

Trace Element Speciation in the Environment: A Mini-Review

Abstract

Trace element speciation refers to the different chemical forms or species in which a trace element (TE) may exist in a given sample or environment and its importance is widely recognized as of fundamental importance in environmental chemistry. The different chemical forms in which TE can exist in different environmental compartments include different oxidation states, their presence as free ions or interacting with other reactive groups that bind and stabilize them, and their occurrence as nanoparticles. The bioavailability, toxicokinetics and toxicodynamic of a TE are greatly dependent on the chemical form in which it is found, which in particular directly impacts the organism's ability to regulate and/or store it, consequently affecting its toxicity expression. This mini-review aims to summarize the latest developments in the field of TE speciation analysis in environmental matrices (mainly water, soil, sediment, and biota), with emphasis on data from the last eight years regarding chromium, mercury, arsenic, selenium, and thallium.

Keywords:

Trace elements speciation • Chromium • Mercury • Arsenic • Selenium • Thallium

Introduction

According to current IUPAC definitions, "speciation" corresponds to the "distribution of an element amongst defined chemical species in a system and "speciation analysis" refers to "analytical activities of identifying and/or measuring the quantities of one or more individual chemical species in a sample" [1]. In the context of trace elements (TE) chemistry, "species" are the specific forms of a given element in terms of isotopic composition, electronic or oxidation state, complex or molecular structure and phase [2]. The importance of characterizing and determining the

Review Article

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different chemical species of a given element ("speciation analysis"), is widely recognized as being of fundamental importance in environmental chemistry. Chemical speciation may be implemented to include functionally defined speciation (e.g., determination of species that are available to plants or present in exchangeable forms), and/or operationally defined speciation, which refers to the determination of extractable forms of an element [3].

The main chemical forms in which TE can occur in the environment include free ions, different oxidation states, metallic nanoparticles and various complexes (organic and inorganic) resulting from the interaction with reactive groups present in the medium that bind and stabilize them [4]. This chemical speciation is affected by a wide range

of physicochemical factors, such as Arsenic temperature, pH, redox potential, greater or lesser presence of reactive chemical species (e.g., organic and inorganic complexing ligands), colloidal matter and other surfaces with adsorption potential [4]. The partitioning and biogeochemical cycling of TE in the different environmental compartments from the loading source depend on the physicochemical properties of their original chemical species and the particular physicochemical of the receiving ecosystem [5]. Then, the toxicokinetics and toxicodynamics of TE also depend on their chemical form, which often greatly affects the organism's ability to regulate and/or store them, therefore exerting a direct influence on the expression of their toxicity [5].

Thus, because TE speciation can have a huge impact on the transition kinetics, partitioning, deposition, and potential resuspension in environmental compartments and on their ecotoxicological effects on living organism, TE speciation analysis has been increasingly recognized as of crucial importance [4]. The most relevant chemical forms to be studied in environmental samples are free ions, kinetically labile (mostly weakly bound) and non-labile (mostly strongly bound) complexes, and the colloidal fraction [6]. Several studies have demonstrated that free ions and some labile complexes constitute the bioaccessible fraction of an element, being its chemical species most easily assimilated by organisms and, in the case of heavy metals, their toxic fraction [7]. Chemical speciation analysis has therefore also become a fundamental tool for assessing the environmental and ecotoxicological risks posed by TE and is currently the core of most metal pollution studies [8].

The importance of speciation analysis is demonstrated by the growing number of publications focused on this type of study [8-11]. Speciation analysis has benefited greatly from the development of highly selective and sensitive analytical methods, which have been implemented mainly through the coupling of chromatographic techniques with sensitive element-specific detectors [12]. Non-chromatographic methods have also been developed, although with a more limited separation capacity, generally limited to specific chemical species [12]. In both approaches, it is important to continue the development of improved methods, which in particular must consider their environmental impact as a crucial parameter to be optimized, as their main

purpose is precisely environment assessment [8]. Novel analytical approaches must focus on avoiding or reducing the undesirable environmental side effects of chemical analysis, while maintaining the required classical analytical features of selectivity, sensitivity/detectability, precision, and accuracy [8]. Several recent reviews on TE speciation methods are available in the literature [8,13,14].

In addition to the scarcity of accurate speciation analytical methods, the lack of certified reference materials (CRM) and widely accepted analytical protocols are major limitations in the field of TE speciation analysis in environmental contexts [15]. The lack of sample collection, conservation, and handling protocols that demonstrably ensure the preservation of the original chemical species between sample collection and analysis is also a much felt gap. This mini-review aims to summarize the latest developments in the field of TE speciation analysis in environmental matrices (water, soil, sediment, biota), with a focus on data from the last eight years and relating to chromium, mercury, arsenic, selenium and thallium. The first four elements have been extensively studied, while thallium is still a somewhat recent arrival to this list of problematic environmental TE. Their most relevant environmental occurring forms in plants, soils, fresh and sea waters, and new or modified analytical techniques for their characterization and determination are presented and discussed in this mini-review.

Discussion

Chromium

Chromium (Cr) has a complex electronic and valence shell structure, with great potential for conversion from one oxidation state to another, existing in several valence states, from 0 to VI [16]. Trivalent (Cr(III)) and hexavalent (Cr(VI)) chromium are the most stable and the predominant oxidation states in the environment [16,17]. Cr(III) occurs mainly as cations (Cr^{3+}), while Cr(VI) generally occurs as oxyanions (chromate: CrO_4^{2-} , hydrochromate: HCrO_4^- , and dichromate: $\text{Cr}_2\text{O}_7^{2-}$). Cr(III) is relatively stable and non-toxic at circum-neutral pH (6.5–8.5) due to the formation of insoluble hydroxides and oxide compounds and strong complexation with environmental chemicals; it has a strong tendency to form kinetically inert hexacoordinate complexes with water, sulfate, ammonia, organic acids, halides, and urea [16]. Soluble Cr(III) species form

complexes with low molecular mass (e.g. succinic, oxalic, malic, citric, malonic) and high molecular mass (e.g., fulvic and humic) organic acids [18]. The oxidation states Cr(II), Cr(IV) and Cr(V) are unstable forms produced during the redox processes of Cr(III) and Cr(VI); under anoxic conditions, Cr(III) is typically the predominant form; under oxic conditions, anionic Cr(VI) species tend to predominate [16]. These are soluble and mobile across the full pH range, presenting high mobility in water systems, which makes Cr(VI) much more toxic than Cr(III) [16]. Microorganisms can reduce Cr(VI) [16].

In plants, Cr is a potentially toxic TE, without any essential metabolic functions [19,20]. There is no specific transporter for Cr uptake by plants and it enters plants mainly through specific and non-specific essential ion channels [19]. Cr accumulates mainly in plant root tissues, with very little translocation to the shoot [19]. Cr causes harmful effects on various biochemical, physiological and morphological processes. It exerts phytotoxicity by interfering with nutrient uptake and photosynthesis, disrupting plant growth [19]. In particular, it induces increased generation of reactive oxygen species (ROS), causing lipid peroxidation and disrupting antioxidant activities [21]. Most soils contain Cr levels in the range of 15-100 $\mu\text{g g}^{-1}$ [22]. In freshwater Cr ranges from 0.1 to 117 $\mu\text{g L}^{-1}$, while seawater contains Cr concentrations below 0.5 $\mu\text{g L}^{-1}$ [22,23]. The range of airborne chromium levels in Europe is 0–3 ng m^{-3} in remote areas, 4–70 ng m^{-3} in urban areas, and 5–200 ng m^{-3} in industrial areas [22,24]. Cr concentrations in plants are generally low, typically ranging from 0.02 to 0.2 $\mu\text{g g}^{-1}$ (dry weight) [16]. Environmental Cr speciation studies have been reported in water, soils and sediments [25,26], soil-plant systems, [19] and biota [27].

There have been several reports of new or modified techniques for Cr speciation. Two reviews specifically address the pros and cons of the analytical speciation methods [13,16]. Selected works relating to the environmental monitoring of Cr are referred in Table 1. Electrolytic separation of Cr(VI) and Cr(III) followed by determination of Cr by graphite furnace atomic absorption spectrometry (GFAAS) was applied by Nugraha et al. on monitoring a soil extraction process [28]. Cr(III) and Cr(VI) from spring, river, and sea waters were selectively analyzed using a dispersive micro-solid phase extraction

(D- μ -SPE) procedure with magnetic graphene oxide as sorbent and flame atomic absorption spectrometry (FAAS) as detection technique [29]. The extraction procedure used strong acids and organic solvents, albeit in small volumes, minimizing its environmental impact. One paper describes a procedure based on magnetic solid phase extraction (MSPE) using magnetic nanoparticles (MNPs) functionalized with iminodiacetic acid combined with GFAAS [30]. The method was applied to determine Cr(III) and Cr(VI) in lake and river water samples. A recent paper by Saiz et al. [31] provided a complete snapshot of the Cr(VI)-Cr(V)-Cr(III) speciation.

The authors describe a combination of ultraviolet-visible (UV-Vis) and electron paramagnetic resonance spectroscopy (EPR) techniques for Cr speciation after a coupled adsorption and reduction process in zirconium metal-organic frameworks (MOF). UV-Vis spectral fingerprints of Cr(VI) and Cr(III) showed distinctive features, which allowed qualitative information about the Cr coordination environment. EPR spectroscopy proved to be highly sensitive in detecting transient Cr(V), in addition to being highly effective in detecting Cr(III), either as isolated or clustered species. Huang et al. [27] reported a study on the location and speciation of Cr in a Chinese plant (*Coptis chinensis*) with the aim of better understand the mechanisms of Cr accumulation and transport and, ultimately, contributing to minimizing Cr transfer to the food chain. The authors used synchrotron radiation microscopic X-ray fluorescence (SR- μ XRF) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) to spatially localize Cr in the plant, X-ray absorption near-edge structure (XANES) spectroscopy for Cr speciation analysis and inductively coupled plasma mass spectrometry (ICP-MS) to determine subcellular Cr levels. XANES data showed that Cr(VI) could be reduced to Cr(III) when the plant was grown with Cr(VI), and provided a novel conclusion: that this plant contained elemental Cr. Another work aimed to develop an analytical method capable of simultaneously providing molecular and elemental information from a single sample injection, which was achieved by coupling high-performance liquid chromatography/diode-array detection (HPLC-DAD) with ICP-MS [32]. Cr(VI) and Cr(III) in water have also been differentiated based on their distinct surface-enhanced Raman scattering (SERS) spectral features [33].

Mercury

In the environment, mercury (Hg) exists in different forms, including metallic/elemental Hg (Hg⁰), inorganic Hg (HgS, HgCl₂), and organic Hg – mainly as methyl Hg (MeHg), but also ethylmercury (EtHg) and phenylmercury (PhHg) [34,35]. Due to its high volatility and susceptibility to oxidation, elemental Hg is the predominant species in the atmosphere, while Hg(II) is the predominant species in water, soil and sediments, and MeHg is the main species in biota [36,37]. The toxic effects of MeHg can be significant due to its bioaccumulation and biomagnification (up to 10⁶) in the aquatic food chain, high affinity for macromolecules and slow metabolism [38]. Several environmental parameters (pH, organic matter, temperature, light, flooding conditions, ionic activity, redox potential, dissolved oxygen, sulfide levels, suspended solids and microbial activity) influence Hg speciation and bioavailability [39]. Mobile Hg-humic or fulvic complexes tend to be susceptible to methylation, whereas Hg bound to larger organic matter (OM) particles hinders methylation. Specific OM compounds can promote Hg²⁺ methylation by increasing bacterial activity [40,41]. OM can also facilitate Hg²⁺ methylation by inhibiting HgS precipitation or enhance HgS dissolution, thereby providing available Hg²⁺ for methylating microorganisms [14].

Soil microorganisms can also transform inorganic Hg(II) into Hg⁰ by the action of Hg reductases, which are found in bacteria such as *Pseudomonas* sp., *S. aureus*, *Thiobacillus ferrooxidans*, *Streptomyces* sp. and *Cryptococcus* sp. that have the Mer gene [41,42]. Sulfate-reducing bacteria are the main agents responsible for MeHg production in coastal sediments [43]. OM can also influence MeHg production by reducing the amount of bioavailable Hg(II) in the dissolved phase and stimulating the activity of methylating bacteria, providing substrate for mineralization [44]. Plants efficiently absorb Hg through their roots, since Hg is highly soluble in water and easily converted into the gaseous phase. Most of Hg absorbed by plants is retained in the roots, and only a small amount is translocated to the aerial part [45]. Hg causes phytotoxicity and impairs numerous metabolic processes even at low amounts, resulting in ROS production, lipid membrane oxidation, DNA and protein damage, inhibition of photosynthesis and growth retardation [14,46].

Uncontaminated freshwaters generally contain total mercury (Hg(t)) levels <5 ng L⁻¹ and background soil concentration is typically between 0.003 and 4.6 µg g⁻¹ [47]. In uncontaminated sediments, Hg(t) levels are typically between 0.2 to 0.4 µg g⁻¹, however, in sediments close to industrial and urban areas, the Hg(t) concentration can reach 100 µg g⁻¹ and MeHg can reach 0.1 µg g⁻¹ [47]. In recent years, a large number of papers have been published on Hg speciation in various environmental matrices (Table 1). Yang et al. [48] used graphene oxide-bounded silica particles as solid phase extraction (SPE) adsorbent for the online preconcentration of Hg (II), MeHg, and EtHg in drinking water, followed by selective determination by HPLC-ICP-MS. In another work, zwitterion-functionalized polymer microspheres (ZPMs) were used as a core adsorbent in an online SPE procedure for the enrichment of mercury species (inorganic, MeHg and EtHg) in environmental waters (surface and marine), also followed by selective determination by HPLC-ICP-MS [49].

MSPE has also been used for Hg analysis. The magnetic Fe₃O₄@SiO₂@ glycidyl methacrylate (GMA)-S-SH nanoparticles were used for the extraction of Hg(II), MeHg and PhHg from water and soil samples, followed by HPLC-ICP-MS determination [50]. The developed method avoids the use of organic solvents and requires only a small volume of dilute acid, demonstrating great potential for routine environmental analysis. In a similar analytical procedure, magnetic Fe₃O₄@SiO₂@ γ-mercaptopropyltrimethoxysilane (γ-MPTS) nanoparticles were prepared and used for the speciation of mercury (Hg (II), MeHg and PhHg) in environmental water, wastewater, tap water, and fish samples [51].

Thallium

In recent decades, thallium (Tl) has become a “technology-critical element” due to its increasing technological use [52]. As Tl present in non-contaminated environmental compartments and that of anthropogenic origin typically exhibit different isotopic signatures, this has been used as a strategy to fingerprint and identify anthropogenic sources of Tl and understand its environmental processes [53]. The two stable isotopes are ²⁰³Tl (29.5%) and ²⁰⁵Tl (70.5%). Tl has two main oxidation states, Tl(I) and Tl(III), both of which are highly toxic to humans and animals, microorganisms

and plants, and is more toxic to mammals than Cd, Pb, and even Hg [22]. Most lake and river waters have low levels of Tl, in the range of 5-10 ng L⁻¹. In seawater, Tl is predominantly as the free ion Tl⁺ and as subordinate dissolved complexes TlCl⁰, and ranges from 0.2 to 20 ng L⁻¹ [54]. Tl concentrations in continental and oceanic crust and rocks are generally less than 1 µg g⁻¹ [22]. Some soils have a naturally high background level, but in general Tl concentrations in uncontaminated surface soils range from 0.1 to 2 µg g⁻¹ [54,55]. Tl is a non-essential element for plants and its average concentration in land plants is typically < 0.1 µg g⁻¹; the average Tl content in air does not exceed 1 ng m⁻³ [11, 54].

The toxicity of Tl-based compounds is due to the similarity between Tl⁺ and K⁺ cations, which results in the disruption of K⁺-associated metabolic processes [56]. Tl(I) is expected to be the dominant species in almost all environmental systems, in equilibrium with atmospheric oxygen and in the absence of complexing agents. From a thermodynamic point of view, the conversion of Tl(I) to Tl(III) is expected only in the presence of extremely strong oxidants and high alkalinity [52], but photochemical reactions in surface waters or microbiological processes may lead to the oxidation of Tl(I) to Tl(III) even under even moderate oxidizing conditions [57]. Recent studies have also highlighted the possible role of Fe(III) and As(V) in the formation of Tl(III) compounds in acid mining drainage [52]. Tl(III) is approximately 50,000 times more toxic than Tl(I) on a free-ion basis [58]. In the terrestrial environment, Tl is usually bound to the soil matrix, which considerably limits its transport, although dissolved Tl (soluble salts) is susceptible to leaching and can be introduced into the aquatic environment [55]. Tl sorption in soils is commonly attributed to ion exchange reactions on Mn oxides, clays, or OM. A very recent paper describes the use of recycled Al beverage can powder (AICP) in Tl soil remediation. AICP was used as a substitute for zero-valent Al to drive the Fenton-like reaction that induced the oxidation of Tl(I) and subsequent precipitation of Tl(III) via medium alkalization [59].

The high concentration of Tl in shallow soil poses a threat due to possible uptake by plant roots and accumulation in plant biomass [55]. The extent of the role played by natural organic matter (NOM), such as humic and fulvic acids, in the bioaccessibility of Tl is still poorly known. One study

investigated the complexation of Tl(I) by a purified humic substance, used as a proxy of NOM [60]. The experiments were carried out with the Donnan membrane technique to separate the free Tl(I) ion from its complex form in the bulk solution. Tl has been reported to be widely distributed in plant tissues. It is thought that most of the uptaken Tl travels along nutrient pathways to the cell cytosol and storage vacuoles [61]. Because Tl⁺ and K⁺ have similar uptake pathways, they can both easily accumulate in plants from the soil, affecting antioxidant enzyme activity and photosynthesis. Tl⁺ can interfere with Na⁺/K⁺-ATPase and pyruvate kinase, inducing oxidative stress, which leads to damage to cell membranes, proteins, lipids and chloroplast pigments, ultimately leading to cell death [62].

Due to its generally very low concentrations, knowledge of the distribution, enrichment, and environmental risks of Tl in different environmental matrices has benefited greatly from the major developments in atomic spectrometry techniques in recent years, especially inductively coupled plasma mass spectrometry (ICP-MS), due to its very high sensitivity, ease of coupling to chromatographic systems for speciation analysis and isotopic analysis capacity [63-66]. Thus, as an example, it was possible to demonstrate that soils and sediments contaminated from industrial emissions exhibited clearly different Tl isotopic compositions compared to the natural background, allowing source tracking and also new insights into the biogeochemical cycle of Tl in soil [66]. Other relevant studies are referred to in Table 1. A fast, reliable and relatively simple procedure for the separation of Tl(I) from Tl(III) was described by Lopez-Garcia [67], using a dispersive liquid-liquid microextraction step to isolate the ion pair formed by Tl(III) and cetylpyridinium chloride in the presence of bromide. In this way, Tl(I) remained in the aqueous phase, which was subjected to analysis, and the concentration of Tl(III) was obtained by difference.

The procedure was applied to Tl speciation in tap, spring, river and sea waters. A magnetic metal-organic framework nanocomposite with MNPs was used for Tl speciation analysis in well, sea, and wastewater samples [68]. Tl(I) was selectively retained by the sorbent, and total Tl was determined using hydroxylamine hydrochloride to reduce Tl(III) to Tl(I). Another paper described the selective and highly sensitive determination of Tl(I) and Tl(III) (as well as total Tl) using a novel ligandless mixed micelle cloud point

extraction and GFAAS [69]. A detection limit of 15 ng L⁻¹ was obtained.

Arsenic

Arsenic (As) rarely occurs in the free state and is typically found in combination with sulfur, oxygen, and iron, so more than 100 arsenic compounds are present in the environment and biological systems [10]. As occurs in four oxidation states, -3 (e.g. arsenic hydride or arsine gas), 0 (e.g. crystalline As), +3 (arsenite: AsO₃³⁻), and +5 (arsenate: AsO₄³⁻), and in a wide variety of organic and inorganic As compounds [70-72]. Trivalent As is 60 times more toxic than oxidized pentavalent arsenate, inorganic As compounds are about 100 times more toxic than the methylated forms [70]. Organic species are common in OM-rich waters and enzymatic methylation of inorganic As occurs through the action of microorganisms (including fungi and bacteria), algae, and phytoplankton, with the formation of organo-As compounds such as monomethylarsonic acid (MMA), dimethylarsinic acid (DMA), trimethylarsine and arsenobetaine [73].

This methylation process can occur in soil, sediments and water bodies, particularly under anaerobic conditions [73]. On the other hand, organo-As can generate inorganic As through hydrolysis and biological degradation [74]. As precipitated in soils, sediments and wetlands can be released back into the environment by bacteria, fungi, and other microorganisms. The ratio of As(III) to As(V) in groundwater is a function of the OM content, biological activity and oxygen levels [72]. In seawater, inorganic As is usually present in the form of As(III) and As(V) [75]. The uptake and accumulation of As by plants varies according to habitats and plant species [76]. Methylated As and As(III) move through the nodulin 26-like intrinsic proteins aquaporin channels, while As(V) is taken up via phosphate transporters [77]. Some plants (e.g. *Pteridaceae* family) exhibit hyperaccumulation behavior toward As in aboveground tissues [78]. Still, in general chelation leads to detoxification of As(III) through complexation with thiol-rich peptides [79].

As is present mainly as arsenobetaine in fish and crustaceans. Arsenosugars are the predominant species in algae, with relevant presence also in bivalves and sponges [74]. The estimated global average level of As in soil is

5 µg g⁻¹, in open seawater 1–2 µg L⁻¹, and in unpolluted surface and groundwater less than 10 µg L⁻¹. The natural marine environment contains As levels ranging from 1 to 5 µg L⁻¹ [70]. Environmental monitoring studies are often limited to a few As species. Most CRMs are only certified for arsenobetaine and DMA, making it difficult to assess the accuracy of analytical procedures for other organo-As species [80]. The use of HPLC-ICP-MS has become the analytical technique of choice in most As speciation studies, although a significant number of studies have resorted to other couplings (LC to other atomic and MS techniques) or methods based on X-ray spectroscopy [13].

There have been many reports of new or modified analytical procedures for speciation of As. A recent comprehensive review [13] addresses speciation methods developed for selective determination of oxidation states, organometallic compounds, coordination compounds and heteroatom-containing biomolecules using atomic spectroscopy. Chromogenic and fluorogenic chemosensors for detection of As species have also been reviewed, by Banik et al. [81], who grouped them into six types: chemosensors based on hydrogen bonding interactions; aggregation induced emission based chemosensors; chemodosimetric (reaction-based chemosensors); metal coordination-based sensing strategies; chemosensors based on metal complex displacement; and metal complexes as chemosensors.

Relevant papers on the environmental speciation of As are presented in Table 1. For instance, a surface ionic imprinted polymer consisting of a template/bifunctional monomer/crosslinker (NaAsO₂: template; 1-vinyl imidazole: bifunctional monomer; divinylbenzene: crosslinker), and acetic acid/methanol porogen on silica-coated Mn-doped ZnS quantum dots were described and applied as a phosphorescence chemosensor for the selective quantification of inorganic As species in fish [82]. A sensitive and field-usable colorimetric method (an adaptation of the classic molybdenum blue method for determination of PO₄³⁻) was modified to achieve a sufficiently low limit of detection for the determination and speciation of As (As(III) and As(V)) in low sample volumes (100 µL) and in the presence of high levels of potentially interfering solutes [83]. The method was used to study As cycling in soil porewater along the flow path of an As-

contaminated brook [83]. Solid-phase extraction has been reported for species preservation in As speciation studies for environmental risk assessment using XANES [83]. Characterization of As species was performed by SR-XAS (synchrotron X-ray absorption spectrometry) in CRMs and candidate materials (including sediments, ash, and ore tailings) at the Korea Research Institute of Standards and Science and was successfully evaluated by comparison with IC-ICP-MS analysis [84]. The use of XANES revealed details of both the composition and distribution of As species in the intact solid samples and shows potential as a complementary technique to existing methods when non-destructive microscopic analysis is required [84,85]. In another study, the toxicity mechanisms of As(III) and As(V) were investigated in marine zooplankton, namely the rotifer *Brachionus plicatilis*, and the copepod *Paracyclopsina nana*; in vivo toxicity and antioxidant responses were evaluated and As metabolites were determined by HPLC-ICP-MS [86].

Selenium

Selenium (Se) naturally exists in various oxidation states [Se(-II): selenide, Se(0): elemental Se; Se(IV): selenite, Se(VI): selenate] and both in inorganic and organic forms, which present distinct biogeochemical behaviors, with different degrees of mobility and bioavailability [87-89]. Six isotopic forms of Se (relative atomic mass: 74, 76, 77, 78, 79 and 80) are known, with ⁷⁸Se and ⁸⁰Se being the most abundant [87]. The bioprocessing of Se in the environment is catalyzed by Se-metabolizing bacteria that are capable of either reducing or oxidizing it and also generating methylated and volatile derivatives [90]. The Se content in soil varies greatly depending on the continent and geographic region (between 0.01–2 µg g⁻¹), with the average content being 0.4 µg g⁻¹ [91,92]. Se levels in marine fish have been reported to be inferior to 0.6 µg g⁻¹, a concentration approximately 50,000 times higher than that found in the environment surrounding these animals [93].

In soils, the presence of Se is influenced by three mechanisms: mineralization / immobilization; redox; and volatilization [94]. The oxyanions selenate (SeO₄²⁻) and selenite (SeO₃²⁻) are commonly present in aerobic soils [95]. Se(VI) exhibits the highest water solubility and mobility and can be readily available for uptake by plants, whereas

Se(IV) has a much greater affinity for soil particles (e.g., metal oxides and OM) [92]. Se(0) is not soluble in water and is poorly bioavailable in soils, so Se reduction procedures have been considered effective mechanisms for removing Se from contaminated waters or for stabilizing polluted soils, and this reduction is enhanced by the presence of OM [92]. Various Se(-II) compounds, such as dzharkenite (FeSe₂) and klockmannite (CuSe), may be present in sulfide deposits as associated minerals [96]. Organic Se compounds are generally produced by biotic activities and exist in air, soil, and plants (following absorption from soil) as volatile methylselenides, trimethylselenonium ions, and selenoamino acids [97]. Several microorganisms have the ability to incorporate Se, derived from either Se(VI) or Se(IV), into organo-Se compounds such as selenocysteine (SeCys) and selenomethionine (SeMet) through the mechanism known as assimilatory Se-reduction [94,98].

Se(VI), the most mobile and bioavailable form in sediments, is immediately delivered to the xylem of plants after absorption via sulfate transporters [92,95]. Se is taken up from the soil in the same way as sulfur and is metabolized in a similar way [92]. Se(VI) in plants is generally reduced to Se(IV) and then to Se(-II), which is then transformed into SeCys and SeMet [94,95]. At low concentrations, Se protects plants from various abiotic stresses, stimulates plant development and improves plant quality [95]. High concentrations lead to the production of ROS that can induce oxidative stress and cause toxic effects on plant photosynthetic systems [95]. Translocation of Se from root to shoot depends on xylem loading and transpiration rate, and Se accumulates in vacuoles and is expelled via sulfate transporters located in the tonoplast [90].

Inorganic Se species are approximately 40 times more toxic than organic species, and the toxicity of Se(IV) is 10 times greater than Se(VI), making Se speciation analysis essential for understanding its effects on environmental compartments [8]. Several papers have addressed Se's environmental challenges in recent years. Some are highlighted in Table 1, Se speciation analysis has generally been performed using complex hyphenated analytical systems such as LC-ICP-MS. Bordash et al. [99] described an approach based on a sequential derivatization and extraction procedure combined with gas chromatography and mass spectrometry (GC-MS) for the simultaneous determination of Se(IV),

Trace element specie	Extraction	Method	Detection	LOD	Sample	Ref
Chromium						
Cr(III)-fulvic acid-like anions and Cr(III)-amorphous ferrihydrite complexes			Combined nanoscale secondary ion mass spectrometry (NanoSIMS), synchrotron-based techniques, μ -XRF and μ -XANES		Rice root tip and mature zone	[103]
Cr-oxalate, Cr-malate, Cr-citrate, Cr-quininate, Cr(VI)		Strong anion-exchange FPLC column of Mono Q HR 5/5 HPLC-ICP-MS	HPLC post-column ID-ICP-MS, high-resolution MS, and laser ablation ICP-MS	0.32 to 0.37 ng mL ⁻¹	Dandelion roots and leaves (<i>Taraxacum officinale</i>)	[20]
Cr(t), Cr(VI)		Two-step sequential extraction	FAAS and XPS		Soils from chrome plating sites	[104]
Cr(III), Cr(V), Cr(VI)	Zr-based MOFs	Coupled adsorption and reduction of MOFs	Dual UV-Vis and EPR		Soil remediation	[31]
Cr(III), Cr(VI)	Na ₂ CO ₃ (leaching reagent)	Microwave-assisted extraction	FAAS and GFAAS	0.02; 0.03 μ g g ⁻¹	Sediments	[26]
Cr(III), Cr(VI)		Dual solution line filtration; Electrolytic separation	GFAAS	0.01 μ g L ⁻¹	Soil monitoring	[28]
Cr(III), Cr(VI)	Carboxylic-functionalized nanoSiO ₂	SPE	ICP-MS	0.02 μ g L ⁻¹	Lake, rain, and river water	[105]
Cr(III), Cr(VI)	Na ₂ CO ₃	Ultrasound-assisted extraction	Ion pairing reversed phase HPLC-ICP-MS	0.08; 0.09 μ g L ⁻¹	Soil extracts	[106]
Cr(0), Cr(III), Cr(VI)			XANES and ICP-MS		<i>Coptis chinensis Franch.</i>	[27]
Cr(III), Cr(VI)	Magnetized graphene oxide	D- μ -SPE	FAAS	0.10 μ g L ⁻¹	Spring, river, and sea water	[29]
Cr(III), Cr(VI)	Iminodiacetic acid functionalized MNP	MSPE	GFAAS	0.0091; 0.0128 μ g L ⁻¹	Lake, and river water	[30]
Cr(III), Cr(VI)					Soil-plant system	[19]
Cr(III), Cr(VI)	Na ₂ CO ₃	SPE	FAAS	17.5 μ g g ⁻¹	Contaminated soil of tannery	[107]
Cr(III), Cr(VI)		Sequential chemical extraction, electron microscopy, electron microprobe	Microfocus XANES		Urban particulate matter from aquatic sediment and road dust sediment	[25]
Cr(III), Cr(VI)	1,5-diphenylcarbazone polymeric matrix	SPE	FAAS	0.030 μ g mL ⁻¹	Raw and treated municipal sewage	[108]
Cr(t), Cr(III), Cr(VI)			AAS and UV-Vis		Water, agricultural soil, vegetables in leather tanning industrial areas	[109]

Mercury						
Hg					Soil-plant environment	[14]
Hg					Soils and water sediments	[37]
Hg			HPLC-ICP-MS			[110]
Hg(t), MeHg		Digestion	Cold vapor atomic fluorescence spectroscopy	6; 0.003 ng g ⁻¹	Soil and plant samples	[111]
Hg(II), MeHg, EtHg	Graphene oxide-bounded silica particles	SPE	HPLC-ICP-MS	0.005; 0.006; 0.009 µg L ⁻¹	River water	[48]
Hg(II), MeHg, EtHg	ZPMs	ZPMs SPE	HPLC-ICP-MS	0.78; 0.63; 0.49 µg L ⁻¹	Surface and seawater	[49]
Hg(II), MeHg, PhHg	Thioether and thiol-functionalized MNPs	MSPE	HPLC-ICP-MS	0.40; 0.49; 1.4 ng L ⁻¹	Farmland water and soil	[50]
Hg(II), MeHg	Fe ₃ O ₄ NPs modified with nanocellulose	MSPE	GC-AFS	5.6; 4.0 µg L ⁻¹	River water	[112]
Hg(II), MeHg	Triton X-114	CPE	HG-AFS	7; 18 µg L ⁻¹	Industrial wastewater	[113]
Hg					Transportation in soils, atmospheric flux	[35]
Hg(II), MeHg		Reduction	Hydride generation (HG) UV-AFS	0.015; 0.081 mg L ⁻¹	Environmental water	[114]
Hg(0), HgCl ₂ , Hg ₂ Cl ₂ , HgSO ₄ , HgS		Thermal desorption	Direct Mercury Analyzer (thermal degradation, amalgamation and atomic absorption (TDAAS))	1 µg kg ⁻¹	Sediments from streams and rivers close to gold mining	[115]
Hg(t), MeHg	Toluene and back-extraction with sodium thiosulphate		HPLC- ICP-MS		Estuary sediments	[116]
Hg ²⁺ , MeHg ⁺ , EtHg ⁺	Nano-MoS ₂	Nano-MoS ₂ solid phase extraction	HPLC-UV-HG-AFS	0.017; 0.037; 0.021 ng mL ⁻¹	Tap and lake water	[117]
¹⁹⁶ Hg, ¹⁹⁸ Hg, ¹⁹⁹ Hg, ²⁰⁰ Hg, ²⁰¹ Hg, ²⁰² Hg, ²⁰⁴ Hg		Sequential extraction	Concentration and stable isotope analysis (CV-MC-ICP-MS)		Soils and sediments	[118]
Hg	CaCl ₂	Sequential extractions and thermal desorption analyses	CV-AFS and ICP-OES		Soils Contaminated	[119]
Hg(II), MeHg, PhHg	Fe ₃ O ₄ @SiO ₂ @γ-mercaptopropyltrimethoxysilane MNPs	MSPE	HPLC-ICP-MS	0.74; 0.67; 0.49 µg L ⁻¹	River and wastewater	[51]
Wide panel of Hg species	NA	Thermo-desorption method	DMA-80 Direct Mercury Analyzer (thermal decomposition, mercury amalgamation + atomic absorption detection)		Soil, beach sand and marine sediment	[120]

Thallium						
Tl(I), Tl(III)	Graphene-Fe ₃ O ₄ composite	Coupling liquid-liquid microextraction MD- μ SPE	GFAAS	0.02 $\mu\text{g L}^{-1}$	Tap, spring, river and sea water	[67]
Tl(I), Tl(III)	IL Aliquat-336, Triton X-114 ion-pair	LL-MM-CPE	GFAAS	0.015 $\mu\text{g L}^{-1}$	Groundwater and coal mine water	[69]
Tl(I), NOM Tl		Donnan Membrane Technique	ICP-MS		River and lake type water, soils	[60]
²⁰³ Tl, ²⁰⁵ Tl		Anion exchange resin	MC-ICP-MS, XANES		Soils	[63]
Tl(t), Tl(III)	Magnetic MOF nanocomposite with MNPs	MSPE	GFAAS	0.0015 $\mu\text{g L}^{-1}$	Well, sea and wastewater	[68]
Tl(I), Tl(III)	8-hydroxyquinoline immobilized onto SDS-coated Al ₂ O ₃ and DTPA	SPE	ICP-MS	0.037; 0.18 $\mu\text{g L}^{-1}$	Soils	[121]
Tl(t), Tl(I), Tl(III)			IC-ICP-MS with cation exchange guard-column Dionex	0.05 mg L^{-1}	Natural stream and spring waters	[52]
Tl(t), Tl(I), Tl(III)			Cation exchange chromatography Dionex CG-2 coupled to ICP-MS		Acid mine drainages, surface waters, springs in mining area	[122]
Tl review						[123]
Tl review						[55]
Tl review						[124]

Arsenic						
As(III), As(V)			Colorimetric method	0.56; 0.47 μM	Porewater extracted from soil	[83]
33 different As species	Methanol	Fractional factorial design	Anion- and cation-exchange HPLC-ICP-MS		Marine Certified reference materials	[125]
Inorganic and organic As, As(III), As(V), DMA, MMA		Anion-exchange PRP-X100 column and nitrate/phosphate mobile phase	ICP-MS/MS		Environmental water	[126]
As(III), As(V)		Non covalently aminated two-column silica SPE (two PDDA@SiO ₂ cartridges) poly (diallyldimethylammonium chloride) of linear structure	ICP-OES and ICP-MS		Mine and well water	[127]
As, MMA, DMA, TMAO		Anion- and cation-exchange chromatography	ICP MS/MS		PM10 samples collected in urban environment	[128]
As(III), As(V)		IIP@ZnS:Mn QDs Mn-doped ZnS quantum dots coated with (3-aminopropyl) triethoxysilane and As(III) ionic imprinted polymer	Room temperature phosphorescence chemosensor probe		Fish	[82]

As(III), As(V), DMA	Zinc oxide nanoparticles		Zinc oxide nanoparticles photochemical reactor	3.20; 3.86; 6.68 $\mu\text{g L}^{-1}$	Water, soil, and sediments from impacted environments	[129]
As(V), As(III), MMA, DMA, AB, AsC		Heat-assisted extraction	HPLC-ICP-MS		Marine zooplanktons, <i>Brachionus plicatilis</i> and <i>Paracyclopsina nana</i>	[86]
As(III), DMA, MMA, As(V)	Nitric acid		LC-HG-AFS	0.005; 0.01; 0.006; 0.009 mg kg^{-1}	Algae	[130]
As(III), As(V)	Magnetic ionic liquids (MILs) [P6,6,6,14][FeCl ₄] and [P6,6,6,14]3[DyCl]	MIL-DLLME	GFAAS	0.017 $\mu\text{g L}^{-1}$	Sediment, soil, dam, river, sea, underground water	[131]
As(III), As(V), phenylarsenics	Octanol (low-density solvent)	Dispersive liquid-liquid microextraction	HPLC-ICP-MS	0.001–0.039 $\mu\text{g L}^{-1}$	Lake and pond water	[132]
As(III), As(V), AsC, AB, DMA, MMA	HNO ₃		HPLC/ICP-MS		Seaweed, sediment, seawater	[133]
As(III), As(V)		Solid phase microextraction (SPME) using multi-functional hybrid monolithic columns	ICP-MS	25; 12.5 ng L^{-1}	Environmental waters	[134]
As review						[10]
As(III), As(V), MMA, DMA, AB, AsC	HNO ₃		HPLC-ICP-MS	0.05; 0.1; 1; 2 ng g^{-1}	Fresh and salt water, suspended particles, zooplankton, sediment	[135]
As(III), As(V), Se(IV), Se(VI)	TiO ₂ NPs	SPE	ICP-MS	0.004; 0.033 $\mu\text{g L}^{-1}$ for As and 0.061; 0.128 $\mu\text{g L}^{-1}$ for Se	Tap water, seawater, agriculture wastewater	[136]
As(t), As(III)		On-line preconcentration system Polytetrafluoroethylene minicolumn	HG FAAS	0.02; 0.03 $\mu\text{g L}^{-1}$	Sea water	[137]
As(III), As(V)	Phosphate buffered saline (PBS)/0.2 M EDTA		HPLC- ICP-MS		Estuary sediments	[116]
As(III), As(V)	DES choline chloride-phenol	Ultrasound assisted deep eutectic solvent based on dispersive liquid liquid microextraction	GFAAS	0.01 $\mu\text{g L}^{-1}$	Lake and river water, sediment and soil	[138]
As(III), As(V), DMA, MMA, AsB	Water : metanol and phosphoric acid	Extraction with sonication	IC-ICP-MS		Seafood and marine sediments	[139]
As(III), As(V)		Anion exchange chromatography	ICP-MS	0.012; 0.019 ng mL^{-1}	Spring, well, and tap water	[140]
eight arsenic species: As(III), As(V), MMA, DMA, TMAO, tetramethylarsonium, AsC, AB		Ion-pair reversed phase high performance liquid chromatography IP-RPC	HPLC-ICP-MS	0.04; 0.07 ng mL^{-1}	Tree moss extract	[141]

As review						[76]
As(III), As (IV)		Liquid phase microextraction	FAAS	0.08 ng mL ⁻¹	Pond, river and industrial waste waters	[142]
As(III), As(V), AB		Anion exchange column	IC-ICP-MS	16.5; 14.1; 6.2 ng L ⁻¹	Spring water	[143]
As(III), As(V)		Nanocomposite-coated microfluidic-based photocatalyst-assisted reduction device as a vapor generation (VG) - HPLC separation	ICP-MS	0.23; 0.34 µg L ⁻¹	Groundwater	[144]
As(III), As(V), MMA, DMA, roxarsone	H ₃ PO ₄ + NaH ₂ PO ₄ solution		HPLC-ICP-MS	0.24–1.52 µg L ⁻¹	Soil	[145]
MMA, DMA, iAs	Supercritical CO ₂ + methanol, Triton X-405, cyclohexane, butanol, thioglycolic acid n-butyl ester	Supercritical fluid extraction	gas chromatography flame-ionization detection (GC-FID)	0.12–1.1 mg kg ⁻¹	Soils and sediments	[146]
As(III), As(V), DMA, MMA		Phosphine modified polymer microsphere (PPMs) SPE	HPLC-ICP-MS	1.2; 0.96; 0.82; 0.91 ng L ⁻¹	Environmental waters	[147]

Selenium						
Se(IV), Se(VI), SeMet	Phosphoric acid lipase/ alpha-amylase solution protease, methanol		HPLC-ICP-MS		Sediments and plants by mine effluent discharge	[94]
Se(IV), Se(VI), dissolved organic selenides (DOSe)			HG-ICP-MS		Surface water	[148]
Se(IV), Se(VI), selenocyanate	Chloroform	Sequential Derivatization-extraction	GC-MS	0.56; 1.67; 0.35 ng g ⁻¹	Mining wastewater	[99]
Se(IV), Se(VI)	1-undecanol	DLLME	UV-Vis	3.4 µg L ⁻¹	River water	[149]
Se(IV), Se(VI)	Nano-SiO ₂	D-µ-SPE	GFAAS	0.0014 ng L ⁻¹	Rain, sea and underground water	[150]
Se(IV), Se(VI)	Adsorption Au NP	Hydride adsorption	UV-Vis	0.007; 0.006 µg mL ⁻¹	River, lake and sea water	[151]
As(III), As(V), Se(IV), Se(VI)	TiO ₂ NPs	SPE	ICP-MS	0.004; 0.033 µg As L ⁻¹ 0.061; 0.128 µg Se L ⁻¹	Tap, sea, agriculture wastewater	[136]
Se(IV), Se(VI)	Magnetic MWCNTs with Bismuthiol II	MSPE	GFAAS	0.003 µg L ⁻¹	River and sea water	[100]
Se(IV), Se(VI)	DES 3,3'-diaminobenzidine	UA-LPME	GFAAS	4.61 ng L ⁻¹	Water	[152]
Se(IV), Se(VI)	nanosilica-IL hybrid Nano-SiO ₂ @ [C12mim][Br]	D-µ-SPE	GFAAS	0.0011 ng L ⁻¹	Sea, rain, river and underground water	[153]
Seven Se fractions		Sequential extraction	XANES		Agricultural soils	[98]

Six Se fractions		Sequential extraction	XAS and XANES		Phosphate mine soils	[154]
Se(IV), Se(VI)	Graphene oxide nanosorbent TiO ₂	SPE	GFAAS	0.04 ng mL ⁻¹	Spring water	[155]

AALME: air-assisted liquid phase microextraction; **AAS:** atomic absorption spectroscopy; **AB:** arsenobetaine; **ADB18C6:** aminodibenzo-18-crown-6; **AsC:** arsenocholine; **As(t):** total arsenic; **CE:** capillary electrophoresis; **CPE:** sequential cloud point extraction method; **Cr(t):** total chromium; **CV-AFS:** Cold vapor atomic fluorescence spectrometry; **DLLME:** centrifuge-less dispersive liquid-liquid microextraction; **DMA:** dimethylarsinate; **D-μ-SPE:** dispersive micro-solid phase extraction; **EPR:** electron paramagnetic resonance spectroscopy; **FAAS:** Flame atomic absorption spectrometry; **FPLC:** fast protein liquid chromatography; **GC-AFS:** gas chromatography coupled to atomic fluorescence detection; **GC-FID:** gas chromatography with flame ionization detection; **GFAAS:** Graphite furnace atomic absorption spectrometry; **GMA:** glycidyl methacrylate; **GO:** graphene oxide; **HG-AFS:** hydride generation atomic fluorescence spectrometry; **Hg(t):**total mercury; **HPLC-ICP-MS:** high-performance liquid chromatography inductively coupled plasma mass spectrometry; **HS-SPE:** headspace solid phase extraction; **iAs:** inorganic arsenic; **ICP-MS:** inductively coupled plasma mass spectrometry; **IDA:** iminodiacetic acid; **ID-ICP-MS:** isotope dilution inductively coupled plasma mass spectrometry; **LL-MM-CPE:** ligandless mixed micelle cloud point extraction; **MC-ICP-MS:** Multi-collector inductively coupled plasma mass spectrometry; **MD-μSPE:** magnetic dispersive micro-solid phase extraction; **MMA:** monomethylarsenate; **MNP:** magnetic nanoparticles; **MOF:** metal-organic frameworks; **MPTS:** methacryloxypropyl trimethoxysilane; **MSPE:** magnetic solid phase extraction; **NOM:** natural organic matter; **oxMWCNTs:** oxidized multi-walled carbon nanotubes; **PFPD:** pulsed flame photometer detection; **SAX:** strong anion exchange; **PIL:** polymeric ionic liquid; **Tl(t):** total thallium; **SeMet:** selenomethionine; **SPE:** solid phase extraction; **SSME:** supramolecular solvent microextraction; **SWASV:** square-wave anodic stripping voltammetry; **TMAO:** Trimethylarsine Oxide; **UA-LPME:** ultrasound-assisted liquid phase microextraction; **UV-AFS:** UV atomization atomic fluorescence spectrometry; **XAS:** X-ray absorption spectrometry; **XANES:** X-ray absorption near edge spectroscopy; **XPS:** X-ray photoelectron spectroscopy; **XRF:** X-ray fluorescence; **XRAFS:** X-ray absorption fine spectroscopy; **ZPM:** Zwitterion-functionalized polymer microspheres.

Table 1. Trace element speciation analysis – selected recent works

Se(VI), and selenocyanate (SeCN⁻) in aqueous mine wastewater. SeCN⁻ was derivatized with triethyloxonium tetrafluoroborate to ethylselenocyanate, which was extracted into chloroform, and the extract was divided into two aliquots. One of the aliquots was acidified and 3,5-bis(trifluoromethyl)-o-phenylenediamine was added for the derivatization of Se(IV) to 4,6-bis(trifluoromethyl)-2,1,3-benzoselenadiazole; to the second aliquot, HCl was added along with 4-nitro-o-phenylenediamine to simultaneously reduce Se(VI) to Se(IV) and derivatize the combined fraction to 5-nitro-2,1,3-benzoselenadiazole.

Benzoselenadiazoles were extracted with chloroform and the extracts were combined for GC-MS analysis. Firouzabadi et al. [100] described a new magnetic dispersive solid-phase extraction procedure, using multi-walled magnetic carbon nanotubes modified with 5-mercapto-3-phenyl-1,3,4-thiadiazole-2-thione (bismuthiol II) potassium salt (MMWCNTs@Bis) as the sorbent, to separate and preconcentrate Se(IV) prior to its determination by GFAAS. Total Se was determined after reducing Se(VI) to Se(IV) by adding HCl and heating. The concentration of Se(VI) was determined from the difference between total Se and Se(IV). The proposed method was used to determine inorganic Se species in river and sea waters. (Table 1)

Legislation

The importance of TE speciation has been poorly reflected in legislation, which seldom refers to specific species, and no relevant changes have been introduced in these last years. Several toxicological studies provided the basis for policymakers to establish a maximum acceptable limit for certain relevant species, rather than for the total elements or, as it was commonly expressed “an element and its species”. Thus, for example, the United States Environmental Protection Agency (U.S. EPA) and the Canadian Council of Ministers of the Environment (CCME) have established limits for different elemental species of Cr, setting maximum concentrations of Cr (VI) and Cr (III) in water and soils. Speciation-based environmental legislation has been developed for other elements, such as Hg, however is not yet considered in environmental legislation relating to other elements relevant to human and animal health, such as As, which is globally regulated in terms of total elemental concentration.

Se is also legislated in terms of its total concentration, although its characteristics, including its toxicity, as mentioned above, depend strongly on the present species. The complexity of the environmental pathways of Se, as

with As, appears to be the main reason preventing the development of species-focused legislation. The U.S. EPA recently modified its guidelines, considering fish egg/ovary Se as the primary indicator when examining a body of water, rather than just looking at its water concentration [101]. A new proposal for a directive of the European Parliament and of the Council on Soil Monitoring and Resilience (Soil Monitoring Law) is under preparation, where the concentration of heavy metals in soil (As, Sb, Cd, Co, Cr (total), Cr (VI), Cu, Hg, Pb, Ni, Tl, V, Zn) are discussed [102].

Conclusions

Better knowledge about TE speciation in different environmental compartments is crucial. It is essential that reliable data from environmental studies can provide a scientific basis for decision-making by risk managers and policymakers. There has been a huge contribution from academia to understanding the partitioning and biogeochemical cycling of TE in different environmental

compartments in the few years, but there is still much to be done regarding the particular topic of its speciation. For better environmental legislation that addresses speciation aspects, more ecotoxicological studies are mandatory. To this end, reliable analytical approaches that are increasingly accessible and expeditious and, in particular, environmentally friendly themselves, are also necessary.

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Conflict of Interest

None to report.

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