



## Review article

## Selenium contamination, consequences and remediation techniques in water and soils: A review



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## ABSTRACT

Selenium (Se) contamination in surface and ground water in numerous river basins has become a critical problem worldwide in recent years. The exposure to Se, either direct consumption of Se or indirectly may be fatal to the human health because of its toxicity. The review begins with an introduction of Se chemistry, distribution and health threats, which are essential to the remediation techniques. Then, the review provides the recent and common removal techniques for Se, including reduction techniques, phytoremediation, bioremediation, coagulation-flocculation, electrocoagulation (EC), electrochemical methods, adsorption, coprecipitation, electrokinetics, membrane technology, and chemical precipitation. Removal techniques concentrate on the advantages, drawbacks and the recent achievements of each technique. The review also takes an overall consideration of experimental conditions, comparison criteria and economic aspects.

## 1. Introduction

As is known to all, selenium (Se) is an essential micronutrient for the creature and it is good for our health at low concentration. However, excessive Se in the environment causes serious pollution in soil, atmosphere and water, and brings severe risk and damage to human health (Sakamoto et al., 2012). Industrial and agricultural activities are the dominant anthropogenic sources of Se pollution. Selenium absence and toxicity lead to contamination in drinking water and in wastewater, which is a latent threat for water systems (Santos et al., 2015b). Therefore, in recent years, selenium contamination has attracted tremendous interests and has been understood more and more deeply around the world (Sakamoto et al., 2015) (Figs. 1 and 2).

Listing in the sixth main group in the periodic table of elements, selenium is a crystalline “metalloid” and possesses similar chemical properties with sulfur. Selenium can occur in environment as various oxidation states such as: selenate ( $\text{SeO}_4^{2-}$ , Se(VI)), ( $\text{SeO}_3^{2-}$ , Se(IV)), selenide ( $\text{Se}^{2-}$ ) and elemental ( $\text{Se}^0$ ). However, Se(IV) and Se(VI) present in aqueous environment commonly. Besides, the Se(IV) is more toxic than Se(VI) (Awual et al., 2015). Selenium is also widely scattered in rock materials. It exists in various rocks due to its dispersive nature, but its concentration usually less than 0.1 mg/kg. The abundance in the Earth's crust is approximately 0.05–0.09 mg/kg, it is about 1/6000 and 1/50 of the respective abundances of sulfur and arsenic (Rodriguez

et al., 2005). In global terms, Se can concentrate in sedimentary more easily than igneous rocks (Rodriguez et al., 2005).

As we know that the chemical form of selenium influences its toxicity greatly. In particular, inorganic and organic selenium compounds have different toxicity profiles, with the latter being much less toxic than the former (Mehdi et al., 2013). The standards of public health for selenium should consider chemical form, because selenium exists in drinking water almost entirely with inorganic form. On the contrary, inorganic forms of selenium in foods are not generally found. Selenium is detected throughout the world in many environmental matrices including soil, air, plants, foods, and drinking waters. In drinking waters, selenium is generally detected at relatively low concentrations (Mehdi et al., 2013). Subsequent investigations indicated that high selenium exposure by drinking water was related to lower blood glutathione peroxidase activity, suggesting an unexpected inverse relation between enzymatic activity and selenium intake through drinking water at these unusually high exposure levels (Lee and Jeong, 2012).

As recently reviewed (Vinceti et al., 2013a), in most countries or regions (e.g., European Union, Australia, Japan, Canada, Thailand and New Zealand, the United States Food and Drug Administration), the upper limit of Se has been set to 10  $\mu\text{g/L}$ , with the exception of Russia, which has set a limit of 1  $\mu\text{g/L}$  as selenium trioxide since 1970, the U.S. Environmental Protection Agency, which has set a limit of 50  $\mu\text{g/L}$  and

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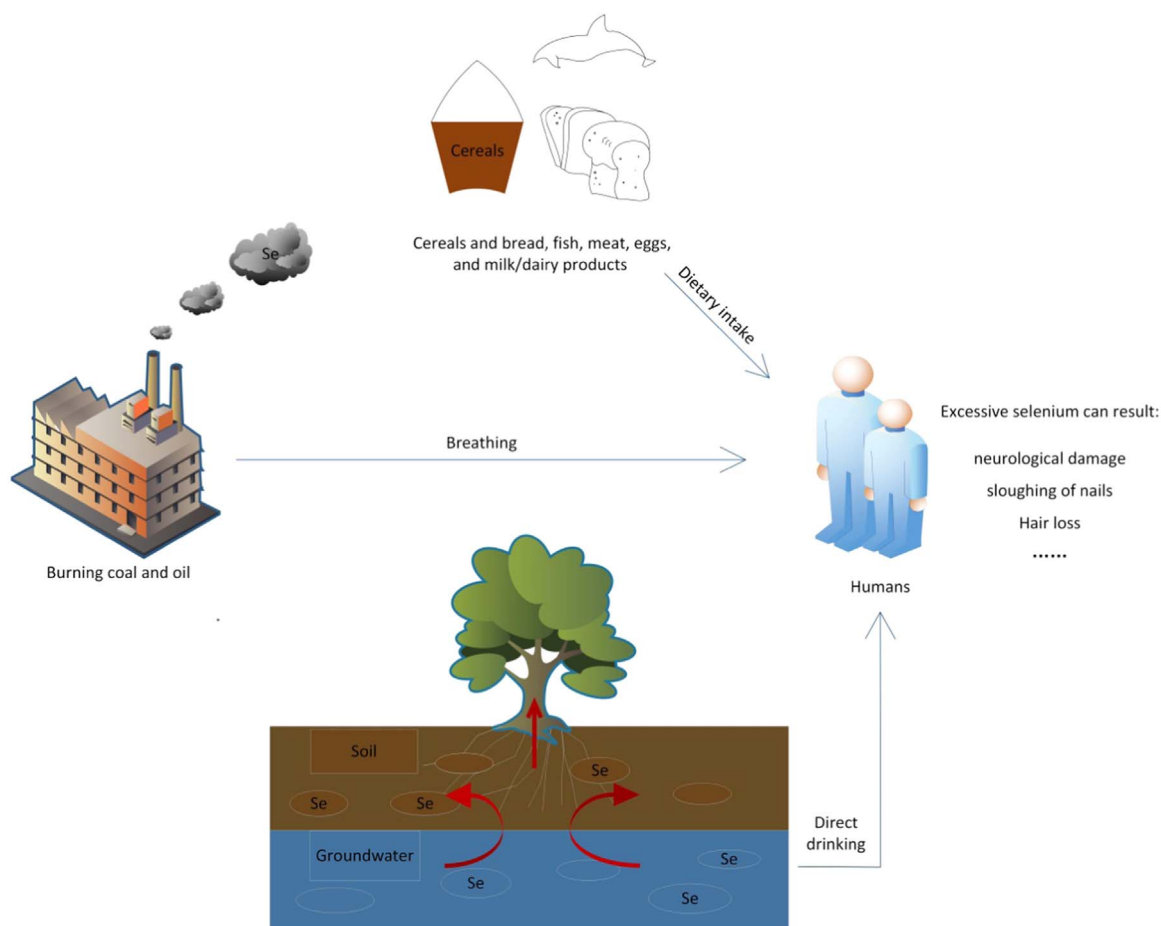


Fig. 1. Schematic diagram shows the transfer of selenium from environment to human beings through daily life. Intake of selenium by human beings causes several diseases.

the California Environmental Protection Agency, which has set a limit of 30  $\mu\text{g}/\text{L}$ . The provisional guideline for selenium of the World Health Organization (WHO) in drinking water was set at 40  $\mu\text{g}/\text{L}$  (Organization, 2011). However, epidemiologic studies investigated that the current commonly used limit of 10  $\mu\text{g}/\text{L}$  for selenium in drinking water applied in most countries or regions should be decreased, and the standard should reduction to 1  $\mu\text{g}/\text{L}$  suggested by Vinceti et al. in order to decrease the risk of adverse health effects, including neoplasms and endocrine and neurological diseases, due to long-term exposure (Vinceti et al., 2013a). Thus, the prevention and treatment of selenium pollution is a crucial project for the human being.

Here, the goals of this review are to compile and analyze the current state of knowledge of the sources of selenium in the environment, health hazards, and remediation of selenium contamination; and to identify knowledge gaps and future research needs. The review is structured into four topics: a) sources of selenium in the environment; b) health hazards; c) remediation of selenium contamination; d) knowledge gaps and research needs.

## 2. Sources of selenium in the environment

The main source of selenium in the environment (e.g., hydrosphere, pedosphere, biosphere and atmosphere) includes natural and anthropogenic sources. The natural source covers marls, gypsum, volcanic eruptions, sea spray, volatilization/recycling via biotic cycling, the weathering of selenium-containing rocks and soils, etc. (Fairweather-Tait et al., 2011; Rodriguez et al., 2005). Anthropogenic sources include mining, agriculture, coal combustion, insecticide production, oil refining, photocells and glass manufacture (Santos et al., 2015a). Emission of selenium to soils annually from human activities outdistances

those from all natural sources summarized. Table 1 shows the selenium concentration of several countries/areas affected by selenium exposure.

### 2.1. Soil

In the worldwide, all the selenium concentration in soil typically exists within the range from 0.01 to 2.0 mg/kg with a general average of 0.4 mg/kg (Fairweather-Tait et al., 2011). The soils present a mass of concentration (up to 1200 mg/kg) originated in seleniferous parent materials, including sandstones, shales, slate, limestones and coal series (Fairweather-Tait et al., 2011). The soil is the primary source of Se that can be transported and accumulated in the leaves by the water stream from solum. Vegetables rich in sulfur, for example, some *Allium* species and *Brassica*, possess a higher capacity of accumulating Se since it can replace S in the proteins. But this accumulation is still limited at low Se concentrations in soil (De et al., 2014).

The selenium in the soil changes depending on the type, texture and organic matter content of soils and rainfall amount. Selenium in soils is mainly from the rocks erosion containing selenites and selenides which are linked to sulfide minerals and with mass fractions less than 1 mg/kg (Mehdi et al., 2013). Selenium has several forms such as ferric selenite and selenate salts or its organic form.  $\text{SeO}_3^{2-}$  and  $\text{SeO}_4^{2-}$  appear frequently in most soils. Its assimilation through the plant is impacted by the physicochemical factors of the soil (e.g., pH and redox status), and microbiological activity. The average concentration of selenium in soil varies from 100 to 700 ppb. For clay soils, it is 800–2000 ppb, while in tropical soils, it is 2000–4500 ppb (Hoet, 2013). Soil acidity decides the assimilate rate of selenium in plants and crops. In general, acid soils tend to release less selenium than alkaline ones. Selenite oxidizes in alkaline soils and forms soluble selenate that can easily assimilate by

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