Part I

The Selenium Cycle

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

Chapter 1

Selenium in the environment

Martina Cappelletti, Valerio Funari,
Giorgio Gasparotto, Enrico Dinelli and
Davide Zannoni

1.1 INTRODUCTION

Chapter 1 is intended to provide the essential background information to assist operators and researchers who use technologies for the treatment of selenium (Se) in environmental (soils, waters, sediments, air) and biological (foods) samples in addition to analysis of Se-molecular speciation in living organisms (plants, microorganisms, animals and humans). In this regard, it is important to underline that numerous reviews and reports have been published in the last decade on this and related topics (Hosnedlova *et al.*, 2018; Khurana *et al.*, 2019; Nancharaiah & Lens, 2015a, b; Preda *et al.*, 2015; Tan *et al.*, 2016; Winkel *et al.*, 2012). Therefore, all readers are kindly invited to refer to the recent literature on the subject – in addition to chapters 2 to 12 of this volume – for complete information on the role and importance of selenium in nature.

1.1.1 Historical background

Selenium ($^{34}_{79}$Se) is a chemical element of great importance for living beings, which was originally mistaken for tellurium (Te) until the Swedish chemist Jacob Berzelius (Berzelius, 1818) recognized it as a distinct element in 1817 (Trofast, 2011). Since Se was closely related to Te, which was named after

© 2021 The Editors. This is an Open Access book chapter distributed under the terms of the Creative Commons Attribution Licence (CC BY-NC-ND 4.0), which permits copying and redistribution for noncommercial purposes with no derivatives, provided the original work is properly cited (https://creativecommons.org/licenses/by-nc-nd/4.0/). This does not affect the rights licensed or assigned from any third party in this book.
The chapter is from the book *Environmental Technologies to Treat Selenium Pollution: Principles and Engineering* by Piet N. L. Lens and Kannan Pakshirajan (Eds.).
doi: 10.2166/9781789061055_0003

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

the Latin word for earth, *tellus* (Klaproth, 1798), Berzelius chose to name this new element selenium, in reference to *selene*, the Greek name for the moon goddess.

Selenium has a long history of being misunderstood since it has repeatedly been mistakenly considered as a strong toxicant, mainly due to inadequate analytical data. Indeed, the crucial role of selenium in the environment and for human beings became evident only in the 1930s, but it was exclusively associated with toxicity – selenosis – that is the result of excessive Se exposure. An example that illustrates the wrong reputation attributed to selenium as a notorious environmental toxin is the case of two livestock diseases, that is, alkali disease and blind staggers, which were initially fully attributed to Se. There are certain types of plants in western North America – commonly known as locoweed and/or crazyweed – which accumulate high amounts of Se that could have been the cause of severe neurological damage to the animals grazing on these lands. Locoweed is a general name for plants that produce swainsonine, a phytotoxin harmful to livestock mostly present in three plant genera of the Fabaceae's family: *Swainsona, Oxytropis* and *Astragalus* (see Section 1.3.3.4 of this chapter). Livestock poisoned by chronic ingestion of large amounts of swainsonine develop a medical condition known as locoism (also swainsonine disease) reported most often in cattle, sheep, and horses. Some locoweed species, including a few that produce swainsonine, accumulate selenium, and this has led to confusion between swainsonine poisoning and selenium poisoning. Even though Se did not cause as many poisoning episodes as were attributed to it, it is now well established that acute or chronically high Se exposure in food or water certainly causes debilitating symptoms and lethality. On the other hand, selenium's bad reputation is unfortunate because most of its roles in the environment are beneficial rather than harmful, and there are far more areas around the world where deficiency is a problem than regions where selenium excess is an issue (Combs, 2001; see also Section 1.1.3). The famous dictum of Philippus Theophrastus Aureolus Bombastus von Hohenheim, the German physician, universally known as Paracelsus, that "*…solely the dose determines what is or it is not a poison…*" seems particularly suitable for describing the role and effects of selenium on living organisms.

1.1.2 The rising of interest in selenium research

Research on selenium has undergone a surge in recent years following new data and discoveries on the importance of this metalloid in the fields of medical biotechnology and human health, but not only in these fields. In fact, selenium has a wide use in electronic applications, solar cells, the glass industry, photocopying, the cosmetic industry and as a dietary supplement (Bodnar *et al.*,

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

2016; Naumov, 2010) thus to be considered a high commercial value element. In agriculture, for example, selenium is applied as fertilizer in Se-deficient soils (Lavu *et al.*, 2012) and as an inhibitor of sulfate – mediated by toxic methyl-mercury production in paddy fields where the addition of selenium (in the form of selenite or selenate) removes free mercury in the soil generating stable Hg-Se complexes (Wang *et al.*, 2016b).

Estimates for world consumption of selenium are in the order of 40% in metallurgy, 25% in glass manufacturing, 10% in agriculture, 10% in chemicals and pigments, 10% in electronics, and 5% in other uses with its global annual production estimated at approximately 2800 tons in 2018 with China, Japan, Germany and Belgium being the major producers (U.S. Geological Survey, 2019) (see details in Section 1.2.3). Electrolytic manganese production is the main metallurgical end-use for selenium in China, where selenium dioxide is used in the electrolytic process to increase current efficiency and the metal deposition rate. Selenium consumption in China has increased in recent years and 51 electrolytic manganese producers were reported to have been operating and consuming selenium in 2017 (the latest information available), up from 47 reported in 2016 (U.S. Geological Survey, 2019). As a matter of fact, while recovery of selenium from anode slime formed as a by-product of metal refining may prove insufficient to meet the global demand of selenium in the future, there is need to reuse and recover selenium from soil/water habitats having an excess of selenium (Oldfield, 2002) using novel and hopefully non-invasive/environmentally compatible approaches to replenish the selenium resources (Nancharaiah & Lens, 2015a, b; Tan *et al.*, 2016) (see Section 1.2.3 of this chapter along with Chapters 6 and 7 of this book).

In addition to its use in industry and agriculture, selenium has a fundamental role in the metabolism of animals and humans (Fairweather-Tait *et al.*, 2010; Huawei, 2009; Papp *et al.*, 2007). To avoid both the lack and excessive intake of selenium, the World Health Organization (WHO, 2011) recommended a dietary allowance ranging from a minimum of 40 to a maximum of 400 µg of Se per day. Indeed, selenium deficiency and toxicity depend strictly on the location and environmental conditions. There are extreme conditions of Se concentration, that is, lack or excess of Se in the soil, only in specific areas of the planet (El-Ramady *et al.*, 2014a, b), such as China, India, the Middle-East and some European countries (e.g., Poland and western Russia), which are known for selenium deficiency in soils which was associated with heart disease and bone disorders (Lemly, 1999). One of the most striking examples is the so called Keshan's disease, a cardiomyopathy caused by a combination of dietary deficiency of selenium and the presence of a mutated strain of the Coxsackie-virus, named after Keshan County of Heilongjiang province in northeast China where symptoms were first noted. These symptoms were later found prevalent in a wide belt extending from north-east to south-west China,

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

all due to selenium-deficient soil (Beck *et al.*, 2003; Ren *et al.*, 2004). Similarly, the disease known as Kashin-Beck, named after the two Russian military physicians N.I. Kashin and E.V. Beck who described it for the first time in regions of south-east Siberia bordering China, is an endemic osteo-arthropathy which is associated with the consumption of grains with a very low selenium content (Fordyce, 2005).

Although there are several million people in the world potentially subjected to selenium deficiency, it is equally true that many sanitary problems due to selenium excess have been recorded in various regions of the planet as well (El- Ramady *et al.*, 2014a). Indeed, selenium tends to bioaccumulate in the aquatic environment and becomes toxic to fish and birds that feed on fish containing elevated levels of this element (De La Riva *et al.*, 2014; Miller *et al.*, 2013; Zhang *et al.*, 2008). Further, its transfer to the food chain has caused additional toxic effects in humans and animals (selenosis) such as nausea, vomiting, dermal and neurological dysfunction or even paralysis and cardiovascular symptoms (De La Riva *et al.*, 2014; Duntas & Benvenga, 2014). Issues related to selenium toxicity are covered in more detail in Chapters 5, 6 and 7 of this book.

1.1.3 Microbial processing of selenium

As also reported in the following Section 1.2, selenium is found in four inorganic oxidation states (−2, 0, +4, +6). Elemental selenium Se(0) is highly insoluble, relatively non-toxic to humans and it occurs as a prevalent species under anoxic conditions (Barceloux, 1999), while selenide Se(−2) is both highly reactive and toxic although rapidly oxidized to Se(0) through inorganic and/or biochemical reactions (Turner *et al.*, 1998). In this respect, selenium bioprocessing in the environment is catalysed by Se-metabolizing bacteria which are able to either reduce or oxidize it, but also to generate methylated and volatile derivatives such as dimethylselenide (CH_3SeCH_3), dimethyl selenyl sulfide (CH_3SeSCH_3) and dimethyl diselenide ($CH_3SeSeCH_3$) (Chasteen & Bentley, 2003). The most oxidized selenium forms, selenite (SeO_3^{2-}) and selenate (SeO_4^{2-}), can be taken up by several species of microorganisms and reduce these oxyanions to less toxic elemental selenium, Se(0). Representative genera include *Wolinella*, *Pseudomonas*, *Sulfurospirillum*, *Enterobacter*, *Thaurea*, *Bacillus*, *Citrobacter*, *Azospirillum*, *Paenibacillus*, *Rhizobium*, *Stenotrophomonas* and *Rhodococcus* (Antonioli *et al.*, 2007; Hunter *et al.*, 2007; Presentato *et al.*, 2018; Sidique *et al.*, 2006; Tugarova *et al.*, 2014; Yao *et al.*, 2014; Zhang & Frankenberger, 2005). Deposition of Se(0) as particles of variable shape and size may occur in the extracellular milieu but also in the cytosolic and/or the periplasmic space in association with the cell wall or membrane (Gerrard *et al.*, 1974; Klonowska *et al.*, 2005; Losi &

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

Frankenberger, 1997; Oremland *et al.*, 2004; Presentato *et al.*, 2018) [see Chapters 3 and 10 for a complete discussion on this topic].

Several microorganisms have the ability to incorporate selenium derived from selenate or selenite into organo- Se compounds as selenocysteine and selenomethionine via the mechanism known as assimilatory Se-reduction (Lenz & Lens, 2009; Sarret *et al.*, 2005). Figure 1.1 shows how bacteria determine the distribution of the main Se oxidation- reduction forms [elemental selenium Se(0), selenite Se(+4) and selenate Se(+6)] in a contaminated habitat as a consequence of industrial and agricultural activities.

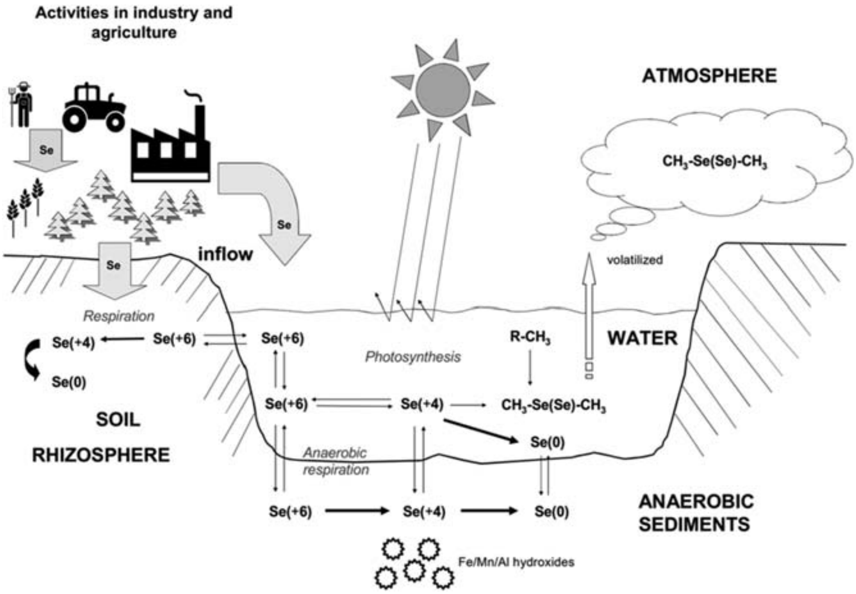


Figure 1.1 Schematic diagram showing the metabolic processes (*respiration*, *anaerobic respiration*, *photosynthesis*) by which bacteria determine the distribution of the main selenium oxidation-reduction forms: elemental selenium Se(0), selenite Se(+4), and selenate Se(+6) in a contaminated habitat as a consequence of activities in industry and agriculture. Natural processes such as weathering, soil leaching and volcanic emissions releasing selenium into the environment, are not shown. The scheme depicts four environmental phases: atmosphere, soil-rhizosphere, anaerobic soil-sediments and water. Symbols and abbreviations: Se, selenium element; R-CH_3, organic methyl groups; and the cloud, volatile CH_3-Se(Se)-CH_3. The thickness of the arrows indicates the prevalent bacterial activity; rough circles symbolize the binding of selenite, mainly Se(+4), to soil/sediment particles of iron (Fe), manganese (Mn) or aluminium (Al) hydroxides. (Modified from Sharma *et al.*, 2015 and Zannoni *et al.*, 2008; see text for further details).

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

1.2 SELENIUM CHEMISTRY

1.2.1 Chemical features of selenium

Selenium belongs to Group VIA of the Periodic Table of the elements and is located between sulfur and tellurium. Its chemical and physical properties are intermediate between those of a metal and a non-metal. Its atomic number is 34 and its atomic mass is 78.96. Selenium has six stable isotopes, namely: ^{74}Se [0.87%], ^{76}Se [9.02%], ^{77}Se [7.58%], ^{78}Se [23.52%], ^{80}Se [49.82%], and ^{82}Se [9.19%]; the relative abundances of these isotopes are indicated in brackets (Hoffman & King, 1997).

Selenium commonly exists in four valence states: −2, 0, +4, and +6, the −2 form being more common for organic compounds. Elemental selenium has a melting point of 217°C and a boiling point of 685°C. Between 74 and 217°C, exothermic modifications of crystalline forms are observed (Langner, 2000). Pure selenium, like sulfur, is allotropic and exists in three forms, including (1) a grey or 'metallic' thermodynamically stable hexagonal form displaying properties of a semiconductor, (2) a red monoclinic form, and (3) a vitreous form.

1.2.2 *Pourbaix* diagram of selenium in water

The behaviour of selenium in aqueous solution is dependent on redox state and pH, as described by the Eh-pH diagrams of Figure 1.2. Selenium is highly mobile under oxidizing, acidic, neutral and alkaline conditions mostly as selenate and selenite. In very oxidizing conditions the Se^{6+} is stable, and selenate [SeO_4^{2-}] is the dominant form in solution under a wide range of pHs, while under very acidic conditions biselenate [$HSeO_4^{-}$] is the common form. Under less oxidizing conditions, Se^{4+} is stable and can be present in solution as selenite [SeO_3^{2-}] at neutral to alkaline conditions or biselenite [$HSeO_3^{-}$] at pH ranging

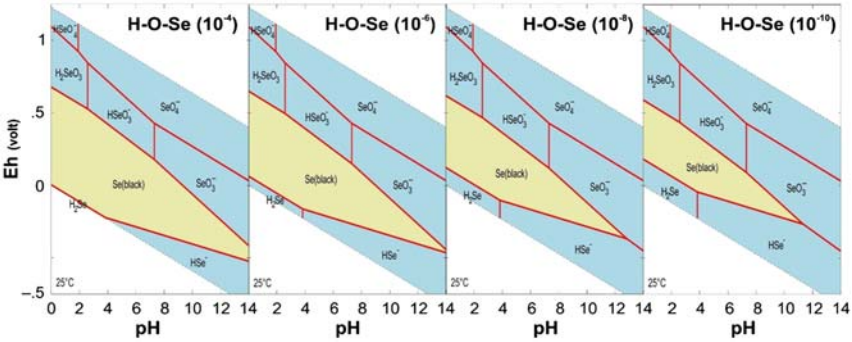


Figure 1.2 Eh-pH diagrams (*Pourbaix* diagrams) for the system Se-O-H at different selenium activities.

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

from neutral to acidic. At lower pH, selenous acid [H_2SO_3] is stable. Selenium mobility decreases in reducing conditions, at neutral to acidic pH, due to the formation of elemental Se whose stability field increases as dissolved selenium activities increase (Figure 1.2). Under reducing conditions, Se tends to form selenide ions that react with metals eventually present in solution, forming stable selenide minerals from aqueous solution even at low metal activities. As suggested by the Eh-pH diagrams, for example, involving Pb (lead) and Ag (silver), reducing conditions lead to the formation of clausthalite [PbSe] or naumannite [Ag_2Se] (Figure 1.3) and possibly other selenides in combination with Fe (iron), Co (cobalt), Ni (nickel) and Cu (copper). Under reducing conditions, Se also tends to replace sulfur in more common minerals such as pyrite, chalcopyrite, pyrrhotite and sphalerite.

The behaviour of selenium in solution is mostly as complexed oxyanion which is strongly influenced by the presence of natural particles of aluminium and iron oxy-hydroxides. These phases, in turn, with their high surface areas and point of zero charge (Chan *et al.*, 2009; Sparks, 2003) might adsorb dissolved selenium species, although it is reported that selenite is less prone to surface adsorption (Christophersen *et al.*, 2013; Meher *et al.*, 2020) due to its high tendency to remain in the aqueous phase. It must be stressed that selenite has been found to be more toxic than selenate and organo-selenium compounds due to its higher solubility and bioavailability (Torres *et al.*, 2011).

The redox chemistry of selenium is complex, given the importance of the biotic transformations involved in its cycling (Lenz & Lens, 2009) and with a range of reactions depending on the environmental conditions (assimilatory and dissimilatory reduction, alkylation, dealkylation and oxidation).

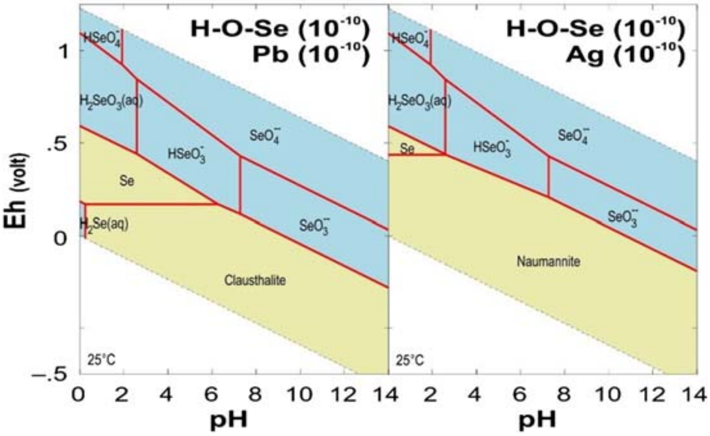


Figure 1.3 Eh-pH diagrams for the system Se-Pb-O-H and Se-Ag-O-H.

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

1.2.3 Global uses of selenium

The selenium content in the Earth's crust averages 0.05–0.09 mg/kg, approximating the typical concentration of cadmium and antimony and ranking above silver, mercury, and uranium. Higher concentrations of selenium are found in volcanic rocks, sandstones, uranium deposits and organic matter-rich rocks. However, the natural occurrence of these minerals can be rarely considered high-grade ore deposits. Although present in many minerals, selenium is generally recovered as a mining by-product from deposits mined for other elements, such as copper, lead, and silver (Langner, 2000). Therefore, selenium is mainly sourced from sulfidic ores in the context of primary ore mining, even if the mean Se/S ratio of magmatic sulfides is rather low (≈0.1). Its principal supply comes from sulfide ores in Canada, the USA, Bolivia, and Russia.

Commercially exploited Se-ore deposits have been referred to four types of mineralization (Stillings, 2017), namely: magmatic, volcanic, hydrothermal, and exogenic. The latter is secondary mineral ore produced by chemical and physical weathering. Many of the secondary mineral sources are high in Se under peculiar conditions (e.g., volcanic soils, and marine shale) owing to erosion transport and deposition from seleniferous parent material or atmospheric selenium supplies. The occurrence of selenium depends upon the composition of the ore, the stratigraphic position of ore minerals, and tectonic settings (Figure 1.4).

Selenium enrichment has been observed in marine samples collected from black smokers and iron-copper massive sulfides associated with the East Pacific Rise. Here, Se-rich mineralization primarily occurs in the inner part of the deposit in equilibrium with hydrothermal fluids. On the other hand, clear examples of exogenic deposits are marine phosphorites that may contain around 300 mg/kg Se. Marine and sub-aerial highly organic shales contain as much as 1500 mg/kg Se because it may accumulate in detrital organic matter (Parnell *et al.*, 2016). High Se concentrations in sedimentary bedrock units likely derive from their depositional origin in marine basins with high primary biological productivity (Presser *et al.*, 2004). As such, organic detritus on the seafloor may experience the consequences of the biomediated Se cycle: with geological time, the loss of organic matter due to diagenesis accumulates selenium and other trace elements in the sediments that may be exhumed today (e.g., the Phosphoria Formation). For this reason, knowledge about the distribution of selenium-rich rocks found in sedimentary basins enriched in organic carbon (Presser *et al.*, 2004) is useful in identifying new selenium resources (Stillings, 2017). Carbon-rich rocks usually show high selenium concentrations owing to the possible selenium substitution for sulfur during diagenesis. Natural resources for potential Se cultivation are coal, marine phosphate deposits, and shales (Presser, 1999) (Figure 1.4).

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

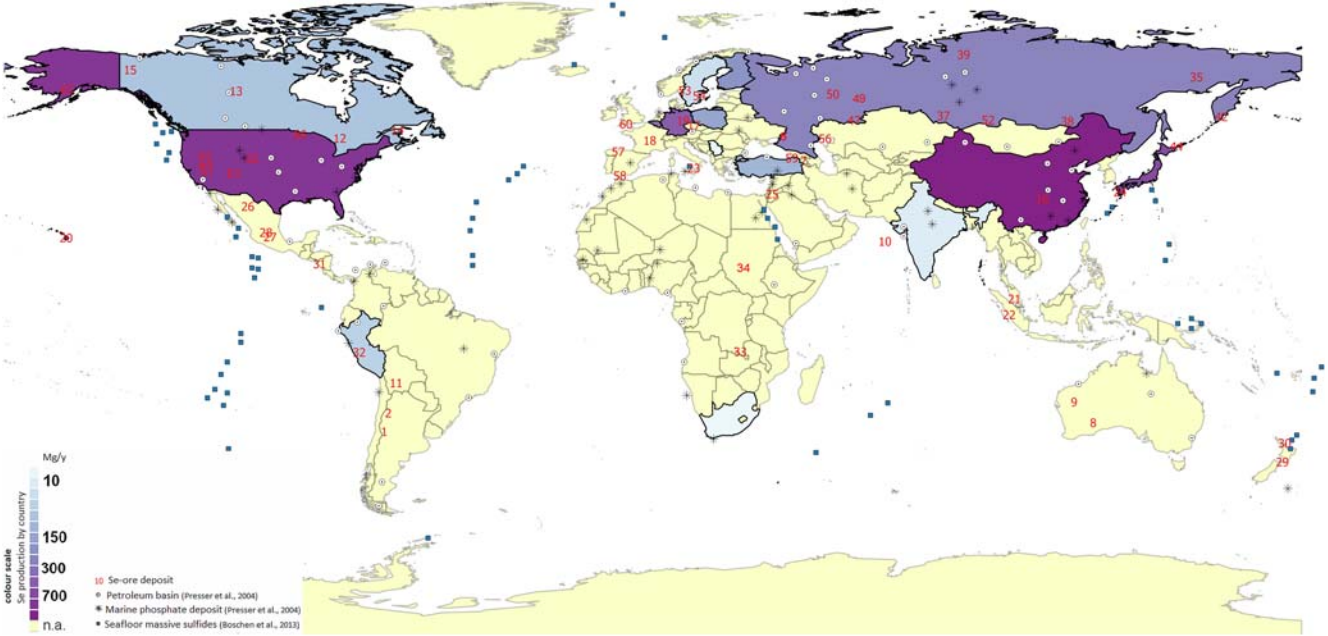
When the host mineral is selenide, the ore deposits can be grouped into four types:

(a) telethermal selenide vein-type
(b) unconformity-related uranium deposits
(c) sandstone-hosted uranium deposits (roll-front type)
(d) gold-silver epithermal volcanic-hosted deposits

Examples of type (a) deposits are the Tilkerode-Zorge-Lerbach deposit in the Harz Mountains (Germany), the Pacajake and El Dragon deposits in Bolivia, Hope's Nose deposit in the United Kingdom, and the Sierra de Umango and Sierra de Cacheuta deposits in Argentina. In these deposits, selenides occur in veins hosted in sedimentary rocks, associated with carbonate minerals, hematite, and rare sulfides (e.g., those containing precious metals, gold and platinum group elements). Type (b) ores are found in veins of the Massif Central (France), the Bohemian Massif in the Czech Republic, and the Athabasca area of northern Saskatchewan in Canada, associated with sulfides, arsenides, hematite, carbonates, and uraninite minerals in Co-Cu-Ni ores. The occurrence of type (c) deposits is from uranium and vanadium sandstone ore deposits in the USA (Colorado Plateau, Oklahoma, Wyoming, and Texas) where Se spots locally at elevated concentrations (from thousands of mg/kg up to 3 weight per cent) were measured in uranium deposits of the Colorado Plateau (Coleman & Delevaux, 1957). Remarkable Se concentrations can be found in Fe-rich selenides (e.g., ferroselite), clausthalite (PbSe), and native selenium. Mineralization of economic importance occurred with other redox-active minerals in dynamic equilibrium between oxidizing and reducing environments. Hatten Howard (1977) hypothesized that continued cycling of oxidative dissolution (of reduced minerals in the unaltered rock) and redeposition (at the redox interface) could concentrate selenium, iron, and the uranium-ore minerals within the Fe-S-Se system. Selenium type (d) deposits occur at low-sulfidation epithermal gold-silver deposits (John, 2001) like those of Japan, Nevada (USA), New Zealand, Mexico, and Russia. In these ore deposits, significant Se concentrations are in silver selenides and, less commonly, in bismuth, copper, antimony, and lead selenides, all associated with sulfides, sulfosalts, gold and native elements. Primary geogenic Se ores have shown conditions that favour the formation of sulfides rather than selenides.

The average selenium content in magmatic and associated hydrothermal sulfides is 0.02%. The selenium estimated content is based on copper production figures: in porphyry copper ore with 0.5% copper, the selenium content is 2.5 mg/kg, or a copper-to-selenium ratio of 2000:1. For many years, selenium production was estimated based on copper production using a factor of 0.0215% or, for very productive ores such as for example the Sudbury basin of the Ontario region, 0.064% (George & Wagner, 2009). Selenium can be present in absolute concentrations of hundreds mg/kg in tuffaceous rocks, and several g per weight

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user



Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

Figure 1.4 Global map of active Se-ore deposits and predictive map of selenium sources associated with organic-rich depositional marine basins (modified from Presser *et al.*, 2004) and seafloor sulfide deposits (modified from Boschen *et al.*, 2013). Borders and country boundaries are from www.thematicmapping.org; Selenium deposits location are from www.mindat.org (Butterman & Brown, 2004; Kogel, 2006; Stillings, 2017). Se-ore deposits by geographic area – as labelled by numbers in figure – are the following: **Africa**: 33. Katanga deposit, Katanga province, Kinshasa, Democratic Republic of the Congo; 34. Shinkolobswe deposit, Democratic Republic of the Congo – **Eastern world** (**including the Middle East**): 3. Agarak deposit, Armenia; 4. Dastakert deposit, Armenia; 5. Dzhindara deposit, Armenia; 6. Kadzharan deposit, Armenia; 7. Miskhana deposit, Armenia; 16. Yutangba Se deposit, Hubei, Central China, China; 21. Redzhang Lebong deposit, Sumatra, Indonesia; 22. Salida and Redzhang Lobong, Indonesia; 24. Hishikari, Japan; 25. Jordan Areva Resources, Amman Governorate, Jordan; 59. Murgul deposit, Turkey – **Europe**: 17. Bohemian Massif of the Czech Republic, Czechia; 18. Massif Central of France, France; 19. Eisenberg, Tilkerode-Zorge-Lerbach deposit in the Harz Mountains, near Korbach, Germany; 23. Lipari Islands, Italy; 53. Glava, Grusen, Moberg, Tinnsjå, Tjøstølflaten, Sweden and Norway; 54. Skrikerum deposit, Småland, Sweden; 55. Idrija, Slovenia; 56. Almaden, Ciudad Real Province, Spain; 57. Providencia Mine, León Province, Spain; 58. Los Reales, Estepona, Málaga Province, Spain; 60. Traour ar Ru, Bahulien, Lannion, Côtes-d'Armor, Brittany Province, France – **Latin America**: 1. Cacheuta Mine, Cerro and Sierra de Cacheuta, Luján de Cuyo, Mendoza Province, Argentina; 2. Sierra de Umango, La Rioja Province, Argentina; 10. Pacajake Selenium Mine, Llallagua, Bolivia; 11. El Dragón mine, Antonio Quijarro Province, Potosí, Bolivia; 26. San Onofre mine, El Doctor, Queretaro, Mexico; 27. El Oro, Mexico; 28. Guanajuato, Mexico; 31. Cerro Negro volcano, León Department, Nicaragua; 32. La Oroya Complex, Peru – **North America**: 12. Sudbury basin, Ontario, Canada; 13. Lake Athabasca area of northern Saskatchewan, Canada; 14. Gaspé Copper mine, Murdochville, La Côte-de-Gaspé, Gaspésie-Îles-de-la-Madeleine, Québec, Canada; 15. Tombstone Mountains, Dawson mining district, Yukon, Canada; 20. Hawaiian Islands, Hawaii, USA; 61. Comstock and Goldfield, Nevada, USA; 62. Shoshone, Jasper, Riverton deposits, Wyoming, USA; 63. Colorado Plateau, Colorado, USA; 64. The western Great Basin, Nevada, USA; 65. Bristol Bay, Pebble deposit, Southern Brooks Range, Red Dog, USA and Alaska; 66. Duluth Complex, Bab-bitt deposit, Minnesota, USA; 67. Humboldt County, National District, Buckskin Mountain, Nevada, USA – **Oceania**: 8. Queen Victoria Springs Nature Reserve, Menzies Shire, Australia; 9. Milgun Variscite Mine (Mount Deverell), Milgun Station, Meekatharra Shire, Australia; 29. Native sulfur-selenium outcrops, New Zealand; 30. The Great Barrier Island, New Zealand – **Russia**: 35. Upper Seymchanskoye deposit, Verina River basin, Far Eastern; 36. Uchaley deposit, Urals; 37. Kirovskoye deposit, Krasnoyarsk, Siberia; 38. Bukuka deposit, Siberia; 39. Noril'sk, Siberia; 40. Kurile Islands, additional Kamchatka locations, Far Eastern; 41. Mendeleev Volcano, Kunashir Island, Far Eastern; 42. Mutnovskii Volcano, Kamchatka, Far Eastern; 43. Paramushir Island, Far Eastern; 44. Prasolovskoye, Kunashir Island, Far Eastern; 45. Karabash group, Tatarstan, Volga; 46. Mauk deposit, Urals; 47. Gay deposit, Urals; 48. III International deposit, Urals; 49. Levikha XIV deposit, Urals; 50. Sibay deposit, Urals; 51. Zyuzel'skoye deposit, Far Eastern; 52. Ust' Uyok deposit, Turan District, Tuva, Siberia.

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

cent (g/100 g) in sulfides that host mercury and antimony deposits. The volcanic deposits of andesite tuffs (e.g., Jasper, Riverton, and Shoshone deposits, USA) yield up to 120 mg/kg selenium while native sulfur deposits can display the highest selenium concentrations (>5% weight). In magmatic sulfide deposits like the Permian-to-Triassic-age Noril'sk group, located inside the Arctic Circle in Russia, and the Sudbury ores in Ontario, selenium may replace sulfur in sulfide veins. The estimated selenium content in such deposits varies between 0.002 and 0.01%, with measured concentrations as high as 200 mg/kg and as low as 3 mg/kg. At Noril'sk, the selenium of extractive interest is in sulfide minerals (e.g., chalcopyrite, millerite, pentlandite, pyrite and pyrrhotite), where it occurs as an isomorphous substitution for sulfur in concentrations of 2 to 74 mg/kg, and can reach up to about 150 mg/kg in massive vein deposits, and sometimes in magnetites. In sulfides of porphyry copper deposits, Se is generally sourced from hypogene fluids and subsequently remobilized during hydrothermal plumbing of the porphyry copper system.

From a mining perspective, no clear quantitative correlation has been found between selenium and any of the associated elements such as copper, lead, nickel, sulfur, or tellurium and precious metals. It is empirically evident that copper ores are a source for selenium while sulfides are prevalent ore minerals, so the close association of selenium with sulfur has a poor significance from the standpoint of absolute concentrations. Besides, selenium can be one of the most mobile elements during rock weathering, and so it can be enriched in a variety of environmental sinks. Fundamental steps in identifying new selenium sources would be to study the relationships between selenium and sulfur and their isotopes in other rock types, to define diagenetic processes of sulfide minerals better, and thereby to probe the interaction of Se-bearing minerals with organic matter and carbon. Despite efforts to standardize the estimation of selenium in sulfide ores, the wide variety of host minerals and, consequently, the highly variable Se concentrations found in ore minerals complicate the definition of Se grades and cut-off values in ore mining.

Selenium is sold in four commercial or refined grades, even though the industry has no specifications for the several classes and some producers provide customers with their specifications. A first, refined grade is 99.5% weight minimum selenium with Te, Fe, Pb and Cu as the main impurities. Materials containing >99.5% selenium are commercially available as powder, granules, and lump. Pigment grade selenium is typically used in colouration and has a purity of 99.7% weight. The high grade ranks as the third grade regarding purity with 99.999% weight minimum selenium. The ultra-high grade is claimed to contain from 99.999 to 99.9999% weight selenium (Hoffman & King, 1997), available as shot or powder. To reach higher purification somewhat inert contaminants (e.g., Na, Mg, Ca, Al, Si) and harmful impurities such as arsenic, iron, mercury, and tellurium must be removed. Generally, the concentration of sulfur, oxygen and halogens must be ensured to be as low as possible for high-purity selenium

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

powder. When estimating elemental purity and grades, any analytical uncertainty linked to accurate selenium quantification should be carefully stated. The suitability of determination methods depends on several factors, such as (i) a proper conversion of selenium after distillation in the coordination compound wanted (that is, suitable for analytical measure), (ii) effective reduction/deposition to elemental selenium when a gravimetric determination is desired, (iii) the presence of possible interfering substances left behind in the sample preparative, (iv) selenium speciation and (v) type of environmental matrices (e.g., organic vs inorganic) in the test sample. With the development of organo-selenium chemistry, an increasing number of organo-selenium compounds have been prepared in the laboratory (mostly as organosulfur analogues): they include the simple alkyl selenide (CHSe) and carbon diselenide (CSe_2) as well as complex heterocyclic compounds and a variety of Se-based polymers thereof. An overview of the main organo-selenium compounds can be found elsewhere (Hoffman & King, 1997). Selenium compounds of strategic importance for the productive industry include selenium dioxide, selenium disulfide, cadmium selenide and sulfoselenide, sodium and other selenites, and some organic selenium compounds (e.g., phosphine selenides are widely used solvents).

The world Se production according to USGS (United States Geological Survey) was estimated around 2710 tons in 2017 (without the USA's quote, assumed around 150–750 tons per year), including China (930 tons per year), Japan (730 tons per year), Russia (150 tons per year), Germany and Belgium (500 tons per year) as main actors among all producers (Stillings, 2017) (Figure 1.4).

The glass industry uses approximately 25% of the total production of selenium. Selenium and its compounds with Na, Cu, Cd, and Te are required mainly to produce flat glass, pressed or blown glass and glassware for colouration and advanced optics in analytical devices (Langner, 2000). A significant percentage of the selenium production (25%) is employed in inorganic pigments (predominantly as cadmium sulfoselenide) used in plastics, paints, enamels, inks, rubber, and ceramics. Around 10–15% of selenium globally produced each year is used in other applications including accelerators, gaseous electric insulation (as selenium hexafluoride), solvents and lubricants, and in rubber production selenides are applied as vulcanizing agents. The remaining selenium globally produced is used in stainless steel and refractory metals, in the electrolytic production of manganese, in medical and pharmaceutical topical preparations (e.g., treatment of dandruff), as fungicide and insecticide in agricultural uses and, finally, it finds application as dietary supplements for humans and livestock. Selenium in the high-purity form is used in electronics due to its semiconductor and photoelectric characteristics, in thermoelements and in xerographic materials. However, applications of selenium in the chemical industry are considered largely dissipative, especially during distillation and recovery from low- concentration sources of primary supply and when required at a high grade.

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

Following the need to maintain the trade-off between supply and demand, selenium may be used to replace strategic metals (European Commission, 2014) in different applications with satisfactory performance: Se can enter in substitution of Sb in industrial applications for hardening of materials and alloys, it can be used in bimetallic catalysts to decrease rhenium's share of the existing catalyst market, or it can replace tellurium in many free-machining steels and rubber compounding. Some selenides show enhanced performance as high-temperature, high-vacuum lubricants instead of tellurides (e.g., selenides of niobium and tantalum in electrically-conducting solid lubricants). Copper indium diselenide is almost as efficient as cadmium telluride in photovoltaic power cells (Fiducia *et al.*, 2019). The substitutability of tellurium with selenium is particularly chased to lessen the criticality of supply for the much more expensive tellurium. However, this trend may revert soon from both a technical and economic standpoint since selenium is gaining increasing attention due to its critical importance in the production of solar cells (George & Wagner, 2009; Stillings, 2017). On the other hand, silicon is the major substitute for selenium in low- and medium-voltage rectifiers while new organic pigments substitute for cadmium sulfoselenide pigments. Sulfur dioxide can also be used as a replacement for selenium dioxide with limited efficiency. Bismuth and tellurium are rather efficient in place of Se due to their similar chemical properties, whereas lead and cerium oxide more frequently suit as substitutes, especially in the glass-making industry, rubber production and free-machining alloys. Amorphous silicon and cadmium telluride are considered the two principal competitors for replacing Se in thin-film photovoltaic solar cells (George & Wagner, 2009). However, market fluctuations control the supply trend of prime metal vs its substitute.

Refinery production of selenium is reported by 14 countries with more than 130 companies trading selenium, of which Mitsubishi Materials Corp., Nippon Mining and Metals Co. (Japan), Noranda Inc., Falconbridge, the Northwest Nonferrous International Investment Co. (Canada), Jiangxi Copper, Yunnan Copper, Jinduicheng Molybdenum Group (China), Norilsk Nickel, the Ural Mining-Metallurgical Company (Russia), Umicore S.A., Retorte Selenium Chemicals & Metals (Europe), Phelps Dodge Refining Corp. and Rio Tinto Zinc are the most famous. The majority of producers are electrolytic copper refineries and, according to USGS estimates, more than 90% of the USA selenium output and more than 8% of the world Se production is derived from the anode mud deposited during the electrolytic refining of copper. However, as only a fraction of the selenium is recovered from copper anode slimes that can contain between 0.5 and 280 kg of selenium per ton of copper effluent (Stillings, 2017), these slimes represent both a potential loss of Se and a contamination source when discharged as wastewater (Kilic *et al.*, 2013). Due to the close connection to major metal deposits, the production of minor metals like Se depends heavily on the production of the host metal (e.g., Cu), resulting in complex demand/supply and price patterns (Hageluken & Meskers, 2010). The dramatic price volatility of

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

Se is apparent due to its application for strategic energy technologies (Lenz & Lens, 2009). For example, the selenium price increased by 440% in the USA between 2003 and 2004, and it reached its all-time high in 2011 (146,000 US$ per ton). As such, innovative strategies like those coming from biotechnologies that allow for the recovery of minor metals are required because they can help to uncouple demand/supply and price patterns from major metals extraction. This, in turn, will open novel recycling possibilities, which may have been overlooked for merely technical reasons.

All commercial processes for the production of selenium involve a finely tuned combination of fundamental methods, such as chemical treatments, physical separation methods, thermal treatments, and electrodeposition. Electrowinning is the preferred option at the final stage of recovery, especially from Cu-Ni ores but also from fly dust and slag of metal foundries (Langner, 2000). Recent advances in membrane separation technologies are adding new perspectives for Se recovery from very fine precipitates or different types of physical and chemical phases. Microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) can be applied, with RO and NF being the most effective for recovery of Se fine precipitates (CH2MHILL, 2010; Santos *et al.*, 2015). Soda ash roasting, roasting with sulfuric acid, wet chlorination, and alkaline autoclaving are primary recovery processes for selenium developed at the full scale (Hoffman & King, 1997).

In Europe, recovery of minor by-products like Se have minimal own production infrastructure, low efficiencies and represent a small contribution to revenues, typically less than 5% (Blengini *et al.*, 2017). Secondary selenium is processed by a small number of primary selenium refiners. No secondary selenium sources have in loco production. Most selenium consumed domestically is dissipated into the environment and assumed to be not recoverable. It is also a common belief that selenium from pigments, fertilizers, animal feeds, chemicals, and pharmaceuticals can be dispersed in soils and other environmental sinks without any possibility of avoiding loss of resource. The selenium from the glass and free-machining alloys industries is not accounted for recycling either, because it probably volatilizes during melting operations. However, mining from secondary and unconventional sources is of utmost importance to secure a stable supply and for diversifying sourcing. Superphosphates can contain about 20 mg/kg selenium, while soil Se concentrations can be higher than 20 mg/kg in the vicinity of copper and lead smelters and refineries. Coal generally contains between 0.5 and 12 mg/kg Se while soil samples associated with coal mine environments in Wyoming showed selenium concentrations up to 26 mg/kg (Stillings, 2017).

A high number of Se-bearing products may end up in landfills considering 1 mg/kg Se is the hazardous waste limit (Guo & Wu, 2017; USEPA [United States Environmental Protection Agency], 1992) or in waste incinerators and thermal treatment plants (Liu *et al.*, 2015), where Se likely volatilizes during combustion. In municipal incineration residues, named fly and bottom ashes, Se

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

is in the range 0.05–10 mg/kg (Allegrini *et al.*, 2014). Subsequent studies have suggested a moderate enrichment factor for selenium calculated with respect to crustal abundance that is similar to the enrichments observed in fly ash from coal-fired power plants and refuse incinerators (Kogel, 2006). Although technically feasible, the recovery of selenium from coal fly ash and municipal solid waste incineration residues does not appear economical, and dedicated processes are thus far unidentified. As such, secondary sources for selenium recovery include coal ash, contaminated soils, municipal fly ash and bottom ash, wastewaters and sludge, landfill leachates and other anthropogenic residues. A most important source is inherently Waste Electrical and Electronic Equipment (hereafter: WEEE), such as factory scrap generated during the manufacture of selenium rectifiers, burned-out rectifiers, spent catalysts, used xerography-copying cylinders and heat-generators, outdated sensors, printed circuit boards (especially advanced microdevice graphics cards), relays, resistors (CdSe), and optical stores (George & Wagner, 2009; Schrauzer, 2004). Selenium can also be recovered from plastics and oil waste, treatment plants for phosphorus production, and abundant mining waste dumps experiencing significant selenium releases in some circumstances (Kogel, 2006).

The WEEE showing high selenium contents like scraps from document copiers and laser printers are the focus of urban mining. As an example, the selenium layer from for example, xerographic photocopier drums is either broken up mechanically, then cleaned and remelted; or dissolved in sodium sulfite or other solvents, then precipitated and eventually purified, generating no more than 50 tons of secondary selenium annually according to the USA report of mineral commodity in 2004 (Butterman & Brown, 2004). Other residual streams for practical urban mining are waste solutions from the production of trigonal selenium (used in photosensitive or photoconductive components) where selenium oxide may be in the form of sodium selenite and sodium selenate and for which a patented process may apply (Goodman *et al.*, 2000). Other methods currently under investigation rely on oxidizers/adsorbents such as Al, Fe, Ti, Si oxides (e.g., anatase), manganese oxide, binary metal oxides [$Al(+3)/SiO_2$, $Fe(+3)/SiO_2$, Fe(+3) and Mn(+3) hydrous oxides], layered double hydroxides (i.e., nanostructured anionic clays, mostly Mg-Al, Mg-Fe, and Zn-Al based), graphene and magnetic graphene oxide nanocomposites, and even peanut shell and rice husk. Membrane separation technologies are typically deployed for the final recovery stage (Figure 1.5a and b).

Industrial emitters are a compelling hot spot of selenium losses in the atmosphere compared to volcanic emissions and natural releases from plants, soils and animals which are minor sources. Selenium concentrations in air primarily depend on coal-burning power plants, copper-refining plants or selenium rectifier plants, zinc-cadmium smelters, fossil fuel combustion, lime industry, and refuse incineration. From the atmosphere, natural and anthropogenic selenium re-accumulates in environmental compartments (e.g., in lakes) or is taken up by

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

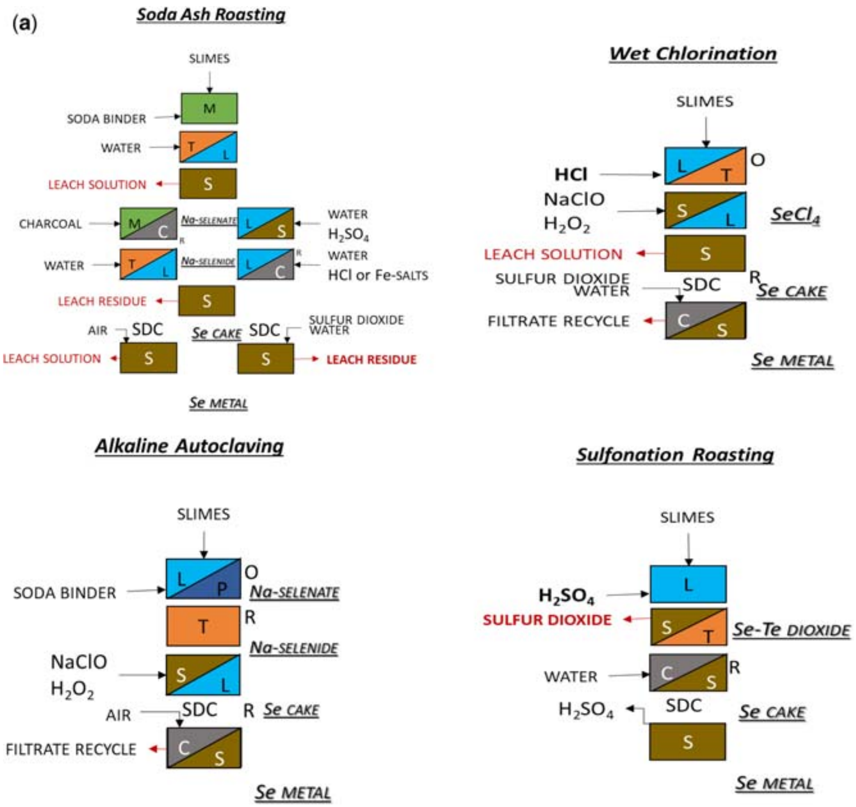


Figure 1.5 (a) Schematic flow designs of selenium recovery processes from primary and secondary ores. Commercial processes (a) and other methods (see Figure 1.5b). The blocks represent critical processing stages, where diverging blocks are possible alternate routes and letters indicate the key process acting: M = mixing, extruding, drying; T = severe thermal treatment (e.g., smelting, roasting); L = chemical leaching; S = physical separation methods; C = coagulation, sorption, flocculation, froth floatation; P = pressure; eC = electro-coagulation; B = bioleaching and biosorption; SDC = stripping, distillation, condensation (mainly) used at the final stage of recovery; MF, NF & RO specify the membrane separation technologies (see text for details); and R and O mean reducing and oxidizing conditions, respectively. Block halves represent co-participated processes. The bold format indicates high inflow/outflow, in red waste or by-products negatively impacting the process, and underlined the selenium fate during the process. *Sources*: Baldwin *et al.* (1985), Hoffman and King (1997), Goodman *et al.* (2000), Kashiwa *et al.* (2000), Overman (2000), Mollah *et al.* (2004), El-Shafey (2007a, b), Geoffroy and Demopoulos (2009, 2011), CH2MHILL (2010), Soda *et al.* (2011), Pickett and Sonstegard (2012), Fu *et al.* (2014), Santos *et al.* (2015), Mierzejewski *et al.* (2017), Stillings (2017).

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

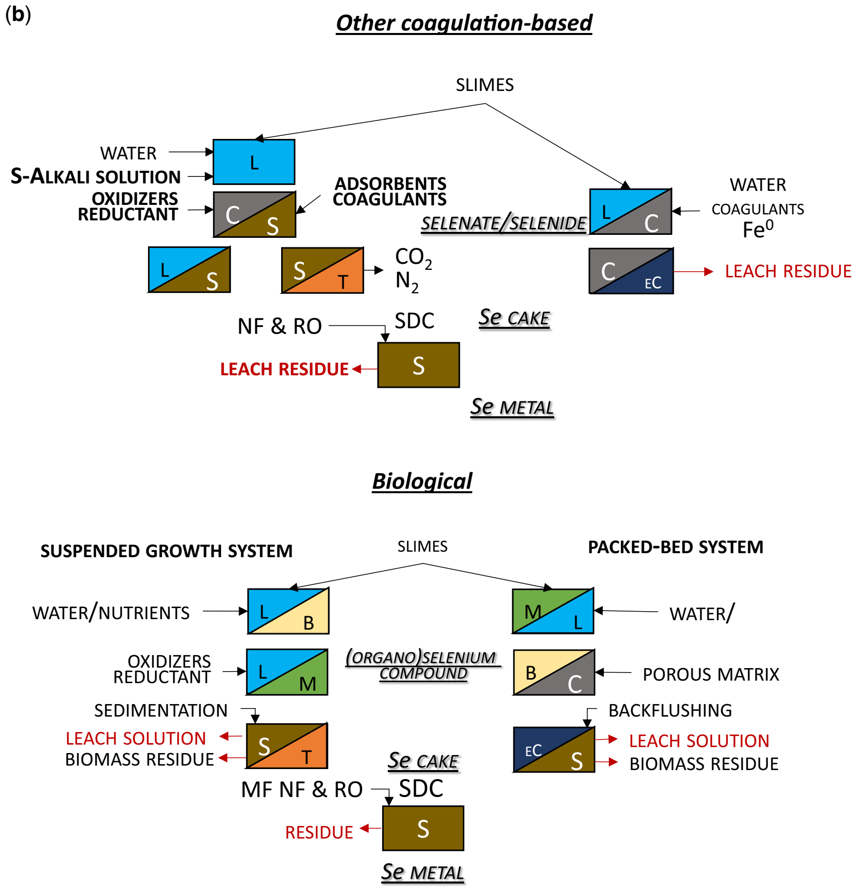


Figure 1.5 (*Continued*). **(b)** Schematic flow designs of other methods, in addition to those of Figure 1.5a, for selenium recovery processes from primary and secondary ores. The block-scheme flow, symbols, abbreviations and references are the same as those used in Figure 1.5a. See text for further details.

plants and converted into organic compounds such as selenomethionine, sometimes serving as a detoxifying mechanism. Microorganisms such as *Escherichia coli*, *Clostridium thermoaceticum*, and *Clostridium sticklandii* seem to crave selenium in their metabolic reactions. Accumulator plants can incorporate from 1000 to 10,000 mg/kg selenium (dry weight): they include *Astragalus* L., *Oonopsis* (Nutt.) Greene, *Oryzopsis* Michx., *Xylorhiza* Nutt., *Mentzelia* L., and *Stanleya* Nutt. (details in Section 1.3.3.4) (Presser, 1999). Significantly high selenium concentrations are also reported in some legumes, nuts, and mushrooms (see

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

Section 1.3.3.5). The presence of bioaccumulators and selenium-tolerant plants prompted the use of different microorganisms for biorecovery and bioremediation. Through bacterial leaching and phytovolatilization substantial amounts of selenium may be removed from Se-contaminated soil. Wetlands are a clear example of demonstrated biological passive treatment for selenium (CH2MHILL, 2010). Even though rapid recovery from biomass is virtually unfeasible, several technologies based on bacterial, fungal and plant metabolism have been tested in the laboratory. For example, species of the genus *Clostridium*, *Bacillus* and *Pseudomonas* (anaerobic and aerobic bacteria), *Aspergillus* spp., *Ganoderma lucidum* and *Phanerochaete chrysosporium* (fungi), *Saccharomyces cerevisiae* (baker's yeast), *Eichhornia crassipes* (water hyacinth), *Lemna minor* (lesser duckweed) and *Cladophora hutchinsiae* (green marine alga) have been tested for Se removal (Nancharaiah & Lens, 2015a, b; Santos *et al.*, 2015). Biological treatment relies on the enrichment and retention of microorganisms that convert soluble selenium oxyanions into the less-toxic elemental selenium. Furthermore, photobioreactors are emerging for the inclusion of microalgae as part of integrated algal-bacterial selenium removal systems, wherein selenium oxyanions are removed by biovolatalization and bioreduction. Selenate reduction has been investigated under methanogenic, sulfate-reducing, denitrifying, and hydrogenotrophic conditions (Nancharaiah & Lens, 2015a, b).

Different bioreactor configurations have been adopted (Figure 1.5a and b), such as up-flow anaerobic sludge blanket reactors, fluidized bed reactors, plug flow reactors, membrane biofilm reactors, and bioelectrochemical systems for retaining selenium-reducing microorganisms as flocs, granular sludge, or biofilms. For the latter purpose, soil, sand, cellulose, glass wool or glass beads can be used as a porous matrix. A significant fraction of the bioreduced selenium can still be present in the bioreactor effluent, necessitating a post-treatment step such as coagulation or electrocoagulation. It should be underlined that many of the suggested technologies are not demonstrated at full-scale for Se recovery and present the disadvantage of the high costs related to chemicals and solid waste disposal (Figure 1.5a and b). Biological selenium removal methods are more attractive than traditional metallurgical routes because of low operational costs and impacts on the environment. The performance of any technology should be evaluated on a case-specific basis, optimized and demonstrated at the pilot scale.

1.3 SELENIUM IN THE ENVIRONMENT

1.3.1 Selenium mineralogy

Since the first observation in 1817 of selenium in sulfides, there are today more than 100 known selenium minerals (123 approved by the International Mineralogical Association (IMA); Krivovichev *et al.*, 2019), classified into: native selenium (1), oxides (1), selenides (85), selenites (without H_2O, 14; with H_2O; 17), selenates (without H_2O, 1; with H_2O, 4) (Krivovichev *et al.*, 2019, Supplementary

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

Materials Table S1). This number is relatively high considering that most selenium is dispersed in other minerals as a substitute of sulfur. When taking into account the geochemical abundance of selenium, these minerals are rarely present as pure terms but rather as mixtures with the far more abundant sulfur-bearing minerals (sulfides and sulfates). The most up-to-date review on selenium minerals is the one of Krivovichev *et al.* (2019) with its Supplementary Materials Table S1. Wang *et al.* (2016a) adopt a slightly different classification into selenides, selenium sulfides, and oxygen-containing selenides. The paper by Stillings (2017) contains a careful listing of Se minerals with chemical formula, date of discovery or IMA approval and geological setting. This paper is an invaluable source of mineralogical and geochemical data for selenium mineralogy and occurrence. Another important source of data is the web site: www.mindat.org.

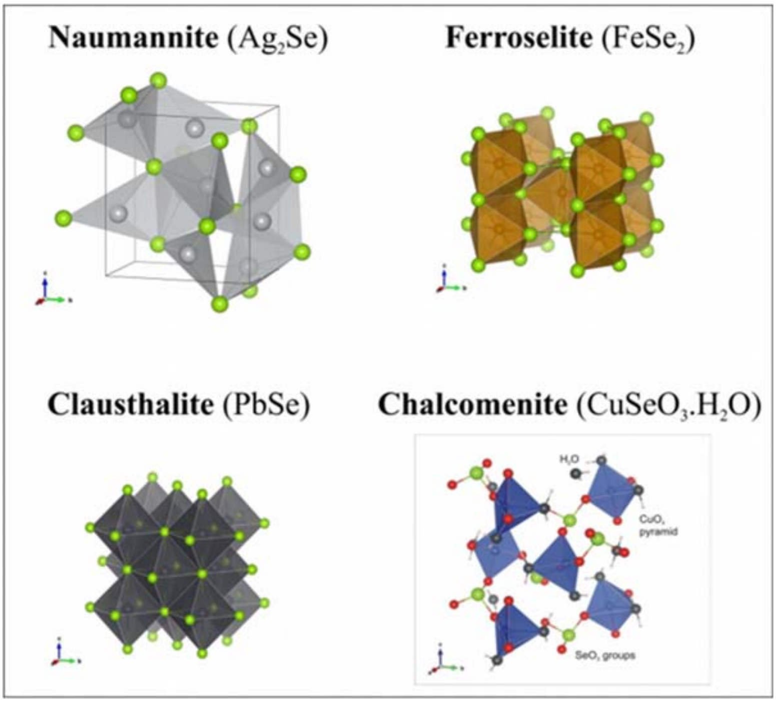
The crystal-chemistry of selenium minerals is complicated and was examined in depth in a paper by Krivorichev *et al.* (2019). Selenium, similarly to sulfur, can assume four oxidation states: −2, 0, +4, +6. The chemical formula resembles most common sulfides and due to the vicinity of the two elements, selenium minerals are very rarely pure terms, as summarized in Table 1.1, while the crystal structure of selenium minerals is variable and, in some cases, quite complex (see Figure 1.6).

A detailed account of the origin of Se minerals is described in Grundmann and Forster (2017) and Pažout *et al.* (2019). The most up-to-date study of the structure and crystal chemistry of Se minerals is the paper by Krivovichev *et al.* (2019) with the attempt to apply the concepts of *mineral ecology* (Hazen *et al.*, 2015). Many Se minerals are common in hydrothermal deposits (selenides), associated with fumaroles (selenites) or in the oxidation zone of sulfide and selenide deposits (secondary selenites and selenides). Selenium minerals rarely occur in high concentration; most often they are dispersed as small grains with other minerals. Most selenium minerals are composed of a narrow range of metals (Fe, Cu, Ni, Zn, Pb, Co, Ag, Pd, Pt, Hg) plus semimetals (As, Sb, Te, Bi) with scarce presence of other elements (K, Na, Al) in oxygen-containing selenides. As most of these minerals resemble most common sulfides, pure Se

Table 1.1 Selenium minerals.

Name	Ion	Example
Selenium	Se^0	Native selenium
Selenide	Se^{2-}	Clausthalite ($PbSe$), Berzelianite (Cu_2Se)
Diselenide	$[Se_2]^{2-}$	Ferroselite ($FeSe_2$), Dzharkenite ($FeSe_2$)
Selenite	$[Se^{4+}O_3]^{2-}$	Molybdomenite ($PbSeO_3$), Chalcomenite ($CuSeO_3.H_2O$)
Selenate	$[Se^{6+}O_4]^{2-}$	Olsacherite ($Pb_2(SeO_4)(SO_4)$), Ramaccioniite ($Cu_4(SeO_4)(OH)_6$)

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user



Naumannite (Ag_2Se)

Ferroselite ($FeSe_2$)

Clausthalite (PbSe)

Chalcomenite ($CuSeO_3.H_2O$)

Figure 1.6 A few examples of crystal structures of selenium minerals. In all examples, the Se ion is presented in green. Naumannite (orthorhombic, a = 4.336, b = 7.067, c = 7.753, Z = 4, V = 237.57), Ferroselite (orthorhombic, a = 4.8001, b = 5.776, c = 3.585, Z = 2, V = 99.40), Clausthalite (isometric, cell dimensions a = 6.147, Z = 4, V = 232.37), Chalcomenite (orthorhombic, a = 6.671, b = 9.193, c = 7.384, Z = 4, V = 452.83). Drawings produced with VESTA (Momma & Izumi, 2011).

compounds are very rare. As previously stated, selenium mineralogy is complicated, and it is not possible to give a simple description of many Se minerals.

1.3.2 Selenium geochemistry

Selenium is a rare element, ranking 65th in average crustal abundance (0.09 mg/kg Se, Rudnick & Gao, 2003). Selenium concentrations in rocks, when reported, are generally very low (a summary of literature data is presented in Table 1.2). The highest concentrations, among the most common rock types are found in shales (average values however well below 1 mg/kg). In igneous rocks, the concentrations are generally low, likely higher in mafic than acidic material, for the occurrence of sulfides, although the impact of volcanic activity in selenium cycling is considered very high (Fordyce, 2013) with an estimate of a

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

Table 1.2 Selenium abundance in rocks.

Rock Type	Mean Value (Range) in mg/kg	Number of Observations	Reference
Igneous rocks Ultramafic rocks	0.07		Koljonen (1992)
Mafic intrusives (post Archean)	0.099	308	Gao *et al.* (1998)
Diorite (post Archean)	0.065	260	Gao *et al.* (1988)
Tonalite-Trondhjemite-Granodiorite (Archean)	0.056	553	Gao *et al.* (1988)
Tonalite-Trondhjemite-Granodiorite (post Archean)	0.052	641	Gao *et al.* (1988)
Granite (post Archean)	0.054	1226	Gao *et al.* (1988)
Granite (Archean)	0.036	402	Gao *et al.* (1988)
Granite	0.05		Bowen (1979)
Granite, Granodiorite	0.025		Koljonen (1992)
Volcanic rocks			
Mafic volcanics (post Archean)	0.111	632	Gao *et al.* (1988)
Felsic volcanics (post Archean)	0.066	972	Gao *et al.* (1988)
Basalt	0.05		Bowen (1979)
Basalt	0.12		Koljonen (1992)
Sedimentary rocks			
Sandstones (Archean)	0.13	121	Gao *et al.* (1988)
Sandstones (post Archean) Sandstone	0.269	2754	Gao *et al.* (1988)
Sandstone	<0.01		Bowen (1979)
	0.01		Koljonen (1992)
Pelites (Archean)	0.217	69	Gao *et al.* (1988)
Pelites (post Archean)	0.499	1341	Gao *et al.* (1988)

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

Shale	0.5		Bowen (1979)
Shale	0.3		Koljonen (1992)
North American shale composite	0.08		Morgan *et al.* (1978)
Marine pelagic clay	0.2		Li (1991)
Marine shales	0.6		Li (1991)
Carbonates (Archean)	0.042	50	Gao *et al.* (1988)
Carbonates (post Archean)	0.126	2038	Gao *et al.* (1988)
Limestone	0.03		Bowen (1979)
Limestone	0.025		Koljonen (1992)
Manganese nodules	0.6		Li (1991)
Black shales, UK and Ireland	18.7 (1.3–42)	44	Parnell *et al.* (2016)
Mediterranean sapropel	24 (0.2–44)		Nijenhuis *et al.* (1999)
Carbonaceous shale	0.77 (0.025–4.6)	12	Wen and Carignan (2011)
Average phosphorite	4.6 (0.5–13)	6	Altschuler (1980)
Phosphate rocks (Peru)	2.4 (0.5–6.0)	12	Bech *et al.* (2010a)
Phosphate rocks (other localities)	7.4 (0.11–44)	35	Bech *et al.* (2010b)
US, Coals	3.6 (0.02–75)	304	Coleman *et al.* (1993)
British, Coals	4.9 (0.3–61.9)	61	Bullock *et al.* (2018, 2019)
Coals	3		Koljonen (1992)
Metamorphic rocks			
Amphibolites (Archean)	0.235	189	Gao *et al.* (1988)
Mafic granulites (Archean)	0.254	128	Gao *et al.* (1988)
Intermediate granulites (Archean)	0.099	136	Gao *et al.* (1988)
Felsic granulites (Archean)	0.084	137	Gao *et al.* (1988)
Meta felsic volcanites (Archean)	0.037	41	Gao *et al.* (1988)

The table is a compilation of literature data regarding the abundance of selenium in rocks, when available the number of observations and the range are reported.

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

contribution of 0.1 g of selenium for every cm^2 of the Earth's surface. Given its volatility, during eruptions selenium is transferred to the atmosphere and not concentrated in rocks, perhaps except for some pyroclastic rocks (Fordyce, 2013). Floor and Román-Ross (2012) reported a range in Se concentrations in volcanic ash, ranging from <0.2 to 7 mg/kg Se, substantially higher than those in rocks, and with the peculiarity of being easily leachable compared to other sources. In metamorphic rocks, they could be related to the origin of the protolith. The highest concentrations reported (in the range of dozens mg/kg as maxima) in other geological material were observed in phosphatic rocks, eventually related to sulfides and organic matter (Altschuler, 1980), and are generally strongly enriched in black shales and coals, again in association with sulfides (Table 1.2).

1.3.3 Source of selenium in the environment

1.3.3.1 Selenium in soils

Soils represent a critical environmental matrix for the interaction with the biosphere, and selenium is usually present in trace amounts in soils, namely: (i) Fordyce (2013) reports a range of 0.01–2.0 mg/kg and an overall mean of 0.4 mg/kg Se; (ii) Kabata-Pendias (2011) reports a range of 0.05–1.5 mg/kg Se and a mean value of 0.44 mg/kg Se, while (iii) He *et al.* (2010) report a range of 0.1–2.0 mg/kg Se and a mean value of 0.2 mg/kg for agricultural soils and a wider variation (<0.1–4 mg/kg) and higher mean value (0.33 mg/kg) for worldwide surface soils. Although bedrock lithology is the primary factor influencing selenium in soils, additional inputs of selenium to soils occur following atmospheric deposition of selenium from natural (e.g., volcanoes and sea spray) or anthropogenic (e.g., fossil fuel combustion) sources or direct accumulation in soils due to sewage or fertilizer application.

The critical point for selenium occurrence in soils is that it can be transferred to the food chain and selenium can be concentrated in plants resulting in toxic concentrations for livestock (Fordyce, 2013), but it has also been realized that problems for livestock occur in Se-deficient areas, leading to a series of symptoms known as the white muscle disease (Levander, 1986). Low intake of selenium can also have effects in humans, in particular interfering with antioxidant systems, thyroid hormone metabolism, immune function and reproduction (Fordyce *et al.*, 2010).

A wider knowledge about selenium distribution in the environment has been obtained from several geochemical mapping projects carried out at different scales and densities around the world, as shown in Table 1.3. Given the important biological role played by selenium, the knowledge of the spatial distribution of this element is extremely important, not only for the identification of high concentrations areas, but also those where the Se concentration is low, eventually leading to Se deficiency in plants and livestock. As seen in Table 1.3, the average values are generally higher than those reported for rocks (Table 1.2) and in a few

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

Table 1.3 Selected data concerning selenium abundance in soils.

	Mean (Range) mg/kg	Median mg/kg	Number of Observations	Reference
Europe				
GEMAS Agricultural soils	(<0.05–3.8)	0.35	2108	Reimann *et al.* (2018a, b)
GEMAS Grazing land soils	(<0.05–6.8)	0.40	2024	Reimann *et al.* (2014)
Topsoil northern Europe	(0.12–9.02)		174	Reimann *et al.* (1997a, b)
Soil, C-horizon, Barents area	(<0.01–1.155)	0.046	605	Reimann *et al.* (1998)
Baltic soil survey				Reimann *et al.* (2003a)
Agricultural soil	(0.02–7.6)	0.14	752	Reimann *et al.* (2003b)
Bottom soil	(<0.01–6.7)	0.08	752	Reimann *et al.* (2003a)
Germany (West)	(0.016–0.65)		499	Hartfiel and Bahners (1988)
Netherlands	(0.05–2.0)		341	Mol *et al.* (2012)
Belgium	(0.14–0.70)		539	De Temmermann *et al.* (2014)
EIRE	(0.08–17.44)	0.74	1310	Fay *et al.* (2007)
Campania Region (Italy)	0.43 (0.065–2.4)	0.40	2333	Petrik *et al.* (2018)
Lombardia Region (Italy)	1.08 (0.5–2.4)		98	Beone *et al.* (2018)
Soil Murcia Region (Spain)	0.43 (0.003–2.7)	0.3	490	Perez-Sirvent *et al.* (2010)
Huelva municipality (Spain)	1.30 (0.08–68.6)	0.35	150	Guillén *et al.* (2011)
North Trøndelag forest soils				
O-horizon	(<0.15–5.27)	0.897	752	Reimann *et al.* (2015a, b)
C-horizon	(<0.5–3.54)	<0.5	752	Reimann *et al.* (2015a, b)
Southern Norway				
O-horizon	(0.4–6.3)	2	45	Reimann *et al.* (2009a)
C-horizon	(<0.1–2.7)	0.45	45	Reimann *et al.* (2009a)

(*Continued*)

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

Table 1.3 Selected data concerning selenium abundance in soils (*Continued*).

	Mean (Range) mg/kg	Median mg/kg	Number of Observations	Reference
Oslo area				
O-horizon	(0.3–3.4)	0.95	40	Reimann *et al.* (2007)
B-horizon	(<0.1–4)	0.5	40	Reimann *et al.* (2007)
C-horizon	(0.1–1.7)	0.4	40	Reimann *et al.* (2007)
England and Wales soils	0.71(0–16)	0.48	5670	Rawlins *et al.* (2012)
Cornwall (5–25 cm)	1(0.1–6.8)	0.9	1154	
Scotland	0.44 (0.115–0.877)	0.433	114	Fordyce *et al.* (2010)
London soil	0.67(<0.2–19.6)	0.6	6288	Scheib *et al.* (2011)
Belgian agricultural soil				De Temmermann *et al.* (2014)
Sandt loam	(0.14–0.4)	0.25	93	De Temmermann *et al.* (2014)
Sandy loam	(0.17–0.45)	0.26	145	De Temmermann *et al.* (2014)
Silt loam	(0.18–0.7)	0.34	297	De Temmermann *et al.* (2014)
Clay	(0.29–0.61)	0.46	4	De Temmermann *et al.* (2014)
Africa				
Malawy	0.19 (0.05–0.62)	0.16	73	Chilimba *et al.* (2011)
Egypt	0.79 (0.17–1.95)	0.73	15	Sabrynal *et al.* (2011)
Australia				
Topsoil	(<0.01–2.01)	0.06	1314	Reimann and de Caritat (2017)
Bottom soil	(<0.01–2.36)	0.06	1314	Reimann and de Caritat (2017)

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

Asia				
Floodplain sediments, China				
top samples (5–25 cm)	0.213 (0.012–128)	0.5	846	Xie and Cheng (2001)
deep samples (80–120 cm)	0.267 (0.044–11.2)	0.17	468	Xie and Cheng (2001)
Average content in Chinese soils	0.29		2904	Chen *et al.* (1991)
Soils in Chinese cities	0.23 (0.03–10.8)	0.23	3799	Cheng *et al.* (2014)
Japan agricultural soil		0.42	180	Yanai *et al.* (2012)
Soil United States				
Topsoil (0–5 cm)	(<0.2–6.9)	0.2	4841	Smith *et al.* (2019)
A-horizon	(<0.2–8.3)	0.2	4841	Smith *et al.* (2019)
C-horizon	(<0.2–7.5)	<0.2	4841	Smith *et al.* (2019)
South America				
Sao Paulo soils	0.12 (0.01–0.7)		30	Rodrigues Nogueira *et al.* (2018)

The data reported include mean (range) and median as well as the number of samples considered in each study. Preference has been given to large-scale geochemical studies.

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

cases very high concentrations were observed (128 mg/kg Se in soils from China) (Xie & Cheng, 2001). Conversely, in large-scale geochemical surveys maxima are below 10 mg/kg Se (e.g., in Europe 6.8 mg/kg Se for grazing land and 3.8 mg/kg Se for agricultural soil; 6.9 mg/kg Se in topsoil from the United States; 2.01 mg/kg Se in topsoil from Australia). When different topsoil textures were considered (e.g., De Temmerman *et al.* (2014) for Belgian soils, Table 1.3) it appears that the mean and median values increase with finer grain sizes. In the cases where different soil layers were sampled, it is frequent to observe higher median and maxima in the upper layers or topsoil (in Table 1.3, results from the Baltic Soil Survey and floodplain sediments from China). Where sampled, the organic rich layers of soils display the highest median among different soil horizons (Table 1.3, North Trøndelag soils and Southern Norway; Oslo area, Norway), confirming a great affinity of Se for organic matter and, in particular, an origin possibly related to sea spray contributions. In soils developed under a warmer and more humid climate, Se could more likely be associated with colloids or Al-compounds (Dhillon *et al.*, 2019; Malisa, 2001).

Results from surveys in urban areas (Table 1.3, Greater London; Chinese cities; Huelva Municipality) reach relatively high concentrations, whose origin has been associated with localized and historical industrial activity. Especially, coal combustion leads to increased Se atmospheric emissions causing wide dispersion of Se, and its deposition negatively affects wide areas in the environment and public health around the combustion plants (Cheng *et al.*, 2014).

The results presented in Table 1.3 are intended to provide a broad picture of natural selenium concentrations and its spatial variability. Several seleniferous areas are recognized in different parts of the world, and in those cases, much higher concentrations in soils can be observed. Selenium-rich soils in the world have been reported in the USA, Canada, Mexico, Colombia, Ireland, Australia and China (Dhillon & Dhillon, 2003; Dhillon *et al.*, 2019) and other places (Oldfield, 2002). In the USA, selenium-rich soils are common in arid and semi-arid regions where selenium-rich shales form the bedrock. Concentrations reaching values of between 20 and 95 mg/kg Se have been reported for several seleniferous areas in the central USA (Dhillon *et al.*, 2019). Seleniferous areas in India are known in Punjab (Dhillon & Dhillon, 1991, 2014) where soils reach a maximum of 4.52 mg/kg Se, with a mean of 2.1 mg/kg Se compared to a mean of 0.4 mg/kg Se for non-seleniferous areas (Dhillon *et al.*, 2019). In Ireland, England and Wales several selenium-rich areas were recognized in central-southern Ireland, with soils reaching concentrations as high as 324 mg/kg Se in County Limerick and 132 mg/kg Se in County Tipperary (Walsh & Fleming, 1952), whereas in England Webb *et al.* (1966) reported maxima of 7 mg/kg Se for North Staffordshire and Derbyshire soils, 4 mg/kg Se for Devon soils and 5 mg/kg Se for Caernarvon soils; further confirmed by Davies and Houghton (1983) who reported a maximum amount of 7.5 mg/kg Se and a median of 2.2 mg/kg Se for some other seleniferous areas in Wales, also

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

Table 1.4 Classification of selenium impact on human health based on soil selenium content.

Soil Selenium Classification	Selenium Content (mg/kg)
Deficient	<0.125
Marginal	0.125–0.175
Moderate	0.175–0.40
High	0.40–1.00
Toxic	1.00–3.00
Excessive	>3.00

associated with mining activities. In China, several areas are reported to be enriched in selenium (Dhillon *et al.*, 2019), for example Chang *et al.* (2019) reported, based on cited references, concentrations up to 7007 mg/kg for a seleniferous area in central China and a geometric mean of 133 mg/kg for soils developed on black shales. Zhu *et al.* (2008) reported values as high as 2018 mg/kg Se for soils, eventually affected by discarded coal spoils in Yutangba (Hubei Province, Central China), whereas the maximum concentration reported for non-polluted soils was 42.3 mg/kg Se, which is far above the normal values reported worldwide.

Based on studies relating soil selenium with human health (Tan *et al.*, 2009; Zhang *et al.*, 2008), a classification of soil types based on selenium concentration has been proposed (Table 1.4), although other authors consider different concentrations as toxic (Bailey, 2017).

Apart from total soil concentrations, the bioavailable forms of selenium demonstrate a critical effect in soils, which is basically controlled by the combination of pH and redox conditions that, in turn, control Se speciation (see Section 1.2.2), and the soil texture and mineralogy. The selenate form represents the most common form in neutral to alkaline soils: it is mobile (Figure 1.2) and readily available for plant uptake (Neal, 1995). Actually, the most widely accepted indicator for plant bioavailability is the water-soluble selenium concentration (Fordyce *et al.*, 2000; Jacobs, 1989) although speciation studies are increasing (Natasha Shahid *et al.*, 2018 and references therein) to further define selenium behaviour in soil systems.

1.3.3.2 Selenium in waters

The estimated representative selenium concentration in surface water (Lemly, 2004; Schrautzer, 2004) is approximately 0.2 µg/L Se in river water and 0.09 µg/L Se in seawater. Selenium is a very mobile element (Gaillardet *et al.*, 2005) which tends to be more concentrated in groundwater as compared to surface water, likely due to water-rock interactions (Hem, 1985).

Table 1.5 summarizes data available on Se concentration in waters. The data confirm that slightly higher average values are seen in groundwater as compared

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

to surface water although there is a large variation that tends to decrease in small-scale studies such as for example those for surface waters in Norway (Reimann *et al.*, 2009a, b, 2018a, b) and Canada (Hu *et al.*, 2009). Notably, the values reported in US groundwaters and aquifers from France and Denmark are particularly high, up to 969 and 247 μg/L, respectively (De Simone *et al.*, 2014; Shand & Edmunds, 2008). Oxidizing conditions and higher pH values are likely to determine the high dissolved Se concentration in the Denver basin aquifer (Bauch *et al.*, 2014), the US area where the highest dissolved Se concentration has been observed (De Simone *et al.*, 2014). High levels of Se were also observed in a shallow alluvial aquifer, whereas deeper wells, generally used for drinking water supply, presented much lower concentrations (<0.4 μg/L Se) (Musgrove *et al.*, 2014). European surface waters (Salminen *et al.*, 2005) are characterized by a large-scale variability, with high values observed in southern Italy and in several areas of Spain and the Netherlands, possibly due to the presence of sulfide mineralization and the effect of seawater intrusion in coastal sand aquifers (Salminen *et al.*, 2005). Groundwaters in volcanic areas might record high values, such as in the case of Mount Etna, Volcano Island (Table 1.5) and other volcanic areas (Floor & Román-Ross, 2002).

European bottled drinking water indicated a low average value (0.054 μg/L Se). Results spread over four orders of magnitude with spikes on wells that could be affected by sulfide oxidation, while the highest value observed was recorded in water from the Czech Republic (Reimann & Birke, 2010). Limited effect is related to bottle leaching since results indicate only 0.018 μg/L Se contribution from glass leaching and 0.012 μg/L Se from soft plastic (polyethylene terephthalate, PET) leaching (Reimann & Birke, 2010). Tap water from Europe and Italy indicated lower median values and generally fits with the drinking water standards of 10 μg/L Se required in many countries, although the World Health Organization (WHO) sets a higher threshold value (40 μg/L). These are not the highest concentrations reported for selenium in tap water, since in many seleniferous areas around the world larger dissolved concentrations (from 1300 up to 2000 μg/L) have been observed, namely: (i) in the Coast Range alluvial aquifer of the San Joaquin Valley in California, (ii) in springs from the Soan-Sakesar valley in Pakistan, or (iii) in shallow wells of the upper reaches of the Colorado River in Utah (Afzal *et al.*, 2000; Deverel *et al.*, 1994; Engberg, 1999; Plant *et al.*, 2014).

1.3.3.3 Selenium in air

Concentrations of Se in the atmosphere are highly variable due to different sources of Se emissions. These can be of natural (e.g. crustal weathering, volcanic eruptions, sea salt and continental and marine biosphere) or of anthropogenic (e.g. industrial processes that involve combustion of coal, oil biomass; nonferrous metal smelting, manufacturing and utilization of agricultural products) origin

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

Table 1.5 Selected data concerning Se abundance in surface water, groundwater, bottled water and drinking water.

	Mean (Range) µg/L	Median µg/L	Number of Observations	Reference
Surface water Europe	(0.01–15)	0.340	807	Salminen *et al.* (2005)
Manitoba, Canada	(0.34–11.6)	0.34	25	Hu *et al.* (2009)
Oppdal area, Norway	(0.01–0.15)	0.04	200	Reimann *et al.* (2018a, b)
Oslo area, Norway	(0.5–1.4)	<0.5	39	Reimann *et al.* (2009b)
River water				
World average	0.07 (0.0.1–0.3)			Gaillardet *et al.* (2005)
Amazon river, Brazil/Colombia	0.051 (0.032–0.050)			Gaillardet *et al.* (2005)
Orinoco, Colombia/Venezuela				Gaillardet *et al.* (2005)
Lena, Siberia	(0.022–0.23)			Gaillardet *et al.* (2005)
Groundwater				
Europe	1.83 (<0.015–247)	0.50	577	Shand and Edmunds (2008)
Norway bedrock	(<0.01–21)	0.2	476	Frengstad *et al.* (2000)
Mt. Etna area, Italy	2.9 (0.6–66.8)		53	Aiuppa *et al.* (2000a)
Volcano, Italy	24.9 (0.8–237)	11	24	Aiuppa *et al.* (2000b)
Groundwater, USA	2.43 (0.02–969)	1	5335	De Temmermann *et al.* (2014)
Drinking water				
European bottled water	(<0.02–371)	0.054	884	Reimann and Birke (2010)
European bottled water	(<0.01–49.3)	0.635	66	Misund *et al.* (1999)
European tap water	(<0.02–15)	0.12	579	Reimann and Birke (2010)
Italian bottled water	(<0.01–2.67)	0.193	152	Dinelli *et al.* (2012)
Italian tap water	(<0.01–2.03)	0.164	169	Dinelli *et al.* (2012)
Ethiopian drinking water	(0.015–7.58)	0.615	138	Reimann *et al.* (2003a, b)

The data reported include mean, range and median as well as the number of samples under analysis in each study. Preference has been given to studies including a large number of samples to explore natural variability.

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

(Wen & Carignan, 2011). Among the natural sources, the marine and continental biosphere represents the most important source of atmospheric selenium (Mosher & Duce, 1987; Nriagu, 1989; Nriagu & Pacyna, 1988), followed by volcanic emissions and contribution from sea spray. Among the anthropogenic sources, coal combustion is dominant followed by nonferrous metal production (Mosher & Duce, 1987; Nriagu, 1989; Nriagu & Pacyna, 1988). The Se concentration in air above the South Pole is 0.06 ng/m^3 and the average value for worldwide air from remote regions is 0.2 ng/m^3 whereas the median for polluted areas is 4.0 ng/m^3 (Reimann & de Caritat, 1998). There is evidence that the ocean is a significant source of Se to coastal areas. Significant enrichment of Se in marine aerosols results from the formation of volatile organoselenium compounds, mainly dimethyl selenide $(CH_3)_2Se$. Increased Se levels in mosses (>1 mg/kg) and peat (>2 mg/kg) in the marine regions clearly indicate the impact of Se volatilization from seawater aerosols (Steinnes, 2003). Selenium is released into the air as hydrogen selenide generated by plants, and as elemental selenium, selenites and selenates in particulate form. The level of selenium in most urban air ranges from 0.1 to 10 ng/m^3, but higher levels may be found in certain areas as well, such as in the vicinity of copper smelters (WHO, 2011). The USEPA has established inhalation exposure limits as follows (in µg/m^3): 12,700 for hydrogen selenide, 400 for Se-hexafluoride, and 200 for other Se-compounds (Fordyce, 2005). According to the guidelines presented by ATSDR (2002), the Se concentration in air may vary from 160 to 1000 µg/m^3. The recommended threshold limit value for Se in a workplace is 200 µg/m^3, whereas in Germany, the MAK (maximum permissible concentration) value at the workplace has been established at 50 µg/m^3, and in Russia at 100 µg/m^3 (Schrautzer, 2004). Selenium released during fossil fuel combustion in Europe was 420 tons in 1979 (Schrautzer, 2004), this source provides for more than 6 kt/y, either as small particles and volatile compounds, accounting for about 40% of the total aerial Se abundance (Kabata-Pendias & Mukherjee, 2007).

1.3.3.4 Selenium in plants

The Se content of plants depends on the amounts of element available in soils (Combs, 2001) also taking into account the fact that there is little evidence that selenium is required for plant growth (Fordyce, 2013; Terry *et al.*, 2000). Indeed, there seems to be a direct relation between the amount of soluble selenium in the soil environment and the one in plants (Kabata-Pendias & Pendias, 2001), with the Se amount in the plant affected by soil pH (Winkel *et al.*, 2015), temperature and rainfall. In plants, similarly to other living organisms, selenium mimics sulfur biochemical properties and it can replace sulfur in amino acids and other biological processes.

Assuming that grasses and other forage plants are the main routes for grazing animals, the concentrations of selenium are in the ng/g dry weight range

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

(Table 1.6). In moderately low Se-soils, *Medicago sativa* grass accumulates more Se than many other forage plants, probably because of the different rooting depth and different selenium translocation to new buds (Mayland, 1994). Interestingly, a few plants are able to accumulate or hyper-accumulate Se in their tissues and are mostly found on seleniferous soils (White, 2016). They can be classified on the basis of the amount of selenium they contain (Plant *et al.*, 2014; Rosenfeld & Beath, 1964), namely:

- Selenium accumulator plants having more than 1000 mg/kg Se
- Secondary selenium absorbers with 50–100 mg/kg Se
- Plants with a concentration <50 mg/kg Se

Among the hyper-accumulators, some plants are operationally defined as 'obligate' because they require selenium for their growth. These include species from the genera *Astragalus*, *Conopsis*, *Xylorhiza*, and *Stanleya* (Ellis & Salt, 2003). In this respect, the species *Astragalus bisulcatus* (Hook) A. Gray is able to accumulate selenium up to 15,000 mg/kg Se dry weight with a seasonal distribution (Galeas *et al.*, 2007). This plant species is common on seleniferous soils and in the arid climate of the Western USA (see Section 1.1.1). There are also plants that are known as 'facultative' accumulators since they do not require selenium for growth but are able to bind selenium in organic form and concentrate it in their tissues. This category includes plants belonging to the genera *Acacia*, *Artemisia*, *Aster*, *Atriplex*, *Castilleja*, *Penstemon*, and *Grindelia* (Plant *et al.*, 2014).

As stated in section 1.3.3.1, and further detailed in Chapter 8, the uptake of selenium in plants occurs in the prevailing form of selenate (SeO_4^{2-}) via sulfate transporters; then, it is first reduced and subsequently incorporated into selenoamino acids by the sulfur (S) assimilation pathway (Sors *et al.*, 2005; Terry *et al.*, 2000; Valdez Barillas *et al.*, 2012). Selenate is reduced to selenite (SeO_3^{2-}) and then to selenide (Se^{2-}), which is incorporated into selenocysteine (SeCys). The non-specific incorporation of SeCys into proteins is presumed to be toxic (Stadtman, 1990). Notably, selenium hyper-accumulators avoid Se toxicity by methylating SeCys to methylselenocysteine (MeSeCys) through the use of a unique enzyme, SeCys methyltransferase, effectively circumventing the misincorporation of SeCys into protein (Neuhierl & Böck, 1996).

1.3.3.5 Selenium in food and feed

Since selenium is necessary for a balanced metabolism, animals and humans acquire Se from their daily diet. In animal tissues selenium is mostly found bound in proteins, as is the case in plants (see Section 1.3.3.4). Due to this, the most important food sources of selenium are cereals (0.1–10 mg/kg) as well as meat and seafood (0.3–0.5 mg/kg), because of their high protein contents. In contrast, foods with relatively low protein levels, such as vegetables and fruits, have low

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

Table 1.6 Representative data concerning Se abundance in plants and grass (ng/g dry weight).

	Mean (Range) ng/g DW	Number of Observations	Reference
Clover/*M. sativa*, Sweden	18–40		Fergusson (1990)
Clover/*M.sativa*, Germany	90 (50–130)		Kabata-Pendias and Pendias (2001)
Clover/*M.sativa*, France	38 (36–39)		Kabata-Pendias and Pendias (2001)
Clover/*M.sativa*, Canada	15 (5–31)		Kabata-Pendias and Pendias (2001)
Grass, Canada	13 (5–23)		Kabata-Pendias and Pendias (2001) Fergusson (1990)
Grass, France	47 (19–134)		Fergusson (1990)
Grass, USA	32 (10–40)		Fergusson (1990)
Grass, Sweden	30 (11–64)		Kabata-Pendias and Pendias (2001)
Grass, Germany	110 (30–210)		Kabata-Pendias and Pendias (2001)
Grass, Finland	11 (1–54)		Kabata-Pendias and Pendias (2001)
Birch leaves, Norway	0.1* (<0.1–0.3)	45	Reimann *et al.* (2015a)
Willow leaves, Norway	0.1* (<0.1–0.4)	45	Reimann *et al.* (2015b)
Juniper leaves, Norway	<0.1* (<0.1–0.2)	46	Reimann *et al.* (2015a)
Heather leaves, Norway	0.2* (<0.1–0.5)	46	Reimann *et al.* (2015b)

*Median values and concentrations as mg/kg.

selenium contents (<0.01 mg/kg) while still applying the general principle that the selenium content of a food reflects the available Se-content of the soils used to produce it (and the feedstuffs used to produce livestock) (Fairweather-Tait *et al.*, 2010; Chapter 9).

The main food groups providing selenium in the diet of a western country such as the UK are: bread and cereals (26%), meat (26%), milk/dairy products (21%), fish (10%), vegetables and fruits (7%) and eggs (4%). As shown in Table 1.7, the selenium content can vary widely from ~ 0.03 up to 30 mg/kg in bread and cereals, respectively (Barclay *et al.*, 1995; Rayman *et al.*, 2008).

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

Table 1.7 Selected data concerning Se abundance in foods (mg/kg) fresh weight.

	Mean (Range) mg/kg	**Number of Observations**	**Reference**
Cereals, USA	(0.06–0.66)		Combs (2001)
Cereals, Germany	(0.03–0.88)		Combs (2001)
Cereals, Venezuela	(0.123–0.51)		Combs (2001)
Wheat grain, Italy	0.071 (0.007–0.245)		Spadoni *et al.* (2007)
Breakfast cereals, France	0.025		Leblanc *et al.* (2005)
Rice Grains, Hainan Island, China	0.08 (0.01–0.43)		Xu *et al.* (2020)
Bread	(0.03–0.09)	$\leq 17 \leq 27$	Barclay *et al.* (1995)
Bread, UK	0.044		Ysart *et al.* (2000)
Bread, France	0.016		Leblanc *et al.* (2005)
Vegetables, USA	(0.005–0.14)		Combs (2001)
Vegetables, England	(0.01–0.09)		Combs (2001)
Brazil nuts	(0.03–500)		Combs (2001) Rayman *et al.* (2008)
Potatoes, UK	0.003		Ysart *et al.* (2000)
Brazil nuts	(0.03–500)		Combs (2001), Rayman *et al.* (2008)
Nuts, UK	0.25		Ysart *et al.* (2000)
Fish, cod	1.5		Fairweather-Tait *et al.* (2010)
Fish, tuna	5.6		Fairweather-Tait *et al.* (2010)
Fish, shark	2.0		Fairweather-Tait *et al.* (2010)
Fish, France	0.17		Leblanc *et al.* (2005)
Chicken, USA	0.2		Fairweather-Tait *et al.* (2010)
Poultry, UK	0.19		Ysart *et al.* (2000)
Beef, USA	(0.25–0.3)		Rayman *et al.* (2008)
Offal, kidney	4.5		British Nutrition Foundation (2001)

(*Continued*)

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

Table 1.7 Selected data concerning Se abundance in foods (mg/kg) fresh weight (*Continued*).

	Mean (Range) mg/kg	**Number of Observations**	**Reference**
Offal, liver	0.93		British Nutrition Foundation (2001)
Offal, heart	0.55		British Nutrition Foundation (2001)
Offal, muscle	0.2		British Nutrition Foundation (2001)
Hen's egg	(0.34–0.58)		Lipiec *et al.* (2010)
Eggs, UK	0.19		Ysart *et al.* (2000)

The predominant species of selenium in wheat and bread are selenomethionine (usually ~55–85%), selenocysteine (~4–12%), and selenate/selenite (~12–19%) (Whanger, 2002).

The selenium content of meat depends on many factors, for example offal contains relatively high levels of selenium, in particular liver and kidneys (Table 1.7). In the US, the average selenium content of chicken meat is ~0.2 mg/kg and beef ~0.25–0.3 mg/kg (Fairweather-Tait *et al.*, 2011). Meat represents a large fraction of the selenium intake in the USA and UK providing one-quarter of the total estimated Se intake. The predominant species of selenium in meat may be selenomethionine (~50–60% of total extractable selenium species) and selenocysteine (20–31 and ~50% of the total extractable selenium species in chicken and lamb, respectively).

The selenium content in fish is relatively high, being between 0.1 and ~5.0 mg/kg (Fairweather-Tait *et al.*, 2010; Reyes *et al.*, 2009). The main selenium species in fish are selenomethionine (29–70%) and selenite/selenate (12–45%) with the species profile differing between fish species and the total selenium content. Hens' eggs contain from ~3 to ~25 mg selenium per whole egg (Lipiec *et al.*, 2010). Selenium supplementation of the hen's diet may increase the selenium content of eggs to 0.34–0.58 mg/kg as Se-enriched eggs are widely produced around the world (Fisinin *et al.*, 2009). The main selenium species in eggs are selenocysteine, selenomethionine, and possibly selenite. Selenomethionine and selenocysteine are the predominant species (>50%) in egg white and egg yolk, respectively (Lipiec *et al.*, 2010). The selenium content of milk and dairy products varies widely; in the UK, milk and dairy products contain ~0.01–0.03 mg/kg selenium. The predominant selenium species in cows' milk are selenocysteine and selenite. Supplementation of dairy cows with Se-enriched yeast

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

alters the species profile in the milk and the major species after supplementation are selenocysteine, selenomethionine, and selenite (Muniz-Naveiro *et al.*, 2007).

Fruit and vegetables typically contain relatively small amounts of selenium in the form of selenate in onions or selenomethionine (53%), γ-glutamyl-Se-methylselenocysteine (31%), Se-methylselenocysteine (12%), and selenate (4%) in garlic with a natural selenium content of <0.5 mg/kg. However, vegetables such as onions, garlic, and broccoli when grown on Se-rich soil can accumulate selenium, resulting in selenium enrichment from <0.5 mg/kg up to 140–300 mg/kg. The main selenium species in Se-enriched vegetables are: γ-glutamyl-Se-methyl-selenocysteine (accounting for ∼45–73% of the species), selenate (∼4–20%) and selenomethionine (5–13%) plus other species at lower levels (Finley *et al.*, 2001; Hurst *et al.*, 2010). Notably, these forms of selenium in vegetables have received attention due to purported protection against cancer in animal models when compared with other forms of selenium (Fairweather-Tait *et al.*, 2011). Therefore, it can be concluded that the amount of selenium in the diet largely depends on where crops are grown and cultivated, the soil/fodder to which animals are exposed, and the actual foods consumed.

1.3.3.6 Selenium in animals and humans

Selenium is an essential trace element for humans and animals, although even low concentrations of selenium, in the order of a few mg/kg, can provoke health disturbances (Vinceti *et al.*, 2001). Also in humans and animals, Se-Cys is incorporated into a very specific location in the amino acid sequence of selenoproteins, and the uncontrolled S substitution of Se may cause toxic effects in humans and animals. At least 11 selenoproteins have been characterized in animal systems. The first characterized was the glutathione peroxidases; more precisely, four selenium-containing glutathione peroxidases (GPx) have been identified: cellular or classical GPx, plasma or extracellular GPx, phospholipid hydroperoxide GPx, and gastrointestinal GPx (Holben & Smith, 1999). These enzymes reduce damaging reactive oxygen species (ROS) oxidizing glutathione. A well-characterized example of this enzyme family is phospholipid hydroperoxide GPx, an antioxidant enzyme protecting cells from oxidative damages. Se-Cys is present also in the active site of the thioredoxin reductase that, in conjunction with the compound thioredoxin, is involved in the regeneration of several antioxidant systems in animal cells, possibly including vitamin C (Mustacich & Powis, 2000). Moreover, maintenance of thioredoxin in a reduced form by thioredoxin reductase is important for regulating cell growth and viability (Di Gregorio, 2008).

Selenium occurs in mammalian tissues in the range from 0.7 in heart tissue to 2.5 mg/kg in muscles. The average Se content in human soft tissues is estimated as 0.11 mg/kg (Li, 2000). Concentrations of Se in kidneys of European people were reported by Zduôska *et al.* (1994) as follows (in mg/kg of fresh weight):

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

Bulgaria, 2.5; Germany 0.7; and Italy, 1.9. In human fluids, mean Se concentrations are (in µg/L): blood, 107; serum, 80; and urine, 22 (Li, 2000). In Finland, the Se level in serum was between 0.63 and 0.76 µmol/L, and after the Se supplementation of fertilizers, it increased to the range of 1.2–1.4 µmol/L (Hartikainen, 2005).

Deficiency symptoms of improper Se supply to humans can be summarized as follows: muscle weakness and pain, inflammation of muscles, fragile red blood cells, degeneration of pancreas, abnormal skin colouration, heart muscle dysfunction, prolonged illness condition, susceptibility to cancer, Keshan disease (KD) and Kashin-Beck disease (KBD). Conversely, the toxicity symptoms are: liver and kidney damage, blood clotting, necrosis of heart and liver, skin lesions, hair and nail loss, nausea and vomiting (Kabata-Pendias & Mukherjee, 2007). On the other hand, selenium seems to be required to stimulate the immune response in humans (Roy *et al.*, 1994), playing a role in regulating the expression of cell signalling molecules called cytokines, which orchestrate the immune response (Baum *et al.*, 2000). Many studies suggest that selenium supplementation at high levels reduces the incidence of cancer in animals and that the methylated forms of selenium are the active species against tumours (Combs & Gray, 1998). In this respect, several mechanisms have been proposed for the cancer prevention effects of selenium: (1) maximizing the activity of antioxidant selenoenzymes and improving antioxidant status, (2) improving immune system function, (3) affecting the metabolism of carcinogens, and (4) increasing the levels of selenium metabolites that inhibit tumour cell growth (Di Gregorio, 2008). Some aspects related to the therapeutic effects of selenium are reported in Section 1.4.

1.4 EFFECTS AND BIOAVAILABILITY OF NANO-SELENIUM (SeNPs)

Various methods have been reported for the synthesis of selenium nanoparticles (hereafter: SeNPs), namely: biological and/or chemical methods (see Chapters 10, 11 and 12). Nanoparticles (NPs) are, in fact, a promising alternative in drug delivery (Ensign *et al.*, 2012) as well as nutritional supplements (Zhang *et al.*, 2011). Numerous studies have dealt with the effects of bioactive compound supplements in nano-particulate preparations (Anal & Singh, 2007; Hadrup *et al.*, 2016; Hu *et al.*, 2012; Zhai *et al.*, 2017; Zhang *et al.*, 2004) and some applications of NPs in nutrition and medicine have also been approved for clinical use (Wacker, 2014). Inclusion of nanotechniques in human nutrition is justified by the possibility of increasing the drug solubility, its protection against oxidation and enzymatic degradation, prolongation of residence time, and effective passage through the gastrointestinal tract enhancing the bioavailability of supplemented substances (Zhang *et al.*, 2004). Figure 1.7 shows some advantages of using NPs. SeNPs have quite promising and interesting results as a unique approach to either prevent or cure a variety of human diseases.

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

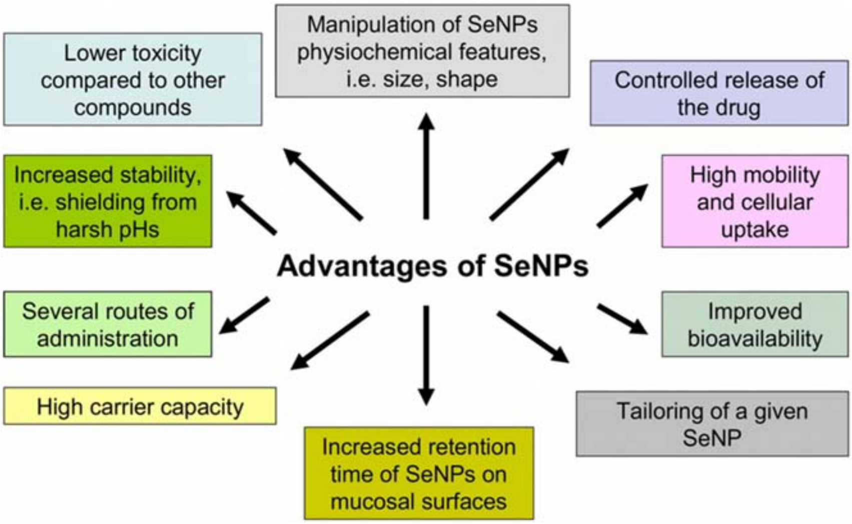


Figure 1.7 Diagram depicting the main advantages of using Se-nanoparticles (SeNPs) in nanomedicine applications (see text and references for details). Modified from Hosnedlova *et al.* (2018) and Khurana *et al.* (2019).

Therapeutic applications of SeNPs were recently reviewed by Khurana *et al.* (2019) and Hosnedlova *et al.* (2018). Besides, many studies have shown the antimicrobial effect (Piacenza *et al.*, 2017) and antifungal activity of nano-Se (Kheradmand *et al.*, 2014). In addition, its protective effects against metal intoxication have been well documented (Hassanin *et al.*, 2013; Prasad & Selvaraj, 2014).

The nano-form of selenium attracts even more attention, thanks to its higher bioavailability and lower toxicity than inorganic (selenite and selenate) and organic (selenomethionine, selenocysteine, and methylselenocysteine) forms (Fajt *et al.*, 2009; Zhang *et al.*, 2008). The advantage of nano-selenium (nano-Se) is the possibility of using selenium in zero oxidation state [Se(0)], which has low toxicity and excellent bioavailability as compared to other oxidation states [Se(+4) and Se(+6)] (Torres *et al.*, 2012; Wang *et al.*, 2007). On the other hand, Se(0) is very unstable and easily transformed into an inactive form although, its stabilization can be achieved by encapsulation into suitable nano-vehicles, for example, chitosan (CS) (Zhai *et al.*, 2017). As expected from the chemical-physical features of the nanoparticles, the biological properties of SeNPs depend on their size: smaller particles have a greater activity (Torres *et al.*, 2012). Indeed, the particle size affects the cellular intake of NPs; for example, *in vitro* absorption of 0.1 µm particles was found to be 2.5 and 6 times higher compared to 1 and 10 µm particles, respectively (Desai *et al.*, 1997). For this reason, in the preparation of dietary supplements, appropriate particle size, morphology, and encapsulation material should be chosen (De Jong & Borm, 2008).

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

Nanoscale selenium has strong effects on the reduction of oxidative stress and it has also been shown that spherical SeNPs have a lower risk of selenium toxicity (Gao *et al.*, 2002). Besides its use as an antioxidant, the immunostimulatory effect of nanoscale selenium has been confirmed (Kojouri *et al.*, 2012; Yazdi *et al.*, 2013) along with its beneficial effects on a number of physiological functions (Hegedüs *et al.*, 2012; Yin *et al.*, 2017). Even more interesting is the fact that SeNPs can be helpful in cancer chemo-prevention as a potential anticancer drug (Chen *et al.*, 2008; Sonkusre *et al.*, 2014) as well as an anticancer drug delivery carrier (Estevez *et al.*, 2014; Liu *et al.*, 2012). SeNPs have interesting anti-proliferation activity and inhibit HeLa cells during the S phase (Luo *et al.*, 2012; Ramya *et al.*, 2015). In the case of A375 melanoma cell lines, SeNPs were decorated with *Spirulina* and/or *Undaria pinnatifida* polysaccharides to improve the NPs biocompatibility and stability (Chen *et al.*, 2008; Yang *et al.*, 2012). Notably, similar results were obtained by capping SeNPs with water soluble polysaccharides-protein complexes from various species of fungi (Wu *et al.*, 2012, 2013).

In addition to biocompatibility and stability, SeNPs need to be selective in their capacity to enter the cells. In this respect, Yu *et al.* (2012) reported that SeNPs decorated with folate-chitosan were found to selectively endocytose inside cancer cells. This latter result is important because it shows the possibility to construct SeNPs for active targeting. Indeed, Zhang *et al.* (2013) synthesized adenosine triphosphate (ATP) surface-functionalized SeNPs which were able to specifically bind to purino-receptors in tumour tissues, thus causing a significant cancer cell apostosis. A further approach, such as the conjugation of SeNPs with other drugs, has also been used to elicit NPs cellular internalization and overcome multi-drug resistance. For example, the combination of adriamycin and SeNPs exhibited synergistic anticancer activity at low concentration compared to the drug used alone in Bel7402 hepatic cancer cell lines (Tan *et al.*, 2009), while bimetallic Se-AgNPs showed antitumour activity against Dalton's lymphoma cells (Kumar *et al.*, 2015). Another aspect related to multidrug resistance is that it may occur due to the mutation in the drug efflux pumps as seen in the case of the overexpression of ATP binding cassettes including P-glycoproteins (reviewed in Khurana *et al.*, 2019). In this respect, SeNPs are interesting carriers for drugs such as doxorubicin and curcumin to be used against *in vitro* lung-cancer cells (Zhao *et al.*, 2017) and Ehrlich's ascites carcinoma mouse model, respectively (Kumari *et al.*, 2017). Similarly, since small interfering RNAs (siRNA) have been used in treating many types of cancer, Xia *et al.* (2017) reported successful targeted delivery of siRNA using functionalized SeNPs against liver carcinoma.

Based on *in vitro* and *in vivo* studies, biogenic SeNPs can be considered as a novel therapeutic agent for the treatment of localized lesions typical of cutaneous leishmaniasis caused by *Leishmania major* (Beheshti *et al.*, 2013). The anti-leishmanial activities of SeNPs against *Leishmania infantum* were also described. SeNPs have more growth-inhibitory effect on promastigotes than

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

selenium dioxide (SeO_2), while the IC_{50} (half minimal [50%] inhibitory concentration) was determined to be 25 and 50 ng/L, respectively (Soflaei *et al.*, 2014).

REFERENCES

Afzal S., Younas M. and Ali K. (2000). Selenium speciation studies from Soan-Sakesar valley, Salt Range, Pakistan. *Water International*, **25**, 425–436.

Aiuppa A., Allard P., D'Alessandro W., Michel A., Parello F., Treuil M. and Valenza M. (2000a). Mobility and fluxes of major, minor and trace metals during basalt weathering and groundwater transport at Mt. Etna volcano (Sicily). *Geochimica et Cosmochimica Acta*, **64**(11), 1827–1841.

Aiuppa A., Dongarrà G., Capasso G. and Allard P. (2000b). Trace elements in the thermal groundwaters of Vulcano Island (Sicily). *Journal of Volcanology and Geothermal Research*, **98**(1–4), 189–207.

Allegrini E., Maresca A., Olsson M. E., Holtze M. S., Boldrin A. and Astrup T. F. (2014). Quantification of the resource recovery potential of municipal solid waste incineration bottom ashes. *Waste Management*, **34**, 1627–1636.

Altschuler Z. S. (1980). The geochemistry of trace elements in marine phosphorites. Part I. Characteristic, abundances and enrichment. *Society of Economic Paleontologists and Mineralogists*, **29**, 19–30.

Anal A. K. and Singh H. (2007). Recent advances in microencapsulation of probiotics for industrial applications and targeted delivery. *Trends Food Science and Technology*, **18**(5), 240–251.

Antonioli P., Lampis S., Chesini I., Vallini G., Rinalducci S., Zolla L. and Righetti P. G. (2007). Stenotrophomonas maltophilia SeITE02, a new bacterial strain suitable for bioremediation of selenite-contaminated environmental matrices. *Applied Environmental Microbiology*, **73**, 6854–6863.

ATSDR (2002). Draft Toxicological Profile for Several Trace Elements. U.S. Dept. Health & Human Services. Agency for Toxic Substances and Disease Registry, Atlanta GA, USA.

Bailey R. T. (2017). Review: Selenium contamination, fate, and reactive transport in groundwater in relation to human health. *Hydrogeological Journal*, **25**, 1191–1217.

Baldwin R. A., Stauter J. C., Kauffman J. W. and Laughlin W. C. (1985). U.S. Patent No. 4 519 913. U.S. Patent and Trademark Office, Washington, DC.

Barceloux D. G. (1999). Selenium. *Journal of Toxicology and Clinical Toxicology*, **37**, 145–172.

Barclay M. N. I., MacPherson A. and Dixon J. (1995). Selenium content of a range of UK foods. *Journal of Food Composition and Analysis*, **8**(4), 307–318.

Bauch N. J., Musgrove M., Mahler B. J. and Paschke S. S. (2014). The quality of our Nation's waters - Water quality in the Denver Basin aquifer system, Colorado. *U.S. Geological Survey Circular*, **1357**, 100.

Baum M. K., Miguez-Burbano M. J., Campa A. and Shor-Posner G. (2000). Selenium and interleukins in persons infected with human immunodeficiency virus type 1. *Journal Infectious Disease*, **182**(1), S69–S73.

Beheshti N., Soflaei S., Shakibaie M., Yazdi M. H., Ghaffarifar F., Dalimi A. and Shahverdi A. R. (2013). Efficacy of biogenic selenium nanoparticles against *Leishmania major*: in

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

vitro and in vivo studies. *Journal Trace Elements in Medicine and Biology*, **27**(3), 203–207.

Beck M. A., Levander O. A. and Handy J. (2003). Selenium deficiency and viral infection. *The Journal of Nutrition*, **133**(5), 1463S–1467S.

Bech J., Suarez M., Reverter F., Tume P., Sánchez P., Bech J. and Lansac A. (2010a). Selenium and other trace elements in phosphate rock of Bayovar–Sechura (Peru). *Journal of Geochemical Exploration*, **107**(2), 136–145.

Bech J., Suarez M., Reverter F., Tume P., Sánchez P., Roca N. and Lansac A. (2010b). Selenium and other trace element in phosphorites: a comparison between those of the Bayovar-Sechura and other provenances. *Journal of Geochemical Exploration*, **107**(2), 146–160.

Beone G. M., Carini F., Guidotti L., Rossi R., Gatti M., Fontanella M. C. and Cenci R. M. (2018). Potentially toxic elements in agricultural soils from the Lombardia region of northern Italy. *Journal of Geochemical Exploration*, **190**, 436–452.

Berzelius J. (1818). Letters to C.L. Berthollet. *Annales de Chimie et de Physique*, **9**, 160–180, 225–267, 337–365.

Blengini G. A. A., Blagoeva D., Dewulf J., Torres de Matos C., Nita V., Vidal-Legaz B., Latunussa C., Kayam Y., Talens, Peirò L., Baranzelli C. E. L., Manfredi S., Mancini L., Nuss P., Marmier A., Alves-Dias P., Pavel C., Tzimas E., Mathieux F., Pennington D. and Ciupagea C. (2017). JRC Technical reports – Assessment of the Methodology for Establishing the EU List of Critical Raw Materials – Annexes. https://doi.org/10.2760/73303.

Bodnar M., Szcyglowska M., Konieczka P. and Namiesnik J. (2016). Methods of selenium supplementation: bioavailability and determination of selenium compounds. *Critical Reviews in Food Science and Nutrition*, **56**(1), 36–55.

Boschen R. E., Rowden A. A., Clark M. R. and Gardner J. P. A. (2013). Mining of deep-sea seafloor massive sulfides: a review of the deposits, their benthic communities, impacts from mining, regulatory frameworks and management strategies. *Ocean & Coastal Management*, **84**, 54–67.

Bowen H. J. M. (1979). Environmental Chemistry of the Trace Elements. Academic Press, London.

British Nutrition Foundation. (2001). Briefing paper: Selenium and Health. www.nutrition.org.uk, **145**, 1–36.

Bullock L. A., Parnell J., Perez M., Armstrong J. G., Feldmann J. and Boyce A. J. (2018). High selenium in the Carboniferous Coal Measures of Northumberland, North East England. *International Journal of Coal Geology*, **195**, 61–74.

Bullock L. A., Parnell J., Feldmann J., Armstrong J. G., Henn A. S., Mesko M. F., Mello P. A. and Flores E. M. M. (2019). Selenium and tellurium concentrations of Carboniferous British coals. *Geological Journal*, **54**(3), 1401–1412.

Butterman W. C. and Brown R. D., Jr. (2004). Mineral Commodity Profiles-Selenium. U.S. Geological Survey Open-File Report **03–018**. Retrieved from https://pubs.usgs.gov/of/2003/of03-018/of03-018.pdf

CH2MHILL (2010). Review of available technologies for the removal of selenium from water – final report. Prepared for North American Metals Council by CH2M HILL Companies, Ltd, Englewood, Colorado. Retrieved from https://www.namc.org/docs/FINAL-NAMC-SWG_Removal_Technologies.pdf

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

Chan Y. T., Kuan W. H., Chen T. Y. and Wang M. K. (2009). Adsorption mechanism of selenate and selenite on the binary oxide systems. *Water Resources*, **43**, 4412–4420.

Chang C., Yin R., Zhang H. and Yao L. (2019). Bioaccumulation and Health Risk Assessment of Heavy Metals in the Soil–Rice System in a Typical Seleniferous Area in Central China. *Environmental Toxicology and Chemistry*, **38**(7), 1577–1584.

Chasteen T. G. and Bentley R. (2003). Biomethylation of selenium and tellurium: microorganisms and plants. *Chemical Reviews*, **103**, 1–25.

Chen J., Wei F., Zheng C., Wu Y. and Adriano D. C. (1991). Background concentrations of elements in soils of China. *Water, Air, and Soil Pollution*, 57–58, 699–712.

Chen T., Wong Y. S., Zheng W., Bai Y. and Huang L. (2008). Selenium nanoparticles fabricated in *Undaria pinnatifida* polysaccharide solutions induce mitochondria-mediated apoptosis in A375 human melanoma cells. *Colloids and Surface B: Biointerfaces*, **67**(1), 26–31.

Cheng H., Li M., Zhao C., Li K., Peng M., Qin A. and Cheng X. (2014). Overview of trace metals in the urban soil of 31 metropolises in China. *Journal of Geochemical Exploration*, **139**, 31–52.

Chilimba A. D. C., Young S. D., Black C. R., Rogerson K. B., Ander E. L., Watts M. J., Lamme J. and Broadley M. R. (2011). Maize grain and soil surveys reveal suboptimal dietary selenium intake is widespread in Malawi. *Scientific Reports*, **1**(72), 1–9.

Christophersen O. A., Lyons G., Haug A. and Steinnes E. (2013). Chapter 16 – Selenium. In: Heavy Metals in Soils: Trace Metals and Metalloids in Soils and their Bioavailability, B. Alloway (ed.), Environmental Pollution Series, 22, Springer Science+Business Media, Dordrecht, pp. 429–463.

Coleman R. G. and Delevaux M. H. (1957). Occurrence of selenium in sulfides from some sedimentary rocks of the Western United States. *Economic Geology*, **52**, 499–527.

Coleman L., Bragg L. J. and Finkelman R. B. (1993). Distribution and mode of occurrence of selenium in US coals. *Environmental Geochemistry and Health*, **15** (4), 215–227.

Combs G. A. (2001). Selenium in global food systems. *British Journal of Nutrition*, **85**, 517–547.

Combs G. F. and Gray W. P. (1998). Chemopreventive agents: selenium. *Pharmacology and Therapeutics*, **79**, 179–192.

Davies B. E. and Houghton N. J. (1983). The selenium content of Welsh soils with special reference to bedrock and contamination from sulphide ores. *Minerals and the Environment*, **5**, 67–70.

De La Riva D. G., Vindiola B. G., Castañeda T. N., Parker D. R. and Trumble J. T. (2014). Impact of selenium on mortality, bioaccumulation and feeding deterrence in the invasive Argentine ant, *Linepithema humile* (*Hymenoptera: Formicidae*). *Science of the Total Environment*, **481**, 446–452.

Desai M. P., Labhasetwar V., Walter E., Levy R. J. and Amidon G. L. (1997). The mechanism of uptake of biodegradable microparticles in Caco-2 cells is size dependent. *Pharmaceutical Research*, **14**(11), 1568–1573.

Deverel S. J., Fio J. L. and Dubrovsky N. M. (1994). Distribution and Mobility of Selenium in Groundwater in the Western San Joaquin Valley of California. In: Selenium in the Environment, W. T. Frankenberger and S. Benson (eds.), Dekker, New York, pp. 157–183.

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

De Jong W. H. and Borm P. J. (2008). Drug delivery and nanoparticles: applications and hazards. *International Journal of Nanomedicine*, **3**(2), 133–149.

De Simone L. A., McMahon P. B. and Rosen M. R. (2014). The quality of our Nation's waters – Water quality in Principal Aquifers of the United States, 1991–2010. *U.S. Geological Survey Circular*, **1360**, 1–15.

De Temmerman L., Waegeneers N., Thiry C., Du Laing G., Tack F. and Ruttens A. (2014). Selenium content of Belgian cultivated soils and its uptake by field crops and vegetables. *Science of The Total Environment*, **468–469**, 77–82.

Dhillon K. S. and Dhillon S. K. (1991). Selenium toxicity in soils, plants and animals in some parts of Punjab, India. *International Journal of Environmental Studies*, **37**, 15–24.

Dhillon K. S. and Dhillon S. K. (2003). Distribution and management of seleniferous soils. *Advances in Agronomy*, **79**, 119–184.

Dhillon K. S. and Dhillon S. K. (2014). Development and mapping of seleniferous soils in north-western India. *Chemosphere*, **99**, 56–63.

Dhillon K. S., Dhillon S. K. and Bijay-Singh (2019). Genesis of seleniferous soils and associated animal and human health problems. *Advances in Agronomy*, **154**, 1–80.

Di Gregorio S. (2008). Selenium: a versatile trace element in life and environment. In: Trace Elements in Human Health and Disease, A. S. Prasad (ed.), Vol 2. Academic Press, New York, USA, pp. 593–622.

Dinelli E., Lima A., Albanese S., Birke M., Cicchella D., Giaccio L., Valera P. and De Vivo B. (2012). Comparative study between bottled mineral and tap water in Italy. *Journal of Geochemical Exploration*, **112**, 368–389.

Duntas L. H. and Benvenga S. (2014). Selenium: an element for life. *Endocrine*, **48**, 756–775.

Ellis D. R. and Salt D. E. (2003). Plants, selenium and human health. *Current Opinion in Plant Biology*, **6**(3), 273–279.

El-Ramady H., Abdalla N. A., Alshaal T., Domokos-Szabolcsy E., Elhawat N., Prokisch J., Sztrik A., Fári M, El-Marsafawy S. and Shams M. S. (2014a). Selenium in soils under climate change, implication for human health. *Environmental Chemistry Letters*, **13**(1), 1–19.

El-Ramady H. R., Domokos-Szabolcsy E., Abdalla N. A., Alshaal T. A., Shalaby T. A., Sztrik A., Prokisch J. and Fári M. (2014b). Selenium and nano-selenium in agroecosystems. *Environmental Chemistry Letters*, **12**(4), 495–510.

El-Shafey E. I. (2007a). Removal of Se(IV) from aqueous solution using sulphuric acid treated peanut shell. *Journal of Environmental Management*, **84**, 620–627.

El-Shafey E. I. (2007b). Sorption of Cd(II) and Se(IV) from aqueous solution using modified rice husk. *Journal of Hazardous Material*, **147**, 546–555.

Engberg R. A. (1999). Selenium budgets for Lake Powell and the upper Colorado River Basin. *Journal of the American Water Resources Association*, **35**, 771–786.

Ensign L. M., Cone R. and Hanes J. (2012) Oral drug delivery with polymeric nanoparticles: the gastrointestinal mucus barriers. Advanced Drug Delivery *Reviews*, **64**(6), 557–570.

Estevez H., Garcia-Lidon J. C., Luque-Garcia J. L. and Camara C. (2014). Effects of chitosan-stabilized selenium nanoparticles on cell proliferation, apoptosis and cell cycle pattern in HepG2 cells: comparison with other selenospecies. *Colloids and Surfaces B: Biointerfaces*, **122**, 184–193.

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

European Commission (2014) Report on Critical Raw Materials for the Eu. *Eucom*, **39**, 1–41. https://doi.org/Ref.Ares(2015)1819595 (accessed 29 April 2015).

Fairweather-Tait S. J., Collings R. and Hurst R. (2010). Selenium bioavailability: current knowledge and future research requirements. *The American Journal of Clinical Nutrition*, **91**(5), 14845–14915.

Fairweather-Tait S. J., Bao Y., Broadley M. R., Collings R., Ford D., Hesketh J. E. and Hurst R. (2011). Selenium in human health and disease. *Antioxidants and Redox Signaling*, **14** (7), 1337–1383.

Fajt Z., Drabek J., Steinhauser L. and Svobodova Z. (2009). The significance of pork as a source of dietary selenium – an evaluation of the situation in the Czech Republic. *Neuro Endocrinology Letters*, **30**(1), 17–21.

Fay D., Kramers G., Zhang C., McGrath D. and Grennan E. (2007). Soil Geochemical Atlas of Ireland.

Fergusson J. E. (1990). The Heavy Elements: Chemistry, Environmental Impact and Health Effects. Pergamon, London.

Fiducia T. A. M., Mendis B. G., Li K., Grovenor C. R. M., Munshi A. H., Barth K., Sampath W. S., Wright L. D., Abbas A., Bowers J. W. and Walls J. M. (2019) Understanding the role of selenium in defect passivation for highly efficient selenium-alloyed cadmium telluride solar cells. *Nature Energy*, **4**, 504–511.

Finley J. W., Ip C., Lisk D. J., Davis C. D., Hintze K. J. and Whanger P. D. (2001). Cancer-protective properties of high- selenium broccoli. *Journal of Agricultural and Food Chemistry*, **49**, 2679–2683.

Fisinin V. I., Papazyan T. T. and Surai P. F. (2009). Producing selenium-enriched eggs and meat to improve the selenium status of the general population. *Critical Reviews in Biotechnology*, **29**(1), 18–28.

Floor G. H. and Román-Ross G. (2012). Selenium in volcanic environments: a review. *Applied Geochemistry*, **27**(3), 517–531.

Fordyce F. M. (2013). Selenium deficiency and toxicity in the environment. In: Essentials of Medical Geology, O. Selinus (ed.), Springer, Dordrecht, The Netherlands, pp. 375–416.

Fordyce F. M. (2005). Selenium deficiency and toxicity in the environment. In: Essentials of Medical Geology, O. Selinus, B. Alloway, J. A. Centeno, R. B. Finkelman, R. Fuge, U. Lindh and P. Smedley (eds.), Elsevier, London, UK, pp. 373–415.

Fordyce F. M., Zhang G., Green K. and Liu X. (2000). Soil, grain and water chemistry and human selenium imbalances in Enshi District, Hubei Province, China. *Applied Geochemistry*, **15**(1), 117–132.

Fordyce F. M., Brereton N., Hughes J., Luo W. and Lewis J. (2010). An initial study to assess the use of geological parent materials to predict the Se concentration in overlying soils and in five staple foodstuffs produced on them in Scotland. *Science of the Total Environment*, **408**(22), 5295–5305.

Frengstad B., Midtgård Skrede A. K., Banks D., Krog J. R. and Siewers U. (2000). The chemistry of Norwegian groundwaters: III. The distribution of trace elements in 476 crystalline bedrock groundwaters, as analysed by ICP- MS techniques. *Science of the Total Environment*, **246**(1), 21–40.

Fu Y., Wang J., Liu Q. and Zeng H. (2014). Water-dispersible magnetic nanoparticle–graphene oxide composites for selenium removal. *Carbon*, **77**, 710–721.

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

Gaillardet J., Viers J. and Dupré B. (2005). Trace element in river waters. In: Treatise on Geochemistry, volume 5. Surface and Ground Water Weathering and Soils, J. J. Drever, H. D. Holland and K. K. Turekian (eds.), Elsevier, NY, pp. 225–272.

Galeas M. L., Zhang L. H., Freeman J. L., Wegner M. and Pilon-Smits E. A. H. (2007). Seasonal fluctuations of selenium and sulfur accumulation in selenium hyperaccumulators and related nonaccumulators. *New Phytologist*, **173**, 517–525.

Gao S., Luo T.-C., Zhang B.-R., Zhang H.-F., Han Y.-W., Zhao Z.-D. and Hu Y.-K. (1998). Chemical composition of the continental crust as revealed by studies in east China. *Geochimica et Cosmochimica Acta*, **62**(11), 1959–1975.

Gao X., Zhang J. and Zhang L. (2002). Hollow sphere selenium nanoparticles: their *in vitro* anti hydroxyl radical effect. Advanced *Materials*, **14**(4), 290–293.

Geoffroy N. and Demopoulos G. P. (2009). Reductive precipitation of elemental selenium from selenious acidic solutions using sodium dithionite. *Industrial and Engineering Chemistry Research*, **48**, 10240–10246.

Geoffroy N. and Demopoulos G. P. (2011). The elimination of selenium(IV) from aqueous solution by precipitation with sodium sulfide. *Journal of Hazardous Material*, **185**, 148–154.

George M. W. and Wagner L. A. (2009). Selenium recycling in the United States in 2004. *U. S. Geological Survey Circular*, **1196-T**, 1–7.

Gerrard T. L., Telford J. N. and Williams H. H. (1974). Detection of selenium deposits in *Escherichia coli* by electron microscopy. *Journal of Bacteriology*, **173**, 3463–3467.

Goodman D. J., Kerollis R. E., Mindler A. B. and Bruns B. (2000). U.S. Patent No. 6 090 290. U.S. Patent and Trademark Office, Washington, DC.

Guillén M. T., Delgado J., Albanese S., Nieto J. M., Lima A. and De Vivo B. (2011). Environmental geochemical mapping of Huelva municipality soils (SW Spain) as a tool to determine background and baseline values. *Journal of Geochemical Exploration*, **109**(1–3), 59–69.

Guo L. and Wu D.-Q. (2017). Study of recycling Singapore solid waste as land reclamation filling material. *Sustainable Environment Research*, **27**, 1–6.

Grundmann G. and Förster H.-J. (2017). Origin of the El Dragón Selenium Mineralization, Quijarro Province, Potosí, Bolivia. *Minerals*, **7**(5), 68.

Hadrup N., Loeschner K., Skov K., Ravn-Haren G., Larsen E. H., Mortensen A., Lam H. R. and Frandsen H. L. (2016). Effects of 14-days oral low-dose selenium nanoparticles and selenite in rat – as determined by metabolite pattern determination. *Peer J – Life and Environment*, **4**, e2601.

Hageluken C. and Meskers C. (2010). Complex life cycles of precious and special metals. In: Linkages of Sustainability, T. E. Graedel and E. van der Voet (eds.), The MIT Press, Cambridge, pp. 163–198.

Hartfiel W. and Bahners N. (1988). Selenium Deficiency in the Federal Republic of Germany. In: Selenium, G. N. Schrauzer (ed.), Humana Press.

Hartikainen H. (2005). Biogeochemistry of selenium and its impact on food chain quality and human health. *Journal of Trace Elements in Medicine and Biology*, **18**, 309–318.

Hassanin K. M., Abd El-Kawi S. H. and Hashem K. S. (2013). The prospective protective effect of selenium nanoparticles against chromium-induced oxidative and cellular damage in rat thyroid. *International Journal of Nanomedicine*, **8**, 1713–1720.

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

Hatten Howard J. H., III. (1977). Geochemistry of selenium—Formation of ferroselite and selenium behavior in the vicinity of oxidizing sulfide and uranium deposits. *Geochimica et Cosmochimica Acta*, **41**(11), 1665–1678.

Hazen R. M., Grew E. S., Downs R. T., Golden J. and Hystad G. (2015). Mineral ecology: Chance and necessity in the mineral diversity of terrestrial planets. *Canadian Mineralogist*, **53**, 295–324.

Hegedüs V., Prokisch J., Fébel H., Kleiner D., Ditrói K., Szijártó A. and Blázovics A. (2012). Nanoselenium treatment in fatty liver. *Zeitschrift fur Gastroenterolologie*, **50**(5), A29.

He Z. L., Xiao J. S. and Yang E. (2010). Manganese and Selenium. In: Trace Elements in Soils, P. S. Hooda (ed.), Blackwell Publishing Co, Chichester, UK, pp. 481–495.

Hem J. D. (1985). Study and Interpretation of the Chemical Characteristics of Natural Water. *USGS Professional Paper*, **2254**, 1–264.

Hoffman J. E. and King M. G. (1997). Selenium and selenium compounds. In: Encyclopedia of Chemical Technology, J. I. Kroschwitz and M. H. Howe-Grant (eds.), John Wiley & Sons, New York, USA, pp. 686–719.

Holben D. H. and Smith A. M. (1999). The diverse role of selenium within selenoproteins: a review. *Journal of the American Dietetic Association*, **99**, 836–843.

Hosnedlova B., Kepinska M., Skalickova S., Fernandez C., Ruttkay-Nedecky B., Peng Q., Baron M., Melcova M., Opatrilova R., Zidkova J., Bjørklund G., Sochor J. and Kizek R. (2018). Nano-selenium and its nanomedicine applications: a critical review. *International Journal of Nanomedicine*, **13**, 2107–2128.

Hu C. H., Li Y. L., Xiong L., Zhang H. M., Song J. and Xia M. S. (2012). Comparative effects of nano-elemental selenium and sodium selenite on selenium retention in broiler chickens. *Animal Feed Science and Technology*, **177**(3), 204–210.

Hu X., Wang F., Mark L. and Hanson M. L. (2009). Selenium concentration, speciation and behavior in surface waters of the Canadian prairies. *Science of the Total Environment*, **407**(22), 5869–5876.

Huawei Z. (2009). Selenium as an essential micronutrient: roles in cell cycle and apoptosis. *Molecules*, **14**(3), 1263–1278.

Hunter W. J., Kuykendall L. D. and Manter D. K. (2007). Rhizobium selenireducens sp. nov., a selenite-reducing α-Proteobacterium isolated from a bioreactor. *Current Microbiology*, **55**, 455–460.

Hurst R., Armah C. N., Dainty J. R., Hart D. J., Teucher B., Goldson A. J., Broadley M. R., Motley A. K. and Fairweather- Tait S. J. (2010). Establishing optimal selenium status: results of a randomized, double blind, placebo-controlled trial. *American Journal of Clinical Nutrition*, **91**, 923–931.

Jacobs L. W. (ed.) (1989). Selenium in Agriculture and the Environment. Soil Science Society of America Special Publication, Madison, 23.

John D. A. (2001). Miocene and early Pliocene epithermal gold-silver deposits in the northern Great Basin, Western United States—Characteristics, distribution, and relationship to magmatism. *Economic Geology*, **96**, 1827–1853.

Kabata-Pendias A. (2011). Trace Elements in Soils and Plants, 4th edn. CRC Press, Boca Raton.

Kabata-Pendias E. and Pendias H. (2001). Trace Elements in Soils and Plants, 3rd edn. LLC, CRC Press/Taylor & Francis Group, Boca Raton.

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

Kabata-Pendias A. and Mukherjee A. B. (2007). Trace Elements from Soil to Human. Springer Science + Business Media, Berlin, Germany.

Kashiwa M., Nishimoto S., Takahashi K., Ike M. and Fujita M. (2000). Factors affecting soluble selenium removal by a selenate-reducing bacterium *Bacillus* sp SF-1. *Journal of Biosciences and Bioengineering*, **89**, 528–533.

Kheradmand E., Rafii F., Yazdi M. H., Sepahi A. A., Shahverdi A. R. and Oveisi M. R. (2014). The antimicrobial effects of selenium nanoparticle-enriched probiotics and their fermented broth against *Candida albicans*. *DARU Journal of Pharmacological Sciences*, **22**(48), 1–6.

Khurana A., Tekula S., Saifi M. A., Venkatesh P. and Godugu C. (2019). Therapeutic applications of selenium nanoparticles. *Biomedicine and Pharmacotherapy*, **111**, 802–812.

Kilic Y., Kartal G. and Timur S. (2013). An investigation of copper and selenium recovery from copper anode slimes. *International Journal of Mineral Processing*, **124**, 75–82.

Klaproth M. H. (1798). On the Transylvanian gold ore, and the new metal contained in it. Chemical Annals for the Friends of Science, Medicine, Economics, and Manufacturing, **1**, 91–104.

Klonowska A., Heulin T. and Vermeglio A. (2005). Selenite and tellurite reduction by *Shewanella oneidensis*. *Applied and Environmental Microbiology*, **71**, 5607–5609.

Kogel J. E. (2006). Industrial Minerals and Rocks: Commodities, Markets, and Uses. Society for Mining Metallurgy and Exploration, Littleton, Colorado, USA.

Kojouri G. A., Sadeghian S., Mohebbi A. and Dezfouli M. R. M. (2012). The effects of oral consumption of selenium nanoparticles on chemotactic and respiratory burst activities of neutrophils in comparison with sodium selenite in sheep. *Biological Trace Elements Research*, **146**(2), 160–166.

Koljionen T. (ed.) (1992). The Geochemical Atlas of Finland, Part II: Till. Geological Survey of Finland, Espoo, Finland.

Krivovichev V., Krivovichev S. and Charykova M. (2019). Selenium minerals: structural and chemical diversity and complexity. *Minerals*, **9**(455), 1–20.

Kumar S., Tomar M. R. and Acharya A. (2015). Carboxylic group-induced synthesis and characterization of selenium nanoparticles and its antitumor potential on Dalton's lymphoma cells. *Colloids and Surfaces B: Biointerfaces*, **126**, 546–552.

Kumari M., Ray L., Purohit M., Patnaik S., Pant A., Shukla Y., Kumar P. and Gupta K. (2017). Curcumin loading potentiates the chemotherapeutic efficacy of selenium nanoparticles in HCT116 cells and Ehrlich's ascites carcinoma bearing mice. *European Journal of Pharmaceutics and Biopharmaceutics*, **117**, 346–362.

Langner B. E. (2000). Selenium and Selenium Compounds. In: Ullmann's Encyclopedia of Industrial Chemistry, M. Bohnet (ed.), 6th edn. Vol 32. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, pp. 203–215.

Lavu R. V. S., Du Laing G., Van De Wiele T., Pratti V. L., Willekens K., Vandecasteele B. and Tack F. (2012). Fertilizing soil with selenium fertilizers: impact on concentration, speciation, and bioaccessibility of selenium in leek (*Allium ampeloprasum*). *Journal of Agricultural and Food Chemistry*, **60**(44), 10930–10935.

Leblanc J.-C., Guérin T., Noël L., Calamassi-Tran G., Volatier J.-L. and Verger P. (2005). Dietary exposure estimates of 18 elements from the 1st French Total Diet Study. *Food Additives & Contaminants*, **22**(7), 624–641.

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

Lemly A. D. (1999). Selenium transport and bioaccumulation in aquatic ecosystems: a proposal for water quality criteria based on hydrological units. *Ecotoxicology and Environmental Safety*, **42**(2), 150–156.

Lemly A. D. (2004). Aquatic selenium pollution is a global environmental safety issue. *Ecotoxicology and Environmental Safety*, **59**(1), 44–56.

Lenz M. and Lens P. N. L. (2009). The essential toxin: the changing perception of selenium in environmental sciences. *The Science of the Total Environment*, **407**, 3620–3633.

Levander O. A. (1986). Selenium. In: Trace Elements in Human and Animal Nutrition, W. Mertz (ed.), Academic Press, London, pp. 139–197.

Li Y.-H. (1991). Distribution patterns of the elements in the ocean: a synthesis. *Geochimica et Cosmochimica Acta*, **55**(11), 3223–3240.

Li Y.-H. (2000). A Compendium of Geochemistry: from Solar Nebula to the Human Brain. Princeton University Press, Princeton.

Lipiec E., Siara G., Bierla K., Ouerdane L. and Szpunar J. (2010). Determination of selenomethionine, selenocysteine, and inorganic selenium in eggs by HPLC-inductively coupled plasma mass spectrometry. *Analytical and Bioanalytical Chemistry*, **397**, 731–741.

Liu W., Li X., Wong Y. S., Zheng W., Zhang Y, Cao W. and Chen T. (2012). Selenium nanoparticles as a carrier of 5- fluorouracil to achieve anticancer synergism. *ACS Nano*, **6**(8), 6578–6591.

Liu A., Ren F., Lin W. Y. and Wang J. Y. (2015). A review of municipal solid waste environmental standards with a focus on incinerator residues. *International Journal of Sustainable Built Environment*, **4**, 165–188.

Losi M. E. and Frankenberger W. T. (1997). Reduction of selenium oxyanions by *Enterobacter cloacae* SLD1a-1: isolation and growth of the bacterium and its expulsion of selenium particles. *Applied and Environmental Microbiology*, **63**, 3079–3084.

Luo H., Wang F., Bai Y., Chen T. and Zheng W. (2012). Selenium nanoparticles inhibit the growth of HeLa and MDA- MB-231 cells through induction of S phase arrest. *Colloids and Surfaces B: Biointerfaces*, **94**, 304–308.

Malisa E. P. (2001). The behaviour of selenium in geological processes. *Environmental Geochemistry and Health*, **23**, 137–158.

Mayland H. F. (1994). Selenium in plant and animal nutrition. In: Selenium in the Environment, W. T. Frankenberger, Jr. and S. Benson (eds.), Marcel Dekker Inc, New York, USA, pp. 29–45.

Meher A. K., Jadhav A., Labhsetwar N. and Bansiwal A. (2020). Simultaneous removal of selenite and selenate from drinking water using mesoporous activated alumina. *Applied Water Science*, **10**, 1–12.

Mierzejewski M., Wismer M. W. and Sathrugnan K. (2017). U.S. Patent No. 9 567 249. U.S. Patent and Trademark Office, Washington, DC.

Miller L. L., Rasmussen J. B., Palace V. P., Sterling G. and Hontela A. (2013). Selenium bioaccumulation in stocked fish as an indicator of fishery potential in pit lakes on reclaimed coal mines in Alberta, Canada. *Environmental Management*, **52**(1), 72–84.

Misund A., Frengstad B., Siewers U. and Reimann C. (1999). Variation of 66 elements in European bottled mineral waters. *Science of the Total Environment*, **243–244**, 21–41.

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

Mol G., Spijker J., van Gaans P. and Römkens P. (2012). Geochemische bodematlas van Nederland. Wageningen Academic Publishers, Wageningen (in Dutch).

Mollah M. Y. A., Morkovsky P., Gomes J. A. G., Kesmez M., Parga J. and Cocke D. L. (2004). Fundamentals, present and future perspectives of electrocoagulation. *Journal of Hazardous Material*, **114**, 199–210.

Momma K. and Izumi F. (2011). VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. *Journal of Applied Crystallography*, **44**, 1272–1276.

Morgan J. W., Higuchi H., Takahashi H. and Hertogen J. (1978). Chondritic Eucrite Parent Body – Inference from Trace- Elements. *Geochimica et Cosmochimica Acta*, **42**(1), 27–38.

Mosher B. W. and Duce R. A. (1987). A global atmospheric selenium budget. *Journal of Geophysical Research*, **92**, 13289–13298.

Musgrove M., Beck J. A., Paschke S. S., Bauch N. J. and Mashburn S. L. (2014). Quality of groundwater in the Denver Basin aquifer system, Colorado. U.S. Geological Survey Scientific Investigations Report **2014–5051**, 1–107.

Muniz-Naveiro O., Dominguez-Gonzalez R., Bermejo-Barrera A., Bermejo-Barrera P., Cocho J. A. and Fraga J. M. (2007). Selenium speciation in cow milk obtained after supplementation with different selenium forms to the cow feed using liquid chromatography coupled with hydride generation atomic fluorescence spectrometry. *Talanta*, **71**, 1587–1593.

Mustacich D. and Powis G. (2000). Thioredoxin reductase. *Biochemical Journal*, **346**, 1–8.

Nancharaiah Y. V. and Lens P. N. L. (2015a). The ecology and biotechnology of selenium respiring bacteria. *Microbiology and Molecular Biology Reviews*, **79**(1), 61–80.

Nancharaiah Y. V. and Lens P. N. L. (2015b). Selenium biomineralization for biotechnological applications. *Trends in Biotechnology*, **33**(6), 323–330.

Natasha Shahid M., Niazi N. K., Khalid S., Murtaza B., Bibi I. and Rashid M. I. (2018). A critical review of selenium biogeochemical behavior in soil-plant system with an inference to human health. *Environmental Pollution*, **234**, 915–934.

Naumov A. V. (2010). Selenium and tellurium: state of the markets, the crisis, and its consequences. *Metallurgist*, **54**, 197–200.

Neal R. H. (1995). Selenium. In: Heavy Metals in Soils, B. J. Alloway (ed.), Blackie Academic & Professional, London, pp. 260–283.

Neuhierl B. and Böck A. (1996). On the mechanism of selenium tolerance in selenium-accumulating plants: Purification and characterization of a specific selenocysteine methyltransferase from cultured cells of *Astragalus bisulcatus*. *European Journal of Biochemistry*, **239**, 235–238.

Nijenhuis I. A., Bosch H. J., Sinninghe Damsté J. S., Brumsack H. J. and De Lange G. J. (1999). Organic Matter and Trace Element Rich Sapropels and Black Shales: A Geochemical Comparison. *Earth and Planetary Science Letters*, **169**(3–4), 277–290.

Nriagu J. O. (1989). A global assessment of natural sources of atmospheric trace metals. *Nature*, **338**, 47–49.

Nriagu J. O. and Pacyna J. M. (1988). Quantitative assessment of worldwide contamination of air, water and soils by trace metals. *Nature*, **333**, 134–139.

Oldfield J. E. (2002). Selenium World atlas. Selenium-Tellurium Development Association (STDA). Grimbergen, Belgium.

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

Oremland R. S., Herbel M. J., Blum J. S., Langley S., Beveridge T. J., Ajayan P. M., Sutto T., Ellis A. V. and Curran S. (2004). Structural and spectral features of selenium nanospheres produced by Se-respiring bacteria. *Applied Environmental Microbiology*, **70**, 52–60.

Overman S. D. (2000). U.S. Patent No. 6 156 191. U.S. Patent and Trademark Office, Washington, DC.

Papp L. V., Lu J., Holmgren A. and Khanna K. K. (2007). From selenium to selenoproteins: synthesis, identity, and their role in human health. *Antioxidants and Redox Signalling*, **9**(7), 775–806.

Parnell J., Brolly C., Spinks S. and Bowden S. (2016). Selenium enrichment in Carboniferous Shales, Britain and Ireland: Problem or opportunity for shale gas extraction? *Applied Geochemistry*, **66**, 82–87.

Pažout R., Sejkora J. and Šrein V. (2019). Ag-Pb-Sb Sulfosalts and Se-rich Mineralization of Anthony of Padua Mine near Poličany–Model Example of the Mineralization of Silver Lodes in the Historic Kutná Hora Ag-Pb Ore District, Czech Republic. *Minerals*, **9**, 430, 1–47.

Pérez-Sirvent C., Martínez-Sánchez M. J., García-Lorenzo M. L., Molina J., Tudela M. L., Mantilla W. and Bech J. (2010). Selenium content in soils from Murcia Region (SE, Spain). *Journal of Geochemical Exploration*, **107**(2), 100–109.

Petrik A., Thiombane M., Lima A., Albanese S., Buscher J. T. and De Vivo B. (2018). Soil contamination compositional index: a new approach to quantify contamination demonstrated by assessing compositional source patterns of potentially toxic elements in the Campania Region (Italy). *Applied Geochemistry*, **96**, 264–276.

Piacenza E., Presentato A., Zonaro E., Lemire J. A., Demeter M., Vallini G., Turner R. J. and Lampis S. (2017). Antimicrobial activity of biogenically produced spherical Se-nanomaterials embedded in organic material against *Pseudomonas aeruginosa* and *Staphylococcus aureus* strains on hydroxyapatite-coated surfaces. *Microbial Biotechnology*, **10**(4), 804–818.

Pickett T. M. and Sonstegard J. N. (2012). 'Selenium Separation and Recovery from Bioreactor Sludge.' U.S. Patent Application No. 12/971,585. U.S. Patent and Trademark Office, Washington, DC.

Plant J. A., Bone J., Voulvoulis N., Kinniburgh D. G., Smedley P. L., Fordyce F. M. and Klinck B. (2014). Chapter 11.2: arsenic and selenium. In: Environmental Geochemistry, B. Sherwood Lollar (ed.), H.D. Holland and K.K. Turekian (executive editors). Treatise on Geochemistry, 2nd edn, volume 11. Elsevier, Oxford, pp. 13–57.

Prasad K. S. and Selvaraj K. (2014). Biogenic synthesis of selenium nanoparticles and their effect on As(III)-induced toxicity on human lymphocytes. *Biology of Trace Elements Research*, **157**(3), 275–283.

Preda C., Vasiliu I., Bredetean O., Ciobanu D. G., Ungureanu M.-C., Leustean E. L., Grigorovici A., Oprisa C. and Vulpoi C. (2015). Selenium in the environment: essential or toxic to human health? *Environmental and Engineering Management Journal*, **15**, 913–921.

Presentato A., Piacenza E., Anikovskiy M., Cappelletti M., Zannoni D. and Turner R. J. (2018). Biosynthesis of selenium-nanoparticles and -nanorods as a product of selenite bioconversion by the aerobic bacterium *Rhodococcus aetherivorans* BCP1. *New Biotechnology*, **41**, 1–8.

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

Presser T. S. (1999). Selenium pollution. In: Encyclopedia of Environmental Science, P. E. Alexander and R. W. Fairbridge (eds.), Springer-Verlag, Berlin, Germany, pp. 554–556.

Presser T. S., Piper D. Z., Bird K. J., Skorupa J. P., Hamilton S. J., Detwiler S. J. and Huebner M. A. (2004). The Phosphoria Formation – a model for forecasting global selenium sources to the environment. In: Life Cycle of the Phosphoria Formation – From Deposition to the Post-mining Environment, J. R. Hein (ed.), Elsevier, Amsterdam, *Handbook of Exploration and Environmental Geochemistry*, **8**, 299–319.

Rayman M. P., Infante H. G. and Sargent M. (2008). Food-chain selenium and human health: spotlight on speciation. *British Journal of Nutrition*, **100**, 238–253.

Ramya S., Shanmugasundaram T. and Balagurunathan R. (2015). Biomedical potential of antibacterially synthesized selenium nanoparticles with special reference to anti-biofilm, anti-oxidant, wound healing, cytotoxic and anti-viral activities. *Journal of Trace Elements in Medicine and Biology*, **32**, 30–39.

Rawlins B. G., McGrath S. P., Scheib A. J., Breward N., Cave M., Lister T. R., Ingham M., Gowing C. and Carter S. (2012). The Advanced Soil Geochemical Atlas of England and Wales. British Geological Survey, Keyworth. www.bgs.ac.uk/gbase/advsoilatlasEW.html.

Reimann C. and Birke M. (eds.) (2010). Geochemistry of European Bottled Water. Borntraeger Science Publishers, Stuttgart.

Reimann C. and de Caritat P. (1998). Chemical Elements in the Environment. Springer, Berlin.

Reimann C. and de Caritat P. (2017). Establishing geochemical background variation and threshold values for 59 elements in Australian surface soil. *Science of the Total Environment*, **578**, 633–648.

Reimann C., Ayras M., Chekushin V. A., Bogatyrev I., Boyd R., de Caritat P., Dutter R., Finne T. E., Halleraker J. H., Jæger Ø., Kashulina G., Lehto O., Niskavaara H., Pavlov V. A. and Raisanen L. (1997a). Environmental geochemical atlas of the central Barents region. Norges geologiske undersôkelser (NGU) Geological Survey of Norway.

Reimann C., Boyd R., de Caritat P., Halleraker J. H., Kashulina G., Niskavaara H. and Bogatyrev I. (1997b). Topsoil (0–5 cm) composition in eight arctic catchments in northern Europe (Finland, Norway and Russia). *Environmental Pollution*, **95**(1), 45–56.

Reimann C., Äyräs M., Chekushin V., Bogatyrev I., Boyd R., Caritat P., Dutter R., Finne T. E., Halleraker J. H., Jæger Ø., Kashulina G., Lehto O., Niskavaara H., Pavlov V. K., Räisänen M. L., Strand T. and Volden T. (1998). Geochemical analysis of soil in the central Barents Region. *PANGAEA*, https://doi.org/10.1594/PANGAEA.686641

Reimann C., Bjorvatn K., Frengstad B., Melaku Z., Tekle-Haimanot R. and Siewers U. (2003a). Drinking water quality in the Ethiopian section of the East African Rift Valley I – Data and health aspects. *Science of the Total Environment*, **311**(1–3), 65–80.

Reimann C., Siewers U., Tarvainen T., Bityukova L., Eriksson J., Giucis A., Gregorauskiene V., Lukashev V. K., Matinian N. N. and Pasieczna A. (2003b). Agricultural Soils in Northern Europe. A geochemical atlas. Geologisches Jahrbuch Sonderhefte Reihe D, Heft 5, E. Schweizerbart'sche Verlangsbuchhandlung, Stuttgart.

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

Reimann C., Arnoldussen A., Englmaier P., Filzmoser P., Finne T. E., Garrett R. G., Koller F. and Nordgulen Ø. (2007). Element concentrations and variations along a 120-km transect in southern Norway – Anthropogenic vs. geogenic vs. biogenic element sources and cycles. *Applied Geochemistry*, **22**(4), 851–871.

Reimann C., Englmaier P., Flem B., Gough L., Lamothe P., Nordgulen Ø. and Smith D. (2009a). Geochemical gradients in soil O-horizon samples from southern Norway: Natural or anthropogenic? *Applied Geochemistry*, **24**(1), 62–76.

Reimann C., Finne T. E., Nordgulen Ø., Saether O. M., Arnoldussen A. and Banks D. (2009b). The influence of geology and land-use on inorganic stream water quality in the Oslo region, Norway. *Applied Geochemistry*, **24**, 1862–1874.

Reimann C., Birke M., Demetriades A., Filzmoser P. and O'Connor P. (eds.) (2014). Chemistry of Europe's Agricultural Soils, Part A. Geologisches Jahrbuch, Band B 102, E. Schweizerbart'sche Verlangsbuchhandlung, Stuttgart.

Reimann C., Englmaier P., Fabian K., Gough L., Lamothe P. and Smith D. (2015a). Biogeochemical plant-soil interaction: Variable element composition in leaves of four plant species collected along a south–north transect at the southern tip of Norway. *Science of the Total Environment*, **506–507**, 480–495.

Reimann C., Fabian K., Schilling J., Roberts D. and Englmaier P. (2015b). A strong enrichment of potentially toxic elements (PTEs) in Nord-Trøndelag (central Norway) forest soil. *Science of the Total Environment*, **536**, 130–141.

Reimann C., Birke M., Flem B., Eggen O. A. and Gasser D. (2018a). Background values of gold, potentially toxic elements and emerging high-tech critical elements in surface water collected in a remote northern European environment. *Geochemistry: Exploration, Environment, Analysis*, **18**(3), 185–195.

Reimann C., Fabian K., Birke M., Filzmoser P., Demetriades A., Négrel P., Oorts K., Matschullat J and de Caritat P., The GEMAS Project Team. (2018b). GEMAS: Establishing geochemical background and threshold for 53 chemical elements in European agricultural soil. *Applied Geochemistry*, **88**(Part B), 302–318.

Ren L. Q., Li X. J., Li G. S., Zhao Z. T., Sun B. and Sun F. (2004). Coxsackievirus B3 infection and its mutation in Keshan disease. *World Journal of Gastroenterology*, **10**(22), 3299–3302.

Reyes L. H., Mar J. L., Rahman G. M., Seybert B., Fahrenholz T. and Kingston H. M. (2009). Simultaneous determination of arsenic and selenium species in fish tissues using microwave assisted enzymatic extraction and ion chromatography inductively coupled plasma mass spectrometry. *Talanta*, **78**, 983–990.

Rodrigues Nogueira T. A., Abreu-Junior C. H., Ferracciú Alleoni L. R., He Z., Soares M. R., dos Santos Vieira C., Frediani Lessa L. G. and Capra G. F. (2018). Background concentrations and quality reference values for some potentially toxic elements in soils of São Paulo State, Brazil. *Journal of Environmental Management*, **221**, 10–19.

Rosenfeld I. and Beath O. A. (1964). Selenium: Geobotany, Biochemistry, Toxicity and Nutrition. Academic Press, New York, USA.

Roy M., Kiremidjian-Schumacher L., Wishe H. I., Cohen M. W. and Stotzky G. (1994). Supplementation with selenium and human immune cell functions. I. Effect on lymphocyte proliferation and interleukin 2 receptor expression. *Biology of Trace Elements Research*, **41**, 103–114.

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

Rudnick R. L. and Gao S. (2003). 3.01 – Composition of the Continental Crust. In: Treatise on Geochemistry, H. D. Holland and K. K. Turekian (eds.), Pergamon, pp. 1–64.

Sabrynal H. H. A., Yahiya N. S. M., Abdel-Rahman E. A. M. and Radwan S. A. (2011). Selenium status in some Egyptian soils. *Environmental Sciences*, **6**, 123–131.

Salminen R., Batista M. J., Bidovec M., Demetriades A., De Vivo B., De Vos W., Duris M., Gilucis A., Gregorauskiene V., Halamic J., Heitzmann P., Lima A., Jordan G., Klaver G., Klein P., Lis J., Locutura J., Marsina K., Mazreku A., O'Connor P. J., Olsson S. Å., Ottesen R.-T., Petersell V., Plan J. A., Reeder S., Salpeteur I., Sandström H., Siewers U., Steenfelt A. and Tarvainen T. (eds.). (2005). Geochemical Atlas of Europe. Part 1 – Background Information, Methodology and Maps. Geological Survey of Finland, Espoo, Finland.

Santos S., Ungureanu G., Boaventura R. and Botelho C. (2015). Selenium contaminated waters: An overview of analytical methods, treatment options and recent advances in sorption methods. *Science of the Total Environment*, **521–522**, 246–260.

Sarret G., Avoscan L., Carriere M., Collins R., Geoffroy N., Carrot F., Coves J. and Gouget B. (2005). Chemical forms of selenium in the metal-resistant bactyerium *Ralstonia metallidurans* CH34 exposed to selenite and selenate. *Applied and Environmental Microbiology*, **71**, 2331–2337.

Scheib C., Flight D., Lister T. R., Scheib A. and Breward N. (2011). Selenium in topsoil. Summary interpretation. Downloaded from https://www.bgs.ac.uk/gbase/londonearth.html

Schrautzer G. N. (2004). Selenium. In: Elements and Their Compounds in the Environment, 2nd edn, E. Merian, M. Anke, M. Ihnat and M. Stoeppler (eds.), Wiley-VCH Verlag GmbH & Co, Weinheim, pp. 1365–1406.

Shand P. and Edmunds W. M. (2008). The Baseline Inorganic Chemistry of European Groundwaters. In: Natural Groundwater Quality, W. M. Edmunds and P. Shand (ed.), Blackwell Publishing Co., pp. 22–58.

Sharma V. K., McDonald T. J., Sohn M., Anquandah G. A., Pettine M. and Zboril R. (2015). Biogeochemistry of selenium: a review. *Environmetal Chemistry Letters*, **13**(1), 49–58.

Sidique T., Zhang Y., Oleke B. C. and Frankenberger W. T. (2006). Characterization of sediment bacteria involved in selenium reduction. *Bioresource Technology*, **97**, 1041–1049.

Smith D. B., Solano F., Woodruff L. G., Cannon W. F. and Ellefsen K. J. (2019). Geochemical and mineralogical maps, with interpretation, for soils of the conterminous United States. U.S. Geological Survey Scientific Investigations Report, **2017–5118**.

Soda S., Kashiwa M., Kagami T., Kuroda M., Yamashita M. and Ike M. (2011). Laboratory scale bioreactors for soluble selenium removal from selenium refinery wastewater using anaerobic sludge. *Desalination*, **279**, 433–438.

Soflaei S., Dalimi A., Abdoli A., Kamali M., Nasiri V., Shakibaie M. and Tat M. (2014). Anti-leishmanial activities of selenium nanoparticles and selenium dioxide on *Leishmania infantum*. *Comparative Clinical Pathology*, **23**(1), 15– 20.

Sonkusre P., Nanduri R., Gupta P. and Cameotra S. S. (2014). Improved extraction of intracellular biogenic selenium nanoparticles and their specificity for cancer chemoprevention. *Journal of Nanomedicine and Nanotechnology*, **5**(194), 1–9.

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

Sors T. G., Ellis D. R. and Salt D. E. (2005). Selenium uptake, translocation, assimilation and metabolic fate in plants. *Photosynthesis Research*, **86**, 373–389.

Spadoni M., Voltaggio M., Carcea M., Coni E., Raggi A. and Cubadda F. (2007). Bioaccessible selenium in Italian agricultural soils: comparison of the biogeochemical approach with a regression model based on geochemical and pedoclimatic variables. *Science of the Total Environment*, **376**(1–3), 160–177.

Sparks D. L. (2003). Environmental Soil Chemistry, 2nd edn. Academic Press, Amsterdam, The Netherlands.

Stadtman T. C. (1990). Selenium biochemistry. *Annual Review of Biochemistry*, **59**, 111–127.

Steinnes E. (2003). Biogeochemical cycling of iodine and selenium and potential geomedical relevance. In: Geology and Health: Closing Gap, H. C. Skinner and A. R. Berger (eds.), Oxford University Press, Oxford, pp. 57–60.

Stillings L. L. (2017). Selenium. In: Critical Mineral Resources of the United States—Economic and Environmental Geology and Prospects for Future Supply, K. J. Schulz, J. H. DeYoung, Jr., R. R. Seal, II and D. C. Bradley (eds.), *U.S. Geological Survey Professional Paper* **1802-Q**, U.S. Geological Survey, Reston, VA U.S.A., 1–55.

Torres J., Pintos V., Gonzatto L., Domínguez S., Kremer C. and Kremer E. (2011). Selenium chemical speciation in natural waters: protonation and complexation behavior of selenite and selenate in the presence of environmentally relevant cations. *Chemical Geology*, **288**, 32–38.

Trofast J. (2011). Berzelius' Discovery of Selenium. *Chemistry International*, **33**(5). http://publications.iupac.org/ci/2011/3305/5_trofast.html

Tugarova A. V., Vetchinkina E. P., Loshchinina E., Burov A. M., Nikitina V. E. and Kamnev A. (2014). Reduction of selenite by *Azospirillum brasilense* with the formation of selenium nanoparticles. *Microbial Ecology*, **68**, 495–503.

Tan L. C., Nancharaiah Y. V., van Hullebusch E. D. and Lens P. N. L. (2016). Selenium: environmental significance, pollution, and biological treatment technologies. *Biotechnology Advances*, **34**, 886–907.

Tan L. C., Jing X., Zhang Y., Tang H., Yao S. and Xie Q. (2009). In vitro study on the individual and synergistic cytotoxicity of adriamycin and selenium nanoparticles against Bel7402 cells with a quartz crystal microbalance. *Biosensors and Bioelectronics*, **24**, 2268–2272.

Terry N., Zayed A. M., de Souza M. P. and Tarun A. S. (2000). Selenium in higher plants. *Annual Review in Plant Physiology and Plant Molecular Biology*, **51**, 401–432.

Torres S. K., Campos V. L., León C. G., Rodríguez-Llamazares S. M., Rojas S. M., González M., Smith C. and Mondaca M. A. (2012). Biosynthesis of selenium nanoparticles by *Pantoea agglomerans* and their antioxidant activity. *Journal of Nanoparticle Research*, **14**(1236), 1–9.

Turner R. J., Weiner J. H. and Taylor D. E. (1998). Tellurite-mediated thiol oxidation in *Escherichia coli*. *Microbiology*, **145**, 33–40.

U.S. Geological Survey (2019). Selenium and Tellurium statistics and information. https://www.usgs.gov/centers/nmic/, pp. 146–147.

USEPA (1992). Method 1311. Toxicity Characteristic Leaching Procedure. *The United States Environmental Protection Agenc*, pp. 1–27.

Valdez Barillas J. R., Quinn C. F., Freeman J. L., Lindblom S. D., Fakra S. C., Marcus M. A., Gilligan T. M., Alford É. R., Wangeline A. L. and Pilon-Smits E. A. (2012). Selenium

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

distribution and speciation in the hyperaccumulator *Astragalus bisulcatus* and associated ecological partners. *Plant Physiology*, **159**(4), 1834–1844.

Vinceti M., Wei E. T., Malagoli C., Bergomi M. and Vivoli G. (2001). Adverse health effects of selenium in humans. *Reviews on Environmental Health*, **16**, 233–251.

Wacker M. G. (2014). Nanotherapeutics – product development along the ‘nanomaterial’ discussion. *Journal of Pharmaceutical Sciences*, **103**(3), 777–784.

Walsh T. and Fleming G. A. (1952). Selenium levels in rocks, soils and herbage from a high selenium locality in Ireland. *Transaction of the 5th International Congress on Soil Sciences*, **2**(A), 178–183.

Wang H., Zhang J. and Yu H. (2007). Elemental selenium at nano size possesses lower toxicity without compromising the fundamental effect on selenoenzymes: comparison with selenomethionine in mice. *Free Radicals in Biology and Medicine*, **42**(10), 1524–1533.

Wang C., Li S., Wang H. and Fu J. (2016a). Selenium minerals and the recovery of selenium from copper refinery anode slimes. *Journal of the Southern African Institute of Mining and Metallurgy*, **116**(6), 593–600.

Wang Y., Dang F., Zhao J. and Zhong H. (2016b). Selenium inhibits sulphate-mediated methylmercury production in rice paddy soil. *Environmental Pollution*, **213**, 232–239.

Webb J. S., Thornton I. and Fletcher K. (1966). Seleniferous soils in parts of England and Wales. *Nature*, **211**(5046), 327–330.

Wen H. and Carignan J. (2011). Selenium isotopes trace the source and redox processes in the black shale-hosted Se- rich deposits in China. *Geochimica et Cosmochimica Acta*, **75**(6), 1411–1427.

Whanger P. D. (2002). Selenocompounds in plants and animals and their biological significance. *Journal of the American College of Nutrition*, **21**, 223–232.

White P. J. (2016). Selenium accumulation by plants. *Annals of Botany*, **117**(2), 217–235.

Winkel L. H., Johnson C. A., Lenz M., Grundl T., Leupin O. M., Amini M. and Charlet L. (2012). Environmental selenium research: from microscopic processes to global understanding. *Environmental Science Technology*, **46**(2), 571–579.

Winkel L. H. E., Vriens B., Jones G. D., Schneider L. S., Pilon-Smits E. and Bañuelos G. S. (2015). Selenium cycling across soil-plant-atmosphere interfaces: a critical review. *Nutrients*, **7**(6), 4199–4239.

World Health Organization (2011). Selenium in drinking water. *Guidelines for Drinking-water Quality*. https://www.who.int/water_sanitation_health/dwq/chemicals/selenium.pdf, pp. 1–22.

Wu H., Zhu H., Li X., Liu Z., Zhen W., Chen T., Yu B. and Wong K.-H. (2013). Induction of apoptosis and cell cycle arrest in A549 human lung adenocarcinoma cells by surface-capping selenium nanoparticles: an effect enhanced by polysaccharide-protein complexes from *Polyporus rhinocerus*. *Journal of Agricultural and Food Chemistry*, **61**, 9859–9866.

Wu H., Li X., Liu W., Chen T., Li Y., Zhen W., Man C. W.-Y., Wong M.-K. and Wong K.-H. (2012). Surface decoration of selenium naoparticles by mushroom polysaccharide-protein complexes to achieve enhanced cellular uptake and anti-proliferative activity. *Journal of Materials Chemistry*, **22**, 9602–9610.

Xia Y., Lin Z., Li Y., Zhao M., Wang C., Guo M., Zhang B. and Zhu B. (2017). Targeted delivery of siRNA using RGDfC-conjugated functionalized selenium nanoparticles for anticancer therapy. *Journal of Materials Chemistry*, **B5**, 6941–6952.

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

Xie X. and Cheng H. (2001). Global geochemical mapping and its implementation in the Asia–Pacific region. *Applied Geochemistry*, **16**(11–12), 1309–1321.

Xu Y., Hao Z., Li Y., Li H., Wang L., Zang Z., Liao X. and Zhang R. (2020). Distribution of selenium and zinc in soil-crop system and their relationship with environmental factors. *Chemosphere*, **242**, 125289.

Yao R., Wang R., Wang D., Su J., Zheng S. and Wang G. (2014). Paenibacillus selenitireducens sp. nov., a selenite reducing bacterium isolated from a selenium mineral soil. *International Journal of System and Evolutionary Microbiology*, **64**, 805–811.

Yanai J., Okada T. and Yamada H. (2012) Elemental composition of agricultural soils in Japan in relation to soil type, land use and region. *Soil Science and Plant Nutrition*, **58**(1), 1–10.

Yang F., Tang Q., Zhong X., Bai Y., Chen T., Zhang Y., Li Y. and Zheng W. (2012). Surface decoration by Spirulina polysaccharide enhances the cellular uptake and anticancer efficacy of selenium nanoparticles. *International Journal of Nanomedicine*, **7**, 835–844.

Yazdi M. H., Mahdavi M., Setayesh N., Esfandyar M. and Shahverdi A. R. (2013). Selenium nanoparticle-enriched *Lactobacillus brevis* causes more efficient immune responses in vivo and reduces the liver metastasis in metastatic form of mouse breast cancer. *DARU. Journal of Pharmaceutical Sciences*, **21**(1), 33.

Yin J., Hou Y., Yin Y. and Song X. (2017). Selenium-coated nanostructured lipid carriers used for oral delivery of berberine to accomplish a synergic hypoglycemic effect. *International Jornal of Nanomedicine*, **12**, 8671–8680.

Ysart G., Miller P., Croasdale M., Crews H., Robb P., Baxter M., De L'Argy C. and Harrison N. (2000). 1997 UK Total Diet Study dietary exposures to aluminium, arsenic, cadmium, chromium, copper, lead, mercury, nickel, selenium, tin and zinc. *Food Additives & Contaminants*, **17**(9), 775–786.

Yu B., Zhang Y., Zhen W., Fan C. and Chen T. (2012). Positive charge enhances selective cellular uotake and anticanver efficacy of selenium nanoparticles. *Inorganic Chemistry*, **51**, 8956–8963.

Zannoni D., Borsetti F., Harrison J. J. and Turner J. R. (2008). The bacterial response to the chalcogen metalloids Se and Te. *Advances in Microbial Physiology*, **53**, 1–71.

Zduôska H., Bloch-BogusŶawska E., Przygoôska J., Þliwka K. and Zachara B. A. (1994). Selenium concentration and glutathione peroxidase activity in the organs of people died a violent death. In: Arsenic and Selenium in the Environment. Ecologic and Analytic Problem, A. Kabata-Pendias and B. Szteke (eds.), Polish Academy of Sciences, pp. 190–193 (in Polish).

Zhai X., Zhang C., Zhao G., Stoll S., Ren F. and Leng X. (2017). Antioxidant capacities of the selenium nanoparticles stabilized by chitosan. *Journal of Nanobiotechnology*, **15**(1), 4.

Zhang Y. and Frankenberger W. T., Jr. (2005). Removal of selenium from river water by microbial community enhanced with *Enterobacter taylorae* in organic carbon coated sand columns. *Science of the Total Environment*, **346**, 280–285.

Zhang J., Wang H., Bao Y. and Zhang L. (2004). Nano red elemental selenium has no size effect in the induction of seleno-enzymes in both cultured cells and mice. *Life Sciences*, **75**(2), 237–244.

Zhang J., Wang X. and Xu T. (2008). Elemental selenium at nano size (Nano-Se) as a potential chemopreventive agent with reduced risk of selenium toxicity: comparison with Se-methylselenocysteine in mice. *Toxicological Sciences*, **101**(1), 22–31.

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user

Zhang S., Luo Y., Zeng H., Wang Q., Tian F., Song J. and Wen-Hsing Cheng W.-H. (2011). Encapsulation of selenium in chitosan nanoparticles improves selenium availability and protects cells from selenium-induced DNA damage response. *Journal of Nutritional Biochemistry*, **22**(12), 1137–1142.

Zhang Y., Li X., Huang Z., Zhen W., Fan C. and Chen T. (2013). Enhancement of cell permeabilization apostosis- inducing activity of selenium nanoparticles by ATP surface decoration. *Nanomedicine: Nanotechnology in Biology and Medicine*, **7**, 74–84

Zhao S., Yu Q., Pan J., Zhou Y., Cao C., Ouyang J.-M. and Liu J. (2017). Redox-responsive mesoporus selenium delivery of doxorubicin targets MCF-7 cells and synergistically enhances its anti-tumor activity. *Acta Biomaterials*, **54**, 294–306.

Zhu J., Wang N., Li S., Li L., Su H. and Liu C. (2008). Distribution and transport of selenium in Yutangba, China: impact of human activities. *Science of the Total Environment*, **392**(2–3), 252–261.

Downloaded from http://iwaponline.com/ebooks/book/chapter-pdf/919134/9781789061055_0003.pdf
by UNIVERSITY OF BOLOGNA (FREE TRIAL) user