LECTURE TEXT

Selenium: widespread yet scarce, essential yet toxic

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Abstract

Selenium (Se) is an essential element for humans and animals, with one of the narrowest ranges between deficiency ($< 40\ \mu g\ day^{-1}$) and toxicity ($> 400\ \mu g\ day^{-1}$). Se is very widespread in all environments (rocks, soils, waters, air, plant and animal tissue) but in very low concentrations. Thus, there are no ores from which Se can be effectively mined. This can create a potential problem in supplying Se for commercial uses or for battling Se deficiency which already affects more than one billion people and is predicted to rise in the future. Besides Se deficiency, there are many incidents where excess Se in water and soil caused deformities in animals and humans. Often high-Se areas are found near past coal mining and burning sites, which have never been remediated and still pose a potential threat to human health. This article aims to inform readers about the general chemical characteristics of Se, environmental cycling of Se, and past incidents of Se deficiency and toxicity. The article also touches on the removal of excess Se from waters and soils, as well as biofortification methods for preventing Se deficiency in humans and animals.

Abbreviations

CIGS cell	A thin-film solar cell that uses layers of copper indium gallium selenide (CIGS) to absorb sunlight and convert it into electricity
GPx	Glutathione peroxidase, an enzyme that catalyzes the reduction of hydrogen peroxide to water and oxygen and peroxide radicals to alcohols and oxygen
KBD	Kashin–Beck disease (KBD), an endemic osteoarthropathy characterized by deformity of affected joint cartilage and epiphyseal plate cartilage of the four limbs
KD	Keshan disease, an endemic chronic heart disease characterized by enlargements of the heart and congestive heart failure
nZVI	Nanoscale zero-valent iron used for in situ remediation
SeCys	Selenocysteine, the 21st amino acid and the selenium analogue of cysteine
SeMet	Selenomethionine, the selenium analogue of methionine

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Chemical characteristics and usage

Selenium is a chemical element discovered in 1817 by Swedish chemist Jöns Jacob Berzelius (20 August 1779–7 August 1848) and named after the Greek word for moon, *selènè*. It was discovered after analyzing a reddish sludge that occurred in the chambers used for sulfuric acid production while burning Falun pyrite. It was first believed to be an arsenic compound, because of its reddish color, then tellurium, because of its strong horseradish smell when heated. After many experiments, Berzelius concluded that it was a new element, calculated the atomic weight of the selenium, and gave formulas of 90 different selenium compounds [1].

Selenium is a metalloid, with properties intermediate between metals and nonmetals, and, together with oxygen, sulfur, tellurium, and polonium, is a part of the chalcogen group, where allotropy is one of the characteristics. Therefore, elemental Se can exist as multiple allotropes (different molecular forms with varying physical properties), both crystalline (red and metallic gray forms) and amorphous (red and vitreous forms) (Fig. 1). The red crystalline form and red and vitreous amorphous forms convert to the metallic gray form, which is the most stable one, at temperatures above 110 °C and at 70–120 °C, respectively [2].

Most outstanding properties of the metallic gray form are its photovoltaic (where light is converted directly into
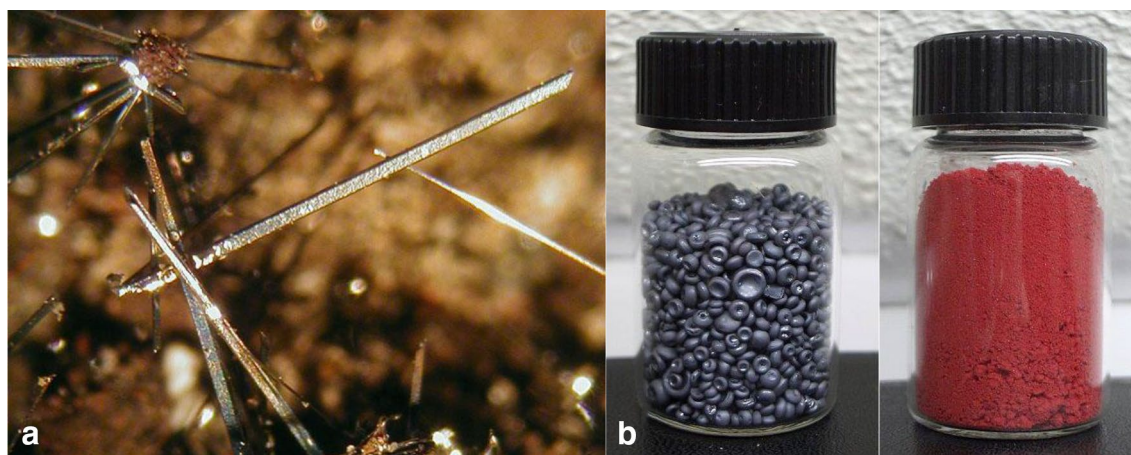
Fig. 1 **a** Prismatic crystals of native selenium from Ronneburg uranium deposits, Germany (© Courtesy of Thomas Witzke, Malvern Panalytical). **b** Black amorphous and red amorphous selenium used in laboratories. (© W. Oelen, public domain)

electricity) and photoconductive (becomes more electrically conductive owing to the absorption of light) characteristics [3]. These properties were widely exploited in the mid-1900s, when Se was used in rectifiers (which change alternating current to direct current) and in the liners of photocopier drums. Although other cheaper or more efficient compounds have replaced selenium in these products, Se is still used in energy-efficient windows that limit heat transfer, in thin-film photovoltaic cells (CIGS cells) that convert solar energy into electricity [4], and in lithium–selenium batteries which are becoming more prominent again [5].

Besides in electronics, selenium has many different commercial uses, with the following latest estimates of world consumption of Se: metallurgy (40%), glass manufacturing (25%), agriculture (10%), chemicals and pigments (10%), electronics (10%), and other (5%) [6].

Occurrence and cycling of Se in the environment

Selenium is found in all environments, including rocks, soils, waters, air, and plant and animal tissue. This is a result of its chemical speciation, where Se can naturally exist in four oxidation states: selenide (−II), elemental selenium (0), selenite (IV), and selenate (VI) [3].

Six isotopes of Se coexist in nature with abundance shown in parentheses: ^{74}Se (0.9%), ^{76}Se (9.4%), ^{77}Se (7.6%), ^{78}Se (23.8%), ^{80}Se (49.7%), and ^{82}Se (8.7%). Five of them are stable, the exception being ^{82}Se, which is considered stable for practical reasons owing to its half-life of approx. 10^{20} years.

^{77}Se isotope is used in nuclear magnetic resonance (NMR) spectroscopy for determining the chemical structure of organic compounds [7]. NMR can be used only with nuclei that have a spin, which is a reflection of more than one energy state in an applied magnetic field. ^{77}Se has spin 1/2 due to an odd number of neutrons (43) and has a wide spectral window, making it ideal for determination of organoselenium compounds [8].

In addition to these six isotopes, there are 24 unstable selenium isotopes, with a half-life ranging from approx. 20 ms to 327,000 years. ^{79}Se radioisotope is of environmental concern as it is present in long-lived nuclear waste [9] with its half-life being 327,000 years [10].

Different Se oxidation states have different geochemical behaviors that affect the mobility, bioavailability, and toxicity of Se in the surface environment [11]. As a result of its wide range of oxidation states and its appearance in both organic and inorganic forms, Se has a complex environmental cycle (Fig. 2). Briefly, Se is released into the atmosphere mainly through biogenic emissions, volcanic eruptions, and fossil fuel combustion [12, 13]. As it is released from volcanic eruptions, not much Se is left behind in volcanoes and therefore the concentration of Se in volcanic rocks is usually less than 0.05 mg kg^{-1} [14].

In the atmosphere, Se is transformed from gaseous phase to particle and aqueous phase, and is transported to the soil and water through dry and wet deposition [13]. In water, Se is taken up by organisms and is further transported via the food chain, volatilized or reduced, and immobilized onto sediments [15, 16].

In the soil, Se is taken up by plants or immobilized through interaction with clay particles, organic matter, or metal (hydr)oxides [17]. When taken up by plants, Se is either volatilized back into the atmosphere, or accumulated in plants which are then ingested by humans and animals [12, 18]. It is then incorporated into selenoproteins which have an important role in human health, or into selenomethionine where Se is a substitute for sulfur [19]. If too
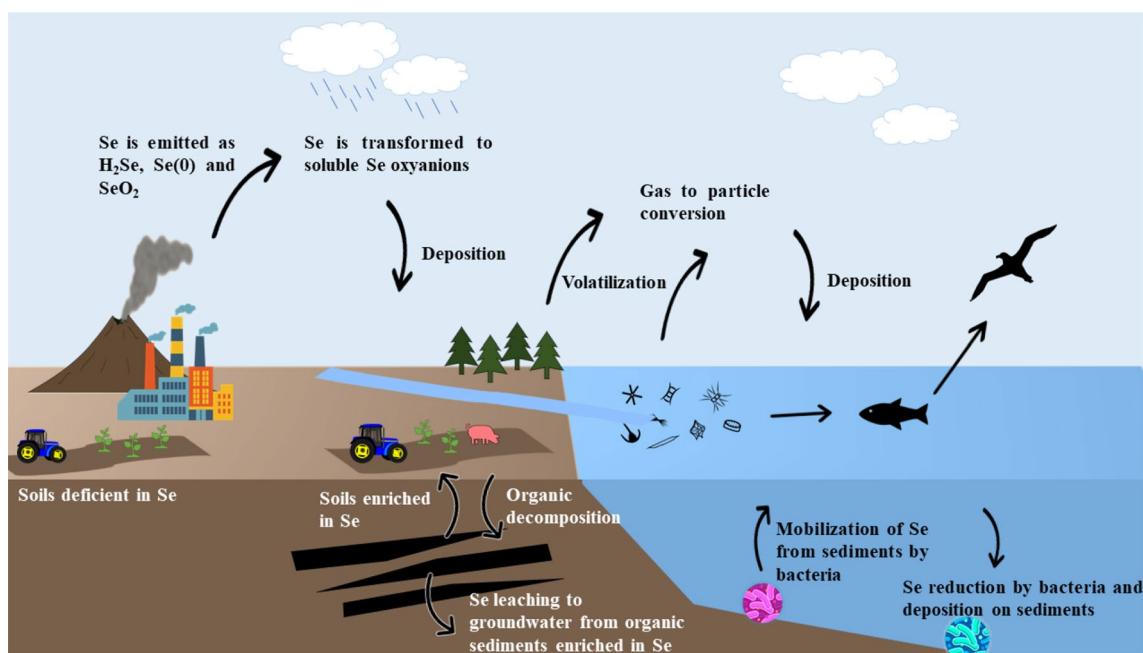
Fig. 2 Simplified biogeochemical cycle of Se

much or too little Se is ingested, it can cause serious adverse effects. After plants and animals die, Se is recycled back into the environment. Microorganisms play an important role in selenium cycling, as different types of bacteria and archaea can reduce and oxidize Se, making it either more mobile or immobilized [20].

Se in rocks and minerals

Selenium is very widely distributed in the Earth's crust; however, its abundance is estimated to be only 0.05 mg kg^{-1} [4].

Se content in volcanic rocks is usually low because volatile selenium escapes as high-temperature gas during volcanic eruptions [14]. Consequently, tuffs (rocks made of volcanic ash) are usually enriched in volatile elements such as Se owing to the adsorption of elements on the ash surface [21, 22]. Besides tuffs, some basic rocks formed during the early stages of crystallization of molten magma may be higher in Se content than other magmatic rocks. The reason could be that, during the early stages of crystallization, sulfides may separate from silicate melt, forming deposits through gravity differentiation [23].

Sedimentary rocks usually have low levels of Se, and since sedimentary rocks account for 75% of the Earth's surface, Se-deficient environments are more widespread than selenium-adequate or selenium-toxic ones [14]. Levels in most limestones and sandstones rarely exceed 0.1 mg kg^{-1} [24]. However, particular types of sedimentary rocks can have high selenium concentrations. Some

phosphatic rocks have high Se content (average 1 mg kg^{-1}, some rocks ≤ 300 mg kg^{-1}) [25], reflecting structural similarities between PO_4^{3-} and SeO_4^{2-} anions [26, 27]. Black shales in Ireland are amongst the highest Se-containing rocks, with an average abundance of 600 mg kg^{-1}, and in some samples up to 1250 mg kg^{-1} [28, 29]. Coals enriched in organic sulfur usually have elevated values of U, Se, Mo, V, and Re. These coals are found in different parts of the world, e.g., in China [30] and Croatia [31] with Se values ranging from 5 to 100 mg kg^{-1}, with an average of 35 mg kg^{-1}. Burning that type of coal produces high levels of SO_2 and ashes with high Se content that can be transported over great distances. Elevated Se values were found in surface water, groundwater, lettuce, and sediments in Croatia which are all consequences of 400 years of mining and burning coal high in Se [31–33]. In addition, the original coal was found to have lower Se content than previously reported, indicating leaching of trace elements by groundwater [34].

As for Se mineralogy, selenium can be found in minerals containing selenium as an essential element, or more often as a substitute for sulfur in sulfide minerals. Minerals containing selenium as an essential element can be divided, according to their genesis, into three groups [35]: (1) selenide minerals, which occur mainly in hydrothermal deposits and are formed from hydrothermal solutions under relatively reducing conditions [36]; (2) secondary selenites and selenates, which are formed in oxidation zones of sulfide and selenide ores [37, 38]; (3) anhydrous selenites which are the product of fumarolic activity and are found in volcanic

fumaroles of the Tolbachik volcano, Kamchatka peninsula (Russia) [39].

So far, 123 Se minerals have been recognized by the International Mineralogical Association (IMA). However, deposits containing independent selenium minerals are rare, and selenium is usually more abundant in sulfide minerals, where it substitutes sulfur owing to their similar ionic radii.

Since Se is dispersed in various minerals in low concentrations, it is only obtained as a by-product and not directly mined. Most of the world's production of selenium is as a by-product from copper, copper–nickel, and lead and zinc sulfide deposits [4, 40]. The rising demand for Se highlights the need for identifying new selenium sources, such as marine phosphate deposits, oil shales, and coals [41, 42]. Some of these resources can contain high but dispersed Se and variously bound Se, which can make Se harder to recover and therefore not economical for mining [4].

Se in the atmosphere

Between 29 and 36,000 tons of Se is released into the atmosphere every year, through natural emissions and anthropogenic emissions [12, 43, 44]. The main natural sources of Se are biogenic emissions (volatilization of Se by terrestrial and aquatic organisms) and volcanic emissions, and in lesser amounts crustal weathering and sea spray. Volatilization of Se by marine organisms is the main source of Se in the atmosphere (approx. 40% of total emissions), while volatilization by terrestrial organisms and volcanic emissions account for approx. 15% and approx. 12% of total emissions, respectively [45].

Anthropogenic emissions (fossil fuel combustion, mining, non-ferrous metal production, manufacturing, and utilization of agriculture products) have greatly increased since industrialization, and it was estimated that the combustion of coal was the main anthropogenic source of atmospheric Se contamination in the northern hemisphere [13, 43]. Currently, anthropogenic emissions account for approx. 33% of total emissions, making it the second biggest source of Se. It should be mentioned that estimations of Se emissions are still an ongoing research topic [45].

Depending on the source, Se can be released as volatile organic Se, volatile inorganic Se, and particulate Se [13].

1. *Volatile organic Se* Volatile organic Se compounds are emitted into the atmosphere through biological activity of marine and terrestrial organisms (bacteria, algae, fungi, animals, humans). Once Se is taken up by organisms, it can be methylated and volatilized as mostly dimethyl selenide ($H_3C–Se–CH_3$) and dimethyl diselenide ($H_3C–Se–Se–CH_3$). The atmospheric lifetimes of dimethyl selenide were estimated as approx. 5 min, approx. 3 h, and approx. 6 h due to reactions with NO_2,

OH^-, and O_3, respectively. It is likely that those reactions form less volatile products that may undergo gas-to-particle conversion [46].

2. *Volatile inorganic Se* Volatile inorganic Se is emitted mostly through volcanic and anthropogenic emissions, primarily in the form of hydrogen selenide (H_2Se), elemental Se(0), and selenium dioxide (SeO_2) [47]. Once emitted, those Se species undergo a series of cooling and oxidation reactions. Potential reactions may go as follows: H_2Se is oxidized to SeO_2 or selenite(IV), while both elemental Se and $SeO_2(g)$ can form particulate Se under normal atmospheric conditions. $SeO_2(s)$ can dissolve in rainwater to form $H_2SeO_3(aq)$ [11].

   Residence time of volatile inorganic Se may be similar to dimethyl selenide and it therefore seems unlikely that atmospheric Se can be transported for a long distance in its gaseous forms. Rather, gaseous Se could be converted to particulate form, and then be transported over long distances, which depends on particle sizes and atmospheric conditions [13].

3. *Particulate Se* Particulate Se is primarily released from sea salts, windblown dust, volcanic ash, fly ash from coal combustion, dust from mining, and metal melting [43]. However, it is believed that most particulate Se is formed by conversion from volatile inorganic Se as mentioned above [13].

Se in the soil

Se in soils originates mainly from atmospheric deposition and parent material. In addition, it can be present in various oxidation states that alter its behavior in soils—mobility and toxicity.

Sources of Se in the soil

The lifetime of atmospheric Se is estimated to be approx. 5 days; particulate Se and soluble oxyanion Se species are transferred from the atmosphere to soils by dry (19%) and wet (81%) deposition. Besides dry and wet deposition, sources of Se in soils are also weathering and leaching of Se from parent material (35 mg ha^{-1} year^{-1}) and Se fertilizers applied on agricultural land [45].

Leaching from parent material and applying Se fertilizers are usually considered as local sources as they add Se over a small range. Therefore, the parent material is usually considered as the main source of Se in alkaline soils developed on shales high in Se content. That can be found in Ireland where soils developed on black shales have levels of Se up to 1250 mg kg^{-1} [28].

However, dry and wet atmospheric deposition are considered as the dominant regional sources, as Se can be transported over greater distances and in much greater

quantity (870 mg ha^{-1} year^{-1}) [11, 20, 25, 27, 45]. Therefore, Mount Etna is considered as the main source of the Mediterranean area owing to the transport of volcanic ash over a larger area [27, 48, 49]. Deposition of Se originating from biogenic processes in the ocean is considered as the main source of Se in coastal areas in all latitudes of Norway [50]. In monsoonal China, precipitation is the main factor in controlling the large-scale Se distribution in soils [51]. Areas that are near coal combustion or mining activities usually have higher Se contents. Haygarth et al. [52] showed a decrease in Se content in soils and plants in the UK after the Clean Air Act (1956). The decrease reflected a reduction in coal combustion which lowered atmospheric input of Se.

Owing to many different inputs of Se, the distribution of Se in soils is highly uneven and can vary from 0.005 to 1200 mg kg^{-1}, and most commonly between 0.01 and 2 mg kg^{-1} [14]. Soils deficient in Se and soils enriched in Se can exist near one another making it hard to map the worldwide distribution of Se in soils [53].

Soils enriched in Se (> 0.5 mg kg^{-1}) are called seleniferous soils and crops grown on those soils usually absorb Se more than the maximum permissible level for animal consumption (4 mg kg^{-1}) [54]. Soils with elevated levels of Se are found in parts of many countries including Australia, China, India, Ireland, and USA [54]. Health problems caused by Se toxicity have been documented in people and livestock in China [55] and aquatic animals and birds in the USA [56].

Soils deficient in Se (< 0.05–0.1 mg kg^{-1}) are also found in many countries (Finland, Sweden, Central China). Soils deficient in Se are more widespread and affect more people than soils enriched in Se [14], and it is predicted that soils will become even more deficient in Se in the future as a result of climate change [57]. Se deficiency affects more than one billion people, and two diseases connected to the deficiency were recognized primarily in China, namely Kashin–Beck disease and Keshan disease [58]. Most often supplementation and usage of Se fertilizers can limit the health problems of Se deficiency. For example, almost all fertilizers in Finland have been supplemented with sodium selenate since 1985 because of the low content of Se in soils and food [59].

However, total Se content does not reflect how much Se will be taken up by plants. For example, Hawaii and Puerto Rico, despite having 6–15 mg kg^{-1} and 1–10 mg kg^{-1} of Se in soils, have not produced vegetation high in Se content [60–62]. On the contrary, soils in South Dakota and Israel with a lower total Se content have produced toxic vegetation [63, 64]. This is because Se in those soils is present in different fractions that are or are not bioavailable to plants [62]. Therefore, bioavailable Se is an accurate measurement for Se status of soils.

Se fractionation in soils

The mobility of Se depends on Se speciation and fractionation in soils, which is mainly controlled by pH and redox conditions. In addition, the mobility of Se is also controlled by microbial activity, precipitation, complexation, and sorption–desorption processes [64–66].

As mentioned before, Se can exist in four oxidation states (−II, 0, IV, VI) that have different acid–base and solubility properties. Considering that pH and redox conditions dictate the Se redox species in soil, the Pourbaix diagram is useful for the prediction of Se species in soils (Fig. 3) [67]. For the determination of Se species, various chromatographic methods can be used [68].

- **Se(VI)** In highly oxidizing soils (pe + pH > 15), Se exists as Se(VI), the most mobile Se species. Theoretically, Se(VI) can exist as doubly protonated species (H_2SeO_4), biselenate ($HSeO_4^-$), and selenate (SeO_4^{2-}) which depends on pH. However, H_2SeO_4 does not exist in nature ($pK_a = -2.01 \pm 0.06$) and considering the average world soil conditions, selenate (SeO_4^{2-}) is the most dominant form of Se(VI) in soils as it exists over a wide pH range (Fig. 3) [14, 27, 67].
- **Se(IV)** In mildly reducing conditions (7.5 < pe + pH < 15), Se exists as Se(IV). It can be present in the environment as all three species—doubly protonated (H_2SeO_3), protonated ($HSeO_3^-$), and deprotonated species (SeO_3^{2-}). However, considering the normal soil conditions, $HSeO_3^-$ and SeO_3^{2-} are common Se(IV) species found in soils. $HSeO_3^-$ is the dominant Se(IV) species in slightly acidic and neutral soil conditions, while SeO_3^{2-} is dominant in slightly alkaline soil conditions (pH ≥ 8) (Fig. 3) [27, 67].

Mobility of Se(IV) is related to adsorption processes on minerals (e.g., Al and Fe oxides, clay minerals, calcite) and organic matter [69, 70]. Se(IV) has a stronger affinity towards adsorbing constituents than Se(VI), and can also be absorbed in the inner sphere of minerals. On the contrary, Se(VI) is mainly adsorbed on the surface [71]. Since the surface ions are more easily mobilized, Se(VI) is more mobile and available for plant uptake.

In addition, Se(IV) can be immobilized by organic matter—fulvic and humic acids. Considering that both Se(IV) ions and organic matter are negatively charged, Se is immobilized by organic matter (OM) in the presence of iron oxyhydroxide, which acts as a bridge metal, forming the complex Se–metal–OM [72].

- **Se(−II) and Se(0)** Se(−II) is found in reducing (pe + pH < 7.5) and organic-rich soils. It is mostly present in soils in organic compounds (e.g., selenomethionine, selenocysteine), metallic selenides, and sulfide minerals; thus it is not mobile or available to plants [27, 67]. Se(−II) can be found in soil solution under strongly reduc-
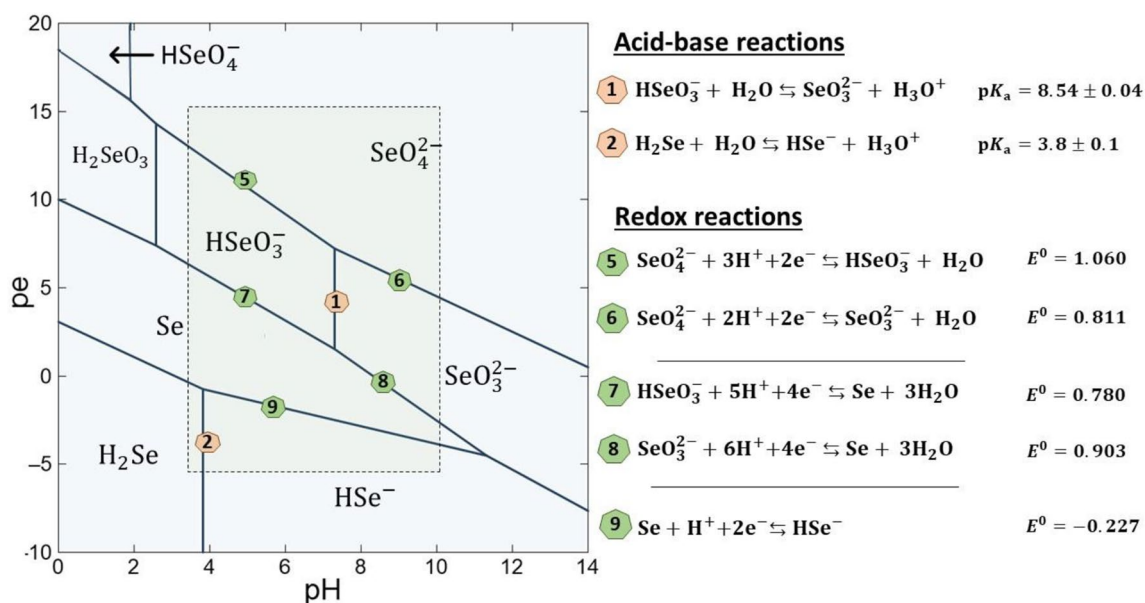
Acid-base reactions

(1) $HSeO_3^- + H_2O \leftrightarrows SeO_3^{2-} + H_3O^+$ $pK_a = 8.54 \pm 0.04$

(2) $H_2Se + H_2O \leftrightarrows HSe^- + H_3O^+$ $pK_a = 3.8 \pm 0.1$

Redox reactions

(5) $SeO_4^{2-} + 3H^+ + 2e^- \leftrightarrows HSeO_3^- + H_2O$ $E^0 = 1.060$

(6) $SeO_4^{2-} + 2H^+ + 2e^- \leftrightarrows SeO_3^{2-} + H_2O$ $E^0 = 0.811$

(7) $HSeO_3^- + 5H^+ + 4e^- \leftrightarrows Se + 3H_2O$ $E^0 = 0.780$

(8) $SeO_3^{2-} + 6H^+ + 4e^- \leftrightarrows Se + 3H_2O$ $E^0 = 0.903$

(9) $Se + H^+ + 2e^- \leftrightarrows HSe^-$ $E^0 = -0.227$

Fig. 3 Selenium pe–pH diagram for Se concentrations of 10^{-10} mol L^{-1} at 25 °C, 1 bar pressure, and 0 ionic strength, with the most relevant acid–base and redox reactions and equilibrium constants. The box framed by broken lines in the diagram represents the soil pe and pH range [67, 80]

ing conditions as HSe^-, the most stable Se(−II) species across the pH range (Fig. 3). Those conditions are found in some soils like gley and wetland [73].

Elemental selenium(0) is formed by reduction processes in soils and is an insoluble and non-toxic form of Se [73]. The reduction processes are governed mainly by microorganisms, which reduce Se(VI) to Se(IV) and further to Se(0) and Se(−II). Many bacterial species (e.g., *Bacillus arseniciselenatis*, *Thauera selenatis*) have been identified to reduce Se by taking Se oxyanions into the cells and reducing them via assimilatory reduction to Se(−II) [74–76]. Besides biotic reduction, Se can also be reduced abiotically by Fe oxides [77].

Oxidation of Se(0) to Se(IV) and further to Se(VI) is also governed by microorganisms [78]. However, the rate of Se(IV) oxidation is much slower than reduction processes. This is visible in the presence of Se(IV) in some soils with oxidizing conditions, where it coexists with Se(VI) [17, 79].

- **Geochemical fractions** Se species in soils can also be classified as geochemical fractions found in soils with descending degree of bioavailability [17, 81, 82]: (1) soluble Se—the most mobile and bioavailable fraction, which mostly refers to Se(VI) oxyanions [83, 84]. (2) Exchangeable Se—which mostly refers to Se(IV) bound to the surface of clay minerals and hydrous oxides. (3) Iron/manganese oxide-bound Se—primarily refers to Se(IV) associated with Fe/Mn, which is difficult for plants to take up but could become mobile with changes

in pH and redox potential [85, 86]. (4) Organic matter-bound Se—includes fulvic acid-bound Se and humic acid-bound Se [87]. Plants can easily absorb fulvic acid-bound Se, but have difficulty absorbing humic acid-bound Se. Humic acid-bound Se is the largest portion in soils in Se-deficient areas in China, while in areas with high and adequate Se in soil, soluble and exchangeable Se are the main species [87]. (5) Elemental Se—highly insoluble and immobile for plant uptake, and only a low level of nanoscale elemental Se(0) can be taken up by plants [88]. (6) Residual Se fraction—primarily occurs in sulfide and silicate minerals as Se(−II) and is unavailable to plants [89].

Se uptake and metabolism in plants

Selenium is an essential element for animals and human health, while no Se requirement has been found for plants [58, 90–92]. Therefore, Se metabolism in plants occurs non-specifically via sulfur metabolic pathways [92]. Plants can take up both inorganic and organic selenium.

Selenate (SeO_4^{2-}) is taken up via sulfate transporters, because of the structural analogy of selenate(VI) and sulfate [93–95], and Se(IV) is taken up via phosphate transporters and Si transporters [96–98]. Uptake of Se in the presence of sulfate and phosphate is suppressed [99, 100], while in the absence of those anions, uptake is increased owing to increased expression of sulfate and phosphate transporter genes to compensate for the lower availability [101].

Once taken up, Se(VI) is reduced to Se(IV) which is further reduced to Se(−II). Se(−II) is then incorporated in organic form—amino acid selenocysteine (SeCys). SeCys is either incorporated into cells, further metabolized into SeMet, or methylated (volatile methylated Se is then emitted into the atmosphere). Detailed metabolic pathways of Se in plants can be found elsewhere [95, 102, 103].

Se at low concentrations can have beneficial effects for plants—simulating plant growth, improving photosynthesis, helping in homeostasis of essential nutrient elements, protecting the plants from a variety of abiotic stresses such as cold, drought, metal stress, etc. [102–107]. However, Se at high concentrations can lead to toxicity causing inhibited growth, chlorosis, and decreased protein synthesis [108, 109].

Inside the plant cells, Se is mostly accumulated in their vacuoles [18, 110]. Plants are categorized into three groups, depending on their ability to tolerate and accumulate Se [111, 112]: (a) non-accumulators, which accumulate Se less than 100 mg Se kg^{-1} dry weight, and cannot survive on Se-rich soils (e.g., grasses and crops); (b) secondary accumulators, which accumulate Se in the range 100–1000 mg Se kg^{-1} dry weight (e.g., *Brassica juncea*, *Brassica napus*, broccoli, *Helianthus*, *Aster*, *Camelina*, *Medicago sativa*); and (c) hyperaccumulators, which accumulate more than 1000 mg Se kg^{-1} dry weight. More than 30 species of Se hyperaccumulators have been identified (e.g., *Stanleya*, *Astragalus* spp., *Conopsis*, *Neptunia*, *Xylorhiza*) [102, 111, 112]. The main form of Se accumulated by Se hyperaccumulators is organic methyl-SeCys, while in other plants a large fraction of Se remains in the inorganic form [113–115]. Unlike Se(VI) and Se(IV), methyl-SeCys does not cause oxidative stress, explaining why some species can tolerate high Se content [29].

Role of Se in health of animals and humans

Higher animals take selenium from crops in both inorganic and organic (selenocysteine, selenomethionine) forms. Selenium gets absorbed mostly in the duodenum and caecum, and the mechanisms of absorption are different depending on the chemical form of the element [116, 117].

Selenocysteine (SeCys)

The role of Se in human health is evident mainly through selenocysteine (SeCys) (Fig. 4), the 21st proteinogenic amino acid. Besides SeCys, a common organic Se compound is selenomethionine (SeMet). The major difference between SeCys and SeMet is that SeMet is randomly incorporated into proteins in place of methionine (a sulfur analogue) and therefore it is not regarded as an amino acid [19]. In comparison, SeCys has all the properties as
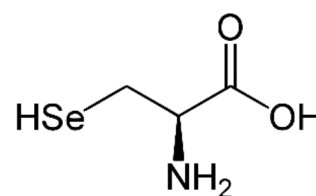
Fig. 4 Structure of ʟ-selenocysteine (SeCys), the 21st amino acid. SeCys is a building block of 30 selenoproteins, which have an important role in human health

common amino acids: it is encoded by DNA and has its own unique codon (UGA), has a unique tRNA and translation machinery [118, 119].

SeCys residues are incorporated in 30 selenoproteins so far identified in human tissues which have an important role in various functions of the body, such as antioxidant defense, the formation of thyroid hormones, DNA synthesis, tumor prevention, fertility, and reproduction [120, 121].

Probably the most characterized selenoproteins include glutathione peroxidases (GPx), which are a family of antioxidant enzymes, whose main function is to neutralize hydrogen peroxide and organic hydroperoxides in the intracellular and extracellular compartments [122]; iodothyronine deiodinases (ID1, ID2, ID3), which play a role in thyroid hormone metabolism [123]; selenoprotein P (Se1P), which is the most abundant selenoprotein found in plasma and plays a role in homeostasis and the transport of selenium in tissues [121, 123]; thioredoxin reductases (TrxR1, TrxR2, TrxR3), which have an antioxidant function, control the intracellular redox potential, and act as a cell growth factor in DNA synthesis and inhibition of apoptosis (programmed cell death) [121, 123, 124], and others.

- **SeCys vs Cys** The insertion of selenocysteine (SeCys) into proteins is much more complicated and requires more energy than insertion of the sulfur analogue amino acid—cysteine (Cys) [125–127]. This caused scientists to question why biological systems would prefer incorporation of SeCys over Cys.

  The main reason why Se is preferable is the chemical difference between Se and S, especially their redox properties. Although S and Se are very similar, Se is heavier and heavier elements generally prefer lower oxidation states [127]. In addition, outer valence electrons of Se are more loosely held and therefore Se has a greater ability to donate an electron pair to form a chemical bond. These properties allowed Se to have faster reaction rates than S [128]. In addition, Se has weaker π bonds in Se oxides which allows Se to cycle between reduced and oxidized states without becoming permanently oxidized [129]. The advantage of resistance to permanent oxidation is visible in its peroxidation cycle (Fig. 5).
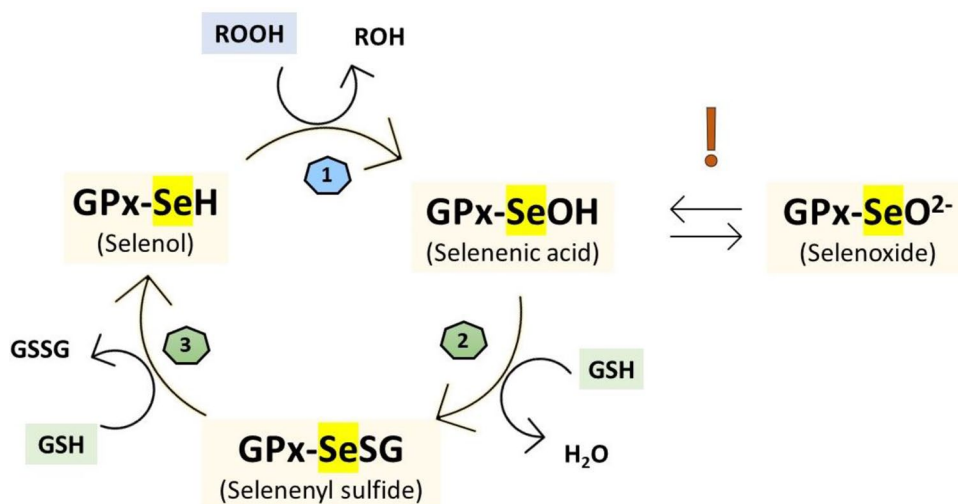
Fig. 5 Glutathione peroxidase (GPx) redox cycle. The main reaction that glutathione peroxidase (GPx) catalyzes is the reduction of hydrogen peroxide and organic hydroperoxides (ROOH) to water and corresponding alcohol (ROH) [122]. The reaction is catalyzed by an active site on GPx which is a selenocysteine residue—selenol. During the reaction, GPx undergoes a redox cycle, where (1) selenol is oxidized by hydroxide peroxide to selenenic acid (GPx-SeOH) [130]. Selenenic acid is then reduced back to the selenol by a two-step process. In the first step, (2) selenenic acid reacts with GSH to form selenenyl sulfide (GPx-SeOH). In the second step, (3) the second GSH reduces selenenyl sulfide back to selenol, producing GSSH as an oxidized form of GSH [131]. Selenenic acid can also be oxidized to Se oxides, which will rapidly be reduced back to continue the active catalytic pathway. This is due to very weak π bonds in Se oxides [129]
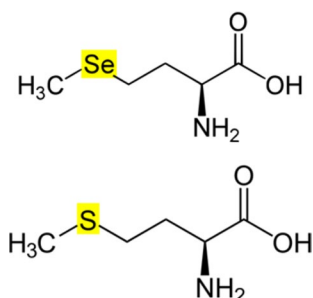

Fig. 6 Similarities between selenomethionine (SeMet) (above) and methionine (Met) (below). SeMet is incorporated into proteins in place of Met with no effects on protein function

Selenomethionine (SeMet)

As mentioned above, SeMet is unspecifically incorporated into proteins, replacing methionine residues (Fig. 6). Proteins containing such unspecifically incorporated selenomethionine residues are not regarded as selenoproteins [17]. Se is also stored as SeMet in the organs and tissues with variable density: 30% in liver, 30% in muscle, 15% in kidney, 10% in plasma, and 15% in other organs [132]. The stored selenium is used when selenium food intake is too low for selenoprotein synthesis [133].

This incorporation of selenomethionine into proteins in place of methionine, without the structural disturbance, became an important experimental tool as a heavy atom label in macromolecular X-ray crystallography, solving the phase problem [134].

Se toxicity and deficiency

Se has one of the narrowest ranges between dietary deficiency (< 40 μg day^{-1}) and toxic levels (> 400 μg day^{-1}), with recommended adult intake approx. 60 μg day^{-1} [14]. Because of to the narrow range, both Se toxicity and deficiency have been recorded in humans and animals.

The toxicity of selenium first became widely known when it was discovered that its toxic effects caused hair and hoof loss in animals during the 1930s, which was known as alkali disease [135]. However, Marco Polo (1254–1324) described selenium poisoning in western China during his travels in the thirteenth century. In his travel diaries, Polo wrote that a poisonous plant caused horses to lose their hair and have deformed hoofs [136].

Berzelius experienced Se toxicity when he had breathed gaseous selenium compounds (hydrogen selenide) and wrote that it "produces a painful sensation in the nose and a violent inflammation which continues for a considerable length of time" [1]. It was not until the 1950s that Se was found to be an essential element in animals, with the discovery that "white muscle disease" in feedstock is caused by selenium and vitamin E deficiency [137].

Past incidents of Se toxicity and deficiency are described below. In addition, the removal of excess Se from waters and

soils, as well as biofortification methods for preventing Se deficiency are discussed.

Occurrence of Se toxicity

Excessive intake of selenium causes Se poisoning of animals and humans called selenosis. It mostly occurs through three pathways [138]: interaction with thiols and generating free radicals [139, 140]; incorporation of excess selenomethionine into structural proteins [138]; and inhibition of selenium methylation metabolism due to excess selenocysteine, causing hydrogen selenide to accumulate [141].

Acute Se poisoning is rarely observed in humans, most often related to inhalation of volatile selenium by industrial workers [14] and overdose of Se supplementation [142]. Acute Se poisoning of nine people in Venezuela was caused by the intake of nuts of the *Lecythis ollaria* tree in a seleniferous area [14]. Chronic exposure to high levels of Se in food and water usually results in hair loss, weak nails, lack of mental alertness, garlic breath odor, and excessive tooth decay and discoloration [143]. Several chronic cases of selenosis in humans and animals have been recorded in history.

In the twentieth century, human selenosis heavily affected the population of Enshi County, Hubei Province of China with the highest prevalence between 1961 and 1964. Yutangba Village was affected the most and therefore evacuated in the late 1960s. The cause of selenosis was coal with high selenium content (more than 300 mg kg^{-1}), which entered the soils and water by weathering. The residents consumed high-Se crops and contaminated water, especially during the highest prevalence of selenosis, when severe drought contributed to the intensity of disease, forcing the villages to eat more vegetables than rice [55]. The reported symptoms were loss of hair and nails, skin lesions, tooth decay, garlic breath odor, and in the most severe cases neurological damage. Average Se intake among individuals showing selenosis was estimated to be 5000 µg day^{-1}. Signs of selenosis were also evident in domesticated animals (hair and hoof loss, inflammation of the feet) and in eggs which had very low hatchability and deformed embryos. In the most affected village, livestock died from Se poisoning [55]. In 2013, Qin et al. [144] reported that water, soils, and crops still have elevated Se content and calculated that the daily Se intake of the residents was approximately 2144 µg day^{-1}, posing a serious risk of chronic selenosis.

Animal selenosis, known as alkali disease, was a major problem in the Great Plains of the USA in the nineteenth century among horses, cows, and pigs, and it was believed that high salt (alkali) waters were the main cause, hence the name. The disease manifested itself through hair and hoof loss and extreme tenderness of the feet. In the 1930s it was discovered that high Se content in crops is the main cause of alkali disease [118].

The most examined case of animal Se poisoning occurred at Kesterson Reservoir during the 1980s [145, 146]. Kesterson Reservoir in San Joaquin Valley (California) was constructed between 1968 and 1975 to receive agriculture drain water and to be used as a part of the wetland wildlife refuge [147]. The main agriculture area from where the water was drained was overlaying a shale with naturally high levels of Se and salt in it. The movement of the water over the shale resulted in the leaching of Se into the water with an average concentration of 300 µg L^{-1}; this water then entered Kesterson Reservoir and bioaccumulated in local wildlife. The bioaccumulation of Se caused mortality of fish populations, deformities of aquatic birds, and their embryos (Fig. 7) [148, 149]. Kesterson Reservoir was closed, and the wetland was transformed into an upland grassland, to remediate the site [146].

After the discovery that selenium toxicity is the main cause, selenosis of aquatic birds was observed in similar environments of the USA—in wetland basins that received waters draining seleniferous soils. Most of these study areas had climate, geology, and hydrology similar to those of San Joaquin Valley [150].

Recently, Se poisoning of fish by coal ash wastewater was observed in Herrington Lake (Kentucky, USA). Coal ash wastewater is discharged into the lake through permitted surface water overflow from ash disposal ponds and through

Fig. 7 Normal (**a**) and deformed (**b**) embryo of black-necked stilts at Kesterson Reservoir. The deformities (eyes missing, protrusion of brain, curled lower beak, upper parts of legs shortened and twisted, one toe on each foot) were caused by selenium bioaccumulation in fish, and therefore in aquatic birds. (© U.S. Fish and Wildlife Service, public domain)

unpermitted discharge from leaks in ash pond dams [151]. Concentrations of Se in water and sediment at some sites were measured as 10 µg L^{-1} and 15 µg L^{-1}, respectively, which is above toxic thresholds for fish reproduction and survival (1.5 µg L^{-1} and 2 µg L^{-1}, respectively) [152–154]; 12.2% of examined juvenile *Micropterus salmoides* exhibited spinal and/or craniofacial malformations [151].

Remediation strategies for polluted water and soil

There are several physical and chemical methods that can be used for removing selenium from polluted water and soil [155, 156], e.g., reduction techniques by nanomaterial—nZVI (nanoscale zero-valent iron). Nanomaterials are both natural and engineered materials, in which at least one dimension is between 1 and 100 nm [157]. One of their main properties is increased relative surface area, which can lead to greater chemical reactivity. This is the main reason why nZVI, a type of nanomaterial, is gaining popularity compared to conventional bulk ZVI (zero-valent iron) materials, usually used in filters and electrodes [158]. nZVI has been promising for in situ remediation as it is effective in reacting with many types of organic contaminants and most heavy metals through surface reduction and complexation. Se(IV) is removed from water via nZVI by chemical reduction to Se(−II) and Se(0) and encapsulation in the nanoparticles [159]. In coagulation–flocculation methods, Se is adsorbed onto Al and Fe-based coagulants. Most often coagulants are Al and Fe salts, which, when added to water, hydrolyze and precipitate as Al and Fe oxide-hydrates [160]. Contaminants, e.g., Se, are then adsorbed and precipitated with coagulants [160, 161]. In precipitation, Se ions precipitate from weak acidic solutions using sodium sulfide [162]. In coprecipitation, the trace element is immobilized in the mineral during crystal growth [163]. Other techniques include electrochemical methods [164], electrocoagulation [165], membrane separation [166, 167], adsorption [156], and electrokinetics which is most effective in treating near-saturated clay soils polluted with metals [156, 168].

Besides physical and chemical methods, there are several biological treatments like phytoremediation and bioremediation. In phytoremediation, Se accumulators are potentially useful in removing Se from water and soil. *Brassica* species have been used for terrestrial remediation [84, 169, 170], while several macrophytes species have been used to clean Se present in agricultural drainage water [171–173]. Choosing a plant for Se phytoremediation includes several factors: a plant needs to grow well under the local conditions, be competitive, grow fast, produce large biomass, be tolerant to Se, and can accumulate or volatilize Se. Phytoremediation efficiency of plants can be enhanced using genetic engineering [174].

Another remediation strategy is bioremediation, where microorganisms convert Se oxyanions to elemental, insoluble Se [175]. Several bacteria species have been isolated and demonstrated as effective in reducing Se(IV) to Se(0), e.g., *Alishewanella* sp. WH16-1, which was isolated from the soil of a copper and iron mine [176]; *Ralstonia* sp., which removed up to 60% of Se from coal-polluted soil [177]. In terms of optimal cost and efficiency, biological treatment is one of the most promising approaches in remediation strategies [178].

Occurrence of Se deficiency

Selenium deficiency in animals was first observed in the 1950s as "white muscle disease" in feedstock. It is a disease caused by a deficiency of selenium and vitamin E in dietary intake and most often affects young lambs and calves. Selenium and vitamin E are antioxidants and therefore deficiencies of these nutrients lead to oxidative damage to cells within the body. The muscle cells are the most vulnerable to damage, and the disease can result in sudden heart failure by mineralization of the heart muscle [179, 180]. Fertilization of Se-deficient soils or supplementation of livestock with Se compounds showed efficiency in preventing the occurrence of the disease [181, 182].

Selenium deficiency in humans is regarded as a major health problem for 0.5–1 billion people worldwide [183], which will probably increase in the future as a result of climate change [57]. Se deficiency has been associated with more rapid HIV-disease progression and higher HIV-related mortality [184, 185] and increases risk of several types of cancer [186].

Prolonged selenium deficiency in humans can result in serious diseases. Two endemic diseases are recognized as being worsened by Se deficiency, Keshan disease and Kashin–Beck disease, both widely distributed in China.

Keshan disease (KD) is an endemic chronic heart disease characterized by enlargements of the heart and congestive heart failure (Fig. 8). It occurs in specific Se-deficient rural areas in China (Keshan province) with peak prevalence in the early 1960s [187]. The disease is associated with low selenium intake due to low selenium levels in food and affects mainly children and pregnant women [188]. It is proposed that, along with low Se content, there are other factors that contribute to the development of the disease. A mutated strain of cardiotoxic Coxsackievirus has been identified as a possible factor, as well as polymorphisms in glutathione peroxidase (GPx) genes causing low activity of that enzyme [189, 190]. Supplementation with selenium funded by government was shown to be effective in reducing and preventing the disease [187, 191]. As a result, acute KD has not been detected for 20 years, while chronic cases are continuously monitored and managed [192].
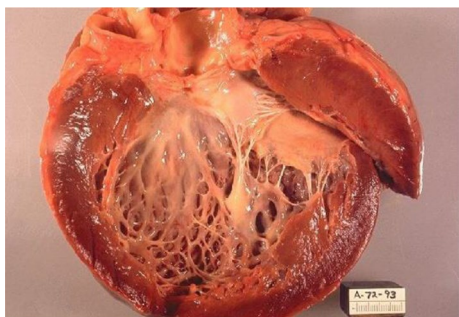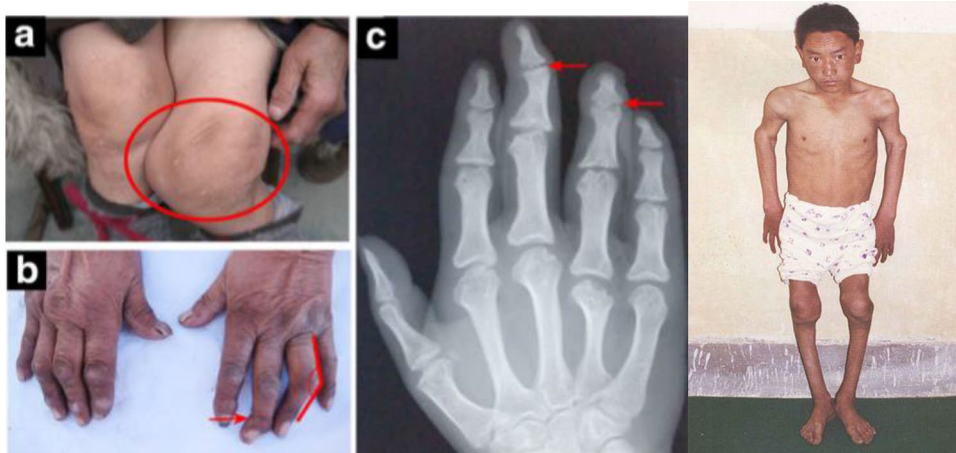
Fig. 8 Keshan disease is endemic dilated cardiomyopathy, characterized by enlargement of the heart. The heart is larger and more rounded than a normal heart. (© Dr. Edwin P. Ewing, Jr., public domain)

Kashin–Beck disease (KBD) is an endemic osteoarthropathy characterized by deformity of affected joint cartilage and epiphyseal plate cartilage of the four limbs (Fig. 9). It primarily occurs in agricultural regions of eastern Siberia, northern Korea, and in the central regions of China [193, 194]. Four factors have been associated with the disease: selenium deficiency, iodine deficiency, contamination of grain by fungi (T-2 toxin and mycotoxin moniliformin), and water pollution with organic material and fulvic acid [193, 195–197]. Se content in cultivated topsoils in affected areas ranged from 0.05 to 0.29 mg kg^{-1} [198]. Se supplementation has been effective in some affected areas, where the rate of KBD declined by 10–50%. However, in some areas Se supplementation has not been effective, indicating that selenium is not an original etiology but an important environmental risk factor [199, 200]. Research indicates that the lower the level of environmental selenium is, the more severe the disease is [201]. Changing fungi-contaminated grain has been an effective method in preventing KBD, and by the end of 2015 KBD was eliminated in more than 90% of the affected areas [192].

Biofortification is one of the promising approaches to combat emerging Se deficiency. Biofortification is a process in which levels of micronutrients in crops are increased to battle micronutrient deficiency, e.g., selenium deficiency [29]. Some of the methods in biofortification include applying inorganic Se-containing fertilizers to soils [59], foliar application of Se(IV) and Se(VI) [203], genetic engineering [169], and using waste products (plant material) from phytoremediation [204].

Se biofortification has many advantages over direct inorganic Se supplementation, e.g., Se in plants is transformed into organic forms, which has a higher bioavailability for humans and animals [205].

Some methods, like applying inorganic fertilizers, can become wasteful, as severalstudies showed that Se was reduced to insoluble forms after it was added to the soil [183]. Foliar application and genetic engineering were shown to be more efficient in terms of wastefulness [29, 183].

Conclusions

Selenium is found in all environments, where it cycles through rocks, atmosphere, waters, soils, and the food chain. It is usually present in relatively low concentrations, making it hard to mine Se. Therefore, identifying and reviewing selenium sources is of great importance for future generations. Se deficiency could become a global problem in the future, which highlights the need for directing research towards mapping Se-deficient areas, identifying Se speciation and fractionation in soils, and developing biofortification and remediation strategies.

Fig. 9 Deformities of **a** knees, **b** interphalangeal joints, and **c** the X-ray radiographs of deformed interphalangeal joints caused by Kashin–Beck disease, an endemic osteoarthropathy (© Tai et al. [202], Open Access), and **d** patient with KBD (© public domain)

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