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Note

What do we know about the natural sources, transport and sinks of antimony in the environment?

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ABSTRACT

Limited attention has been given to antimony present in detrital form in the different environmental compartments except for highly polluted systems related in some way to ore deposits. In highly polluted systems, the ultimate sinks of Sb may be the minerals tripuhyite ($FeSbO_4$) or perhaps schafarzikite ($FeSb_2O_4$) but how about Sb dynamics in the much more abundant, weakly polluted or 'non-polluted' systems? This deficiency in our knowledge is probably related to the perception that the element is mostly present 'dissolved' in waters and to a focus on the role of its binding to iron oxyhydroxides in solid phases. Here we evaluate the state of our knowledge in the Sb journey from geological matrices to detrital forms in soils and waters and identify key aspects that require further investigation. In high-temperature environments, Sb demonstrated its striking incompatibility by fractionation into aqueous fluids or sulfide/metallic melts, or by uptake in a few common minerals that accept this element (e.g., rutile or pyrite). In low-temperature environments, Sb enters the structures of minerals with different formation rates and solubilities, creating a confusing impression of being mobile and immobile at the same time. The estimates of Sb concentration in the upper continental crust are scattered and the Sb-bearing mineral(s) there have not yet been identified. Given that sedimentary rocks are consistently enriched in Sb, the carriers could be the clay minerals. In surface water bodies, Sb could be carried predominantly in the particulate fraction, despite the popular belief of the opposite. An important point to consider is the transport of Sb within the suspended particulate matter, not on its surface. In soils, many studies employed sequential extractions to show that Sb accumulates in the 'residual' fraction, without ever asking what the nature of this fraction is. Based on these facts (i.e., knowns), we have identified the unknowns regarding detrital Sb on our planet that should preferentially be addressed by future projects if our understanding is to improve.

1. Introduction

Antimony (Sb), like any chemical element, is present in different environmental compartments (e.g. water, soil, atmosphere, etc.) either bound to a solid phase (on the surface or in the structure) or 'dissolved' (Town and Filella, 2002). Although this distinction is operational because in reality there is a continuum of particle sizes (Filella, 2007), it is widely used and useful when exploring aspects such as transport or bioavailability. However, this size-based classification does not tell us anything about the actual solid phase in which the chemical element is present. To address this question, a panoply of operational methods has been developed, mainly bulk approaches involving the establishment of correlations (e.g., sequential extractions) (Filella, 2011). The application of molecular-level methods, such as X-ray absorption spectroscopy (XAS), is often restricted to heavily polluted systems (e.g., in artificial laboratory mixtures or soils near mines, smelters, and shooting ranges) due to analytical sensitivity limitations.

In the case of Sb, extensive research on the element over the last twenty years has led to the general acceptance that the element is mostly 'dissolved' in waters and therefore mobile, whereas in soils (with a dependence on the redox state), it is mostly immobile (Filella, 2021). This apparent incongruity can be tentatively explained by an interplay of thermodynamics and kinetics (Majzlan, 2021). Reflecting on the problem shows that, in fact, very little is known about how Sb is present in the 'solid phase' in environmental systems. An exception is the mineralogy of Sb minerals in ore deposits and their weathering products, where tripuhyite ($FeSbO_4$) and schafarzikite ($FeSb_2O_4$) were identified as the 'ultimate sinks' of Sb in the environment. It seems, though, that

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ore deposits are local anomalies that can be neglected if the entire budget of an element is to be considered. Interestingly, antimony is the 'most striking example' of highly concentrated occurrence in ore deposits that are cheap to mine and process (Laznicka, 1999). The global endowment of Sb was estimated to ~7.3×10^6 metric tonnes (Laznicka, 1999). Assuming that this global endowment pertains to the uppermost 500 m that are amenable to mining, we calculate that about 0.00002 % Sb in the available crust (available by means of the current exploitation technology) is stored in the ore deposits; the rest is dispersed and moved by natural processes or unintentionally by humans. For copper, as a comparison, Kesler and Wilkinson (2008) estimated that the ore deposits contain 0.08 % of the entire copper budget of the crust.

Discussing what is known, why it is relevant and how progress could be made are the objectives of this article. It is organised as follows: first, the incompatible nature of the element is discussed, followed by consideration of its behaviour and mobility in high-temperature systems before moving on to low-temperature systems and the upper continental crust. Once these fundamental aspects are discussed, existing knowledge on water and soils is considered and interpreted. The topical order is by no means a reflection of the natural flow of antimony between the reservoirs. The flow is circular and facilitates the exchange of Sb (and other elements) between lithosphere, hydrosphere, and atmosphere, with a significant and increasing interference from humans. The importance of this study lies in the blend of the summary of what is known and the perspective of what should be investigated to fill the major gaps in our knowledge. The latter is more urgent than the former, and will hopefully spur future research on antimony and its global cycle.

2. Notation of the oxidation state of antimony and other elements

In this work, we are considering elements in their reservoirs in rocks, minerals, soils, aqueous phase, and air. For clarity, we refer to ions in minerals with their formal charge as Sb^{3+} or Sb^{5+}, etc. In aqueous solutions, such ions never exist isolated, and the species that contain Sb^{3+} as the central ion are labelled as Sb(III), those with Sb^{5+} as Sb(V), etc. One may object that similar species, i.e., coordination polyhedra, exist also in solids. They are, however, bonded to surrounding polyhedra whereas, in an aqueous medium, the species are separated from each other by bulk water. In addition, even though the definition of coordination polyhedra appears to be simple in oxides or silicates, the more covalent bonding in sulfides presents a problem for a clear-cut definition of which atoms still belong to a coordination polyhedron of a central cation and which ones do not.

3. Antimony as an incompatible element

Antimony is one of the least compatible elements, comparable, in terms of incompatibility, to cerium (see Fig. 5 in Gao et al., 1998). We recall that compatibility, as defined in geochemistry, means that ability of the element to be incorporated into the crystal structure of common rock-forming minerals. Elements which are excluded from such common minerals (e.g., feldspars, pyroxenes, amphiboles) are called incompatible. This property dictates the behaviour of elements, including antimony, in igneous, metamorphic, and sedimentary environments through its mineralogy. The incompatibility is caused by

- electronic configuration of Sb^{3+} ($[Kr]4d^{10}5s^2$) that involves a lone s^2 electron pair. This electron pair must be accommodated in a structure such that the electrostatic repulsion forces are minimized. The Sb^{3+} ion requires mostly trigonal pyramidal coordination where the lone electron pair is positioned in the direction opposite to the three ligands. Therefore, substitution of Sb^{3+} for all common octahedrally or tetrahedrally coordinated ions (e.g., Fe^{3+}, Al^{3+}, Si^{4+}) is impeded. The ion Sb^{3+} is taken up readily in structures of sulfides where the structural units (blocks, rods, ribbons) form interfaces that can accommodate the lone electron pairs (Makovicky, 2006). An example thereof is the crystal structure of the most common Sb mineral stibnite, Sb_2S_3 (Kyono et al., 2002). Despite its simple stoichiometry, the topology of the stibnite structure is much more complicated than those of other chemically simple sulfides, such as PbS or ZnS.
- high charge of the Sb^{5+} ion that usually assumes octahedral coordination. In terms of ionic radii, Sb^{5+} is similar to Fe^{3+} and limited, but substantial substitution of these two elements are known, for example in iron oxides (Ackermann et al., 2008; Burton et al., 2020) or jarosite-group minerals (Courtin-Nomade et al., 2012). In these structures, the charge difference is likely compensated by deprotonation which is not an option in most rock-forming minerals.

4. Antimony in high-temperature systems

These properties steer and control the behaviour and mobility of Sb in high-temperature and surficial environments. Under high-temperature conditions (i.e., hydrothermal, metamorphic to igneous regimes), Sb can

- fractionate strongly into H_2O-rich fluids. Stibnite and related minerals have high solubility (> 100 mg kg^{-1} Sb above 300 °C, Williams-Jones and Normand, 1997) that can be rarely attained or exceeded in fluids in "normal" rocks. The most abundant species in hydrothermal fluids are $Sb(OH)_3$ and $HSb_2S_4^-$ (Bessinger and Apps, 2005). Hence, the aqueous solubility of Sb^{3+} can be enhanced in the presence of reduced sulfur but even in its absence, it remains high.
- be temporarily stored in oxide minerals which accept greater degree of substitution of Sb into their structures. Among the common minerals, the most viable alternative is rutile (nominally TiO_2). It is able to accommodate complex charge-compensated substitutions of divalent to hexavalent (Fe^{2+}, Fe^{3+}, Sb^{5+}, Nb^{5+}, W^{6+}) ions into its structure (Agangi et al., 2019; Majzlan et al., 2021). Uptake of Sb^{5+} into rutile is supported by experimentally determined distribution factors (https://earthref.org/GERM/) or studies of natural rocks. Zack et al. (2002) showed that in their eclogite samples, rutile carried >90 % of the total Sb load. Upon prograde metamorphism, rutile breaks down to titanite, a mineral that is not able to store Sb and will release it into the metamorphic fluid.
- be temporarily stored in sulfide minerals which accept greater degree of substitution of Sb into their structures. Among the common minerals, the most viable alternative is pyrite (FeS_2). Antimony enters the structure of pyrite most likely as Sb^-, substituting for S^-. A substitution of Sb^{3+}, in a fashion similar to the substitution of As^{3+} (see Fig. 2 in Deditius et al., 2014), is possible but was never investigated. Upon prograde metamorphism, pyrite breaks down to pyrrhotite and releases S, Au, As, and Sb into hydrothermal fluids (Pitcairn et al., 2015; Agangi et al., 2019).
- fractionate into a sulfide melt. Antimony prefers sulfide melt over silicate melt (Li and Audétat, 2012). Such processes are of importance only in magmas contaminated with sulfur and are manifested by a plethora of Sb minerals in orthomagmatic deposits of Ni-Cu-PGE (Spiridonov et al., 2015).
- fractionate into a metallic melt. Such processes were certainly of great importance during the initial differentiation of the Earth into the primitive mantle and core (Taylor and McLennan, 1995) and are supported by distribution coefficients determined on natural materials (Klöck and Palme, 1988). In today's crust and mantle, they are probably negligible.

5. Antimony in low-temperature systems

In low-temperature (i.e., weathering) regime, Sb is exposed to atmospheric O_2 and H_2O and rapidly attains the highest oxidation state Sb (V) (Leuz et al., 2006). Mineralogy of Sb(V) is known only from polluted sites whose material is amenable to mineralogical techniques, including chemical analyses with an electron microprobe, X-ray diffraction, and spectroscopy. The question of scaling these results down to weakly polluted systems (e.g., those distal to pollution sources, affected only by atmospheric deposition) is unresolved. Antimony in weathering environments is

- initially bound in transient Sb(III) oxides such as kermesite (Sb_2S_2O) or valentinite (Sb_2O_3). They succumb fairly quickly to oxidation.
- potentially bound as Sb(III) to the octahedral nets of sheet silicates as a tridentate hexanuclear inner-sphere complex. This complex is a fragment from the crystal structure of chapmanite [$Fe_2Sb(Si_2O_5)O_3(OH)$] (Majzlan et al., 2021).
- is associated with Fe-Al-Mn oxides via adsorption or incorporation into their structure (e.g., Burton et al., 2020).
- thought to be mobile as Sb(V) in the environment (e.g., Ashley et al., 2003).
- thought to be immobile as Sb(V) in the environment (e.g., Diemar et al., 2009).

The last two statements, based on geochemical and mineralogical arguments, appear to be in a direct conflict. They can be reconciled if the Sb(V) minerals and their properties are considered (Majzlan et al., 2016). During the early stages of weathering, Sb can be released into aqueous solutions and quickly form minerals with high solubility, such as brandholzite [$Mg[Sb(OH)_6]_2 \cdot 6H_2O$] (e.g., Borčinová Radková et al., 2020). Such minerals can provide ample supply of Sb into the solutions and Sb appears to be mobile. They crystallize and dissolve rapidly. Given enough time, Sb will unite with iron to form much less soluble minerals, such as tripuhyite ($FeSbO_4$). Field work suggests that formation of tripuhyite requires years to decades (Majzlan et al., 2011) and locks Sb in a phase with very low solubility (Leverett et al., 2012). Hence, the question of mobility of Sb is an interplay of thermodynamics and kinetics. In immature systems, Sb will appear to be more mobile, in mature systems, it will be immobile.

6. Implications for antimony dispersal in upper continental crust

Even though the continental crust represents only 0.6 wt% of the entire Earth, it houses 20–70 % of the entire budget of incompatible elements (Rudnick and Fountain, 1995). The estimates of Sb concentrations in the upper continental crust (UCC) are scattered (Gao et al., 1998; Rudnick and Gao, 2003; Togashi et al., 2000, see Table 1). For the purposes of recognizing which minerals carry Sb in the UCC rocks, this scatter is of less importance because we have to openly admit that we have hardly any information on the speciation and mineralogy of Sb in UCC rocks. This deficiency is in stark contrast with a good handle on the mineralogy of Sb minerals in ore deposits and their weathering products.

Antimony, together with arsenic, appears to be markedly enriched in sedimentary rocks (by a factor of 2–3), when compared to their young igneous counterparts (Togashi et al., 2000). This enrichment can be detected for sediments of various geological age, although there is no obvious trend of Sb concentrations with age (Gaschnig et al., 2016). Antimony shows broad correlation to the alteration index (CIA) of the UCC rocks (Gaschnig et al., 2016), correlation with Te and As (Hu and Gao, 2008), with Ce (Sims et al., 1990), or no correlation with trace elements at all (Gaschnig et al., 2016). It has been suggested that Sb is bound to clay minerals (Gaschnig et al., 2016) and such suggestions are supported by results of local studies focused on Sb (Drahota et al., 2023). Furthermore, studies show consistently that Sb is lost rapidly upon metamorphic overprint of sedimentary rocks. Such studies deal either with the composition of UCC (Togashi et al., 2000) or the formation of Au–Sb deposits (Patten et al., 2023). In the latter work, the source of Sb was assigned to metasedimentary rocks. Recently, Goldfarb and Pitcairn (2023) argued that the Au–Sb deposits originate as a result of metamorphism, not igneous activity. The implicit corollary thereof is that Sb is indeed sourced from the metasedimentary rocks.

Table 1
Published antimony upper continental crust (UCC) concentrations.

UCC (mg kg^{-1})	Reference	Comments
0.2	Taylor (1964)	Hypothesis: “composition of the continental crust can be represented by a mixture of equal quantities of basic and acidic rock”. Basalt average (0.2) and granite average (0.2) from Turekian and Wedepohl (1961). In Turekian and Wedepohl (1961): “Data from Onishi and Sandell (1955). These authors were not completely satisfied with their results and claim they should be taken tentatively. In the absence of any later information these are the best estimates available”
0.6	Brunfeldt and Steinnes (1969)	Analysis of rocks by NAA: “antimony content of basic rocks is higher on average than for granitic rocks” + composition hypothesis in Taylor (1964)
0.2	Taylor and McLennan (1985)	“Value from the compilations in the *Handbook of Geochemistry* (Wedepohl, 1969)”
0.2	Taylor and McLennan (1995)	“Adapted from Taylor and McLennan (1985), with minor alterations”
0.45 ± 0.08	Sims et al. (1990)	Continental crust rocks of different geological ages, midocean ridges and ocean islands; analytical method: NAA
0.31	Wedepohl (1995)	“Analysis of shales, loesses, and greywackes in the assumption that erosion and sedimentation produced an average sample of exposed crust”. Rock averages from Onishi and Sandell (1955)
0.31	Gao et al. (1998)	905 composite samples produced from over 11,000 individual rock samples covering an area of 9.5 × 10^5 km^2 in eastern China; analytical method: atomic fluorescence (digestion method not given)
0.61	Togashi et al. (2000)	Upper crust of the Japan Arc; higher Sb and As concentrations than in previous UCCs; 166 specimens analysed; analytical method: ICP-MS (digestion method not given)
0.4 ± 0.1	Rudnick and Gao (2003, 2014)	Average of values in Wedepohl (1995), Sims et al. (1990) and Gao et al. (1998). Taylor and McLennan (1985) excluded because derived from same source as Wedepohl’s
0.75 ± 0.11	Hu and Gao (2008)	Value deduced from correlation Te:Sb in loess samples and Sb:As in sedimentary samples (excluding CIA > 72) and UCC for Te; analytical method: ICP-MS after high-pressure HF/HNO_3 digestion
0.418 ± 0.174 0.382 ± 0.156	Gaschnig et al. (2016)	Glacial dimictites; first value (preferred): filtered to remove carbonate-rich samples; analytical method: ICP-MS after high-pressure HF/HNO_3 digestion
No best value proposed	Rudnick (2018)	Max/min values = 3.75, considering Taylor and McLennan (1985, 1995), Wedepohl (1995), Gao et al. (1998), Togashi et al. (2000), Hu and Gao (2008), Gaschnig et al. (2016)

The available hints point indeed at the clay minerals as the carriers of Sb in the sedimentary rocks. As mentioned above, Sb has affinity to the octahedral nets on the surfaces of the clay minerals. The tridentate hexanuclear inner-sphere complexes on clay minerals appear to be a viable alternative for the storage of trace amount of Sb in sediments. The questions to verify or refute this hypothesis include

- the oxidation state of Sb in the sediments. The inner-sphere complexes proposed here are formed only by Sb(III).
- composition of the clay minerals, namely their Fe/Al ratio. Chapmanite itself is an iron-rich sheet silicate [$Fe_2Sb(Si_2O_5)O_3(OH)$] and

it seems that Sb prefers adsorption onto such surfaces. The detrital sheet silicates, on the other hand, are Al-dominated. The authigenic clay minerals, formed in aqueous environments as biologically induced are, however, Fe-rich (Konhauser and Urrutia, 1999). The mass balance of detrital and authigenic clays is not known and it is not clear if the authigenic clays can be seen as important Sb carriers.

The clays could also uptake Sb^{5+} as a substitution for Fe^{3+}/Al^{3+}, coupled with local deprotonation. Although such substitution is viable, this form of Sb would probably not be as labile as required by the observation that even low-grade metamorphism forces most of Sb out of the metasediments (Patten et al., 2023).

7. 'Particulate' antimony in natural waters

Although it has been repeatedly pointed out that the distinction between 'particulate' and 'dissolved' fraction of chemical elements in natural waters is arbitrary and of uncertain value, it is now widely entrenched in standards (APHA, 2022; USEPA, 2022). Typically, filters of 220 or 450 nm pore size are used as an arbitrary boundary between the two fractions. In the case of Sb, it is widely accepted that the element is mostly present as 'dissolved' (Filella et al., 2009). Geochemists often use 'distribution' or 'partition' coefficients (*K*d) to describe and predict the partitioning of chemical elements between the 'dissolved' and 'particulate' phases in natural systems. Such coefficients are defined as the quotient between the concentration of the element in the particulate phase (*C*p), in mass of the element per unit weight of solid phase, and its 'dissolved' concentration (*C*d) in mass of the element per unit volume of solution determined after filtration. Reported values of *K*d ($L\ g^{-1}$) for Sb in rivers are scarce and range from 0.43 to 33 (Table 2). These *K*d values are usually interpreted to mean that Sb has a low affinity for natural particles. This limited affinity may be true, but it should be noted that the conclusion here is based on the conceptualisation of *K*d as a measure of sorption on a solid matrix that does not contain the element itself (i.e., the assumption that *K*d is based on the existence of an underlying C-type sorption isotherm). However, the possibility that *C*p reflects Sb contents in detrital particles cannot be excluded and was not considered so far.

In principle, and derived from its definition, *K*d should not show any dependence on the concentration of suspended solid particle. In practice, however, all possible types of behaviour (i.e., no correlation, positive and negative correlations) have been reported for Sb (Table 2). In general, the decrease in *K*d values with increasing particle concentrations has been attributed to the formation of colloids and their subsequent coagulation into larger filterable particles, as coagulation leads to less surface available for sorption (Li et al., 1984), again reasoning based solely on sorption. The change in particle quality (i.e., origin) has also been evoked in the case of high particle concentrations in flood events but, curiously, the presence of detrital Sb has not been taken into account in the interpretation of the observations.

Since Sb is mostly 'dissolved' in waters, it is generally assumed that it is mostly transported as such in rivers and that the contribution of 'particulate' Sb to the oceans is therefore insignificant. However, although somewhat counter-intuitive, Fig. 1 illustrates that, as the percentage of any chemical element present in the 'dissolved' fraction depends not only on the *K*d values but also on the amount of total

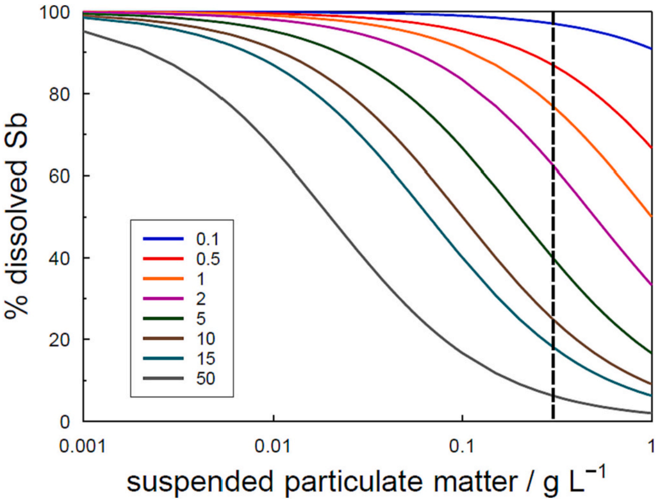

Fig. 1. Theoretical percentage of 'dissolved' Sb as a function of the concentration of suspended particulate matter, SPM, for different values of *K*d ($L\ g^{-1}$) covering the range of *K*d found for Sb calculated following Gaillardet et al. (2014) as: % dissolved Sb = 100(1/(1+ *K*d SPM)). Vertical dashed line corresponds to the world mean value of particulate matter for large rivers as estimated by Gaillardet et al. (2003) at 0.350 g L^{-1}. Adapted from Filella and Rodríguez-Murillo (2021).

Table 2
Reported values of partition coefficients, *K*d ($L\ g^{-1}$), for antimony in surface waters. Values for antimony radioisotopes not included. Values from mining-related studies (e.g., Johnston et al., 2020) or where the 'particulate' antimony was clearly not total antimony (e.g. Javed et al., 2020) were not taken into account. Values in chronological order of publication. Updated from Filella and Rodríguez-Murillo (2021).

System	*K*d / L g^{-1}	Correlation with suspended particulate matter (SPM)	Digestion particulate matter	'Dissolved' Sb / ng L^{-1}	Reference
Thames River	33	–	NAA	270	Habib and Minski (1982)
Rhône River	5.3	–	not given	487	Guieu et al. (1993)
Waikato River, New Zealand	Summer: 4.5 (median, n = 12) Winter: 15.2 (median, n = 12)	–	*aqua regia*	300–900	Wilson and Webster-Brown (2009)
Gironde Estuary, France	16.2 (mean, n = 96)	–	HF–HCl–HNO_3	92–292	Masson et al. (2009)
Gironde Estuary, France	12.0 (median, n = 50)	no correlation	HF–HCl–HNO_3	205–245	Masson et al. (2011)
Rhône River, France	6.6 (median, n = 41)	decreasing values with increasing SPM	"acid digestion"	163–644	Ollivier et al. (2011)
Kamo River, Japan	1	–	HF–$HClO_4$–HNO_3	160	Asaoka et al. (2012)
Oda River, Japan	1.0 (median, n = 18)	decreasing values with increasing SPM	HF–$HClO_4$–HNO_3	9–39	Matsunaga et al. (2013)
Gironde Estuary, France	8.0 (median, n = 93)	increasing values with increasing SPM	HF–HNO_3–HNO_3	80–400	Gil-Díaz et al. (2016)
Yangtze Estuary, China	0.70	–	not given	1119	Yin et al. (2016)
Yangtze Estuary south branch (95 % discharge), China	0.43	increasing values with increasing SPM	HF–$HClO_4$–HNO_3	not given	Feng et al. (2017)
Lot-Garonne River system, France	15.8 (median, n = 1057)	no correlation	HF–HNO_3–HNO_3	~200	Gil-Díaz et al. (2018)

particulate matter in the water, some scenarios are possible where a relatively high percentage of Sb is not 'dissolved' in rivers. Notice that, even if many rivers have just a few milligrams of suspended particles per litre, the world mean value of particulate matter for large rivers has been estimated at 350 mg L^{-1} (Gaillardet et al., 2003). Taking this concentration at its face value, Fig. 1 shows that for $Kd = 5$, 40 % of Sb will be transported as dissolved and 60 % as associated with particulate matter.

Viers et al. (2009) estimated the riverine flux of particulate Sb to the oceans at 33 kt y^{-1} by using a value of 15 Gt y^{-1} for the world suspended matter flux (Berner and Berner, 1987) and their own compiled average value of Sb in suspended sediments (2.19 μg g^{-1}). According to their results, Sb is one of the elements (only second to Cd) with the highest enrichment in the riverine particulate fraction when compared to the average UCC concentration. Numerically, the enrichment factor is ~10, but there is no explanation of this enrichment so far. Considering a total water discharge of 3.74×10^4 km^3 y^{-1} (Berner and Berner, 1996), the estimated riverine 'dissolved' Sb flux would be 2.6 kt y^{-1} (Gaillardet et al., 2003). This value is much lower than the estimated load of particulate Sb in rivers, implying that Sb is mainly transported in the solid phase. In practice, up to 90 % of the suspended particles are deposited when river water mixes with seawater (Milliman and Farnsworth, 2013) and, consequently, only a small percentage of the continental material and its associated chemical elements reaches the open ocean. These data illustrate that the 'particulate' fraction of Sb should not be neglected when considering the cycling of Sb in the environment.

8. Soils

Existing information on Sb speciation in soils has been mainly obtained by applying sequential extraction techniques (Filella, 2011). These methods use the sequential action of progressively more powerful extractants in order to simulate the conditions under which trace elements associated with certain components of solids can be released and thus identify the binder phases. Most existing methods are based on a scheme first introduced by Tessier et al. (1979) for sediments. Ever since then, the approach has become popular in spite that many criticisms have been made, both of the methodological approach itself and of the use of specific extractants and conditions (Pickering, 1981; Martin et al., 1987). Despite attempts to establish reference methods (e.g., Ure et al., 1993), curiously in practice almost all authors introduce small 'clever' changes to pre-existing procedures, which further complicates the comparison of results. The reader not familiar with the subject will find a comprehensive description of the main schemes in Filgueiras et al. (2002). In the case of Sb, low to very low extraction yields by mild extractants have been reported in single extraction experiments and the majority presence of Sb in the so-called 'residual' fraction in sequential methods (Filella, 2011). The Sb extracted by the sequential methods is mainly associated with 'iron oxide' fractions, but the total fraction of extracted Sb is generally very small in most of the soils studied. Hence, the amount of Sb bound to iron oxides is in fact low. Nearly all these results stem from soils close to mines, smelters, or roads, though. Therefore, the usefulness of the results in the context of understanding how Sb is present in soils that are not heavily polluted needs to be considered with care. Since the publication of Filella (2011), the use of sequential extractions proliferated, mainly in the context of multi-element studies, largely due to the explosion of studies by Chinese scientists. The general message remained the same, namely that most of the Sb is found in the residual fraction. The nature of this fraction, including its mineralogical composition, was not studied.

Several geochemical mapping projects have been carried out by geological surveys over the last 20 years. The areas surveyed cover large regions up to entire continents and allow for the mapping of elemental distributions. In the case of Sb, six continental surveys (> 1,000,000 km^2) have been produced. They have recently been described and discussed by Reimann and Fabian (2021). In Europe, broadly speaking, there is a strong difference in Sb concentration in soils in southern (high Sb) and northern/central Europe (low Sb). A similar pattern emerges for other elements, e.g., for arsenic (Reimann et al., 2015). Sodium, as an example of a major element, shows consistently higher concentrations in the north than in the south of Europe. These patterns may be related to lithological differences between older crystalline rocks in the north and their weathering products moved southward by glaciation, and younger sedimentary and volcanic rocks in the south. The observed difference probably reflects differences in soil age and thus weathering rates after the last glaciation period. An interesting by-product of these studies is that the reported Sb concentrations are highly dependent on the chemical digestion methods applied: when *aqua regia* is used, the average concentration value is three times lower than when soils are digested with a four-acid (HNO_3, $HClO_4$, HF, HCl) extraction. This divergence suggests that a significant part of the soil Sb is present in refractory minerals.

9. Suggestions for future research

Much work has been expended to understand the speciation and mobility of the element Sb in various environmental compartments (Filella et al., 2009; Filella, 2021) but, surprisingly, limited attention has been paid to Sb present in detrital form. In this work, the evaluation of our knowledge of Sb occurrence from geological matrices to detrital forms in soils and waters has allowed us to identify known and unknown aspects. These are concisely detailed in Table 3.

A possible approach that could help to advance our understanding of the role of detrital Sb could be the application of mineralogical identification techniques to fractions that accumulate this element. Such fractions could be the residual fraction in soils, or a specific size fraction separated from rocks or waters, applying appropriate separation techniques. In fact, identification of the minerals that have leached in each extraction, using X-ray diffraction or automatized mineralogical analysis, has already been suggested in order "to decrease the uncertainty" for exploration purposes (Dold, 2003) and the approach has sometimes been applied to mine remediation (e.g., Caraballo et al., 2009) but not, to our knowledge, to the study of Sb speciation in suspended particulate matter in waters, sediments, and soils.

CRediT authorship contribution statement

Juraj Majzlan: Conceptualization, Data curation, Validation, Visualization, Writing – original draft, Writing – review & editing. **Montserrat Filella:** Conceptualization, Data curation, Validation, Visualization, Writing – original draft, Writing – review & editing.

Table 3
Main identified knowns and unknowns.

Known/assumed	Unknown
Sedimentary rocks have higher Sb concentrations than their igneous counterparts; they lose Sb readily upon metamorphism	What are the carriers of Sb and why are they relatively labile?
Much of the data that we have is based on samples from heavily polluted systems	Can such data be applied or extrapolated to weakly polluted or unpolluted systems?
The concentration of Sb in the riverine particulate fraction is ~10 higher than the average UCC concentration of Sb	Is this enrichment owing to systematic analytical errors (e.g., in the UCC concentrations), to pollution, or to some natural processes?
Most of the Sb carried by the world rivers is found in the particulate fraction	Is the mode of association of Sb with the particles via adsorption onto surface or inherited inside the particles from the geological source?
Most Sb in the soils is stored in the residual fraction of the sequential extraction procedure	What is the mineralogical composition of this fraction and which phases are the Sb carriers?

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.

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