural ecosystem. When animals absorb or accumulate extremely high concentrations of selenium it can cause reproductive failure and birth defects [35–37].

### 2.4 Selenium in humans with epidemiological perspective

Water, food and air in decreasing order are identified earlier as source of human toxicity from selenium [38]. Moreover, drinking water sources remains to be a concern in geogenic selenium contamination. For instance, in many French regions, geogenic sedimentary sources of selenium were identified as responsible for the selenium concentrations exceeding the European limit in many wells designated to produce drinking water [36]. Selenium toxicity is prevalent in 1000 ha in Hoshiarpur and Nawanshahar of Nigerian districts where about 11 and 4% of groundwater samples were found unfit for drinking and irrigation purposes, respectively [35].

Selenium carries the narrowest range between its nutritional deficiency (< 40 µg/d) and toxicity (> 400 µg/d) with respect to the daily intake [17] (Table 1). Selenate and selenite have an oxidant mode of action in living organisms and are very toxic. In humans, the toxic effects of long-term high level environmental selenium exposure are manifested in dermatological effects, nails, hair and liver problems [39].

Selenium exposure can result in either acute or chronic health problems. An acute exposure is explained by selenium neurotoxicity while the chronic exposure is explained by the toxic effect on endocrine function especially in the synthesis of thyroid hormones and if the dose exposed is relatively lower [39, 40]. For instance, a report from China indicated that clinical and biochemical signs occur at a daily intake above 0.8 mg. Conversely, inadequate concentration of selenium in Chinese diet is a cause for Keshan disease which is the degeneration of articular cartilage between joints, thyroid disease and different forms of cancer [26, 38].

To get the nutrient benefit from selenium diet fortification became an alternative. Care should be taken as in product labeling; otherwise, toxicity outbreak is inevitable as exhibited in the identified outbreak due to the selenium in a liquid dietary supplement in a certain town in the United States. Based on epidemiological observation, the median estimated dose of selenium consumed was 41 749 µg/d with frequently reported symptoms that include diarrhea, fatigue, hair loss, joint pain, nail discoloration or

**Table 1** Commonly accepted drinking water quality guidelines for selenium [62, 63]

Constituent	Drinking water standards recommended by Bureau of Indian Standard (BIS) and the World Health Organization (WHO) (mg/l)			Undesirable effect when present beyond acceptable limit in drinking water
	BIS (2012)		WHO (2011)	
	Acceptable limit	Permissible limit in the absence of alternative source	Guideline values	
Selenium	0.01	No relaxation	0.01	Very low selenium status in humans has been associated with juvenile, multifocal myocarditis and chondrodystrophy. Very high selenium status causes gastrointestinal disturbance, skin discoloration and tooth decay

brittleness, and nausea [41, 42]. Nevertheless, acute toxicity problem is rare due to diet diversity despite the rising concern over environmental selenium contamination in the United States.

Elsewhere in New Zealand and Venezuela, acute selenosis was observed due to the selenium rich food consumption [43]. In a related fact the daily intake of Venezuelan children with clinical signs was estimated to be about 0.7 mg. Effects on synthesis of a liver protein were also seen in a small group of patients with rheumatoid arthritis given selenium at a rate of 0.25 mg/d in addition to selenium intake through food. No clinical or biochemical signs of selenium toxicity were reported in a group of 142 persons with a mean daily intake of 0.24 mg (maximum 0.72 mg) from food [44].

### 3 Environmental fate of selenium

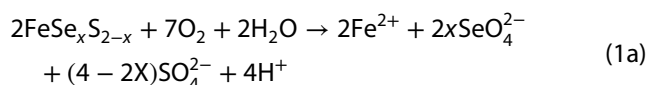
Selenium in the whole environment can be either from natural or anthropogenic sources forming cycles between them (Fig. 2). The natural bases of selenium include the weathering of selenium-containing rocks and soils and volcanic eruptions [45]. Anthropogenically, selenium pollution in the environment is hugely contributed by the coal mining and the use of selenium rich fossil fuels in industries that can account 40% of selenium in air as well as the aquatic systems that resulted in wastewater discharge limit of 5 µg Se/l [34, 37]. In that regard, selenium contamination in groundwater and surface water in numerous river basins worldwide has become a critical issue in recent decades [46, 47], especially due to the geogenic contamination. In order to foresee the mineralization, mobilization, and toxicity extent of selenium to plants, animals and human in natural systems understanding of its oxidation state is important. In geological formations, selenium transformation and speciation depend on the presence of nitrate (NO<sub>3</sub>), organic

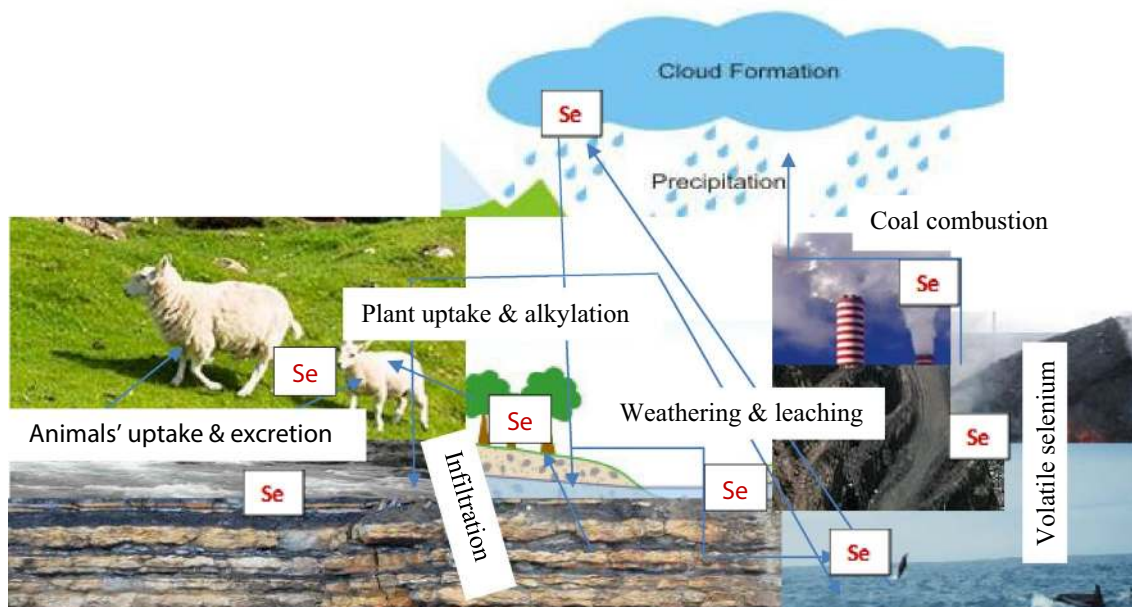
materials and clay content, pH and carbonates/bicarbonates for mobility and hence the risk associated [48–51].

Selenium concentrations in soils vary widely, from 5 to 1, 200, 000 µg/kg, being higher in soils of more recent volcanic origins. It is normally found in concentrations ranging 50–90 µg/kg of soil, but higher concentrations can be associated with some volcanic, sedimentary and carbonate rocks. Selenium occurs in environmental soils in several forms, according to its possible oxidation states: selenides (Se<sup>2-</sup>), amorphous or polymeric elemental selenium (Se<sup>0</sup>), selenites (Se<sup>4+</sup>) and selenates (Se<sup>6+</sup>) (IPCS, 1987; UK EGVM, 2002).

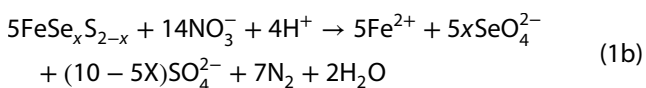
Regarding selenium speciation, acidic and reducing conditions reduce inorganic selenites to elemental selenium, whereas alkaline and oxidizing conditions favor the formation of selenates in the environment. Since selenites and selenates are both soluble in water, selenium is leached from oxic alkaline soils that favor its oxidation. In contrast, the elemental and selenides forms are insoluble in water; consequently, selenium inclines to be retained in wet and anoxic soils. Thus, selenium in alkaline soils is accessible by plants; however, the availability of selenium in acidic soils inclines to be restricted by the adsorption of selenites and selenates to iron and aluminum oxide soils (NRC 1983).

Based on the species extraction using 0.1 mol/l NaOH, all the four selenium compounds are present as anionic species based on their pKa values at a pH of 13. Being in state of dissolution or precipitation and absorption or desorption, selenium is present in almost all soils, particularly in irrigated agricultural aquifer systems underlain by or adjacent to shale formations containing seleno-pyrite where SeO<sub>4</sub> can be released through autotrophic reduction of O<sub>2</sub> or NO<sub>3</sub> [52] (Eqs. 1a, 1b).



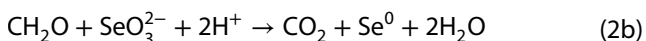


**Fig. 2** Selenium cycle in the environment near the surface of the earth. (Redrawn from [1] with permission from John Wiley and Sons. © 2016 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim)



Selenate is mobilized in oxidizing condition and is interfered by reducing condition as well as adsorption. Irrigation and agriculture are associated with Se mobility. In addition, selenium is subject to cycling in the plant–soil system similar to other nutrients such as nitrogen (N), phosphorus (P), and sulfur (S).

Selenium mobility and risk of toxicity are not limited to physico-chemical phenomena. Microbially-mediated chemical reduction reactions reduce  $\text{SeO}_4$  to  $\text{SeO}_3$  [Eq. (2a)] and  $\text{SeO}_3$  to either immobile  $\text{Se}^0$  [Eq. (2b)] or mobile selenomethionine (SeMet) suggesting the possible mitigation pathways for  $\text{SeO}_4$ . Almost all of the selenium removal techniques include reduction of  $\text{SeO}_4$  to  $\text{SeO}_3$ ,  $\text{Se}^0$ , or SeMet that in most case it is inhibited by the presence of  $\text{O}_2$  and  $\text{NO}_3$  which act as electron acceptors. However, it is suggested that there is a concentration of  $\text{NO}_3$  at which  $\text{NO}_3$  reduction and  $\text{SeO}_4$  reduction can even occur simultaneously [53].



The risk of selenium toxicity in the environment is affected by its mobility. In that regard experimental study by Bassil and co-workers revealed that even though the less fraction (10%) of selenium was mobilizable, 70% of it was Se (IV) which is the most soluble species [54]. Environmentally, the selenium pool exists much in the lithosphere followed

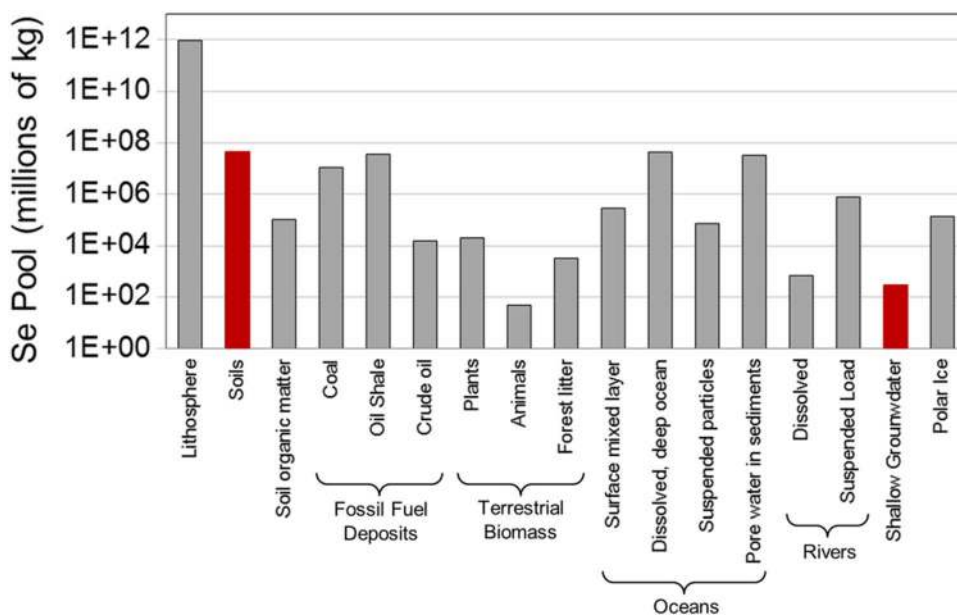
by the fossil fuel deposits and oceans (Fig. 3), thus, its geochemistry and hence the associated risk is also affected by climate variability [55].

#### 4 Geochemistry of selenium and bioavailability

Worldwide the occurrence of selenium is irregular. Selenium is widely distributed in the environment, but its natural geogenic concentration level is generally below  $1 \mu\text{g}/1$  in natural waters or below  $1000 \mu\text{g}/\text{kg}$  in rocks and soils provided that anthropogenic influences are only moderate [56]. Their distribution ranges from selenium deficit regions like the United Kingdom with a daily intake of  $< 55 \mu\text{g}$  to selenium rich regions like Canada with a daily intake between  $100$  and  $200 \mu\text{g}$ . Again, the intake amount is explained on the fact that selenium soil concentration is determined in many countries. Countries like Ireland, parts of the United State and India are in the toxic range while Yugoslav and Finland are deficient (Fig. 4).

Following its spatial variation, the daily selenium intake varies worldwide by country. For some regions of the world, selenium occurrence is scarce and raises issue of nutrient limitations rather than issue of toxicity. Accordingly, different countries attempted to trace its occurrence and dietary implication, whether its removal or fortification would be needed in their water supply scheme or not. Thus, selenium in Africa appears to be within limit, if not nutrient fortification is essential for most countries (Fig. 5).

**Fig. 3** Mass of selenium (in millions of kg) in various environmental pools worldwide. (Reprinted by permission from Springer-Verlag Berlin Heidelberg, *Hydrogeol J* [5]. © Springer-Verlag Berlin Heidelberg 2016)



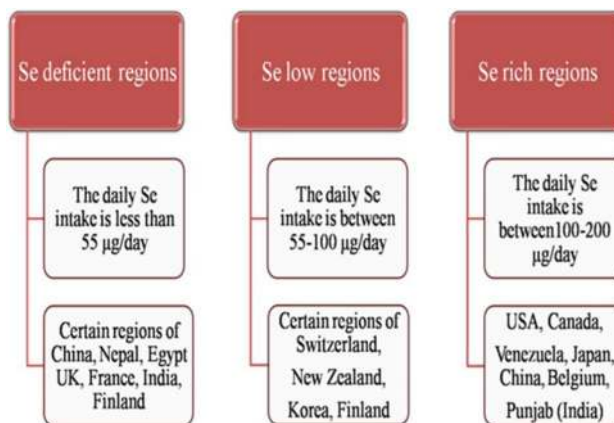
Interestingly, recent studies report the importance of selenium in reducing the risk of arsenicosis due to selenium mediation [57, 58], arsenic hit regions may even need selenium supplement to tackle arsenicosis. Selenium is widely distributed in the environment with average occurrence of 0.09 ppm and its occurrence or distribution has been investigated in rocks, soils, minerals, groundwater and surface water [27].

#### 4.1 Selenium in rocks

High selenium concentrations are associated with some phosphatic rocks, organic-rich black shales, coals, and sulfide mineralization, whereas most other rock types contain very low concentrations. Selenium deficient environments are far more widespread than selenium-containing ones. However, it should be recalled that health outcomes are not only dependent on the total selenium content of rocks and soils but also on the amount of selenium taken up into plants and animals as bioavailable selenium from its cycle in the environment (Fig. 2) [32].

#### 4.2 Selenium occurrence and distribution in minerals

Selenium naturally occurs in a number of inorganic forms, namely selenide, selenate, and selenite, but these minerals are rare. Selenium rarely occurs in its elemental state or as pure ore compounds in the earth's crust. It is found in metal sulfide ores, where it partially replaces the sulfur. Likewise, the organic compounds of selenium and



**Fig. 4** Outline of occurrence of selenium in different regions of the world as selenium-deficient, selenium-low and selenium-rich regions [7]

tellurium are known since the late nineteenth century [8]. Selenium is found as a major constituent of 40 minerals and a minor component of 37 others, chiefly sulfides [27].

Based on a reconnaissance survey conducted in South Africa by K Sami and AL Druzynski, selenium is not related to rock-forming silicates, and is most abundant in sulfide minerals, such as galena (commonly 0–15 ppm), arsenopyrite (42–57 ppm), pyrrhotite (5–63 ppm), marcasite (0–11 ppm), chalcopyrite (commonly between 10 and 50 ppm), pyrite (commonly between 0 and 50 ppm), and sphalerite (commonly between 10 and 50 ppm, can be as high as 900 ppm) [60].

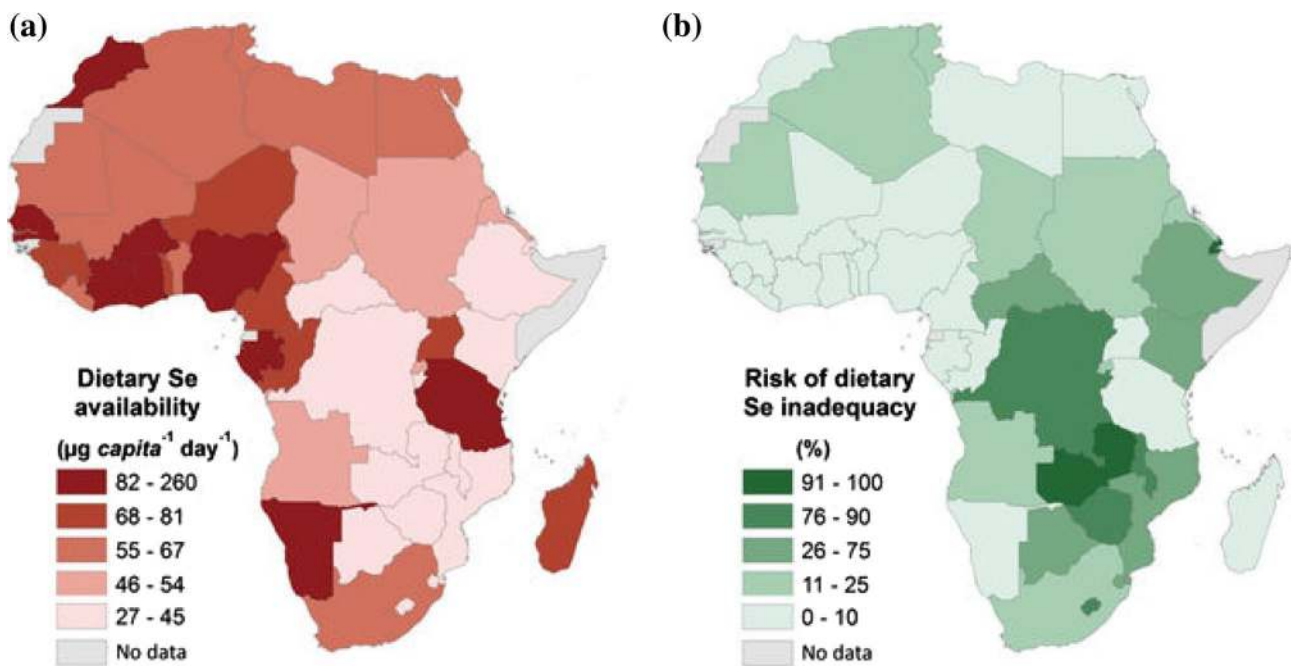


Fig. 5 Dietary selenium availability and risk of inadequacy in Africa. (Source: [59])

### 4.3 Selenium occurrence and distribution in soils

The occurrence of selenium in different soils is mainly a reflection of the underlying rock as well as practice of irrigation with selenium rich groundwater. The soluble selenite and selenate species in soil enter into plant metabolism; however, leaching and formation of insoluble complex by selenite accounted for losses into the environment like other insoluble selenium species. Most soils showed a selenium content ranging between 0.1 and 0.2 ppm while a maximum of 100 ppm is detected in the United States. However irregular concentrations have been measured in different regions of the world including China. In that regard sedimentary rocks are most reported contributor to soil selenium and to plants. In relation to that predicting selenium mobility in soils is proposed as researchable area in order to address either deficiency or toxicity issues [10, 27, 51]. In fact, selenium is also present in air though it is detected to nano scale concentration especially in urban air [43].

### 4.4 Selenium occurrence and distribution in groundwater and surface water

Based on reports, selenium content in natural water exists in the range of 0.1–400  $\mu\text{g/l}$  and sometimes reaching up to 6000  $\mu\text{g/l}$ . In such water bodies the predominant species are those biogeochemically relevant selenite and selenate from mobility and bioavailability points of views [61].

Selenium poisoning may result from water systems whenever new agricultural runoff flow through a normally dry, undeveloped lands. This process leaches natural soluble selenium compounds (such as selenates) into the water, which may then be concentrated in emerging wetlands. Selenium pollution of waterways also occurs when selenium is leached from coal flue ash, mining and metal smelting, crude oil processing, and landfill.

Recently issues of selenium water contamination are associated with selenium biochemical risks. For instance, from the 210 ground water samples taken in Nigeria, selenium concentration of  $7.33 \pm 6.22$ – $46.3 \pm 22.4$   $\mu\text{g/L}$  is reported following the needed assessment vis-à-vis risk of geogenic contamination which is almost greater than that of WHO's limit of 10  $\mu\text{g/l}$  [35] (Table 1). The distribution of selenium was fairly uniform in the samples studied in different locations that suggested the influence of geogenic factors. More than that, in some parts of the United States dark-gray shale sampled from 51 locations in Colorado, New Mexico, and Utah, many of the groundwater samples were found saline with selenium concentration of 1000  $\mu\text{g/l}$  [2] which is 100 times beyond the limit recommended by the WHO.

Locally, selenium occurrence is rarely checked including the status in groundwater. There is a report noting that selenium content in Ethiopia is generally low, though a concentration of 15–7600  $\mu\text{g/l}$  [64] is reported for ground waters of the rift valley region of the country; and the median values being lower for spring and surface water

sources. Yet, this range of selenium concentration is over the limit value set by WHO. However, selenium health effect, either deficiency or toxicity, is not known or unreported. Moreover, that same region is a concern for other geogenic water contamination in which fluoride is the most explored one [65–67].

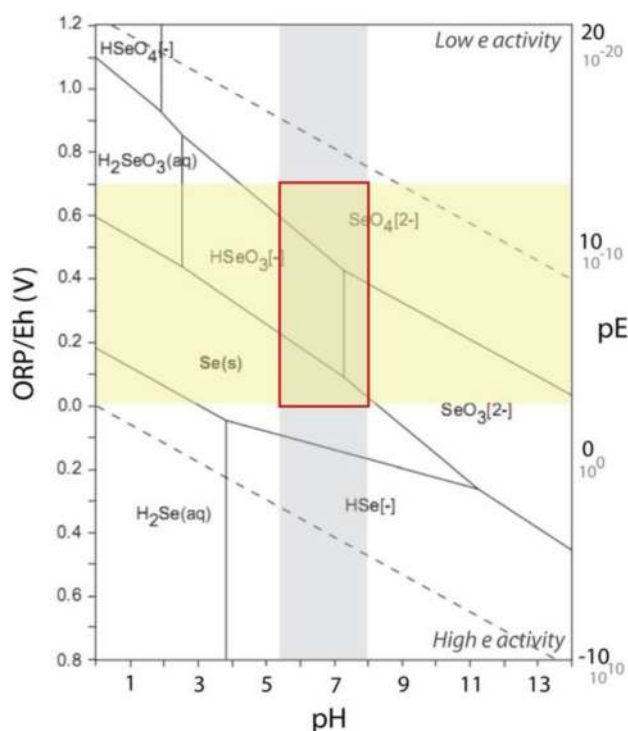
The selenium enrichment in groundwater may be caused by the contact with sedimentary formations. The selenium behavior as function of pH was similar in the ultrapure water that can determine its leaching behavior (Fig. 6) [36, 68]. Thus, medium-range oxidation–reduction potential (ORP) and neutral pH are critical conditions for the toxic selenium to exist or to become dominant as species.

#### 4.5 Reactivity and mobility conditions of selenium species

In the environment pH and reduction conditions play role in selenium species and mobility. Acidic and reducing conditions reduce inorganic selenites to elemental selenium, whereas alkaline and oxidizing conditions favor the formation of selenates as described earlier. Consequently, since selenites and selenates are soluble in water, selenium is leached from well-aerated alkaline soils that favors its oxidation. Conversely, elemental selenium and selenides are insoluble in water; therefore, selenium tends to be sorbed to wet and poorly aerated soils. Thus, reducing conditions of the environment favor those forms. As a result, selenium in alkaline soils is available for uptake by plants, whereas the availability of selenium in acidic soils tends to be limited by the adsorption of selenites and selenates to iron and aluminum oxide soils (Figs. 7, 8) [5, 69]. Further, temperature, moisture, the concentrations of water-soluble selenium, climate condition, organic matter content and microbial activity also determine selenium mobility.

As an anthropogenic activity, agriculture does not only increase the selenium content in soil but it can also increase selenium concentrations in surface water, as selenium is brought along with irrigation drainage water [70]. In that regard, factors controlling selenium release into the groundwater system, soluble Na- and Mg-SO<sub>4</sub> salts represent the primary mobile reservoir of selenium in the Mancos Shale and associated alluvium, with only minor contributions from relatively insoluble gypsum. These salts are more prevalent in alluvium than Mancos Shale, and thus the alluvium represents a potential large source of readily mobilized selenium, which has been reported in other irrigated alluvial valleys particularly in the Western United States and China [71].

Generally, selenium species typically have greater reactivity towards oxidants and attract oxidants comparably greater than sulfur that is determined by their scavenging



**Fig. 6** Phase diagram of selenium speciation. (Reprinted with permission from Springer-Verlag Berlin Heidelberg, *Hydrogeol J* [5]. © Springer-Verlag Berlin Heidelberg 2016)

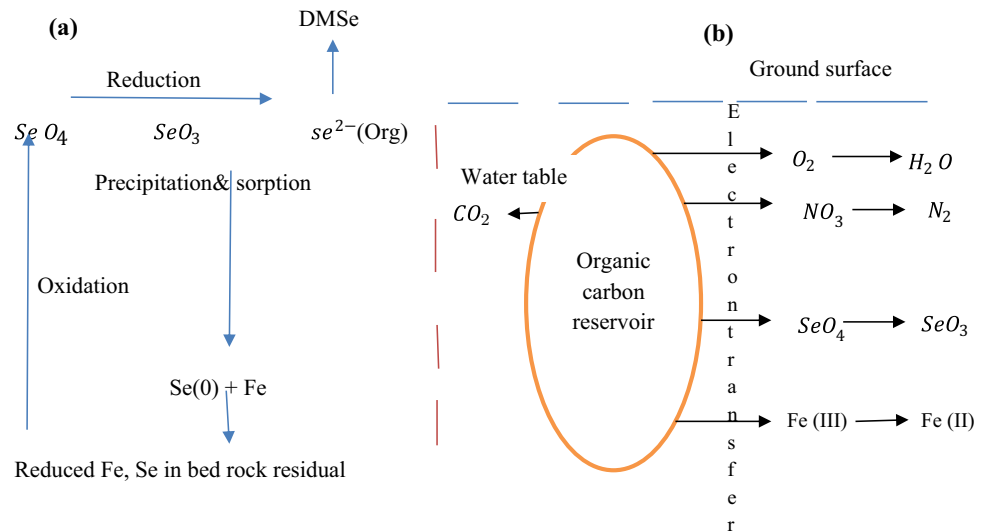
efficient on oxidants including hypochlorous acid, especially in living systems. Such reactivity of selenium brings implications of pros and cons in living system [72, 73]. Besides, its acid forms in the activation of  $\pi$ -bonds in diynyl esters giving to conjugate structures are recently reported [74, 75].

## 5 The selenium biochemistry

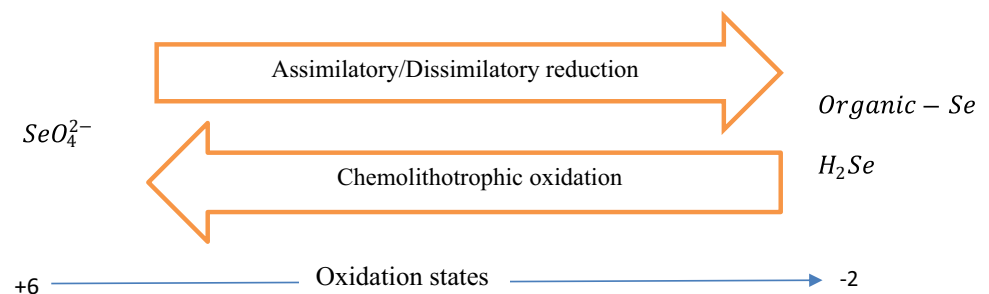
In the environment whereby inorganic selenium is transformed into volatile forms including (CH<sub>3</sub>)<sub>2</sub>Se by the microbial action of fungi and plants, organic selenium is found in biotic systems [61]. Selenium metabolism is found in all domains of life, such as in bacteria, *archaea*, and eukarya and viruses. The chalcogen, selenium, plays an important role in animals, plants and microbes and their enzymes [76] especially after the major finding that uracil guanine and adenosine (UGA) termination codon is used to direct the covalent insertion of selenocysteine. Selenocysteine is viewed as the 21st amino acid by many scientists in terms of ribosome-mediated protein synthesis-into certain selenium-dependent enzymes [77, 78]. Selenium is incorporated into amino acids, such as cysteine, and then into selenium-containing proteins. Three types of redox enzymes that contain selenium in the form of



**Fig. 7** Selenium species and transformation pathways between the species in **a** soil-groundwater-shale system; dissolution, organic incorporation, volatilization, precipitation, and **b** the succession of terminal e-accepting processes in a soil-groundwater system, showing the chemical reduction of  $SeO_4$  to  $SeO_3$  only after  $O_2$  and  $NO_3$  have been reduced [5]



**Fig. 8** Selenium cycle in nature and role of organisms



selenocysteine have been isolated so far and they are characterized from bacterial sources, whereas only one, glutathione peroxidase, is known in mammals [79].

In nature the selenium cycle (Fig. 8) is partially maintained by selenium reducing bacteria (SeRB). The role of selenium cycling is played partly by the microorganisms that use selenate and selenite as terminal electron acceptors whose selenium biomineralization mechanisms gave ways to selenium environmental biotechnological applications [80].

In bacteria and *archaea*, selenium is readily metabolized and involved in a range of metabolic functions that include assimilation, methylation, detoxification, and anaerobic respiration. In that regard, anaerobic digesters treating organic waste and operating at high ammonia concentrations are operated stably with selenium supplement at 0.16 mg selenium per kg of fresh organic matter feed [81–83].

In a related fact, after ingestion, selenium is absorbed by the human body mainly in the duodenum and caecum via active transport through a sodium pump. The mechanisms of intestinal absorption of selenium differ depending on the chemical form of the element. When it is in excess, it is excreted through the urine and feces. Its

homeostasis is based on reserves of selenomethionine in the kidney and liver [76, 84–87]. Humans can get selenium from food items such as Brazil nuts, kidney, liver wheat (grown in selenium rich countries) and drinking water [88].

Regarding the biochemistry of selenium, whether it is essential for higher plants metabolism or not, is debatable though most argue it is not [19, 21]. However, there is a possible incorporation of trace amount of the element into specific selenoproteins for which the “S-assimilation” pathway is proposed where selenium is metabolized by the enzymes of sulphate assimilation both in accumulators and non-accumulators. Further, the accumulation selenium varies within the plant where shoot and root are most accumulators [21]. Whether selenium benefits higher plants metabolism or not, a more concern as well as an opportunity is the issue of phytotoxicity and its implication to human. On one hand, hyper-accumulators do benefit through phytoremediation of selenium contaminated sites, on the other hand consumption of selenium pounded plants could result in human selenium toxicity while the less-accumulators would open the potential to human nutrient supplement [89].

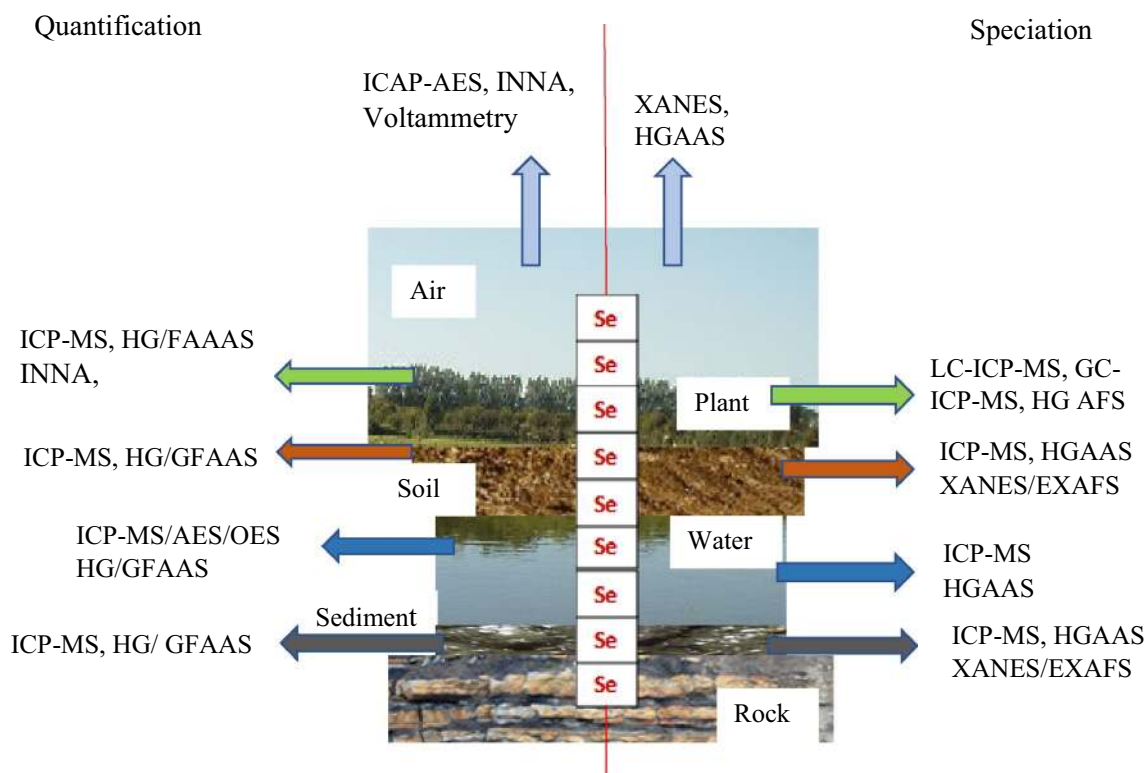
## 6 Selenium quantification in an environmental sample

Several instrumental and analytical methods including microwave digestion and fluorescence detection are applied to determine selenium in environmental samples in the recent past [61, 88]. Due to the narrow margin between the essential selenium and selenium toxicity, the detection sensor material, electrode surface modifiers and chelators that overcome various challenges and achieve better detection limit, range, reproducibility, stability, selectivity, sensitivity, and so forth got advanced as reported by Devi et al., and Paikaray. Further the type of sample matters on the choice of a particular or group of detection methods as well as whether quantification or speciation is sought. In that regard a recipe depicting various environmental samples versus quantification and speciation is given in Fig. 9 [1, 17, 61].

Generally, selenium detection techniques can apply either the destructive method that includes the inductively coupled plasma mass spectroscopy (ICP-MS), a hydride generation atomic fluorescence spectrometer (HG-AFS) or the hydride generation atomic absorption spectroscopy (HGAAS). The non-destructive methods such

as the Instrumental Neutron Activation Analysis (INAA) are also gaining attention. If the desire is routine detection but a simultaneous detection of multielement per sample, then the use of ICP-MS is advised [1, 90]. The INNA can, especially be applied to low detection ( $10^{-8}$ – $10^{-9}$  g) multi-elemental analysis in an air sample though better detection limits and selenium speciation in an environmental sample can be achieved using HGAAS (0.1  $\mu\text{g}$ ) [1, 91–94]. In spite of the advances in detection of selenium in an air sample, obtaining composite air sample is complicated and field-deployable air sampling method has been challenging until a simultaneous preconcentrating analysis method is forwarded [95].

However, conventionally, gas chromatography (GC), high-performance liquid chromatography (HPLC), ICP-MS, neutron activation analysis (NAA), atomic fluorescence spectrophotometry (AFS), AAS, electrothermal AAS, and graphite furnace AAS (GF-AAS) are widely applied. Moreover, for improved detection and speciation, hyphenated separation methods including Ion chromatography (IC) and capillary electrophoresis (CE) are used in conjugation with various atomic spectrophotometry detection systems such as Electrothermal AAS and plasmic optical emission spectroscopy (POES) [5].



**Fig. 9** Selenium detection from an environmental sample for speciation and quantification. (Redrawn from [1] with permission from John Wiley and Sons. © 2016 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim)

For trace analysis of toxic elements, it is not only necessary to determine the total content of the element in question at lower and lower levels, but it is also necessary to elucidate the binding state in order to evaluate the ecotoxicity and to follow the pathways of these elements in the environment and their metabolism in biological systems. Speciation of toxic as well as the essential elements are therefore important through the detection of forms of selenium.

Therefore, as applied to unravel selenium sorption mechanisms that rely on an interaction of some source of X-ray excitation and a sample, diverse advanced detection techniques are emerging which include energy-dispersive X-ray spectroscopy (EDXRS), Fourier-transform infrared spectroscopy (FT-IR), powder X-ray diffraction (PXRD), extended X-Ray absorption fine structure (EXAFS) and X-ray absorption spectroscopy (XAS) [96].

## 7 Management of the excess selenium in water and soil media

Diverse technologies are being applied to remove selenium from water, soil, sediment and sludge [97]. These technologies are applied at laboratory, pilot and full-scale levels [46, 98]. By their working principle, these technologies encompass physico-chemical and biological methods. For instance, the full-scale application systems in selenium removal include fixed bed biological filters, constructed wetlands and reverse osmosis. Table 2 below gives a glimpse of the classes of selenium remediation technologies with the corresponding examples that are partly detailed in Table 3 including the advantage and disadvantage as well as process description.

### 7.1 Conventional selenium management techniques

Numerous physicochemical methods have been used to reduce the level of selenium from drinking water as well as to meet discharge limits by the process industries. For instance, the order of 1–5 µg/l is sought in the United States and other selenium rich nations. Conventionally

the following techniques are applied to meet standards in drinking water supply.

1. Biological reduction following pretreatment.
2. Ion exchange,
3. Activated alumina (AA),
4. Reverse osmosis (RO), and
5. Distillation.

Ion (anion) exchange can reduce selenium by up to 95%, in which the selenate ion is strongly preferred. Although Se (IV) is more difficult to oxidize compared to As (III) which is oxidized to As (V), this can readily be accomplished with the application of excess chlorine. The optimum amount of oxidation is obtained between pH 6.5 and 8.0 where Se (IV) can be converted to Se (VI) within five minutes at a free chlorine concentration of 2 mg/l. At pH 9.0, only 15% of the Se (IV) has been found to be converted with 2 mg/l of free chlorine. Other techniques used for selenium removal include distillation (> 98% reduction), reverse osmosis (RO) (> 90% reduction) and activated alumina (85–95% reduction) [87, 99, 100] (Table 3).

Removal of the excess selenium from drinking water entered to a conventional scale especially in selenium rich countries through the application of the biological reduction technique. In such regard, fixed-film fluidized bed reactor (FF-FBR), commercially called “ABMet”, has got wider application. Recently, developments on the application of this biotechnology to mineralize selenium as extracellular and intracellular precipitation of selenium biominerals have been reported using selenate respiring bacterium [101].

Comparatively, despite its pretreatment and management cost, pressure driven separations including RO are also applied to full scale. Some removal techniques are at pilot scale and few are still on a rigorous study especially the electrocoagulation method as explained in Table 3.

### 7.2 Recent developments on selenium management research

Since selenium contamination in groundwater and surface water in numerous river basins worldwide has become a

**Table 2** Brief summary of classes of selenium removal technologies with examples

No	Classes of technology	Examples
1	Chemical	Ion exchange with adsorption, catalyzed reduction
2	Adsorption	Activated carbon, peanut shell, activated alumina, ferrihydrite
3	Phytoremediation	Wet land, algal volatilization
4	Coagulation precipitation	Electrocoagulation
5	Bioremediation (excluding phytoremediation)	Enzymatic selenium reduction, enhanced in situ microbial reduction, algal–bacterial removal
6	Pressure driven separations	Nano-filtration and reverse osmosis

**Table 3** Description and pros and cons of selected selenium removal technologies [106]

Technology	Description	Advantage	Disadvantage
Fixed-film fluidized bed reactor (FF-FBR) (commercially named as ABMet)	The ABMet applies an attached growth (comprised of a biofilm, or a layer of microorganisms that grow on the surface of a solid phase media) downflow granular activated carbon bed filter	It is commercially available technology that has been demonstrated to remove selenium to low levels (e.g., <5 µg/l) in pilot scale and full-scale applications. This process technology uses naturally occurring microbes and molasses-based nutrient feed to maintain biomass. Biologically reduced elemental selenium is in an insoluble form as nanoparticles integral to the biological solids	Potential need for pretreatment to remove suspended solids. Backwash water is required to periodically slough off excess microbial growth, prevent short-circuiting of flow and for de-gassing. Presence of an excessive nitrates will require proportional amount of carbon or energy source. This excess carbon source will also generate some additional biomass. External carbon source is required if the soluble influent organic content is insufficient. Wasted biomass residuals contain elemental selenium that may be hazardous. Media replacement may be compulsory over the life of the system. Biological residuals will need to be thickened and dewatered before landfill disposal
Activated alumina	Activated alumina is a general term for various granular, porous oxides and hydroxides of aluminum that have been exposed to sodium hydroxide at high temperature and have a high surface area that has the properties of providing physical adsorption of selenium similar to ferrihydrite.	This technology is demonstrated only at laboratory scale	This technology is demonstrated only at laboratory scale
Catalyzed selenium reduction (cementation)	The addition of copper or nickel to a zero-valent iron treatment process has been demonstrated to catalyze the reduction of selenium by creating a greater electrochemical potential between the elemental iron and soluble selenium	Basic technology is demonstrated in laboratory studies to remove selenite and selenate to low concentrations	The technology has not been proven in full-scale application. Potential for long residence times. Spent media must be removed, disposed of and replaced. May require disposal as hazardous waste. Sludge disposal may be significant cost. Media replacement may be a significant cost. Other potential issues with copper and nickel discharges
Electrocoagulation	A physical adsorption process where ferrous iron is produced by applying direct electrical current to the water where an iron anode oxidizes to form ferrous iron that can reduce selenate and the resultant ferric iron can co-precipitate selenite	Advantages are not provided for technology demonstrated at laboratory scale only	Disadvantages are not provided for technology demonstrated at laboratory scale only

**Table 3** (continued)

Technology	Description	Advantage	Disadvantage
Nanofiltration	It is a pressure driven membrane process similar to reverse osmosis that retains selenium and other dissolved salts between 0.001 and 0.01 microns but it is operated at pressures approximately at one-third of reverse the osmosis	Operates at one-third of the pressure requirement of reverse osmosis technology. Small space requirements, modular type construction, and easy expansion. Can offer improved recoveries by rejecting a smaller portion of the salts including selenium, thereby reducing scale potential. Concentrates the selenium thereby reducing the volume for ultimate reduction treatment	Not tested at full-scale for selenium removal. No actual performance data are available yet for selenium removal. Requirements for pretreatment and chemical addition (micro filter, mixed media filter) to reduce scaling/fouling. Frequent membrane monitoring and maintenance. Pressure, temperature, and pH requirements to meet membrane tolerances. Requires treatment and disposal of the reject stream. Temperature operating issues due to viscosity effects at extreme low and high temperatures.
Permeable reactive barriers	Permeable reactive barriers are a type of passive, on site treatment for shallow groundwater (generally employed at depths less than 50–70 ft) and can be employed for source zone treatment	Lower cost alternative than other technologies. Low maintenance. Can be used as a source control measure to mitigate exposure to downgradient receptors	Finite life span. Potential to be clogged due to precipitation of secondary metals. Has not been fully demonstrated to achieve low µg/l levels in the effluent (less than 5 µg/l).
Reverse osmosis	Reverse osmosis is a membrane separation process that uses high pressure to force a solution through a membrane that retains the soluble selenium (e.g., selenite and selenate) and other dissolved salts less than 0.001 microns on the reject side of the membrane and allows the purified water pass to the permeate side	Demonstrated at full scale to remove selenium (selenite or selenate) to less than 5 mg/l. Produces a high water quality with relatively high recoveries as a function of scale treatment. Small space requirements, modular type construction and easy expansion. Concentrates the selenium reducing the volume for ultimate reduction treatment	Higher capital cost to purchase, install, and operate than other membrane separation processes. Requirements for pretreatment and chemical addition (microfilter, mixed media filter) to reduce scaling/fouling. Pressure, temperature, and pH requirements to meet membrane tolerances. Frequent membrane monitoring and maintenance. Requires treatment and disposal of the brine (reverse osmosis reject stream). Reverse osmosis permeate stream will require treatment (pH and total dissolve solids buffering) prior to discharge to receiving waters to meet aquatic toxicity test. Operating issues will result from viscosity changes at extreme low and high temperatures

critical issue in recent decades [46], researches in selenium environmental management are gaining wider attention. Among the various endeavors attempted, phytoremediation, sorption and use of characteristically identified microbes are worth to mention.

Basically, phytoremediation is a biological approach to pollution control or management activities that apply selenium selective plants species as portrayed on Fig. 10 [102, 103]. The mechanism by which plants take up, transport and transform selenium is nearly similar as illustrated in Fig. 11. Accordingly, a selenium concentration of 1 g/kg DW of plants is reported from phytoremediation of contaminated site using hyper accumulator plant species (Fig. 10). In that regard, the hyper accumulators including giant reed to clean selenium-contaminated sites are also conveyed in recent publications [7, 55, 76]. In a related study water hyacinth (*Eichhornia crassipes*) were tested for their pollutant metal sequestering potential [104] that can also potentially be considered for selenium removal [105]. However, the later management of the biomass will be a challenge for future research.

Organo-selenium, selenite and selenate in the soil are taken up through the plants' physiological system involving the root transport system and are either incorporated in selenium-protein, accumulated in their leaf or dissipated into the air after methylation (Fig. 11) [95].

Sorption of selenium is another attractive removal technology which is proved efficient in removing selenium from an environmental media and yet it is an older technique. For instance, sorption of selenium using minerals

like hydrated lime and calcium-based particles proved to be efficient based on an XRD evaluation [107, 108]. Adsorption of selenium is a phenomenon that co-occurs during a metabolic process [10].

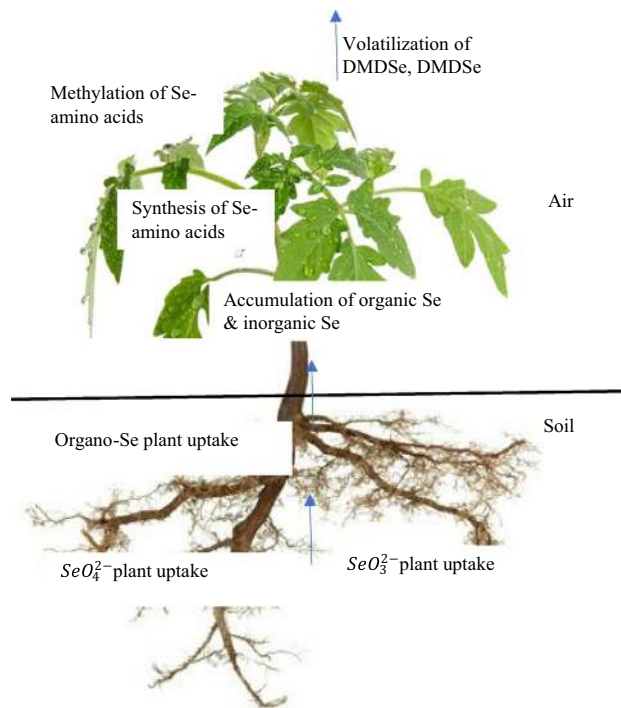
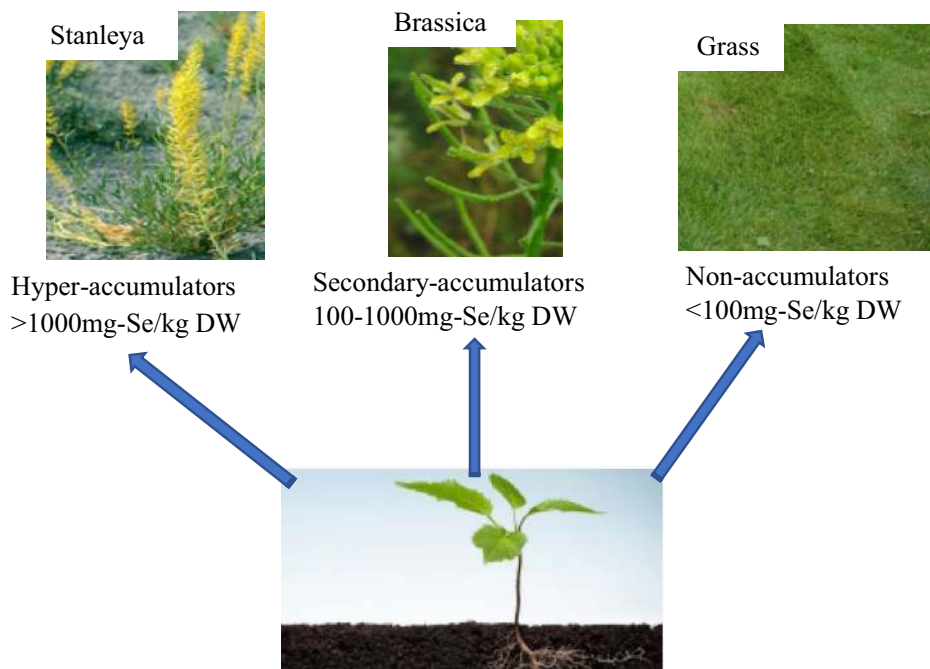


Fig. 11 Selenium uptake by plants. (Adapted from [50])

Fig. 10 Classification of plants depending upon selenium accumulation as hyperaccumulators, secondary accumulators and non-accumulators. (Source: [7])



In a related current study, sorption of selenium is tested using rare earth hydroxide since the contents of selenium in industrial wastewater, agricultural runoff, and drinking water have to be constrained to a value of 50  $\mu\text{g/l}$ , as the maximum concentration limit [109]. This recent experimental research reported that selenium can be sequestered efficiently from its aqueous solution using a structurally well-defined cationic layered rare earth hydroxide,  $\text{Y}_2(\text{OH})_5\text{Cl}\cdot 1.5\text{H}_2\text{O}$  (Fig. 12) with maximum sorption capacities of selenite and selenate reported are 207 and 124 mg/g, respectively, both representing the new records among the inorganic sorbents. In the low concentration region,  $\text{Y}_2(\text{OH})_5\text{Cl}\cdot 1.5\text{H}_2\text{O}$  is able to almost completely remove selenium from aqueous solution even in the presence of competitive anions such as  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ , and  $\text{HPO}_4^{2-}$ . The resulting concentration 10  $\text{A } \mu\text{g/l}$  is achieved. The sorption kinetics is well fitted in the Langmuir model in two different pH levels, 7 and 8.5; however, the selenium sorption decreased at the higher pH (Fig. 13).

Observing the surface phenomena closely, the sorption mechanism was unraveled by the combination of advanced techniques like EDS, FT-IR, PXRD, and EXAFS. Selenate ions were exchanged with chloride ions in the interlayer space, forming outer-sphere complexes. In comparison, besides anion exchange mechanism, the selenite ions were directly bind to the  $\text{Y}^{3+}$  center in the positively charged layer of  $[\text{Y}_2(\text{OH})_5(\text{H}_2\text{O})]^+$  through strong bidentate binuclear inner-sphere complexation, consistent with the observation of the higher uptake of selenite over selenate [109].

Waste sludge of domestic or industrial origin is becoming another selenium mine sites. Like other recovery operations, selenium is being obtained through sludge mining: *Pseudomonas stutzeri* NT- I to reduce the soluble selenium compounds to elemental selenium,  $\text{Se}(0)$  [110] in another study. Michihiko Ike and colleagues at Osaka University, have developed a process to mineralize selenium through microbial recovery though the technique is obscured. This element is also present in industrial wastewater streams, for instance, from copper production [111].

However, much of the recovery efforts are on a laboratory scale which is mainly due to gaps in the method applied and the associated cost implications.

## 8 Conclusion

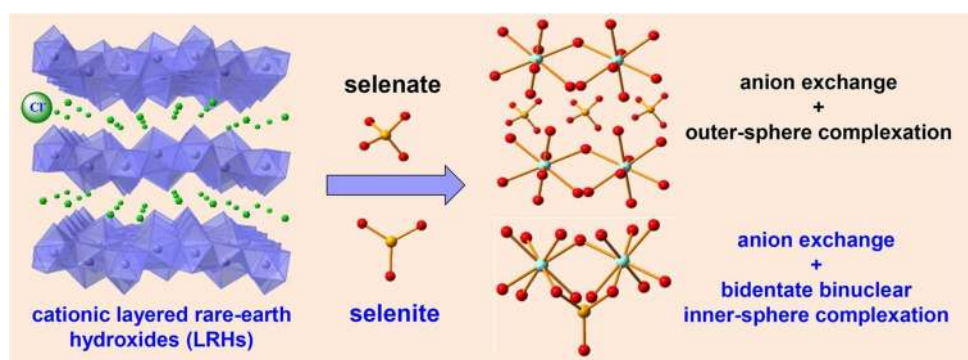
Selenium occurrence, geochemistry, nutrient and toxicity effect remained concerns worldwide. Advances in analytical methods and instrumentation, selenium detection and speciation helped in understanding selenium's environmental process in more detail. Selenium's natural distribution is globally uneven; for some it is scarce but for others, it needs removal from an environmental medium. In addition, the selenium intake by animals involves both food and water and hence the toxicity risk has to consider both factors. Furthermore, the selenium mobility associated risk is largely the selenium species specific, environmental pH and redox potential dependent.

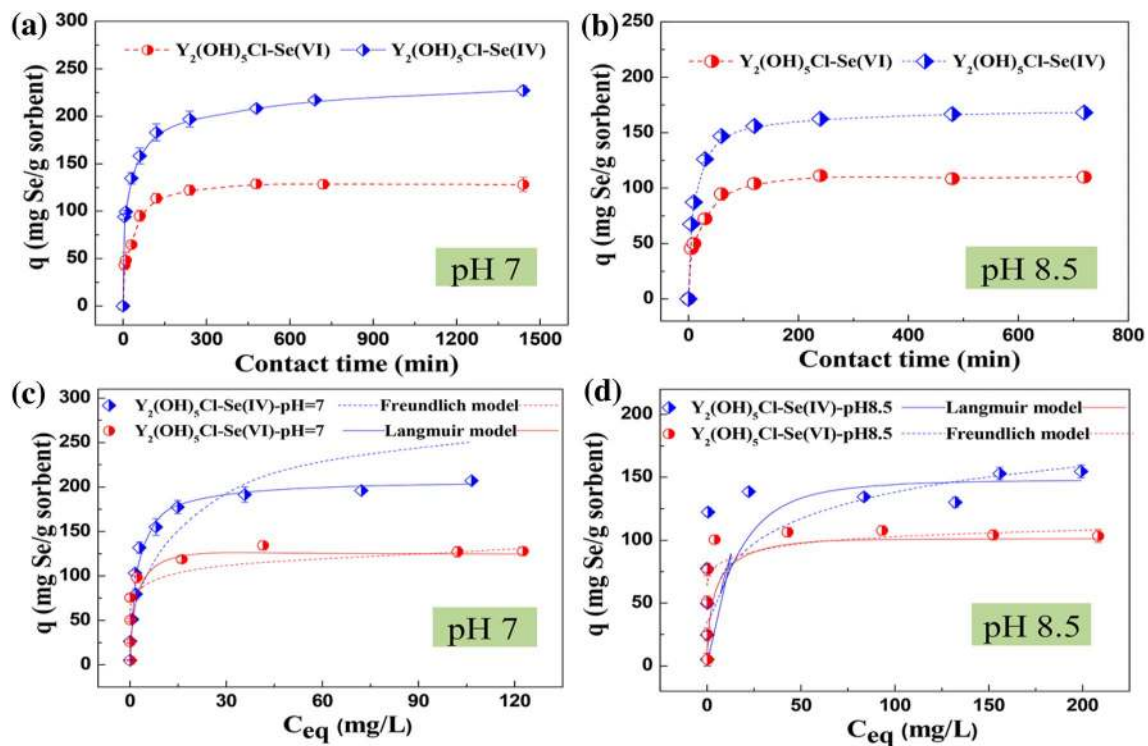
Regarding selenium management, reduction is the most feasible chemical technology to remove selenium. The biological methods are most established, especially in using phytoremediation and microbial reduction, the latter being largely applied in drinking water supply systems. Similarly, the application of surface phenomena to remove selenium is advancing with time. Thus, selenium sorption and isotherm are elucidated in recent works.

Yet, selenium remains to be a concern in geogenic and anthropogenic contamination as well as in nutrient supplement effect. The recovery of selenium from anthropogenic sources of release is also equally important. However, there is a huge geographical imbalance in selenium studies and publications, the least studies being in the African continent.

Research and development towards implementation and provision of an adequate institutional framework and marketing chains to increase the use of recovered selenium materials require feasibility studies. Furthermore, technologies for efficient recovery and reuse of recovered selenium with consideration of speciation, purity and

**Fig. 12** Selenium adsorption in rare earth hydroxide. (Adapted with permission from [109]. © 2017 American Chemical Society)





**Fig. 13** Sorption kinetics of Se (IV) and Se (VI) on  $Y_2(OH)_5Cl \cdot 1.5H_2O$  at **a** pH 7 and **b** 8.5. Sorption isotherms of Se (IV) and Se (VI) on  $Y_2(OH)_5Cl \cdot 1.5H_2O$  at **c** pH 7 and **d** 8.5. (Phase ratio=2 g/l, contact

time=12 h, background=0.01 M NaCl. (Adapted with permission from [109]. © 2017 American Chemical Society)

value are highly sought. In such regard, integrating selenium sequestered plants as source of selenium requires those advanced separation techniques. However, the extraction of the plant sequestered selenium is a future challenge that needs to be addressed.

**Acknowledgements** We are thankful to the African Center of Excellence for Water Management, Addis Ababa University, Ethiopia for the kind support it has made.

## Compliance with ethical standards

**Conflict of interest** The authors declare that they have no conflict of interest.

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