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Please cite this article as: S. Etteieb, S. Magdouli, M. Zolfaghari, et al., Monitoring and analysis of selenium as an emerging contaminant in mining industry: A critical review, *Science of the Total Environment* (2019), https://doi.org/10.1016/j.scitotenv.2019.134339

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Monitoring and analysis of Selenium as an emerging contaminant in mining industry: A critical review

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September, 2019

Abstract

Selenium is an indispensable trace element for humans, however, its release at high concentrations become a major concern for terrestrial and aquatic ecosystems due to its bioaccumulation potential. Mining and metal-mineral processing are among the main sources of selenium released into the environment. Excessive levels of selenium may induce toxicity in human as selenosis, in grazing animals as alkali disease and in aquatic organisms as larval and developmental deformities and mortality. Due to the introduction of new policies for Se monitoring in the mining industry mainly setting the guidelines for selenium level in freshwaters as recommended by the Canadian Council of Ministers of Environment and Environment and climate change Canada, an improved understanding of Se occurrence, mobility, bioavailability and treatment technologies for efficient removal is timely and required. In this context, this review updated the understanding of mining-related selenium occurrence in surface water, soil and plant, with a focus on its mobility and bioavailability. Selenium uptake, translocation, accumulation, and metabolism in plants are further presented. Selenium monitoring and treatment is the key to adopt the corrective measures to mitigate highly contaminated effluent and to minimize the associated adverse health effects. Future research directions and recommendations for selenium analysis and treatment processes are also discussed.

1. Introduction

Increased mining activities have led to large amounts of undesired toxic contaminants being released into the environment, such as selenium (Se), aluminum, cadmium, arsenic, copper, iron, lead, nickel, and zinc. Se pollution released from mining exploitations is of particular concern as an emerging contaminant entering the water, soil and plants, bioaccumulating and inducing serious health and ecological risks (Khamkhash et al., 2017; Palmer et al., 2010). Se belongs to the chalcogen group in the periodic table and is frequently found in sulfur-containing minerals. In the natural environment, Se generally exists in different oxidation states as selenide (-II), elemental Se (0), selenates (VI) and selenites (IV), and organic forms (Zhang et al., 2014a) (Table 1). Selenate is the most soluble and bioavailable form, predominates in the oxidizing environment; while, selenite is mostly adsorbed in soils under a more reducing environment. Under anoxic environment, selenide (-II) precipitates as metal selenides and elemental Se in a rather insoluble and unavailable form. Organoselenium includes volatile methyl selenide and nonvolatile organic selenides (selenomethionine, selenocysteine).

Se could be introduced into the environment through natural or anthropogenic sources. Se is naturally originated from volcanic emanations, metallic sulfides, sedimentary rocks and shales, petroleum source rocks, coals ore deposits, and phosphorites (Ryan and Dittrick, 2000). On the contrary, the main anthropogenic activities consist of metal mining, fossil fuels refinement and irrigation of Se-rich soils (USEPA, 2016). For a decade, Se had been widely applied mainly in electronics, paint industry, glass industry, ceramics, metallurgy, chemical industry, and pharmaceutics and in agriculture (Mehdi et al., 2013). During mining activities, Se can be mobilized after rock overburden excavation and natural weathering generating significant levels in mine effluents. Consequently, Se may leak into downstream surface water, soil and plants through the oxidation of waste rock and the generation of elevated levels of effluents (Diehl et al., 2012; GolderAssociatesInc., 2009; Griffith et al., 2012; USEPA, 2016). Hence, mining effluent represents the initial route of Se introduction into surface water and soil-plant system through acid mine water drainage (Chapman, 2006; Lemly, 2004; Wellen et al., 2015). Therefore, it is crucial to assess the biogeochemical behavior, mobility and bioavailability of Se in surface water, soil and plant environments based on its speciation and fractionation (Peng et al., 2017; Wang et al., 2013). The mobility, fate and the behavior of Se in the soil are affected by its speciation as well as different geochemical processes mainly oxidation-reduction, biomethylation, sorption, precipitation, and complexation. These processes are governed by soil factors such as pH, redox potential, organic matter, mineral composition, soil type, microbial activity and competing anions (Nakamaru and Altansuvd, 2014; Winkel et al., 2015; Xing et al., 2015). Moreover, Se bioavailability for plant uptake and metabolism is closely related to Se soil content. The cumulative available Se content in the soil allows finding adequate Se contents in plants after its uptake, translocation, accumulation, and metabolism, and consequently, it permits enhancing the Se intake by living organisms (Saha et al., 2017; Shahid et al., 2018)**.**

Although the wide range of applications and its crucial function in antioxidant defense, cells protection, human immunity amelioration and carcinogenesis prevention, Se can exert adverse effects on human and animal health once, it reaches the food chain (Lopes et al., 2017; Zhang et al., 2014a). Se can cause acute toxicity by generating respiratory, gastrointestinal, cardiovascular difficulties and hypertension, or chronic toxicity inducing mental problems, damages in hair and nails, extreme tooth decay and staining and chronic alkalosis (Beatty and Russo, 2014; Brodowska et al., 2016; GolderAssociatesInc., 2009; Plak and Bartmiński, 2017; Rogers et al., 1990; WHO, 2011). Excess of Se in contaminated water bodies can also affect the reproduction of egg-laying vertebrates, bioaccumulate and promote teratogenic effects (Table 2). Recently, metal mining is encountering more strict regulations for Se in discharge waters from mining operations. Besides, Se occurrence in drinking water, fresh water, agricultural run-off, and soil has also attracted a major environmental consideration and has been subjected to guidelines in different countries to regulate its release into the environment (Table 3).

Subsequently, monitoring and pollution control efforts for Se have been widely expanded to alleviate its associated potential risks. Thus, recent improvements in analytical methods facilitated the detection of even low levels of Se in the environment (Plant et al., 2014).

However, total Se determination is not sufficient and the main challenging task is Se speciation, which influences Se mobility, bioavailability, bioaccumulation, biogeochemical cycle and the overall toxicity (Kumkrong et al., 2018). Therefore, sophisticated and accurate analysis methods have been employed for the speciation analysis of Se during the two steps of separation and detection. Inductively coupled plasma mass spectrometry (ICP-MS) and other analytical methods based on selective reduction such as Hydride generation atomic fluorescence spectrometry (HG-AFS) and Hydride Generation Atomic Absorption Spectrophotometry (HG-AAS) have been used to analyze Se. Volatile Se species were analyzed by Gas Chromatography techniques coupled to Mass Spectrometry (MS). Progress in analytical chemistry mainly that use hyphenated techniques using High-performance liquid chromatography (HPLC) coupled to MS and ICP-MS have become popular and widely used for Se speciation in environmental samples (LeBlanc et al., 2016; Zembrzuska et al., 2014).

Moreover, knowledge of Se speciation analysis is also necessary when selecting a suitable option of treatment, since most of the treatment technologies are effective for a specific chemical form of Se species. Therefore, the treatment of mine water is a challenge due to the complex chemistry of this element, the presence of additional components found in the same matrix, the strict regulations to meet the required discharged levels as well as the irrespective cost (EnvirogenTechnologies, 2011; Skousen et al., 2017; Stefaniak et al., 2018). Many types of treatment such as physical (membrane filtration and ion exchange), chemical (precipitation, adsorption, and reduction) and biological treatments (*in-situ* microbial reduction, bioreactors, bed reactor, algal volatilization, wetlands) have been evaluated in terms of their advantages versus limitations (Holmes and Gu, 2016).

The current review updated the existing literature on mining-related Se contamination, occurrence in surface water, soil, and plant. Se speciation and the different biogeochemical processes that govern its mobility in the soil and its bioavailability for plant uptake, translocation, accumulation, and metabolism are discussed. This paper also provides recommendations for Se monitoring, pretreatment, analytical instrumentation selection, and quality control of Se in mine industry. Finally, progress and challenges in Se water treatment using physical, chemical and biological processes are presented. The scope of the current review urges scientists to explore novel remediation schemes toward better management practices for Se contamination reduction in natural systems, to provide global environmental protection and human health safety.

2. The occurrence of Se contamination in surface water, soils, and plants

Many previous studies worldwide reported that different mining industries, such as gold, silver, copper, lead, zinc, uranium, etc.), phosphate and coal mining are the main sources of Se release into the environment. However, Se-rich tailings not only resulted from waste rock weathering,

but also from the leakage of ore processing. Generally, Se combined with sulfide minerals is released from waste rocks through weathering (El-Ramady et al., 2015; Khamkhash et al., 2017). Thus, acid mine drainage (AMD) is principally originated from the pyritic bedrock by the waste weathering, sulfide oxidation and leaching in the case of coal mining in the Elk River Valley in southeastern British Columbia (Griffith et al., 2012; Lindberg et al., 2011); the surface uranium mine in northern Saskatchewan (Muscatello and Janz, 2009), phosphate mining in southeastern Idaho (Vance et al., 2009; Wellen et al., 2015) and coal mining in the central Appalachian Coalfields in USA. Besides, ore processing mainly based on froth flotation and cyanidation may result in dissolution and leaching of Se, especially in downstream water systems such as the case of Se-rich tailings discharge process in Kinross Fort Knox gold mine and Fort Knox gold mine operating in Alaskan region (Khamkhash et al., 2017). In coal mining, Se is being leaked from mined coal through rainwater percolation or coal washing prior to transportation to power plants. Se may also be released either directly from combustion and coal burning from power generation or indirectly through the disposal of the fly ash. Subsequently, Se can be leached out by rainwater, leading to surface water, soil and plants contamination (Izquierdo and Querol, 2012; Khamkhash et al., 2017). Previous findings have reported that different Se concentrations in water, soil and plant environments are affected by diverse mining activities. Hence, the occurrence of different Se levels in mine effluents reported by previous studies (Bond, 2000; Bujdoš et al., 2005; Cutter and Cutter, 1995; Desborough et al., 1999; Khamkhash et al., 2017; Nriagu and Wong, 1983) is presented in Figure 1.

2.1 Se in surface water

Leachates from Se-bearing wastes and process tailings derived from the mining activities have contributed to the dispersion of Se in downstream environments, reaching nearby surface waters and leading to river contamination (Sharma and Vance, 2007). For instance, Swain (2007) reported that Se concentration in the Elk River water below Sparwood exceeded 5 µg/L (Swain, 2007); however, it did not exceed 1 µg/L in the Prairie Waters of Southern Manitoba (Hu, 2008), which showed the correlation between mining activities and . Se concentration in surface water. Most of Se concentration in liquid surface exceeded the existing selenium water quality guidelines for the protection of freshwater and marine aquatic life (1 µg/L) set by the Canadian Council of Ministers of Environment (CCME, 2007). This confirms the severity of Se contamination exceeding such guideline values and endangering the aquatic life in water systems affected by mining activities. In water environment, the occurrence of Se in four oxidation states (VI, IV, 0, -II) depends on pH, redox potential, major elements, organic matter, and microbiological activity (Donner et al., 2018; Meseck and Cutter, 2006). Thus, Se speciation is governed by diverse physical, chemical, and biological factors, which affects the oxidation state and the distribution of Se species, as well as their transformations. These biogeochemical processes, and Se speciation are influencing the fate and transportation of Se in surface water. Redistribution of dissolved Se species to different microenvironments is impacted by water circulation and mixing (Lemly, 2004). The occurrence of dissolution and desorption processes releasing the selenium from the solid phase into the liquid phase has a great influence on the

variability of selenium concentration in surface water. The Se levels in the surface water are time and climate-dependent as Se load significantly increases by more than twice in wet seasons (Wellen et al., 2015). Under most pH and redox conditions, selenite and selenate predominate as inorganic forms next to non-volatile organic selenides (selenocysteine and selenomethionine) and volatile methylated selenides (dimethyl selenide and dimethyl diselenide) (El-Ramady et al., 2015). Selenate predominates under oxidizing and alkaline conditions; while under reducing environment selenite is predominant. Selenite can be adsorbed to manganese and iron oxyhydroxides at the sediment-water interface; however, further reduction of these oxyhydroxides will release it back into the water (Belzile et al., 2000). In oxygenated surface waters, dissolved Se is represented mainly by selenate, selenite, and dissolved organic selenide. Particulate organic and inorganic species in water bound to suspended sediments and organic matters (Meseck and Cutter, 2006). Se in the oxic surface water is often present as selenite, selenate, metal selenides, organo-selenides and volatile methylated species (Wallschläger and Feldmann, 2010). However, in the case of mine effluent leakage into surface water, aqueous selenite tends to predominate due to the temperature, pH, and redox conditions related to the process (USEPA, 2016). In fact, selenite predominates especially in the most acidified waters of mine tailings discharge registering a very low pH (Bujdoš et al., 2005).

2.2 Se in Soils

Se is leaching from the mine effluents to be spread on soils. Se concentration in the soil can vary from 0.1 to 435 mg/kg (Favorito et al., 2017; Xing et al., 2015; Zhang et al., 2014a). This abundance is closely related to the number of biogeochemical processes occurring in the soil, as well as its fractionation and speciation that may govern Se mobility.

2.2.1 *Se Speciation affecting Se mobility*

Mobility of Se depends not only on the total Se content in the soil but also on its speciation (Peng et al., 2017; Wang et al., 2013). Se speciation in the soil is influenced by soil conditions, which may promote the oxidation, reduction, mineralization or immobilization of Se (Funwie, 2012). Besides inorganic forms of Se, organic forms in the soil such as selenomethionine (SeMet), selenocysteine (SeCys) and methylselenocysteine (MeSeCys) may occur (Pyrzynska, 2009). Selenate is more soluble and bioavailable than selenite, which is highly more adsorbed to different soil constituents (Peng et al., 2017; Tolu et al., 2011). However, elemental Se and metal selenides are insoluble and unavailable. Thus, given that the bioavailability and mobility of Se accentuate under oxidizing alkaline conditions, Se mobility in mining-affected soils is supposed to decrease under reducing acid environment. Next to its diverse chemical forms, Se occurs in different geochemical fractions in the soil mainly in the soluble and exchangeable fractions or bounded to carbonate, organic, amorphous Fe and Al hydroxides, amorphous and crystalline Mn-oxides, crystalline Fe-oxides or in residual fractions (Favorito et al., 2017; Qasim et al., 2015; Shaheen et al., 2017; Shahid et al., 2018). Like Se speciation, Se fractionation in the soil indicates Se transformation, bioavailability, and mobility (Peng et al., 2017; Wang et al., 2013; Xing et al., 2015). The water-soluble fraction of Se particularly reflects the Se

bioavailability (Xing et al., 2015). Many efforts still need to be deployed for the Se speciation in different soil fractions as large amounts of unidentified species in soil extracts, mainly organo-Se compounds, were reported (Winkel et al., 2015).

2.2.2 *Biogeochemical processes affecting Se mobility and bioavailability*

The mobility, fate, and behavior of Se in the soil are depended on various biogeochemical processes such as sorption, oxidation-reduction, precipitation, biomethylation and complexation (Alfthan et al., 2015) (Figure 2). These processes are susceptible to a variety of soil factors mainly pH, redox conditions, organic matter, soil texture, biological and microbial activity, Se contents, and competing anions (Saha et al., 2017; Shahid et al., 2018; Xing et al., 2015). First, Se Oxidation-reduction process is impacted by the redox potential and pH (Antanaitis et al., 2008; Xing et al., 2015). In fact, in the presence of acid mine effluent drainage and under reducing conditions, selenite predominates in a redox potential ranging from 0 to 200 mV. Then, above 200 mV potential, selenite will be oxidized into selenate and under more oxidizing conditions at 450 mV, selenate predominates by 75% for pH around neutrality and by 95% at pH values from 8.5 to 9. Therefore, Se mobility and bioavailability is inhibited in soils affected by acid mine effluents discharge and a reducing environment (Shahid et al., 2018). This Se mobility inhibition could be accentuated by the impact of microbial activity in the soil. In fact, microorganisms may help Se retention and decrease Se mobility by reducing selenate and selenite to elemental Se, especially under anaerobic conditions. Secondly, the solubility and bioavailability of Se is enhanced by the microbial reduction and methylation of selenite to organic forms and mainly volatile organic Se species like dimethyl selenide (DMSe), dimethyl diselenide (DMDSe) and dimethyl selenenyl sulfide (DMSeS) (Saha et al., 2017; Simmons and Wallschläger, 2005; Winkel et al., 2015). However, Se biomethylation is inhibited under acid pH and reducing environment in the case of soil contamination by mine effluent (Frankenberger and Karlson, 1989; Masscheleyn et al., 1990). Third, Se mobility is closely related to the sorption either on mineral surfaces or on organic matter. Se sorption is mediated by its oxidation state, as selenite has more adsorption capacity than selenate, with the best affinity for metallic oxides and hydroxides mostly iron, manganese, and aluminum (Lopes et al., 2017). Selenite adsorption is favorable in mining-affected soil and acid medium with a pH between 4 to 6; while, it rapidly declines for soils with pH superior to 8. The sorption mechanism of selenite is based on a ligand exchange reaction with formation of an inner-sphere surface complex with soil particles producing covalent (Fernández-Martínez et al., 2009). Se organic compounds mainly selenomethionine may also be adsorbed onto iron oxyhydroxide (Tam et al., 1995). The mobility and the bioavailability of Se are also greatly affected by competitive anions such as SO_4^{2-}, PO_4^{3-}, CO_3^{2-}, and Cl^-, which tend to compete for sorption sites (Goh and Lim, 2004). In mine-affected acidic topsoil, selenite also interacts with organic matter such as humic substances (Li et al., 2017). Se is bounded to organic matter through sorption sites, metal complexes or through microbial reduction and interaction with humic substances mainly fulvic acids (Bruggeman et al., 2007; Darcheville et al., 2008; Jordan et al., 2013). Therefore, the mobility and bioavailability of inorganic Se are positively correlated with pH increase, clay and iron oxide content decrease in

the soil and the decrease of immobilization with organic matter. Then, Se mobility in soil is affected by its interaction with inorganic cations results in mineral precipitation, which is identified using equilibrium thermodynamic reactions. Under acid tailing- impacted soil, the most occurring minerals in acid soils are copper selenide (Cu_2Se) and antiferromagnetic selenite ($MnSeO_3$). Under reducing conditions, FeSe (achavalite), $FeSe_2$ (ferroselite), and solid elemental Se are predominating, and under neutral to alkaline conditions lead selenide (PbSe) and Tin selenide (SnSe) are the most stable minerals (Galkaduwa, 2015). Finally, Se mobility in the soil is also governed by its possible complexation with inorganic cations in the aqueous phase. For mining-impacted soils and under reducing condition, where the potential is inferior to 0 mV, the only hydroselenide exists in solution; while under less reducing conditions with potentials range from 0 to 400 mV, aqueous calcium selenite ($CaSeO_3$) and selenite (SeO_3^{2-}) occur. Under the oxidizing condition, where the potential is superior to 400 mV, both aqueous selenate (SeO_4^{2-}) and calcium selenate ($CaSeO_4$) predominate. It should be mentioned that the Solubility Product Constant (pK_{sp}) of calcium selenate and calcium selenite is 3.09, 5.53, respectively (Séby et al., 1998).

2.3 Se in Plants

Se bioavailability widely varies depending on soil content and the aptitude of plants to accumulate Se. The understanding of Se behavior in the soil allows the prediction of its availability for plant uptake and its intake by herbivores organisms (Dumont et al., 2006). Se bioavailability for soil-plant uptake, translocation and then metabolism are shown in Figure 2. Se bioavailability and uptake are influenced by Se speciation and concentration, plant species, phases of development, salinity, pH, membrane transporters and competition with sulfate (Winkel et al., 2015). Organic Se compounds are the most bioavailable form due to their great phytoavailability, followed by selenate, selenite, and finally metal-selenide and elemental Se with least bioavailability for the plant-life (Gupta and Gupta, 2017; Kikkert and Berkelaar, 2013; Sors et al., 2005). In mine-affected soil at acidic pH, Se plant uptake decreases especially in sandy and loamy soils. However, in rich organic matter soil, Se uptake is inversely proportional to pH increase, as the Se adsorbed by organic matter rather than plants (Winkel et al., 2015). Although the Se bioavailability is supposed to decrease in organic matter-rich soils, positive correlations between organic matter and Se uptake have also been reported and justified by the aptitude of organic matter to develop soil structure and promote oxidizing conditions thus rising bioavailability (Schilling and Wilcke, 2011). Moreover, Se bioavailability increases in fulvic acid-rich soils because of its weak bound comparing to its strong bound to humic acids (Wang et al., 2013). In the presence of competing anions such as sulfate and phosphate, Se plant uptake may be reduced. Under acidic soil, Se plant uptake is reduced by sulfate because of the common metabolic pathway of Se and sulfur (González-Morales et al., 2017). Thus, Se mobility and bioavailability is a complex process susceptible to the combined interactions between soil characterization, mainly, pH, clay content, ionic composition, microbial community and climatic factors (Yasin et al., 2015).

Selenate and selenite are taken with different mechanisms by transporters present in the root cell membrane. In fact, selenate is uptaken via sulfate transporters in the plasma membrane of root cells (Cabannes et al., 2012; Gupta and Gupta, 2017), while selenite is transported via phosphate transporters (Wan et al., 2016; Winkel et al., 2015; Zhang et al., 2014b). In fact, different species of Se shows rather different behaviors within plants. Pyrzynska (2009) declared that absorbed selenite is converted into selenide, more likely accumulate in roots, whereas selenate is translocated by xylem and continues to reproductive organs by phloem without being converted into other chemical forms (Pyrzynska, 2009; Sharma et al., 2010; Winkel et al., 2015; Zhu et al., 2009). Organic Se, mainly SeMet and SeMeSeCys, on the other hand, are transferred only by phloem (Carey et al., 2012). Consequently, some Se species are more accumulated in plant shoots than in roots depending on accumulation potential of different plant species (Cartes et al., 2005). In fact, plants can be classified as non-Se accumulators, primary accumulators, secondary accumulators, and hyperaccumulators. Non-Se accumulating plants hold up to 50 mg Se. kg^{-1}, while primary accumulators contain up to 100 mg.kg^{-1}.Secondary accumulators such as *Atriplex, Castilleja, Grindelia, Gutierrezia, Brassica juncea, Brassicanapus, Broccoli, Helianthus, Aster, Camelina, Medicago sativa* contain up to 1000 mg.kg^{-1} ; finally, Se hyperaccumulators (Brassicaceae (*Stanleya*), Fabaceae (*Astragalus*) and Asteraceae (*Xylorhiza*, *Oonopsis*, *Symphyotrichum*) contain up to 15,000 mg.kg^{-1} of Se (Winkel et al., 2015). In accumulating plants, Se could be found in leaves, vegetative stage, seeds, and reproductive stage; yet, in non-Se accumulators, Se found equally in roots and seeds (Terry et al., 2000), to be noticed that Se content is higher in non-edible parts compared to edible parts.

Se species are being metabolized in plants (Figure 2) by reducing selenate to selenite in the chloroplast under the effect of ATP sulfurylase (APS) and APS reductase (APR) enzymes (Gupta and Gupta, 2017). Subsequently, selenite is reduced to selenide using glutathione (GSH) (Wallenberg et al., 2010), which is later converted into selenocysteine under the action of cysteine synthase enzyme coupled with O-acetylserine. Selenocysteine may adopt different conversion pathways depending on plant species and environmental conditions. First, selenocysteine could be transformed into Se^0 under the activity of selenocysteine lyase (SL) enzyme; second, it could be converted into methyl-SeCys by selenocysteine methyltransferase (SMT) enzyme; third, selenocysteine transformed into selenomethionine (SeMet) under the sequential action of the cystathionine-ɣsynthase (CɣS), cystathionine-b-lyase and methyl synthase enzymes (Gupta and Gupta, 2017). Finally, selenomethionine is transformed into methyl-SeMet and then to Dimethylselenide (DMSe) (Gupta and Gupta, 2017; Pilon-Smits and Quinn, 2010). An exception is made in Se accumulating plants where selenocysteine is bi-methylated to dimethyl diselenide (DMDSe) (Ellis and Salt, 2003). The transformation of selenomethionine to volatile and non-toxic Dimethylselenide represents a detoxification mechanism in the plant (Gupta and Gupta, 2017). According to the accumulated chemical forms in the plant tissues, Se speciation is determined (Eiche et al., 2015). For instance, in the case of *Brassica juncea,* mushrooms, nuts, grains, wheat and barley, the most predominant forms are selenate, selenomethylselenocysteine (Se-MeSeCys) and SeMet while, Se-MeSeCys predominates in the tissue of garlic onions and Oryza sativa (Poblaciones et al., 2014).

3. Recommendations for Se monitoring in mine industry

For an accurate Se quantification using analytical instrumentations, quality control measures should be implemented not only in the analysis phase but also in the pre-analysis during all steps of sample collection, storage, preparation, and pretreatment. Firstly, for Se analysis in water, samples should be collected in a container made of quartz, borosilicate glass, propylene, high-density polyethylene, fluoroethylene polymer, polycarbonate, or polytetrafluoroethylene washed with detergent, cleaned, rinsed with nitric acid or mixture of nitric and hydrochloric acid, and soaked in or filled with nitric or hydrochloric acid for at least 24 h before being rinsed with ultrapure water (U.S. EPA-600/4-82-029 and ISO 5667-3) (Desborough et al., 1999). Later, water samples must be immediately filtered through 0.45 μm polycarbonate or cellulose esters-membrane filters under minimal air exposure to avoid Se co-precipitation with iron and manganese oxide (Kumkrong et al., 2018). It is recommended to perform Se analysis immediately to avoid adsorption, co-precipitation and complexation and reaction with microorganisms. Otherwise, sample preservation for Se analysis was not subjected to guidelines, therefore, Wu and Pichler (2016) recommended a preservation with 0.5 M EDTA at 4 °C in the dark for low Se concentrations (5 to 15μg/L) associated with high levels of iron and manganese, while nitric acid preservation was not recommended as it will react later with sodium borohydride and the Se hydride signal can be decreased (Kumkrong et al., 2018; Wu and Pichler, 2016). Moreover, samples pretreatment to remove organic matter is needed using derivatization of water samples and digestion or extraction of solid samples (Plant et al., 2014). Drying soil samples is not recommended prior to digestion to avoid Se volatilization (Ralston et al., 2008). Digestion of solid samples must be performed under strongly oxidizing acid mixture, such as HNO_3/H_2O_2 at elevated temperature and pressure to obtain a liquid sample (Ralston et al., 2008). The digestates should be then suitably diluted to overcome the issues associated with acidity and spectral interferences. In order to assess Se speciation in soils, sequential extraction for soil fractionation should be checked for reproducibility by running matrix replicates due to lack of reference compounds (Ralston et al., 2008). Furthermore, using analytical instruments for Se analysis should take into consideration many quality control measures. Indeed, detection limits depend on the detector type, pre-concentration efficiency, and injection volume and it should be determined by analyzing at least three blanks (Table 4) (Kumkrong et al., 2018; LeBlanc et al., 2018). The analytical reproducibility should be ensured by analyzing samples to replicate and avoiding the problem of matrix interferences. In order to guarantee the accuracy of analytical procedure and verify sensitivity, the measurement of standard or certified reference materials for its Se concentration and samples spiking in replicate should be performed (Plant et al., 2014). Validation of the calibration curves should be conducted based on the curve of an independent standard of known concentration with a maximally allowed difference of 10% between the measured and the theoretical concentration (Ralston et al., 2008). Se in each species should be quantified using two separate Se isotopes with the acceptable matching between the resulting concentrations. Also, the identification of Se species based on retention time should also be confirmed using matrix spikes and molecular mass

spectrometry to avoid the shift of retention times of known Se species due to matrix effects (Ralston et al., 2008).

In addition, for the analysis of total and Se species in water and soil, many types of analytical methods have been developed. Inductively coupled plasma-mass spectrometry (ICP-MS) has high sensitivity and multi-element on-line detection capacity and speed for Se detection (Pettine et al., 2015). The analysis of total Se in water by ICP-MS was recommended by US EPA methods 200.8 and 6020. The application of MS allows not only to obtain the information on the qualitative and quantitative contents of the sample, but also to determine the structure and molar masses of chemical compounds (Yu et al., 2019). However, ICP-MS application for Se analysis requires high analytical skills in the recognition and correction of spectral, chemical and physical interferences. In the case of complex matrix waters, low detection limits < 0.1μg/L for total Se in water is difficult to reach due to matrix interferences. ICP-MS may have two types of interferences; the first one is related to changes in the sample uptake rate in the nebulizer due to changes in sample viscosity and high salinity and it can be rectified by using internal standardization. The second interference is related to changes in the plasma properties and increased or decreased ionization by organic carbon and/or by high sodium concentrations. This fact is might be rectified by either internal standards that mimic the ionization properties of Se or by isotope dilution (Ralston et al., 2008). For an acceptable total Se determination, at least two Se isotopes must be measured and the difference should not be higher than 10%, while all other Se isotopes should provide higher results. The lowest detection limits being posed for ^{80}Se and ^{78}Se isotopes because of interferences of the polyatomic Argon Ar2þ of the mass of 80 with (^{80}Se). Unfortunately, this interference problem cannot be solved with correction equations included in the ICP-

MS software, as the correction factor was not specified by the U.S. EPA Method 200.8 (Ralston et al., 2008). Therefore, in the perspective to lower the sensitivity and increase the detection limits, the use of reaction or collision cells or dynamic collision cells was recommended (Plant et al., 2014; Tsoi and Leung, 2011; Wallschläger and London, 2004). ICP-MS with Collision/Reaction Cell (CRC) Technology decreases Se detection limits and permits the determination of Se using ^{80}Se and/or ^{78}Se, while avoiding polyatomic interferences from sample constituents or Argon from the plasma (Yu et al., 2019). Although the collision cell-based instruments were efficient for quantification using ^{78}Se, results need to be confirmed using the minor isotopes ^{77}Se or ^{76}Se to solve the problem of ^{80}Se and ^{82}Se isotopes interferences with HBr^+ in bromide-rich waters. To overcome these limitations, triple quadrupole ICP-MS (ICP-QQQ-MS) instruments have been developed similarly to collision/reaction cell instruments, but with the advantage of extreme selectivity and ability to avoid most interferences, given the presence of mass analyzer before and after the collision cell (Kumkrong et al., 2018). Another useful method is hydride generation, HG, reported for its sensitivity, specificity, affordability, and their few spectral matrix interferences and for their efficiency in the increased sample introduction resulting in lower detection limit. For Se determinations, HG is being used coupled with the atomic fluorescence spectrometry (AFS) given its lower detection limits, simpler and cheaper piece of instrumentation, high sensitivity in measuring small fluorescence signal relative to no background compared to atomic absorption spectrometry (AAS) (Fu et al., 2012; Ralston et al., 2008; Santos et al., 2015; Zhong et al., 2011). However, HG suffers from a number of different interferences related mainly to another metal occurrence. This technique also requires the conversion of all Se species

present in the sample into selenite prior to the measurement by verifying the availability

of supposed Se species in each sample using separate blank and matrix spikes. Thus, HG

needs digestion of samples to inorganic forms and optimization of the reduction

procedure for Se.

Graphite furnaces (GF) are efficient even for solid samples, but they require experienced operator (Niedzielski and Siepak, 2003; Ralston et al., 2008). Additionally, Inductively Coupled Plasma with Atomic Emission (ICP-AES) was reported to achieve lower detection limits than GF (Xiong et al., 2008). All in all, the use of ICP-MS has been recommended for total Se analysis in water over all the above-discussed methods and to overcome interferences issues, ICP-MS with CRC technology is highly recommended (Yu et al., 2019). For the total Se determination in soil, digestion under high acidity and strong residual chemical oxidants pose a problem for both ICP-MS sensitivity and for HG procedure, which is based on a reduction process. However, in the presence of high Se concentrations in soil digests, dilutions and the use of post-digestion spikes could resolve these problems. ICP-MS or HG-AFS/AAS determination of total Se in soil was reported to achieve good detection limits (Niedzielski and Siepak, 2003; Ralston et al., 2008). To obtain low detection limit for Se speciation using ICP-MS, Capillary electrophoresis (CE) method, which is based on the migration of ions through a capillary to which an electric field is applied, was recommended. CE permits a high resolving power unless sample preconcentration using a solid-phase extraction step prior to CE-ICP-MS is properly performed (Deng et al., 2007; Liu et al., 2014; Lu and Yan, 2005). Furthermore, for the Se speciation in waters, anion exchange chromatography (AEC) is a common separation method used to identify Se oxyanions species in waters by their retention time and quantify them individually (Tsoi and Leung, 2011; Wallschläger and Bloom, 2001). Low detection limits were accomplished by directly coupling AEC to ICP-MS. The further use of a dynamic reaction cell (DRC) increased the sensitivity and allowed to reach lower detection limits in the order of ng/L for selenium speciation (Tsoi and Leung, 2011). Recent developments in anion-exchange HPLC and MS techniques make it possible to determine Se isotope abundances and concentrations in selenamino acids including selenocysteine and selenomethionine (Plant et al., 2014). The online combination of a chromatographic separation and suitable atomic spectrometry detection is recommended for the direct determination of Se species. The coupling of HPLC with ICP-MS is highly recommended for performing direct or "hyphenated" Se speciation analyses in water because the ICP-MS detector yields a species-independent response (Niedzielski, 2005; Yu et al., 2019). In fact, Se species could be separated using liquid-chromatographic (LC) separation mode before feeding them online into an ICP-MS detector, which does not require any other sample treatment after separation. LC-based Se speciation methods perform well in characterizing even unexpected Se species in unknown water compounds mixture and they provide equal detection limits and reproducibility for all Se species (Niedzielski and Siepak, 2003). This chromatographic process succeeded in eliminating matrix effects and interferences in the detection process by

banning the interferent from passing into the LC column (Ralston et al., 2008). For inorganic Se speciation analysis, AEC-CD system represented the most cost-effective with the minimal needed sample preparation (Xu et al., 2012). To avoid interference coming from the high conductivity of the used mobile phase, an eluent suppression could be used but sometimes it is not applicable for organic Se speciation due to their incompatibility with membrane suppressors. For volatile species analysis, gas chromatography can be coupled with mass spectrometry (MS) detector having the ability to identify analytes based on their mass spectra (Ghasemi and Farahani, 2012). Another popular detector coupled to GC instruments is the flame ionization detector (FID) having a universal nature and an ability to identify any volatilizing Se species present in sample (Najafi et al., 2012). Most widely applied to GC is an instrument employing electron ionization (EI) or Chemical ionization (CI) which can be associated with either a single or triple quadrupole mass analyzer. However, derivatization approaches are needed for non-volatile inorganic and organic Se to permit the preconcentration of the analytes and/or removal of interfering components in the sample. However, the chosen resin may not be Se-selective and therefore interference from competing ions in solution may cause lowered retention efficiencies (LeBlanc et al., 2018). Additionally, the use of HG-AFS or HG-AAS has usually the limitation of detecting some species with lower sensitivity and they present the inconvenient of needing a pretreatment process to convert Se species into selenite. Thus, the use of hyphenated techniques of HPLC coupled to MS and ICP-MS is highly recommended for Se speciation in water and soil.

Besides the advances in analytical speciation techniques, quantitative evaluation of some reduced species such as Se(0) and polyselenides still represent the main challenge for Se speciation, chiefly in reducing environments, due to their occurrence as colloidal species and the unavailability of certified standards. As an alternative the use of X-ray based techniques, including X-ray absorption and X-ray fluorescence spectroscopy was recommended for Se (0), which was reported to account for about 30–60% of total Se in sediments of aquatic systems (Pettine et al., 2015). Spectroscopic technique X-ray absorption methods, such as extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge spectroscopy (XANES) permit reaching good detection limits but they require the use of synchrotron-based X-ray radiation sources and are consequently less accessible and hard to be interpreted.

Most of the above described methods used for selenium quantification, mainly ICP-AES, HG-AFS, HG-ICP-AFS, ICP-MS, HG-ICP-MS and LC-ICP-MS have detection limits lower than the permitted discharged levels of selenium in freshwater (1 µg/L) as recommended by the Canadian Council of Ministers of Environment and Environment and climate change Canada, as well as the guideline value of 10 µg/L for drinking water recommended by Health Canada. Moreover, the lowest detection limit of 0.001-0.006 µg/L was achieved using Hydride generation - Inductively coupled plasma with mass spectroscopy, which confirms the robustness of this method in selenium quantification even at very low concentrations (Table 4).

Overall, the choice between analytical methods is very sensitive and depended on intervention factors for Se quantification. However, ICP-MS with CRC technology and the hyphenated

techniques using HPLC or HG coupled to MS and ICP-MS were highly recommended for total Se analysis and Se speciation, respectively.

4. Progress and challenges in Se treatment processes

The bioaccumulative nature of Se in organisms' tissues and food chain, inducing hazardous impacts and toxicity in animal and human life, makes Se treatment an urgent issue for environmental preservation. However, Se removal from wastewater has represented a major challenge, as a result of its different solubility, oxidation states and its competition with other components. Hence, identifying the Se risks in water systems, and adequate removal technology requires a deep understanding of its biogeochemistry and speciation. In fact, different selenium species represent a different degree of toxicity and it is well-established that selenite is relatively simple to remove with conventional water treatment compared to complex removal of high oxidation state selenate (Holmes and Gu, 2016). As shown in Figure 3, different Se removal technologies have been developed to meet the guidelines of mine effluent discharge. Se removal can be achieved by physical treatment (reverse osmosis, nanofiltration and ion exchange), chemical (iron precipitation and reduction), and biological treatment (bioreactors, fluidized bed reactor, wetlands, passive bioreactor, in situ microbial reduction, algae treatment and evaporation ponds) (Stefaniak et al., 2018). These treatment technologies have been intensively reviewed by many previous studies (CH2MHILL, 2010; Frankenberger et al., 2004; GolderAssociatesInc., 2009; Holmes and Gu, 2016; Khamkhash et al., 2017; Moore and Mahmoudkhani, 2011; Skousen et al., 2017; Stefaniak et al., 2018). In biological and chemical reduction methods, reduction of selenate to selenite, and then to elemental Se allows its removal through conventional liquid and solid separation before disposal (Khamkhash et al., 2017). During precipitation method, selenite and selenite are rather adsorbed or co-precipitated by complex metal hydroxide matrix. For phytoremediation as mentioned above, specialized plants are deployed to concentrate selenium residual from water and soil into their tissues. In membrane technology, oxyanions include selenium organic and inorganic species are concentrated in the brine solution. Similarly, ion exchange capture those anions, which later concentrated in regenerated solution, mainly caustic one. The advantages and disadvantages of Se treatment technologies are summarized in Table 5. Moreover, the overall performance of these different treatment technologies could be assessed based on their achievable discharge concentrations, cost-effectiveness, efficiency in treating selenite, an influent volume that can be treated, needed time, energy consumption, temperature-dependence, post-treatment management of by-products, and treatment scale (Sobolewski A., 2005). The selection and efficiency of any treatment process are contextual and site-specific (Skousen et al., 2017).

Nevertheless, most of the technologies are encountering many challenges for Se removal. Firstly, they are limited by Se speciation chiefly at dilute concentrations and high flow rates. Secondly, they are dependent on the variability in wastewater characteristics e.g. temperature, pH, total dissolved solids, contaminants composition, and influent flow. Thirdly, most treatment

options are limited by their high cost, insufficiency of removal levels, system dimensions and operating parameters. Indeed, full-scale treatment of Se has not been deployed for Canadian mine sites with flow rates more than of 250,000 m^3/day (GolderAssociatesInc., 2009). Industrial-scale pilot has been tested only for reverse osmosis, reduction by iron, active and passive microbial reduction, *in situ* microbial reductions, and wetlands. Taken all together, selenate removal is considered as an economical and performance challenge for treatment process, as the concentration of total selenium in many cases did not reach the level of 5 µg/L (Sobolewski A., 2005). Management of concentrated by-products such as brines or wash solutions for membrane filtration and ion exchange, or sludge should be taken into consideration (EnvirogenTechnologies, 2011).

Furthermore, biological treatment was reported for its efficiency in reaching regulatory Se limits, despite low operating cost compared to physical and chemical treatment methods. As the selenium reduction happens under anaerobic conditions, its effectiveness remains unchanged in cold climates. Several different types of passive and *in situ* microbial reduction demonstrated 90% removal of total Se with the lowest operating costs but have not been advanced at full-scale to the same extent as active microbial systems (GolderAssociatesInc., 2009). Fixed-film biological treatment technology was also reported to reduce a wide range of initial concentrations of Se in influent to less than 5 µg/L in a short residence time, low operating cost, and low solids generation (EnvirogenTechnologies, 2011). Microbial technologies Inc (2005) have also confirmed the efficiency, cost-effectiveness, and adaptation to the cold climate of the in-situ biological treatment when used to treat coal-mining wastewater in West- Central Alberta in Canada. Biological treatment methods still encounter some challenges to meet the strict guidelines recommended of USEPA due to site specificity, composition complexity of the influent, competition between the different contaminant e.g. metals, nitrate, and other competing electron acceptors, nutrient requirement, pH and temperature adjustment, residual sludge management. As well, the removal of organic Se forms has been receiving less attention, even though they are bioavailable and bioaccumulative than selenite and selenate. Other treatment methods like nanofiltration and reverse osmosis are efficient, but energy reduction should be implemented on a large-scale application. Although USEPA has recommended the application of ferrous hydroxide reduction of selenate to selenite followed by co-precipitation with ferrihydrite, this method is less effective in high redox potential and it still has the limitation of high chemical cost and hazardous sludge disposal. Reduction/adsorption techniques using metal oxides were recommended for Se removal but they still depend on the surface area properties and the competition of Se oxyanions with other anions for active sites available for adsorption or reduction (Stefaniak et al., 2018). Adsorption technologies onto activated and coated surfaces are widely tested, given its simpler operation and possibility of regeneration and reuse of several adsorbents; yet, they are usually dependent on pH and metal speciation and most of adsorbent are restricted to laboratory experimentation. The application of adsorption process on field is also hindered by the clogging of the filter material, resulting the lifetime reduction of the filter (Shankar and Shanker, 2014). On the other hand, nanomaterials are being developed to increase surface area, reactivity, catalytic potential and selectivity to Se

oxyanions (Holmes and Gu, 2016). Adsorption or reduction are two main emerging nanotechnologies applied for Se removal from industrial wastewater. The limitations of nanotechnology are it's upscaling for full-scale treatment of real wastewater, relatively high cost with the exception of titanium dioxide and iron oxide, operating pH as nano-adsorbents maximize their adsorption capacities under low pH ranges, and unidentified health impacts (Holmes and Gu, 2016).

In order to overcome these challenges in Se removal, a combination of biological, chemical and physical techniques may be employed in the development of a cost-effective treatment strategy. An implementation of a hybrid process, such as a combination of the physical or chemical process with biological treatment is highly favorable. A combined system using reverse osmosis followed by a biological reduction for the treatment of brine solution may hold promise for generating low Se discharge and transforming Se to a solid form ready for disposal (Vance et al., 2009). A combination of nanotechnology with a conventional method is also recommended to enhance the removal rate until reaching concentrations inferior to 5 ppb. In fact, nanomaterials could be specifically used as a polishing step to remove ultra-low concentration selenium by selective formation of oxyanions complexes (Holmes and Gu, 2016).

5. Future perspectives

Due to the widespread of industrial activities and economic development, Se occurrence in the environment is widely increasing. As mentioned, an excessive level of Se represents a major threat to living organisms leading to irreversible ecosystem disruption. Therefore, Se contamination of water, soil, and plant need to be well understood and assessed in order to prevent its harmful impacts on the environment as well as on human health. A recent development in analytical chemistry permits the rapid monitoring of potential Se threat toward ecosystems. However, these advanced techniques are costly in terms of installation and maintenance. For regular monitoring, new emerging sensitive and cost-effective analysis techniques should be further investigated. The mitigation of contaminated mine effluents with toxic levels to aquatic organisms, human and the overall biota should be established by approving and respecting the guidelines for safe levels of Se discharge from mining industries into the environment. Given the challenges for Se treatment, preventative measures are usually favored over treatment systems to reduce Se concentrations and subsequently decrease the risks for humans, animals, and the environment. The levels of Se released could be minimized by controlling and treating the effluents from mining operations. Mitigation measures should be also investigated to reduce Se release in the environment from the mining industry through tailings and wastewater discharge. Cost-effective wastewater purification technologies, which have practical applications in dealing with large volumes of mining effluents should be further optimized. In addition, some remediation techniques may be applied to reduce the mining pollution risks and hazards such as solid backfilling and development of technosols made of carbonates, biochars, and crop residues, to rehabilitate physical structure of soil and restore biological activity in the impacted areas.

6. Conclusions

Se has emerged as a contaminant of concern in mining industries. It is disturbing both aquatic and terrestrial ecosystems and has consequently attracted a major environmental consideration. The current paper examined the Se contamination occurrence in water, soil, and plant as released from mining activities. This review also discussed the effect of speciation, fractionation and the different biogeochemical processes mainly oxidation-reduction, sorption, precipitation, biomethylation and complexation on Se mobility in the soil. The bioavailability of Se for plant uptake, translocation, and accumulation, as well as its metabolism in plants, were widely explained. Analytical methods for Se speciation quantification were also presented. Thus, as no Se speciation methods were officially recommended by government agencies, an appropriate analytical method should be selected and optimized to reach better sensitivity especially in the presence of interfering matrix components. Particularly, the hyphenated techniques using HPLC or HG coupled to MS and ICP-MS were highly recommended for Se speciation given their effectiveness in reaching extremely low detection limits, performing high accuracy and reproducibility and resolving the problem of interferences. Hence, monitoring of emerging contamination by Se is highly required for a consequent implementation of efficient treatment approaches to ensure environmental preservation next to resource exploration and economic development. However, many challenges are encountering the efficiency of Se removal as this latter is governed by the economical consideration, complexity of Se chemistry, the complexity of wastewater composition mixtures, and the strict regulations to meet the mandated levels. In order to overcome these challenges in Se removal, a combination of biological treatment with chemical or physical methods are expected to optimize Se removal and to ensure environmental protection and human health safety.

Acknowledgements

Conflicts of Interest

The authors declare no conflict of interest.

7. References

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Figure 1. Range of selenium concentrations in different aquatic media especially mine effluents (Bond, 2000; Bujdoš et al., 2005; Cutter and Cutter, 1995; Desborough et al., 1999; Khamkhash et al., 2017; Nriagu and Wong, 1983).

Figure 2. Selenium mobility in the soil and bioavailability for plant uptake, translocation and metabolism

Figure 3. Overview of six main selenium treatment methods

Table 1

Physical and chemical properties and main species of selenium (Se)

Characteristics	Selenium (Se)
Atomic number	34
Molecular weight	78.96
Melting point (°C)	221 (red); 220.5 (grey); 180 (black)
Boiling point (°C)	685
Vapor pressure (Pa)	1 mm Hg at 356°C (grey)
Water solubility	insoluble
Se species	*Inorganic species*

Inorganic species

- Selenate [Se(VI)]: SeO_4^{2-}, Selenic acid $H_2SeO_4^0$, hydrogen selenate $HSeO_4^-$
- Selenite [Se(IV)]: SeO_3^{2-}, Selenous acid $H_2SeO_3^0$, Hydrogen selenite $HSeO_3^-$, selenium dioxide SeO_2
- Elemental Se [Se(0)]: Se^0
- Selenide [Se(-II)]: Hydrogen selenide H_2Se, Se^{2-}, HSe^-

Organic species

- Dimethyl selenide (DMSe): $(CH_3)_2Se$
- Dimethyl diselenide (DMDSe): $(CH_3)_2Se_2$
- Dimethyl selenium sulfide: $(CH_3)_2SeS$
- Dimethyl selenium-disulfide: $(CH_3)_2SeS_2$
- Selenodiglutathione: GSSeSG
- Selenocysteine (SeC): $HSeCH_2CHNH_2COOH$
- Selenomethionine (SeM): $CH_3Se(CH_2)_2CHNH_2\text{-}COOH$
- Trimethylselenonium: $(CH_3)_3Se\text{-}$
- Selenocyanate: $SeCN^-$
- selenoproteins

Table 2

Toxicity of selenium to humans, animals, and aquatic organisms (Rogers et al., 1990;

WHO, 2011; Beatty and Russo, 2014)

Animals	**In grazing animals:** - For soil selenium levels exceeding 3 to 9 mg/kg DM resulted in alkali disease (dullness, lack of vitality, emaciation, rough coat, sloughing of the hooves, erosion of the joints and bones, anemia, lameness, liver cirrhosis, and reduced reproductive performance). - Blind staggers (impaired vision and blindness, anorexia, weakened legs, paralyzed tongue, labored respiration, abdominal pain, emaciation, and death) **In Birds:** - Selenium levels exceeding 10-20 µg/g dw in liver and 6-15 µg/g dw in eggs caused death or deformation of embryos.
Humans	- Dietary intake exceeding 900 µg/day resulted in selenosis: Hair and nail loss, tooth decay and discoloration, skin lesions, nervous system disorders, paralysis, and death respiratory effects, dyspnea, bronchitis and pulmonary edema and pneumonia, gastrointestinal and cardiovascular effects and irritation of eyes due to acute exposure. - Vomiting and diarrhea, hair and nail loss. - Discoloration of the skin, hair loss, deformation of nails, excessive tooth decay and discoloration, a garlic odor to the breath, weakness and a lack of mental alertness due to chronic exposure.
Aquatic organisms	**In fish:** - Selenium levels exceeding 4-9 µg/g dw in whole body, 8 µg/g dw in muscle, 12 µg/g dw in liver and 10-20 µg/g dw in egg/ovary: Developmental malformations and deformities: skeletal Deformities, craniofacial deformities, edema, facial deformities (eye, jaw, and mouth), Body deformities (kyphosis, lordosis, scoliosis) and fin deformities - Larval deformities and mortality - Reduction in fish growth **In invertebrates:** - Selenium levels exceeding 1-30 µg/g dw in internal tissue: Embryonic mortality and abnormalities - Developmental anomalies **In aquatic plants:** - Growth inhibition, reduced chlorophyll, wilting and drying of leaves, reduced protein synthesis, and death of immature plants, incipient inhibition

Table 3

Summary of guidelines for selenium in drinking water, freshwater, agricultural water and

soil

Guideline	Discharge limit (μg/L)	Reference
Drinking water		
Health Canada	10	HC (2019)
World Health Organization	40	WHO (2011)
Japan Ministry of Environment	10	JEM (1993)
United State Environmental Protection Agency	50	USEPA (2009)
Australian National Health and Medical Research Council and Natural Resource Management Ministerial Council	10	ANWQMS (2011)
Freshwater		
International Joint Commission	≤ 1	IJC (1981)
Canadian Council of Ministers of Environment	1	CCME (2007)
Ontario Environment and Energy	100	MoEE (1987)
United State Environmental Protection Agency	5	USEPA (2016)
Ministère du Développement durable, de l'Environnement et des Parcs du Québec	5	MDDEP (2009)
Australian and New Zealand Environment and Conservation Council	5	ANZECC (2000)
The Netherlands Water pollution control	0.09 (long-term) 5.4 (short-term)	Warmer and van Dokkum (2002)
Colorado Department of Public Health and Environment	4.6	CDPHE (2007)
Indiana Water Pollution Control Board	35	IWPCB (2009)
Agricultural water uses of crop irrigation and livestock watering		
Canadian Council of Ministers of Environment	20-50 for irrigation; 150 for livestock	CCME (2007)
Soil		
Canadian Council of Ministers of Environment	1 μg/g for agricultural, residential or parklands and 2.9 μg/g for commercial and industrial lands	CCME (2007)

Table 4 Comparaison of analytical methods parameters for determining Selenium in environment samples

Analytical method	Detection limit (µg/L)	References
Inductively coupled plasma with atomic emission spectrometry (ICP-AES)	Se_{total}: 0.1	(Xiong et al., 2008)
Hydride generation - Inductively coupled plasma with atomic emission spectrometry (HG-ICP-AES)	Se_{total}: 0.055-1.2	(Niedzielski and Siepak, 2003)
Capillary electrophoresis- Hydride generation - Inductively coupled plasma with atomic emission spectrometry (CE–HG-ICP-AES)	Se_{total}: 2.1	(Deng et al., 2007)
Hydride generation - atomic fluorescence spectrometry (HG-AFS)	Se_{total}: 0.024 - 0.06	(Fu et al., 2012)
	Se(IV): 0.05	(Zhong et al., 2011)
	Se(VI): 0.06	
	Org-Se: 0.06	
Capillary electrophoresis- Hydride generation- atomic fluorescence spectrometry (CE-HG-AFS)	Se(IV):25	(Lu and Yan, 2005)
	Se(VI): 33	
Anion exchange chromatography - Hydride generation - atomic fluorescence spectrometry (AEC-HG-AFS)	Se(IV): 0.026	(Wallschläger and Bloom, 2001)
	Se(VI): 0.033	
	$SeCN^-$: 0.034	

Hydride generation - Inductively coupled plasma with atomic fluorescence spectrometry (HG-ICP-AFS)	Se $_{total}$: 0.003	(Niedzielski and Siepak, 2003)
Atomic Absorption Spectrometry (AAS)	Se $_{total}$: 0.06	(Zhang et al., 2007)
Hydride generation atomic absorption spectrometry (HG-AAS)	Se $_{total}$: 0.1	(Santos et al., 2015)
High-performance liquid chromatography - Hydride generation atomic absorption spectrometry (HPLC–HG-AAS)	Se $_{total}$: 2.4	Niedzielski (2005)
Graphite furnace atomic absorption spectrometry (GF-AAS)	Se $_{total}$: 0.5-2	(Niedzielski and Siepak, 2003)
Inductively coupled plasma with mass spectroscopy (ICP-MS)	Se $_{total}$: 0.1	(Pettine et al., 2015)
	Se(IV): 0.02	(Zheng et al., 2008)
	Se(VI): 0.02	
Anion exchange chromatography - Inductively coupled plasma -dynamic reaction cell – mass spectrometry (AEC-ICP-DRC-MS)	Se(IV): 0.0022	(Tsoi and Leung, 2011)
	Se(VI): 0.0019	
Hydride generation - Inductively coupled plasma with mass spectroscopy (HG-ICP-MS)	Se $_{total}$: 0.001-0.0064	(Niedzielski and Siepak, 2003)
Hydride generation - Inductively coupled plasma -dynamic reaction cell – mass spectrometry (HG-ICP-DRC-MS)	Se(IV): 0.00015	(Wallschläger and London, 2004)
	Se(VI): 0.00027	
	SeCN−: 0.00019	
Capillary electrophoresis- Inductively coupled plasma with mass spectroscopy (CE-ICP-MS)	Se(IV): 2.31	(Liu et al., 2014)

	Se(VI): 2.23	
	SeMet:1.48	
	SeCys$_2$: 1.27	
	MeSeCys: 1.33	
Liquid Chromatography- Inductively coupled plasma with mass spectroscopy (LC-ICP-MS)	Se $_{total}$: 0.03-0.2	(Niedzielski and Siepak, 2003)
Gas chromatography-flame ionization detector (GC-FID)	Se $_{total}$: 0.05-0.11	(Najafi et al., 2012)
	Se(IV): 0.05	
	Se(VI): 0.05	
Gas chromatography- mass spectrometry (GC–MS)	DMSe: 0.016	(Ghasemi and Farahani, 2012)
	DMDSe: 0.011	
Anion exchange chromatography -conductivity detector (AEC-CD)	Se(IV): 0.8	(Xu et al., 2012)
	Se(VI): 0.4	

Table 5

Advantages and disadvantages of selenium treatment technologies

Treatment Technologies	Advantages	Disadvantages
Reverse osmosis	-capable of reducing selenium concentration below 5μg/L in industrial scale -Reduced space, easy expansion -Concentrated selenium in low volume brine solution -Production of high-quality distilled water	-High capital and operation costs (CAPEX &OPEX) -requirement of coagulation/flocculation and/or ultrafiltration as a pretreatment step -Frequent maintenance and control -Treatment of Brine prior to discharge
Nanofiltration	-High selenium rejection -A third of transmembrane pressure comparing with reverse osmosis -Less fouling, and control issue	-High CAPEX &OPEX -No available results for industrial-scale treatment - Treatment of Brine prior to discharge
Evaporation pond	-Low cost -Easy operation	-High space requirement -only for salty water in hot and/or arid climate

		-Risk of infiltration in groundwater
		-Risk for the ecosystem
		-Dry residuals management
Evaporation Crystallization	-production of sitliated water and salt solution	-Possibility of need for pretreatment
		-High CAPEX & OPEX
	-mainly used for high salt content water or reject stream of reverse osmosis, nanofiltration and ionic exchange	-High cost of control and maintenance
		-Solid waste management
Ionic exchange	-Reduction of selenium concentration below 5μg/L at pilot scale	-Anions competition
		-Rejection of the resin if not regenerated
	-Concentrate the selenium in regeneration solution for final treatment	-Regeneration solution treatment
Ferrihydrite coprecipitation	-Stablished process information	-Low removal efficiency
	-Best available technology according to USEPA	-Disposal of a large volume of iron residuals containing selenium
	-Simplicity and low CAPEX and OPEX	-pH adjustment (optimal pH from 4 to 6)
		-Deficiency in selenate removal
Zero valent Iron Reduction	-Treatment of selenite and selenate at low concentrations	-Low information at the pilot and industrial scale
		-Long hydraulic retention time

		-Disturbed by dissolved oxygen and other anions
		-High chemical Usage due to Fe^0 replacement
		-Storage and disposal of sludge
		-Adjustment of temperature and pH
Biological reduction	-Adsorption of selenium in biomasss	- Large space requirement
	- No pretreatment step	-Requirement of nitrate removal
	-Low CAPEX	- Long hydraulic retention time
	-Available pilot scale data	-Biosolid management
Advanced Biological Metals Removal Process (ABMet)	- High selenium removal efficiency	-Probable pretreatment step for total suspended solids and biological oxygen demand
	- Adsorption of selenium in biomass	-Large space requirement
		- Addition of carbon and nitrogen source
		- Backwash requirement
		- Production of a large volume of sludge
Fluidized bed reactor	- Simplicity of process	- Lack of pilot tests
	- Adsorption of selenium in biomasss	- Addition of nutrient (carbon and nitrogen sources)
	- Lower sludge production	- Biosolid management
	- Small space requirement	
	- No pretreatment step	
	- No need for periodic washing	

Wetlands	- Simple technology due to passive treatment - Minimal supervision - Feasibility in cold climate if the flow is under the surface - Application for high flow of effluent	- Long hydraulic retention time, need for big space - Inconsistent selenium discharge concentration below 5μg/L - Low efficiency in low temperature if the flow is superficial - Constant monitoring of selenium bioaccumulation and toxicity -Risk of groundwater contamination
Passive bioreactor	- Low capital, operation, and maintenance cost - Available full-scale information - Minimal supervision - Passive treatment - Feasibility in cold climate	- Risk of selenium contamination in the environment - Large space requirement - Inconstant in reaching Se discharge below 5μg/L - Addition of nutrients
Permeable reactive barrier	- Low CAPEX and OPEX - Low capital, operation, and maintenance cost - Available full-scale information	- Addition of nutrients - Clogging - Low selenium removal efficiency
Algae treatment	- *in situ* application - Easier sludge management: algae could be applied as a dietary supplement or	- Risk of water eutrophication - Seasonality (temperature and sunlight) - Large space requirement

biofuel production	- No available results in pilot scale
	- Not demonstrated to treat to less than 5μg/L Se
	- High level of bioavailable Se in the final effluent

Highlights

- **Release of selenium at high concentrations is of a major environmental concern**

- **The mobility, bioavailability, and fate of selenium depended on various factors**

- **Monitoring of Se contamination in mine industry is highly required**

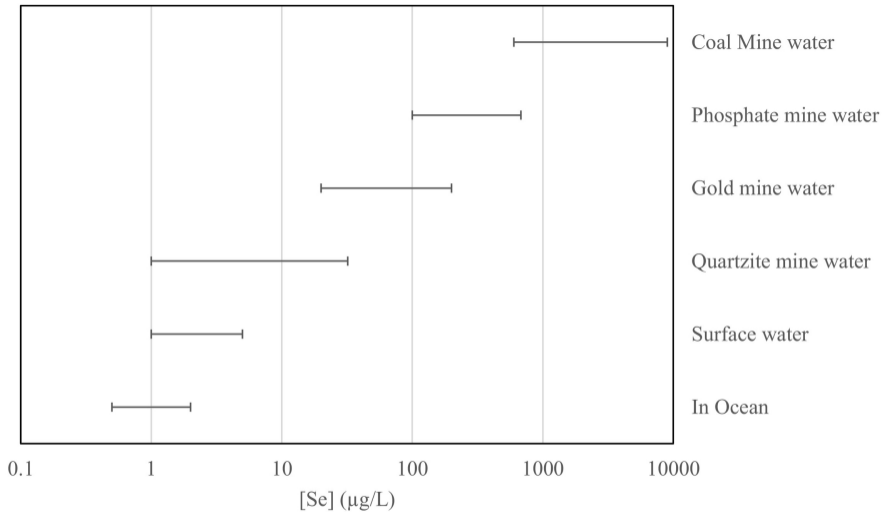- **Recommendations are made to mitigate selenium pollution in the environment**
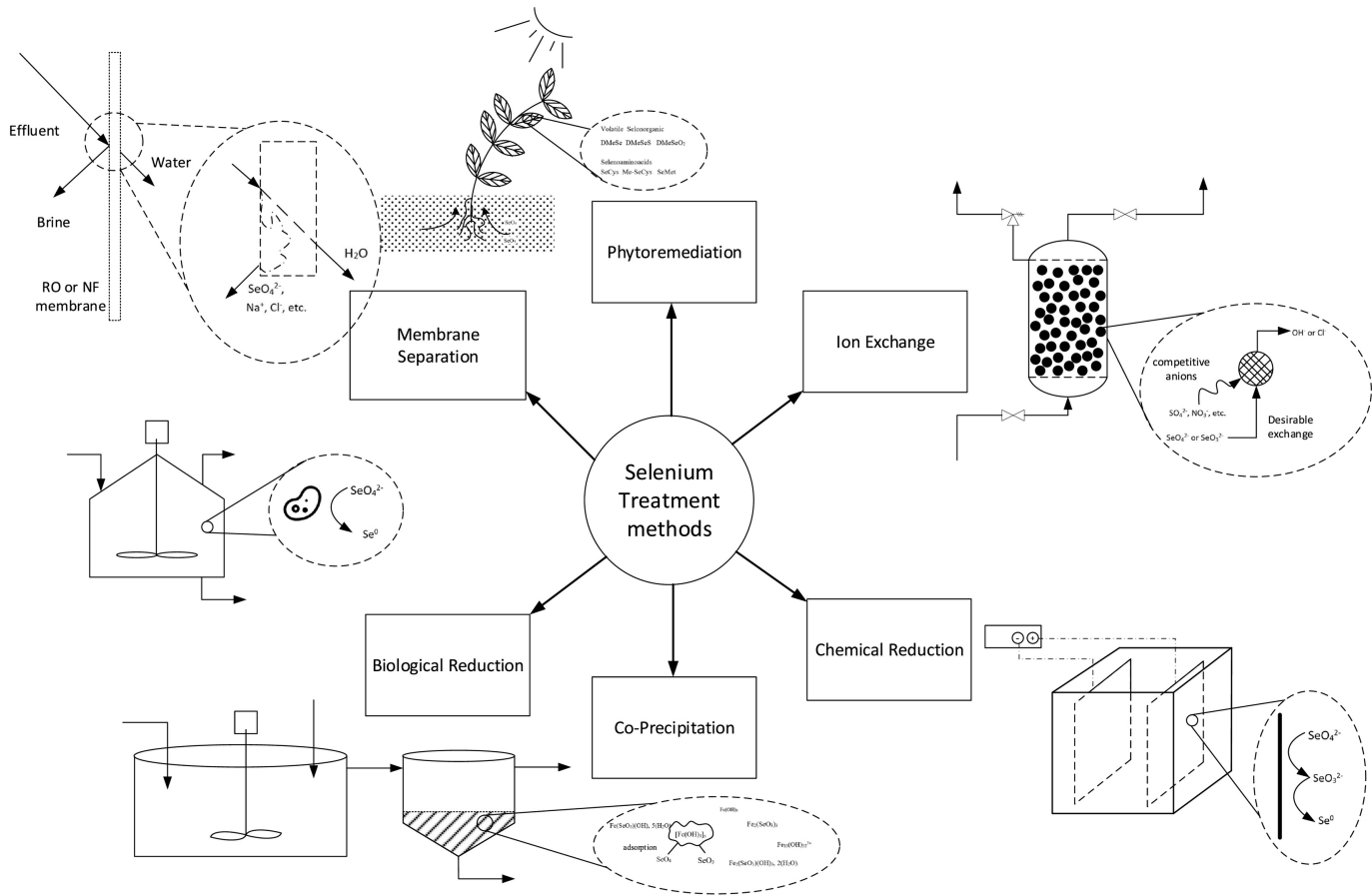
Figure 1

Figure 2

Figure 3