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Review

# The accessibility, necessity, and significance of certified reference materials for total selenium content and its species to improve food laboratories' performance

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ABSTRACT

Micronutrients are one of the most important groups of nutrients that our body needs daily in trace amounts to tackle deficiencies. Selenium (Se) is a mineral that occurs naturally in foods and is an essential component of selenoproteins that support the healthy functioning of the human body. Therefore, monitoring dietary Se concentrations must be a higher priority to meet daily intakes. Fulfillment can be addressed through applying various analytical techniques, and the certified reference materials (CRMs) tool plays a crucial role in quality assurance/quality control (QA/QC). The availability of certified CRMs for total Se content with addition to their species is presented. The review emphasizes the necessity of incorporating more food matrix CRMs certifying Se species, apart from total Se content, to meet method validation requirements for food analysis laboratories. This would help CRM producers bridge the gap between available food matrix materials that are not certified for Se species.

## 1. Introduction

In ecosystems, food webs serve an important function in connecting organisms by allowing the transfer of energy and nutrients from one species to another. Ecosystems involve the exchange of energy and nutrients from an organism to an organism (Padariya, Rutkowska, & Konieczka, 2021). The terrestrial and aquatic food webs are also interconnected, with one organism supplying nutrients to the other (Soininen, Bartels, Heino, Luoto, & Hillebrand, 2015). Nutrients are essential for the proper functioning of life, while micronutrients are a subset of nutrients that our bodies require in limited amounts. Selenium (Se) is a chemical element that is on the list of important micro elements for the proper functioning of mammalian organs, and its importance is recognized in the clinical field. Selenium presents in inorganic form elemental form ($Se^0$), in inorganic forms of selenides ($Se^{2-}$), selenates ($SeO_4^{2-}$), or selenites ($SeO_3^{2-}$) in the environment (Kieliszek, 2019), and in organic forms directly bound to carbon (methyl compounds, selenamino acids, selenoproteins) and others in which selenium is covalently bound to carbon (selenomethionine, selenocysteine) (Bodnar, Konieczka, & Namiesnik, 2012).

Selenium, a contradictory nutrient, has aroused the curiosity of biomedical science in recent decades (Kieliszek, 2022). In contrast to the effects of Se on human health, the ingested dose determines whether Se is an essential or toxic element. Therefore, a certain level of selenium must be maintained in the human diet. As a trace element, selenium is required for many biological activities, including thyroid hormone

*Abbreviations:* AIST, National Institute of Industrial Science and Technology; BCR, the Bureau Communautaire des Références; CAGS, The Chinese Academy of Geological Sciences; CRMs, Certified reference materials; EMCHJ, Environmental Monitoring Centre in Heilong Jiang; ERM, the European Reference Materials; IAEA, International Atomic Energy Agency; IGGE, Institute of Geophysical and Geochemical Exploration; IRMM, European Community's Institute for Reference Materials and Measurements; IUCN, The International Union for Conservation of Nature; JIS Q, Japanese Industrial Standards, area division Q (Management System); JRC, Joint Research Center; JSAC, The Japan Society for Analytical Chemistry, Metrology Management Center; LGC, Laboratory of the Government Chemist; LRM, Laboratory reference material; NIES, National Institute for Environmental Studies Center for Environmental Measurement and Analysis; NIST, United States National Institute of Standards and Technology; NMIJ, National Metrology Institute of Japan; NMIs, National Measurement Institutes; NRC, National Research Center; QA/QC, Quality assurance/quality control; Se, Selenium; SeCys, selenocysteine; SeMeSeCys, selenomethylselenocysteine; SeMet, selenomethionine; SINR, Shanghai Institute of Nuclear Research; SMI, Second Marine Institute.

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metabolism, the body's antioxidant defense systems, strengthening the immune system, and preventing some malignancies. Therefore, the recommended daily intake must be achieved to prevent deficiency, which depends on age and gender. Apart from the pedosphere, selenium occurs in all other environmental compartments [i.e., lithosphere, hydrosphere, biosphere, and atmosphere], all of which play a role in the global biochemical cycling and distribution of Se (Nancharaiah & Lens, 2015). Selenium can potentially enter the environment in several ways, either naturally (physical and chemical weathering of source rocks, volcanic activity) or as a result of anthropogenic activities (agriculture, industrial processes) (Ullah et al., 2022). Aquatic and terrestrial environments are thought to contain trace amounts of selenium (Wells & Stolz, 2020). Selenium compounds are biologically methylated by higher plants, fungi, and other microorganisms. The volatile product (dimethyl selenide) of this reaction plays an important role in the geochemical cycle. In the terrestrial food chain, plants uptake Se as a micronutrient source from soil (50–200 μg/kg in soils) (Reilly, 2006). However, aquatic organisms take up essential Se from aquatic plants and the surrounding water. Selenium is transported further up the food chain, and food products eventually serve human nutrition. The detailed representation of the Se cycle in terrestrial and aquatic food webs is shown in Fig. 1. The initial transport of Se begins with the soil to the plant system and continues through herbivores to scavengers. The inorganic forms of Se are mainly taken up by plants because their bioavailability is greater in the environment.

A comprehensive literature search was performed to identify relevant articles indexed in Scopus, SciFinder, Web of Science together with a metasearch in Google Scholar based primarily on the following keywords: 'Certified reference materials (CRMs)', 'Food safety', 'Quality control/Quality assurance', 'Selenium', 'Selenium speciation. References contained in the identified articles were also assessed. This review is based on the data gathered in this query and also on the authors' personal experience in the field.

## 2. Selenium sources in the human diet: Unraveling the role of the aquatic food web

Selenium is released into the aquatic environment as part of natural and anthropogenic activities. The main transport pathway of Se to the aquatic environment is desorption from ecotone, wet and dry deposition from air, and runoff. The aquatic environment is ecologically sensitive to the accumulation of trace elements, and it is difficult to detoxify such a concentrated region. The aquatic portion of the environment has long been a habitat for aquatic plants, fish, waterfowl, and air-breathing aquatic animals. Concerns have been raised about selenium deposition in the marine environment (Okonji, Achari, & Pernitsky, 2021; Reilly, 2006). In natural water, Se content can be found in varying amounts from $< 2$ ng $l^{-1}$ up to 300 μg $l^{-1}$ (Sager, 2006).

In continental Europe, selenium can enter the aquatic environment primarily through agricultural runoff (selenate-containing fertilizers), animal excreta from selenium-fed livestock, and fossil fuel combustion and ash (particulate matter) (Sager, 2006). Selenium is required for aquatic habitats to have healthy growth, development, and flesh quality. Seafood and freshwater organisms (plants, fish) are the staple foods of Europeans, providing the necessary source of daily Se intake (Sager, 2006). As the food chain progresses, humans who consume aquatic organisms with high selenium content are poisoned by biomagnification. The recent studies indicate that toxic levels of Se were found in birds and fish (Liaskos et al., 2023; L. Wang et al., 2022).

## 3. Selenium sources in the human Diet: Unveiling the role of the terrestrial food web

In the pedosphere, the soil has different forms of Se depending on redox reactions, moisture, and soil pH (Macías & Camps-Arbestain, 2020). Inorganic forms of selenium are generally bioavailable and stable in soil and are not converted to organic forms, except for a small amount of oxidation by microbes. The presence of Se in the soil varies widely from country to country and from area to area, with Se content in plant foods and animal feed (forage) depending in part on the bioavailability of Se in soil (G. Wang et al., 2021). Selenium concentrations in European arable soils are generally in a limited range compared with regions in the United States, Australia, and India, which have much higher levels of Se (Loomba et al., 2020). Soil has a variety of nutrients and minerals that can be absorbed by crops. Conventional crop cultivation affects both the loss and the quality of the soil. Selenium is one of the micronutrients that is affected by soil quality and is less bioavailable to be taken up by plants. Since in some parts of the world,

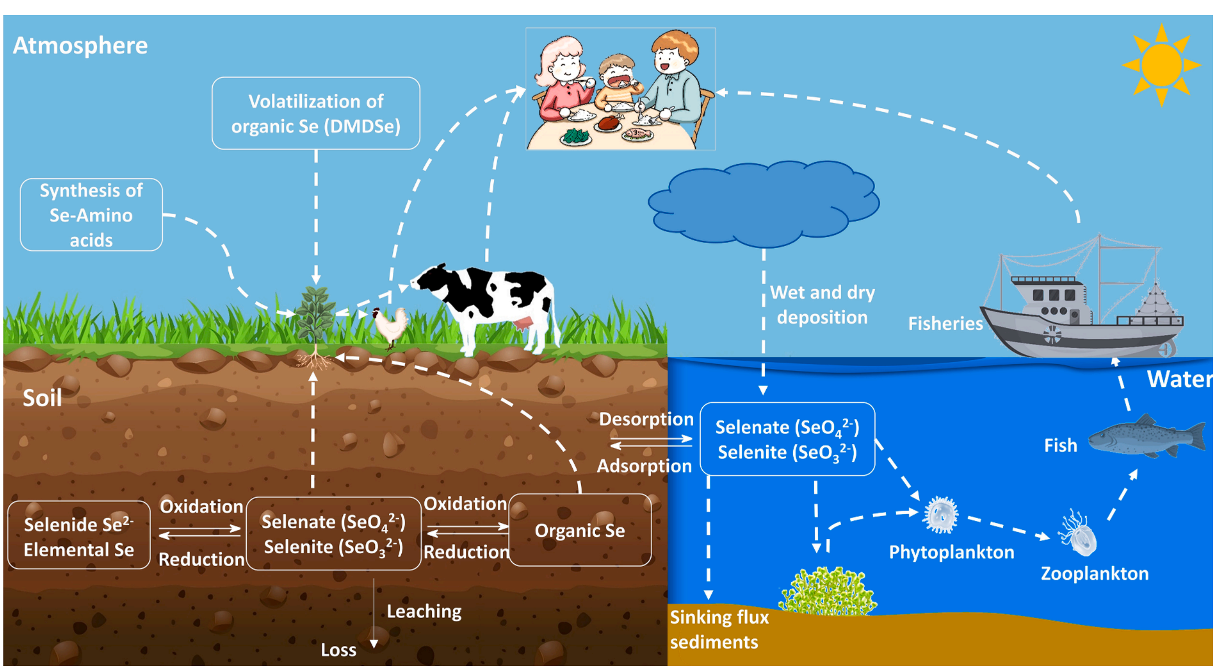


**Fig. 1.** General transport pathways of Se in terrestrial and aquatic environments.

the Se content in soil is excessive, remediation of Se content needs to be considered before growing crops. However, several steps have been taken in recent years to remediate Se content at several sites in these countries (Rajendran et al., 2022; D. Wang, Rensing, & Zheng, 2022). Therefore, it is extremely important to regularly analyze the Se content in the soil.

In soil, the bioavailability of Se and its species have a significant impact on the transport of Se from soil to plant (Jones et al., 2017). Well-drained alkaline soils are rich in bioavailable selenates that can be readily taken up by plants. In acidic environments and poorly drained soils, it usually occurs as unavailable selenides and may be found in its elemental form. It is unlikely that selenium is an essential component for plants, although some plants can accumulate selenium and convert it into biologically active compounds (Bodnar et al., 2012). Based on this, plants can be divided into three categories based on their ability to accumulate Se: Se non-accumulators, Se accumulators, and Se hyper-accumulators (White, 2016). Certain plant species are resistant to Se and accumulate large amounts of Se (Se-accumulators > 100 Se mg $kg^{-1}$ dry weight), whereas most plants do not accumulate Se and are sensitive to it (Se-non-accumulators < 100 Se mg $kg^{-1}$ dry weight) (Pilon-Smits, Winkel, & Lin, 2017; Reilly, 2006; White, 2016). Selenium hyper-accumulators can accumulate Se concentrations of > 1000–15,000 Se mg $kg^{-1}$ dry weight in some plant species (White, 2016). The study by White et al. provides data on Se concentrations in angiosperm species (flowering plants) designated as Se (hyper)accumulators, i.e., species in which plants with shoot Se content >1000 Se mg $kg^{-1}$ dry weight were sampled from a natural environment (White, 2016). In the food chain, humans consuming edible plant species and animals (dairy products, meat) with high selenium contents are poisoned by biomagnification.

## 4. Seleno Species: Uncovering their presence and importance in food for human health

Once selenium in inorganic form is absorbed by an organism, it is converted into an organic or biological form of selenium. However, it is also worth noting that inorganic species such as selenate (VI), and selenite (IV) are present in food (VI) and are not converted to organic forms during the metabolism process (Thiry, Ruttens, De Temmerman, Schneider, & Pussemier, 2012). Such organic compounds are mainly in the form of selenomethionine (SeMet) in plants and selenocysteine (SeCys) in animals (Khanam & Platel, 2016). In addition, selenoneine is an important compound found in livestock (pork and chicken) and fish (tuna, mackerel, squid, and tilapia) (Alhasan, Nasim, Jacob, & Gaucher, 2019; Rayman, 2012).

However, Se metabolism in the plant system differs due to the nature of the accumulation capacity of plants and changes in the formation lineage of the organic forms (Saha, Fayiga, & Sonon, 2017). Water-soluble non-protein compounds such as selenomethylselenocysteine (SeMeSeCys) are present in the majority of accumulator plants (Jacques, 2012; Muleya et al., 2021). It is noteworthy that plants with high Se accumulation produce SeMeSeCys to protect against seleno toxicity, but this is beneficial to animals and presumably to humans as it reduces tumors (Whanger, 2002). However, the nature of Se metabolism in animals differs from that in plants. Selenoproteins are formed from the amino acid residue (SeCys), which is the major form of Se in the cell (Zhu, Pilon-Smits, Zhao, Williams, & Meharg, 2009).

## 5. Importance of QA/QC in the validation of a method for selenium in food and from the surrounding environmental matrix

Quality assurance (QA) of ingredient analysis is of paramount importance for accurate food quality assessment. Food is the main source of macro, micro, and trace elements that may have toxic, nutritional, or other biologically important functions for humans. The safety and quality of food depend on the concentration of these elements. For this reason, the allowable levels of toxic or potentially toxic elements in foods must be regulated. Reliability is therefore critical for compliance verification. In laboratories dealing with food analysis, a proper quality control system must be implemented to obtain reliable and accurate data. Quality control (QC) of food analyses can be addressed through the intentional use of certified reference materials (CRMs). Certified reference materials are useful in the quality assessment system, for example, to ensure product quality and metrological traceability, validate analytical measurement methods or calibrate instruments (Padariya et al., 2021).

Certified reference materials are considered as expenisve products. The significant cost impact occurs during material production, certification, and storage. Therefore, it is important to consider the approach to the production and certification of CRMs for defining the price as following (Venelinov & Quevauviller, 2003):

- Preliminary study (research and development of material);
- Production and certification of candidate CRM (results of preliminary study);
- Certification of CRMs (market introduction);
- Storage of CRM, stability testing, and production and certication of a replacement batch (financed by sales revenue).

The price of the actual CRM also depends on which material is certified for which analytes (organic or inorganic analytes). Usually CRMs certified for organic species are more expensive (e.g., for seleno species) due to the high maintenance costs during the storage period under cool conditions, which increases the price of CRMs and also the expensive shipping of such a material. This can make it difficult for laboratories in developing countries to acquire them. However, experts are discussing about the use of laboratory reference materials (LRMs), which can be used for routine analyses and are less costly than CRMs or measurements with significant economic and environmental impact. It is questionable whether there is a well-established network for monitoring compliance with the minimum quality requirements for produced material (LRM) (Venelinov & Quevauviller, 2003).

In the past decades, there has always been sensational research works on the determination of Se and its species in different environmental matrices and different research fields such as biomedicine, environmental, food and nutritional science (Chen, Zhao, & Zhang, 2021; Méplan & Hughes, 2020; Sakr, Korany, & Katti, 2018; Z. Wang, Wang, Gomes, & Gomes, 2022). The attention of reference materials manufacturers (RMPs) is focused on meeting the needs of analytical laboratories with the preparation of suitable CRMs in different matrices. One type of material widely available in the commercial market is certified for total Se concentration in different matrices and some for their speciation (in food matrices). Concerning Se, food quality monitoring is a top priority due to the presence of Se in foods of various origins and is recommended. As the research is moved more towards selenium speciation, it might be more attention drawing for RMPs to produce the CRMs that are certified for selenium speciation in food products other than total Se content. Selenium species CRMs are in demand for routine determination of organic Se compounds in food laboratories as a QA/QC tool. According to ISO Guide 35:2017, it is usually necessary to provide an interval that includes a large fraction of the values that could reasonably be attributed to the property being certified (Standardization, 2017). It is a simpler approach to apply the standard deviation of the mean and characterize using interlaboratory comparison. In contrast, when compared to the interlaboratory calculation, uncertainty may have higher values (Olivares, Souza, Nogueira, Toledo, & Marcki, 2018).

The screening of available CRMs for seleno compounds has been done using the proposed COMAR database, EVISA database, and individual producer's websites (COMAR Database, n.d.; EVISA Database, n.d.). The availability of CRMs is distributed according to the certification of total selenium content for the matrix, as shown in Fig. 2. Two of the

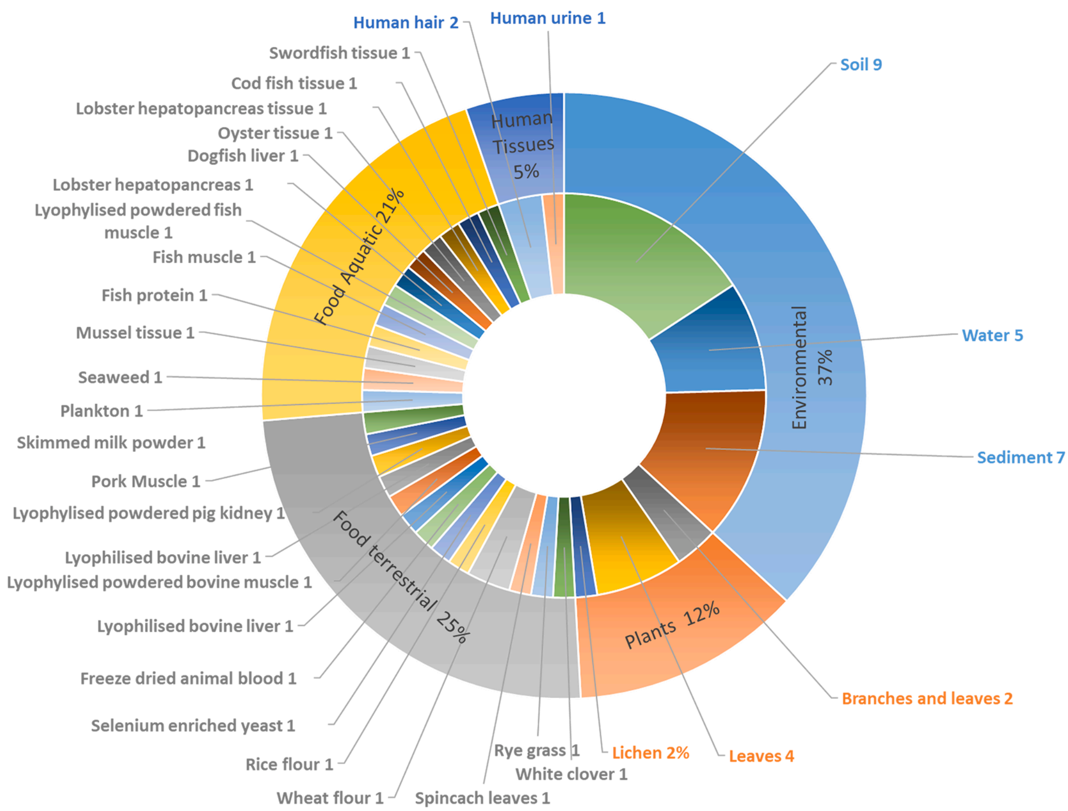


**Fig. 2.** Certified CRMs for total selenium content and selenium species (marked in red color). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

CRM manufacturers (LGC Limited (ERM-BC210) and NRC (SELM-1)) produced only two CRMs certified for organo-compounds (SeMet) as well as with total selenium content, as shown in Fig. 2.

## 6. The availability of CRMs certified for total Se and its species in various matrix materials

Links from different levels of the food chain play an important role in determining the path of nutrients and other substances through ecosystems and where various substances can be stored. The cycling of Se begins in the soil with the terrestrial food chain and continues in plants and animals. In contrast, Se is transported from water and sediments through primary producers to consumers in the aquatic food chain. Humans consume plant and animal foods containing Se as primary consumers (vegans) or quaternary consumers (carnivores), depending on their diet.

The trend is constant in the production of certified CRMs for total Se in various environmental matrices and foods, but not for seleno species as shown in Table 1. The possibility of expanding some CRMs to include Se species would preferably open new avenues for the validation of methods used in food and analytical laboratories. Despite the relatively wide range of CRMs with matrices associated with aquatic and terrestrial environments and certified for total selenium, only a few are mentioned for organoselenium compounds. There is an increasing demand for CRMs characterized by a complex matrix composition and a certified content of one selenium species (SeMet). While considering CRMs availability throughout the ecological food chain, environmental matrices must also be considered. These matrices include soils, sediments (rivers, lakes, estuaries, offshore and marine areas), water (rivers, coastal waters, drinking water, wastewater), and living organisms. Presented CRMs are intended to be used in the development, validate analytical methods, and assure quality control of analytical methods for the determination of total Se and SeMet in materials of a similar matrix.

### 6.1. *Environmental matrix certified reference materials for accurate selenium analysis: Enhancing precision in environmental monitoring*

Twenty one CRMs available as certified reference materials suitable for environmental purposes; however, 7 of the CRMs are materials made from plant parts (leaves and twigs), which are also considered environmental matrices because they are not edible. Commission Directive 2009/90/CE provides the legal basis for the implementation of analytical methods and gives technical specifications for chemical monitoring (European Commission, 2009). Based on the requirements of this directive, the application of internal and external quality control measures, such as the use of blank samples, standards, (certified) reference materials, or regular participation in laboratory comparisons, is strongly recommended.

The quality and comparability of analytical results obtained by laboratories entrusted by the competent authorities of the Member States with the chemical monitoring of sediments and biota under Directive 2014/101/EU amending Directive 2000/60/EC should be ensured (Commission of the European Communities, 2014). The European Environment Agency has been implementing the Thematic Strategy for Soil in Europe since 2006, which identifies trace metal pollution as one of the main threats to soil (European Commission, 2006). However, the new EU Soil Strategy for 2030 sets out a framework and considers measures to protect and restore soils and ensure their sustainable use (European Commission, 2021). It aims to improve soil quality from 2030 to 2050. The EU Soil Strategy 2030 replaces the previous Soil Protection Strategy from 2006.

The objectives of existing legislation relevant to soil protection are mostly pursued as a result of achieving environmental goals and are not so focused on soil, such as reducing pollution, offsetting greenhouse gas emissions, and preventing other environmental hazards, and the following directives are important to be implemented: Regulation (EU) 2019/1010 amending Directive 2004/35/EC) (The European

**Table 1**
Available CRMs certified for their total Se content in various matrices for environmental analysis purposes. Two of CRMs wheat flour (ERM-BC210) and Se-enriched yeast (SELM-1) are additionally certified with SeMet.

| Producers | Matrix | CRM name | Certified value with standard deviation or uncertainty* | Physical parameters | Certification date* / Revision date* / Validity date* | References |
|---|---|---|---|---|---|---|
| **Environmental** | | | | | | |
| NCRM | Soil | GBW 07411 | (0.51 ± 0.13 SD) ug/g | | Feb. 1991<br>Unknown<br>Feb. 2016 | (GBW 07411, 1993) |
| NRRC | Soil | GBW 07419 | (0.14 ± 0.04 SD) ug/g | | 1997<br>Unknown<br>Unknown | (GBW 07418 - GBW 07422, 1997) |
| NRRC | Soil | GBW 07420 | (0.11 ± 0.06 SD) ug/g | | 1997<br>Unknown<br>Unknown | (GBW 07418 - GBW 07422, 1997) |
| LGC Limited | Soil | ERM-CC135a | (0.9 ± 0.3) mg/kg | | Sept. 1997<br>Mar. 2007<br>Unknown | (ERM-CC135a, 2003) |
| JSAC | Contaminated soil | JSAC 0462 | (71.6 ± 2.1) mg/kg | | Jul. 2007<br>Unknown<br>Unknown | (JSAC 0461 - JSAC 0466, 2007) |
| JSAC | Contaminated soil | JSAC 0463 | (141.5 ± 3.6) mg/kg | | Jul. 2007<br>Unknown<br>Unknown | (JSAC 0461 - JSAC 0466, 2007) |
| JSAC | Contaminated soil | JSAC 0464 | (291.9 ± 5.8) mg/kg | | Jul. 2007<br>Unknown<br>Unknown | (JSAC 0461 - JSAC 0466, 2007) |
| JSAC | Contaminated soil | JSAC 0465 | (587 ± 13) mg/kg | | Jul. 2007<br>Unknown<br>Unknown | (JSAC 0461 - JSAC 0466, 2007) |
| JSAC | Contaminated soil | JSAC 0466 | (1175 ± 26) mg/kg | | Jul. 2007<br>Unknown<br>Unknown | (JSAC 0461 - JSAC 0466, 2007) |
| NMIJ, AIST | River water | NMIJ CRM 7202-b | (1 ± 0.06) ug/kg | pH – 1.3 Density – 1.000 g/cm$^3$ Temperature - (25℃) | Aril 2011<br>Unknown<br>2019 | (NMIJ CRM 7202-b, 2011) |
| JSAC | River water | JSAC 0302–3 | (5 ± 0.2) ug/L | | Jul. 2008<br>Unknown<br>Unknown | (JSAC 0302-3, 2008) |
| NMIs | Acidified coastal sea water | NMIA MX014 | (3.17 ± 0.28 ug/L) | Density 1.0339 ± 0.0016 kg/L | Mar. 2014<br>Unknown<br>Oct. 2017 | (NMIA MX014, 2014) |
| LGC Limited | Hard drinking water | ERM-CA011c | (11.13 ± 0.47) ug/L | pH < 2 Density – 0.999054 g/cm$^3$ | Nov. 2015<br>Nov. 2018<br>Unknown | (ERM-CA011c, 2015) |
| LGC Limited | Hard drinking water | LGC6026 | (10.19 ± 0.59) ug/L | pH < 2 Density – 0.999054 g/cm$^3$ | Feb. 2020<br>Jun. 2022<br>12 months from date of shipment | (LGC6026, 2011) |
| JRC | Wastewater | ERM-CA713 | (4.9 ± 1.1) ug/L | pH – 1.6 | Apr. 2013<br>Unknown<br>Unknown | (ERM-CA713, 2013) |
| LGC Limited | River sediment | LGC6187 | (1.2 ± 0.2) mg/kg | | Jun. 2000<br>Mar. 2009<br>12 months from date of shipment) | (LGC6187, 2000) |
| IEC | River sediment | GBW 08301 | (0.39 ± 0.1) ug/g | | 1986<br>Unknown<br>Unknown | (GBW 08301, 1986) |
| NMIJ, AIST | Lake sediment | NMIJ CRM 7303-a | (0.24 ± 0.04) mg/kg | | Mar. 2002<br>Unknown<br>Mar. 2021 | (NMIJ CRM 7303-a, 2002) |
| NIST | Estuarine sediment | SRM 1646a | (0.193 ± 0.028) mg/kg | | Jan. 1995<br>May 1998<br>Sep. 1998<br>Feb. 2004<br>Unknown | (SRM 1646a, 2004) |
| NRC | Marine sediment | HISS-1 | (0.050 ± 0.007) mg/kg | | Feb. 1997<br>Oct. 2014<br>Dec. 2019 | (HISS-1, 2019) |
| SMI | Offshore marine sediment | GBW 07314 | (0.16 ± 0.04) ug/g | | 1994<br>Unknown<br>Unknown | (GBW 07314, 1994) |

(continued on next page)

**Table 1** (*continued*)

| Producers | Matrix | CRM name | Certified value with standard deviation or uncertainty* | Physical parameters | Certification date* / Revision date* / Validity date* | References |
|---|---|---|---|---|---|---|
| NMIJ, AIST | Marine sediment | NMIJ CRM 7302-a | (0.61 ± 0.07) mg/kg | | Mar. 2002<br>Nov. 2010<br>Mar. 2021 | (NMIJ CRM 7302-a, 2002) |
| **Plants (branches and leaves)** | | | | | | |
| IGGE | Bush branches and leaves | GBW 07602 | (0.184 ± 0.013) ug/g | | 1991<br>Unknown<br>Unknown | (GBW 07601-GBW 07605, 1991) |
| IGGE | Bush branches and leaves | GBW 07603 | (0.12 ± 0.02) ug/g | | 1991<br>Unknown<br>Unknown | (GBW 07601-GBW 07605, 1991) |
| IGGE | Poplar leaves | GBW 07604 | (0.14 ± 0.02) ug/g | | 1991<br>Unknown<br>Unknown | (GBW 07601-GBW 07605, 1991) |
| NIST | Apple leaves | SRM 1515 | (0.050 ± 0.009) ug/g | | Jan. 2019<br>Unknown<br>Mar. 2027 | (SRM 1515, 2022) |
| NIST | Peach leaves | SRM 1547 | (0.120 ± 0.017) ug/g | | Apr. 2019<br>Nov. 2022<br>Mar. 2027 | (SRM 1547, 2022) |
| NIST | Tomato leaves | SRM 1573a | (0.054 ± 0.003) mg/kg | | Aug. 2018<br>Unknown<br>Aug. 2027 | (SRM 1573a, 2018) |
| IAEA | Lichen | IAEA-336 | (0.22 ± (0.18–0.26) 95% Confidence interval) mg/kg | | Jun. 1999<br>Oct. 1994<br>Unknown | (IAEA-336, 1999) |
| **Food (terrestrial)** | | | | | | |
| JRC | White clover | BCR-402 | (6.70 ± 0.25) mg/kg | | Nov. 1991<br>May 2007<br>12 months from date of shipment | (BCR-402, 1991) |
| JRC | Rye grass | ERM-CD281 | (0.023 ± 0.004) mg/kg | | May 2010<br>Unknown<br>12 months from date of shipment | (ERM-CD281, 2010) |
| NIST | Spinach leaves | SRM 1570a | (0.117 ± 0.009) mg/kg | | Feb. 2014<br>Unknown<br>Aug. 2023 | (SRM 1570a, 2014) |
| NIST | Wheat flour | SRM 1567b | (1.14 ± 0.10) mg/kg | | Mar. 2014<br>Unknown<br>Nov. 2023 | (SRM 1567b, 2014) |
| NIST | Rice flour | SRM 1568b | (0.365 ± 0.029) mg/kg | | Jun. 2013<br>Unknown<br>Jun. 2025 | (SRM 1568b, 2013) |
| LGC Limited | Wheat flour | ERM-BC210 | (17.23 ± 0.91) mg/kg<br>**Selenomethionine** (27.4 ± 2.6) mg/kg | | Jun. 2011<br>Apr. 2018<br>12 months from date of shipment | (ERM-BC210, 2011) |
| NRC | Selenium enriched yeast | SELM-1 | (2059 ± 64) mg/kg<br>**Selenomethionine**<br>(3448 ± 146) mg/kg | | Jun. 2005<br>Dec. 2006<br>May 2010<br>May 2015 | (SELM-1, 2005) |
| IAEA | Freeze dried animal blood | IAEA-A-13 | (0.24 ± (0.15–0.31) 95% Confiedence interval) mg/kg | | Jan. 2000<br>Unknown<br>Unknown | (IAEA-A-13, 2000) |
| JRC | Lyophilised bovine liver | BCR-185R | (1.68 ± 0.14) mg/kg | | Nov. 1998<br>Sep. 2013<br>12 months from date of shipment | (BCR-185R, 1998) |
| JRC | Lyophilised powdered bovine muscle | ERM-BB184 | (0.45 ± 0.04) mg/kg | | Aug. 2012<br>Sep. 2013<br>12 months from date of shipment | (ERM-BB184, 2012) |
| JRC | Lyophilised bovine liver | ERM-BB185 | (2.99 ± 0.18) mg/kg | | Dec. 2018<br>Mar. 2019<br>12 months from date of shipment | (ERM-BB185, 2019) |
| JRC | Lyophilised powdered pig kidney | ERM-BB186 | (10.3 ± 0.9) mg/kg | | Aug. 2012<br>Oct. 2013<br>12 months from date of shipment | (ERM-BB186, 2012) |
| SINR | Pork muscle | GBW 08552 | (0.049 ± 0.05) ug/g | | 1995<br>Unknown | (GBW 08552, 1995) |

(*continued on next page*)

**Table 1** (*continued*)

| Producers | Matrix | CRM name | Certified value with standard deviation or uncertainty* | Physical parameters | Certification date*<br>Revision date*<br>Validity date* | References |
|---|---|---|---|---|---|---|
| | | | | | Unknown | |
| JRC | Skimmed milk powder | ERM-BD150 | (0.188 ± 0.014) mg/kg | | Aug. 2013<br>Jan. 2017<br>12 months from date of shipment | (ERM-BD150 and ERM-BD151, 2013) |
| JRC | Skimmed milk powder | ERM-BD151 | (0.19 ± 0.04) mg/kg | | Aug. 2013<br>Jan. 2017<br>12 months from date of shipment | (ERM-BD150 and ERM-BD151, 2013) |
| **Food (aquatic)** | | | | | | |
| JRC | Plankton | BCR-414 | (1.75 ± 0.10) mg/kg | | Mar. 1992<br>Jun. 2017<br>12 months from date of shipment | (BCR-414, 2017) |
| JRC | Seaweed | ERM-CD200 | (0.088 ± 0.010) mg/kg | | Jan. 2014<br>Unknown<br>12 months from date of shipment | (ERM-CD200, 2013) |
| JRC | Mussel tissue | ERM-CE278k | (1.62 ± 0.12) mg/kg | | Oct. 2012<br>Oct. 2013<br>12 months from date of shipment | (ERM-CE278k, 2012) |
| NRC | Fish protein | DORM-4 | (3.56 ± 0.34) mg/kg | | Jun. 2012<br>Unknown<br>Jun. 2022 | (DORM-4, 2012) |
| JRC | Fish muscle | ERM-CE101 | (0.113 ± 0.011) mg/kg | | Mar. 2019<br>Unknown<br>12 months from date of shipment | (ERM-CE101, 2019) |
| JRC | Lyophylised powdered fish muscle | ERM-BB422 | (1.33 ± 0.13) mg/kg | | Aug. 2012<br>Oct. 2013<br>12 months from date of shipment | (ERM-BB422, 2012) |
| NRC | Lobster hepatopancreas | TORT-3 | (10.9 ± 1.0) mg/kg | | Apr. 2013<br>Unknown<br>Apr. 2023 | (TORT-3, 2013) |
| NRC | Dogfish liver | DOLT-5 | (8.3 ± 1.8) mg/kg | | Aug. 2014<br>Unknown<br>Aug. 2019 | (DOLT-5, 2014) |
| NIST | Oyster tissue | SRM 1566b | (2.06 ± 0.15) mg/kg | | Aug. 2019<br>Unknown<br>Jun. 2030 | (SRM 1566b, 2019) |
| NRC | lobster hepatopancreas tissue | LUTS-1 | (0.641 ± 0.054) mg/kg | | Jun. 1989<br>Aug. 1995<br>Jan. 2005<br>Nov. 2013<br>Dec. 2017 | (LUTS-1, 2013) |
| NMIJ, AIST | Cod fish tissue | NMIJ CRM 7402 –a | (1.8 ± 0.2) mg/kg | | Aug. 2009<br>Mar. 2010<br>Mar. 2016 | (NMIJ CRM 7402-a, 2009) |
| NMIJ, AIST | Swordfish tissue | NMIJ CRM 7403-a | (2.14 ± 0.11) mg/kg | | Aug. 2009<br>Unknown<br>Mar. 2019 | (NMIJ CRM 7403-a, 2009) |
| **Human tissues** | | | | | | |
| JRC | Human hair | ERM-DB001 | (3.24 ± 0.24) mg/kg | | May 2013<br>Unknown<br>Unknown | (ERM-DB001, 2013) |
| NIES | Human hair | NIES No.13 | (3.24 ± 0.24) mg/kg | | Jan. 1996<br>May 2016<br>Apr. 2021<br>Unknown | (NIES No.13, 1996) |
| NIES | Human urine | NIES No.18 | (0.059 ± 0.005) mg/L | | Jun. 2000<br>Unknown<br>Unknown | (NIES No.18, 2000) |

* Certified values are presented as same as certificates. Moreover, the certified date, revision date, and expired date are collected from certificates. The lack of some data information can be related to revision and expiration date. Some of the CRMs producers like JRC has provided the expiring date as "12 months from date of shipment" as they are probably monitoring the stability of materials every year.

Parliament and the Council of the European Union, 2019), Industrial Emissions Directive (Industrial Emissions Directive 2010/75/EU) (The European Parliament and the Council of the European Union, 2011), Environmental Impact Assessment Directive (EIA Directive (85/337/EEC)) (The European Parliament and the Council of the European Union, 2014), Sewage Sludge Directive (86/278/EEC) in force since 1986 (The European Parliament and the Council of the European Union, 2022), Fertilizer Regulation (Regulation (EU) 2019/1009) (The European Parliament and the Council of the Eurpean Union, 2019), Mercury Regulation (Regulation (EU) 2017/852) (The European Parliament and the Council of the Eurpean Union, 2017), Regulation on land use, land use change and forestry (Regulation (EU) 2018/841) (The European Parliament and the Council of the Eurpean Union, 2018), Common Agricultural Policy (CAP) (European Commission, 2022). According to Regulation (EU) 2019/1010, the soil must be protected because the inclusion of contaminants in food and feed plants may have an impact on the quality of products that are freely traded in the internal market and pose a risk to human and animal health (The European Parliament and the Council of the European Union, 2019).

The availability of soil CRMs would potentially be helpful to laboratories meeting regulatory limits for Se concerning the above guidelines. Three major producers of soil matrix CRMs are NRCCRM, LGC-limited, and JSAC. The National Research Centre for Certified Reference Materials, Office of CRM (NRCCRM), has produced three CRMs for soils certified for total selenium content (GBW 07411, GBW 07419, GBW 07420) (GBW 07411, 1993; GBW 07418 - GBW 07422, 1997). This representative set of soil material standards was introduced to meet the needs of soil geochemical testing for agricultural and environmental research, to accurately determine the content of all elements in soil, and to improve analytical quality.

ERM - CC135a is the soil CRM produced by LGC-limited. Originally, the European Reference Material ERM - CC135a was certified as LGC6135 Batch 001 in September 1997 (ERM-CC135a, 2003). LGC was responsible for its production and certification of the material under the technical guidelines for European Reference Materials. Stability tests were performed and the certificate was revised in 2007. In the absence of suitable reference materials, the material may also be used for other matrices.

JSAC produced the CRMs of contaminated soil (brown forest soil) JSAC 0461-0466 in a set of 6 levels (JSAC 0461 - JSAC 0466, 2007). However, JSAC 0462-0466 are fortified with selenium and the target concentration of JSAC 0466 was achieved at the highest concentration of 1200 mg $kg^{-1}$ for Se.

Soil and water (surface water and groundwater) are closely interconnected. Surface water and groundwater bodies are affected as soon as the soil is contaminated. The extensive EU water legislation helps in the management and is an expression of the global concept of "integrated water resources management". Since 2001, a common implementation strategy has been in place to implement the Water Framework Directive (WFD) (Commission of the European Communities, 2014). The Water Framework Directive applies to inland, transitional, and coastal surface waters and groundwater. However, coastal and marine waters are covered by the Marine Strategy Framework Directive. Both the Water Framework Directive and the Marine Strategy Framework Directive include trace metals and their compounds in an indicative list of major pollutants (The European Commission, 2017). As for the aquatic environment, the selenium content in the aquatic environment is low compared to the other environmental components. According to the guidelines, it is important to have control material that complies with the prescribed limits.

The CRM producers (NMIJ, AIST, NMIS, LGC limited, JRC, IEC, NIST, NRC, and SMI) produce CRMs from aquatic matrices. For water matrix CRMs, spiking is required because selenium is present in low concentrations. In addition, the water CRMs present are treated with nitric acid as a preservative for the metals. Water samples are in a chemically dynamic state, and chemical, biological, and/or physical processes that alter their composition can begin the moment they are taken from the sample site. The concentration of analytes can be altered by effects such as volatilization, sorption, diffusion, precipitation, hydrolysis, oxidation, and photochemical and microbiological processes.

Water samples are generally preserved or stabilized by acidification with nitric acid ($HNO_3$) for common metals. Inorganic analytes may also form precipitating salts. If the sample is not properly prepared, these precipitates will stick to the sides of the collection bottle and prevent proper analysis. Most commonly, the precipitation of metal oxides and hydroxides occurs as a result of the reaction of metal ions with oxygen. The addition of nitric acid prevents this precipitation; the combination of a low pH $< 2$ and nitrate ions keeps most metal ions in the solution. Because CRMs have a longer shelf life, their storage time is also extended. Therefore, it is important to consider the preservation of analytes by the manufacturers of RM while following procedures for the preparation of CRMs.

NMIJ CRM 7202-b, this material (natural river water) was produced according to the NMIJ management system in compliance with ISO Guide 34:2000 and ISO /IEC 17025:2005 (NMIJ CRM 7202-b, 2011). This material was prepared by adding nitric acid and an appropriate amount of Se solutions to the natural river water.

The JSAC produced JSAC 0302-3 from river water (Doshi River) (JSAC 0302-3, 2008). Nitric acid and Se standard solution were added to the river water because it is present only in small amounts. This reference material is suitable for the analysis of the presented inorganic components, including Se in river water or water with a similar matrix, and the analytical values obtained by parallel analysis of this material are compared with the certified values. NMIA MX014 is a certified reference material that is acidified coastal seawater bottled in 120 ml units from the coast of Curl Beach, Sydney, Australia. A certified value for the mass fraction and mass concentration of Se is provided.

ERM-CA011c is a CRM prepared from hard drinking water from the Tamworth (Staffordshire, UK) drinking water network (ERM-CA011c, 2015). If more definitive reference materials are not available, the material may apply to other similar matrices. Participants in the interlaboratory study were asked to measure other elemental contents, including selenium. Using a measured density of 997.98 kg $m^{-3}$, the IDMS value, determined as a mass fraction, was converted to mass/volume. However, LGC produced an LGC6026 whose material source is ERM-CA011c, which complies with the limits of the European Drinking Water Directive and the UK Water Supply (Water Quality) Regulations 2016 and is also certified for total selenium, although the certified value differs slightly from ERM-CA011c (LGC6026, 2011).

ERM-CA713, which was produced by the IRMM (ERM-CA713, 2013). It is intended to be used as a quality assurance and quality control tool, particularly by laboratories responsible for mandatory monitoring under the Water Framework Directive (WFD). ERM-CA713 was substituted for three wastewater-based reference materials: BCR-713, BCR-714, and BCR-715 due to legislative changes. ERM-CA713 is not representative of all wastewater, according to the IRMM. The targeted concentration values were based on the certified values of the BCR-713 material and the environmental quality standards specified in legislation 6.

Aquatic ecosystems often face pollution problems that can be uncontrolled and dynamic (Padariya et al., 2021). As part of the aquatic environment, sediment aggregates a large number of trace substances thanks to sediment flux. Therefore, it is important to consider sediment chemical monitoring guidelines. One of these guidelines is the Guidance Document for Chemical Monitoring of Sediments and Biota under the Water Framework Directive (Guidance Document No. 25) (Commission of the European Communities, 2000). The main objective of the WFD is to achieve good chemical status for all water bodies, which are highly dependent on the matrix for specific substances. Therefore, sediment is a recommended matrix for assessing the chemical status of some metals in marine and lentic bodies. Selenium is not included in the list of priority substances in Directive 2013/39/EU for trend monitoring of sediments and biota (The European Parliament and the Council of the European Union, 2013). However, it has been found that high levels can accumulate in sediments (Lino, Kasper, Carvalho, Guida, & Malm, 2020). Therefore, monitoring of selenium in sediments is also advocated to comply with regulatory limits.

LGC6187 is a river sediment material recovered from a lagoon at a monitoring station on the Elbe River near the Czech-German border (LGC6187, 2000). GBW 08301, A CRM is intended for use in the calibration of equipment and methods used in the analysis of fluvial sediments and other materials with trace element matrices similar to those of fluvial sediments (GBW 08301, 1986). This certified reference material was obtained from the Xiangjing River in Hunan Province, China.

The NMIJ CRM 7303-a was prepared and processed from natural lake sediment (near an industrial area in Japan) according to ISO Guide 34:2000 using NMIJ's management system (NMIJ CRM 7303-a, 2002). This CRM can be used in the analysis of trace elements in sediments or similar matrices to control the precision of analysis or to check the validity of analytical methods or equipment. This CRM is certified for 14 elements, including Se. They are expressed in mass fractions after being corrected to dry mass.

The NIST introduced SRM 1646a that is intended to be used as calibration of instruments and to assess the reliability of analytical methods for determining major, minor, and trace elements (including Se) in estuarine sediments and similar matrices (SRM 1646a, 2004). The material for this SRM was collected from the Chesapeake Bay under the supervision of M. Unger, Virginia Institute of Marine Sciences, Gloucester Point, VA. HISS-1 is produced by NRC and prepared from marine sediments collected from the Hibernia shelf off the coast of Newfoundland (HISS-1, 2019). HISS-1 is primarily intended for the calibration of procedures and development of methods for determining trace and matrix constituents in marine sediments and materials of a similar matrix. Second Marine Institute of the NMB Office of CRMs. GBW 07314 is prepared from offshore marine sediments and is used for analytical quality control of marine surveys and monitoring, verification, and evaluation of the accuracy of analytical methods, and calibration of analytical instruments (GBW 07314, 1994). The reference material can be used to measure the value transfer. The NMIJ CRM 7302-a was prepared from natural marine sediments (bay near an industrial area (NMIJ CRM 7302-a, 2002). This certified reference material (CRM) was prepared using the NMIJ management system and ISO Guide 34:2000.

The European Food Safety Authority (EFSA) ensures the safety of food and feed in the EU (European Parliament and Council, 2019). However, it is important to understand the contamination in plant parts (leaves and shrubs) and trees (leaves and branches of shrubs), which provide information about the contamination with contaminants as they would be distributed in the plant system and the food produced from it after uptake from the soil.

The three plant CRMs (GBW07602-GBW07604) are mainly used in regional environmental geochemistry and exploration geochemistry, as well as in agriculture, forestry, and medicine for chemical analysis as calibration samples and measurement quality monitoring samples. GBW07602 is prepared from twigs and leaves of a bush as a composite sample from the Dachaidan district. GBW 07603 is a composite of bush twigs and leaves from the lead–zinc mining area of Xitieshan, Qinghai Province. GBW 07604 is made from poplar leaves collected in Beijing and Langfang, Hebei Province (GBW 07601-GBW 07605, 1991).

The NIST SRM 1515 was prepared from plant material (apple leaves of Golden Delicious and Rome varieties) under the direction of C.B. Smith, University of Agriculture, The Pennsylvania State University, University Park, PA (SRM 1515, 2022). SRM 1547, the plant material for this SRM was collected and prepared under the direction of R.A. Isaac, Laboratory for Soil Testing & Plant Analysis, The University of Georgia University of Agriculture (SRM 1547, 2022). Leaves of healthy Georgia peach trees, cultivar 'Coronet', were harvested from a Peach County field. Fungicide and insecticide sprays were controlled to minimize heavy metal contamination.

RM 1573a, this plant material was prepared from the mature tomato leaves of "count II" tomato plants grown at the Horticultural Research Farm in Rock Springs, PA (SRM 1573a, 2018). This CRM was prepared under the direction of C.B. Smith, University of Agriculture, The Pennsylvania State University, University Park, PA. IAEA-336 was prepared from the epiphytic lichen *Evernia prunastri (L.) Ach.* collected on trees of the species *Cistus ladanifer* and *Quercus* in Portugal (Gavião, Ourique, and Serra do Cladeirão) far from sources of pollution (IAEA-336, 1999). This sample will be used as reference material for the measurement of trace and trace elements in lichens.

### *6.2. Terrestrial food matrix certified reference materials for reliable selenium analysis: Ensuring quality and safety in selenium-rich food assessment*

The quality of feed has a significant impact on the quality of food derived from animals and thus on human health and is one of the working areas of EU legislation, such as Regulation (EC) No. 1881/2006 (The European Commission, 2019b), Regulation (EU) 2022/2418 (The European Commission, 2022a), and Regulation (EU) 2019/1869 (The European Commission, 2019a). Numerous elements are extremely important due to their nutritional or toxic properties (McDowell, 2003). Elements of high nutritional content include B, Cu, Cr, Mg, Mn, K, Ni, P, Se, Sn, and Zn. However, their role in nutrition is determined by their presence in animal feed. Too much of a nutrient can be toxic. The tolerance level of a nutrient depends on both the animal species and the composition of the nutrient in the feed. Many significant nutritional and biochemical interactions between feed components have been identified. For example, Cu metabolism is strongly related to Mo content, and the presence of vitamin E, and Se protects against metals such as Cd, Hg, As, and Pb. Knowledge of the nutrient content of feeds helps to develop a balanced diet for animals (McDowell, 2003).

Detection of elements such as Se is necessary to avoid adverse health effects in domestic animals. Failure to detect such elements may result in reduced production (economic loss) or adverse health effects on consumers of animal products (milk, meat, cheese, etc.). Some elements, such as Se, occur in the environment in greater amounts due to both natural and man-made activities. Since they can play an important role in the subsequent health of humans and animals, close and careful control of feed is necessary. Some elements, such as Se, need to be measured to monitor the environment and control pollution.

The determination of toxic elements is necessary to avoid damage to the health of animals, which could lead to reduced production or even pose a risk to the consumer of animal products, e.g., milk, meat, etc. As a result, numerous directives have been adopted by the Council of the European Communities (e.g. Commission Regulation (EC) No 152/2009 (The European Commission, 2022b). CRMs are needed to control the quality of determinations of various elements and consequently the quality of feed.

BCR-402, Colver, and grass for animal feed are routinely screened for nutrient-rich elements (e.g., Se) and potential toxicity (BCR-402, 1991). The need to determine whether these nutrients can be used to improve the health and growth of companion animals. Diets must be balanced, so staple foods often need to be supplemented with trace and major elements. The BCR of the Commission of the European Communities was requested to produce a series of CRMs for this purpose and to complete the series of plant materials, it was decided to produce white clover material for trace element quality control. This material (BCR 402) has been certified for Se of the highest interest. It was deliberately selected to have a high value for Se content. This material is not intended for use as a calibrant.

Preparation and Certification of Rye Grass (ERM-CD281) are carried out by the European Commission, Directorate General Joint Research Center, and Institute for Reference Materials and Measurements (ERM-CD281, 2010). This CRM replaces the withdrawal of BCR-281. The main purpose of the material is to evaluate the performance of methods, i.e., to verify the accuracy of analytical results. Like any reference material, it can also be used for control charts or validation studies. SRM 1570a was prepared from chopped frozen spinach supplied by the Oregon Freeze-Drying Corp. in Albany, OR (SRM 1570a, 2014). This standard reference material (SRM) is primarily intended to assess the dependability of analytical methods for determining trace elements, proximates, calories, and total dietary fiber in plant materials with a similar matrix. In 2013, the material left over from the production of SRM 1567a was recycled to produce SRM 1567b (SRM 1567b, 2014). SRM 1567b was prepared by blending and mixing wheat flour from hard red spring wheat and hard red winter wheat is grown primarily in South Dakota.

SRM 1568b was produced from residues from the production of SRM 1568a (SRM 1568b, 2013). SRM 1568b rice flour is produced from 100% Arkansas long grain river rice. This SRM can also be used to ensure quality when assigning values to internal reference materials. ERM-BC210 is one of the certified reference materials for total selenium and selenomethionine (ERM-BC210, 2011). Wheat flour doped with 76Se enriched selenomethionine was used as the material. This certified reference material is primarily used to validate methods for the determination of selenium and selenomethionine in foods and dietary supplements.

SELM-1 is the second certified reference material for selenium speciation prepared from a dry, commercial selenized yeast sample (yeast grown in Se-rich media) (SELM-1, 2005). This reference material is certified for total Se, selenomethionine, and methionine intended for instrument calibration and method evaluation for the determination of SeMet, Met, and total selenium in yeast or similar materials. This material is not intended for use for nutritional, medical, or diagnostic purposes.

Blood analysis is crucial for biological research. However, due to the complex composition of the sample matrix, it is extremely difficult, especially in the determination of trace elements in the low range. IAEA-A-13 is processed material from fresh bovine blood collected at a slaughterhouse and freeze-dried at Seibersdorf (IAEA-A-13, 2000).

Meat is an important part of the typical European diet. Therefore, great attention is paid not only to the nutritional benefits of meat and meat products but also to safety aspects, especially the presence of harmful organic and inorganic substances. In all EU countries, there is legislation setting out the minimum public health requirements for meat. In addition, the Commission has adopted a directive on the control of residues in fresh meat (Directive 83/90/ EEC OJ L59 26, March 5, 1983, and Commission Regulation (EC) 194/97, Jan. 31, 1997). This Commission Regulation is currently being amended to establish maximum levels for certain contaminants in food. Bovine liver CRM BCR-185R is one of three available meat reference materials produced by the JRC (BCR-185R, 1998). It was developed for the control of contaminants in the liver. CRM 184 bovine muscle, which has lower contaminant concentrations, and CRM 186 porcine kidney, which has even higher contaminant concentrations, are the other two reference materials (BCR-185R, 1998).

After BCR-185R, ERM-BB184 was prepared from bovine muscle from two healthy cattle slaughtered in Belgium and delivered to IRMM (ERM-BB184, 2012). Trace element mass fractions were determined in three different types of bovine muscle samples: Boot muscle, rib muscle of a fatty type, and leg muscle. The mass fractions for most elements were similar to those certified in BCR-184. Selenium content in all samples was about twice that in BCR-184.

CRM BCR-185R (elements in the bovine liver) was replaced with ERM-BB185 material and certified with the same elements (ERM-BB185, 2019). CRM was prepared from raw livers of slaughtered Belgian cattle. This material was produced according to ISO Guide 34:2009 and is certified according to ISO Guide 35:2006. It can be used like any other reference material to generate control charts and validation studies.

The developed ERM BB186 is replaced by a reference material to CRM BCR-186 (porcine kidney) (ERM-BB186, 2012). The starting material for ERM BB186 consisted of fresh pig kidneys from Belgium and the processed material was transported to IRMM. GBW 08552 was prepared from fresh pork loin collected from a slaughterhouse in Da Chang, Shanghai, China (GBW 08552, 1995).

Skim milk powder contains a matrix similar to that of many dairy products, the only difference being that it has been heated and dehydrated. Spray drying of milk produces a fine powder that is expected to be homogeneous within the sample holding range of current elemental analysis techniques. In addition, the powder is expected to remain stable at room temperature during the anticipated 10-year sales period of the reference materials. The spiking was performed to ensure that the impurity content is high enough to be measured accurately and to provide reference values with a manageable level of uncertainty for the control of quantitative measurement techniques.

Both CRMs (ERM-BD150, ERM-BD151) are replacements for BCR-150 and BCR-151 (skim milk powder) (ERM-BD150 and ERM-BD151, 2013). This project was conducted by IRMM to certify the mass fractions of trace elements with target levels at natural levels for Se and others spiked to two levels. The amount of spike added was determined to produce a material (ERM-BD150) with mass fractions of one-tenth of the permitted limits for food contaminants in milk and other foods (EC466/2001 and amendment 1881/2006) and the material ERM-BD151 with mass fractions close to the regulatory limit.

### *6.3. Aquatic food matrix certified reference materials for precise selenium analysis: Enhancing accuracy in selenium in aquatic food*

Analysis of phytoplankton and zooplankton is important to determine the role of these organisms in biogeochemical cycling and the transfer and uptake of toxic elements along the trophic chain. In addition, plankton can be used as an indicator of water pollution and to compare pollution levels in different water bodies. The determination of trace elements is difficult and prone to error.

BCR-414 is one of the CRMs where the laboratory of the Rural Resources, Water, and Ecosystems Unit of the JRC Institute for Environment and Sustainability (IES) conducted a series of measurements (BCR-414, 2017). The plankton material was collected in 1988 from several ponds near the Po River and later certified in 1992. The certificate was reviewed under the responsibility of the Joint Research Centre of the European Commission in 2017. These measurements should provide CRM users with more information about the matrix composition of this material.

The certified reference material ERM-CD200 was developed to meet the needs of laboratories performing environmental and food safety analyses (ERM-CD200, 2013). The material was produced following ISO Guide 34:2009. Although the European Water Framework Directive 2000/60/EC amended by Directive 2014/101/EU does not set limits for metal concentrations in algae, it recommends the use of (macro)algae as an indicator of water quality (Commission of the European Communities, 2006, 2014). The ERM-CD200 is primarily intended for testing the accuracy of trace element measurements in algae and similar matrices. Due to their higher uptake capacity compared to red and green algae, brown algae have proven to be an efficient class of biosorbents, especially for Cd, Cu, Zn, Pb, Cr, and Hg in water and wastewater.

*Fucus vesiculosus* and *Ascophillum nodosus* are increasingly used for environmental monitoring, especially for water quality control (Amer, Ostapczuk, & Emons, 1999). Some European countries (notably Finland, Sweden, Germany, and the United Kingdom) use macroalgae (especially *Fucus vesiculosus*) as marine bioindicators.

In addition, brown algae are used in the production of food, cosmetics, and pharmaceuticals due to their nutritional and therapeutic properties, which makes them interesting for analysts and scientists involved in monitoring the content of trace elements (Arora, Kumar, Bose, Li, & Kulshrestha, 2021). The material is intended for quality control or validation studies as well as method performance evaluation.

The CRM ERM-CE278k was a replacement for ERM-CE278 and was made from mussel tissue (*mytilus edulis*) (ERM-CE278k, 2012). The purpose of developing this CRM was to certify bulk fractions of trace elements with target levels at natural levels comparable to ERM-CE278 and below regulatory limits for food contaminants (EC466/2001 and amendment 1881/2006). This CRM is intended for quality control of trace element measurements. The material may be particularly useful for measurements made to support compliance with EC guidelines, such as the quality of drinking water sources (75/440/ CEE, 79/869/ CEE, 80/778/ CEE), groundwater (80/68/ CEE, 91/676/ CEE), or for the protection of fish (78/659/ CEE), as well as for food safety measurements (EC466/2001) (Commission of the European Communities, 2000). DORM-4, a CRM was prepared from a fish protein homogenate from NRC (DORM-4, 2012). This reference material is certified for mass fractions of 17 trace elements, including Se.

Chemical pollution of surface water is a threat to the aquatic environment, causing acute and chronic toxicity to aquatic organisms, accumulation in the ecosystem, loss of habitat and biodiversity, as well as a threat to human health. Directive 2014/101/EU of the European Parliament and of the Council of 30 Oct. 2014 establishing a framework for Community action in the field of water policy sets out a strategy to combat water pollution and requires additional specific pollution control measures and environmental quality standards (EQS) (Commission of the European Communities, 2014; The European Parliament and the Council of the Eurpean Union, 2013). Directive 2008/105/EC establishes environmental quality standards following the provisions and objectives of Directive 2000/60/EC (The European Parliament and the Council of the Eurpean Union, 2013). Member states are required to participate in it.

In addition, Directive 2009/90/ EC establishes technical specifications for chemical analysis and monitoring of water status in support of Directive 2000/60/ EC and recommends that methods be validated according to EN ISO /IEC 17025 (European Commission, 2009).

ERM-CE101 is a matrix material certified for mass fractions of elements (e.g., Se) (ERM-CE101, 2019). This material was produced following ISO Guide 34:2009 and is certified following ISO Guide 35:2006. The material was produced from the fresh muscle of brown trout (*Salmo trutta*) and Nile perch (*Lates niloticus*).

Concerns about the sustainability of the European cod fishery have increased since the preparation of BCR-422 began in Jan. 1989 with the capture of cod for raw material (ERM-BB422, 2012). Cod has been included in the International Union for Conservation of Nature (IUCN) "Red List" of endangered species. As the price of cod has increased and landed quantities have decreased, food manufacturers and consumers have sought other white-fleshed marine fish as cod substitutes. To replace BCR-422, which is no longer available, another fish was chosen as the raw material to produce the candidate CRM. Pollock (*Pollachius virens*, NL: koolvis, FR: lieu noir, DE: pollock/chum) was selected because its matrix and trace element content is similar to that of cod muscle. Pollock belongs to the Gadidae (cod-like fish) family, which also includes cod (*Gadus moruha*). The matrix composition of pollock was expected to be similar to that of cod based on the sample preparation methods used as part of the measurements that the CRM is designed to control.

A wholesaler in Belgium supplied fresh saithe fillets. The fish were caught in the North East Atlantic region of Europe (code FAO27) and further transported to IRMM. ERM-BB422 is certified for the contents (mass fractions) of 8 elements, including Se. TORT-3, this reference material was prepared using edible-grade lobster tomalley (*Lobster hepatopancreas*) (TORT-3, 2013).

DOLT-5, Guelph Food Technology Center (Guelph, ON, Canada) procured and prepared frozen dogfish livers (DOLT-5, 2014). The reference material was prepared for the development of methods for trace elements in marine vegetation and materials with a similar matrix. Bon Secour Fisheries, Inc, Bon Secour, AL, provided NIST with the oysters (*Crassostrea virginica*, an American Eastern oyster) used to produce SRM 1566b (SRM 1566b, 2019). All certified values for trace elements are reported as the mass fraction of the material.

The LUTS-1 reference material is a second-generation reference material made from edible-grade lobster tomalley (LUTS-1, 2013). It was processed at the Canadian Institute of Fisheries Technology at the Technical University of Nova Scotia in Halifax, Nova Scotia. LUST-1 is certified for 16 trace elements, including Se.

Production of LUST-1 was used to calibrate procedures and develop methods for the analysis of biological materials, particularly those with high lipid content. NMIJ CRM 7402 -a, the cod for this CRM was caught in the northern part of the Sea of Japan (NMIJ CRM 7402-a, 2009). After filleting the fish, only muscle tissue was collected. This certified reference material was prepared using the NMIJ quality system and in accordance with JIS Q 0034 (ISO GUIDE 34). The certified values are expressed as mass fractions.

The swordfish for this CRM, NMIJ CRM 7403-a, was nabbed in Japan's Pacific Ocean (NMIJ CRM 7403-a, 2009). After filleting the fish, only muscle tissue was collected. This certified reference material was prepared using the NMIJ quality system and following Japanese Industrial Standards, area division Q (Management System) (JIS Q) 0034 (ISO GUIDE 34) to be used as a method validation tool for determining elements (e.g., Se) for a similar matrix with presented concentration as mass fractions.

### *6.4. Human tissues matrix certified reference materials: Enhancing accuracy in selenium analysis for biomonitoring and health assessment*

Human tissues serve as valuable matrix materials for the analysis of total selenium content (Cardoso et al., 2019). Total selenium analysis in human tissues is of great importance in assessing selenium status, studying its distribution in different organs, and understanding its implications for human health. Various human tissues can be used for total selenium analysis, including blood, plasma, serum, urine, hair, nails, and tissues obtained through biopsies or post-mortem examinations. Each tissue type offers unique insights into selenium levels and metabolism within the body.

Blood, plasma, and serum samples are commonly analyzed to evaluate selenium status and assess nutritional adequacy (Cardoso et al., 2019). Selenium in these fluids is primarily associated with selenoproteins, such as glutathione peroxidase and selenoprotein P. These measurements help in determining selenium deficiencies or excesses and monitoring the effects of dietary interventions or selenium supplementation. Urine is another important sample for total selenium analysis, as it reflects the excretion of selenium and provides insights into selenium intake and excretion rates. Measuring selenium in urine can be particularly useful in occupational or environmental exposure assessments.

Hair and nails are non-invasive sample types that accumulate selenium over time (Hadrup & Ravn-Haren, 2021). Analysis of selenium in these matrices can provide information about long-term selenium exposure and status. Human hair is widely used as a marker for measuring various contaminants, such as those caused by chemical plants or other urban emissions, in medical diagnostics to provide key data for disease treatment, and as an indicator of physiological stress (Chojnacka, 2018; Hadrup & Ravn-Haren, 2021). Some agencies, including the U.S. Environmental Protection Agency and the International Atomic Energy Agency, have proposed using hair as an important biological material for global environmental monitoring.

As a result, the ERM-DB001 certified reference material is intended to provide a common point of reference for a variety of potentially toxic elements in an expanding field of research that encompasses multiple analytical and medical areas (ERM-DB001, 2013). The ERM-DB001 was prepared from natural human hair obtained from various donors. NIES No. 13, 1980 Japanese male scalp hair was collected from three barber shops in Tokyo and Tsukuba (NIES No.13, 1996). This CRM is intended for evaluating the accuracy of analysis of elements (e.g., Se) in human hair and other samples with a similar matrix. NIES No. 18, a composite stock of urine collected from nonoccupationally exposed Japanese males, serves as the source material for this CRM (NIES No.18, 2000). It was produced and distributed by the National Institute for Environmental Studies in Japan.

## 7. Conclusions

The food industry is reliant on quality control programs that include the measurement of food constituents. The analytical data has high importance in nutritional research for dietary nutritional content. Therefore, the availability of quality control tools is of utmost importance for food control laboratories. Following a screening of CRMs, significant efforts are still needed to fill gaps and address the lack of Se species in the food matrix to ensure food safety in the EU. As matrix material, the presented CRMs provide a wide concentration range for total Se content in the different mentioned fields of applications. The reported contents range available for total Se from (0.050 ± 0.007) mg/kg to (1175 ± 26) mg/kg as environmental matrix material, from (0.050 ± 0.009) ug/g to (0.22 ± (0.18–0.26) 95% Confidence interval) mg/kg as the matrix of plants (branches and leaves) material, from (0.023 ± 0.004) mg/kg to (2059 ± 64) mg/kg, and SeMet from (27.4 ± 2.6) mg/kg to (3448 ± 146) mg/kg as food (terrestrial) matrix material, from (0.088 ± 0.010) mg/kg to (10.9 ± 1.0) mg/kg as food (aquatic) matrix material, from (0.059 ± 0.005) mg/L to (3.24 ± 0.24) mg/kg as matrix material of human tissues. The reported concentration range for total Se and SeMet in presented CRMs helps decide on the ideal CRM for total Se and SeMet analysis in comparable matrices.

Most of the CRMs mentioned are certified for their total Se content. However, since selenium speciation is of great interest in research areas such as clinical and agricultural research, it would be necessary for CRMs to be certified for seleno species for specific matrix materials (i.e. plants, and animals). Therefore, it would be necessary for CRM manufacturers to produce them to meet the requirements considering validation strategies. Since living organisms are capable of converting inorganic to organic Se, food is the main source of seleno-species uptake; therefore, CRM producers need to focus more on producing another matrix material for selenium speciation.

Revision is needed for each CRM as stability is considered the most important property. In addition, the COMAR database should update the available information on CRMs (certification date, revision date, validity). Most of the CRMs manufactured in the 1990s and important information (e.g., revision of certificate, the expiration date of CRM) are not updated by the manufacturer, even in the certificate and report. However, such CRMs are still available on the market, as shown in Table 1 (e.g., NRRC). In addition, CRM manufacturers such as LGC Standards, JRC, and NRC properly manage and provide accurate details of CRMs.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

No data was used for the research described in the article.

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