Tellurium in the environment: current knowledge and identification of gaps

Montserrat Filella, A,G Clemens Reimann, B Marc Biver, C Ilia Rodushkin D,E and Katerina Rodushkina E,F

B Geological Survey of Norway, PO Box 6315 Torgarden, N-7491 Trondheim, Norway.
C Bibliotheque Nationale de Luxembourg, Annexe Kirchberg, 31, Boulevard Konrad Adenauer, L-1115 Luxembourg, Luxembourg.
D Division of Geosciences and Environmental Engineering, Lulea University of Technology, S-971 87 Lulea, Sweden.
E ALS Laboratory Group, ALS Scandinavia AB, Aurorum 10, S-977 75 Lulea, Sweden.
F Present address: Ghent University, Department of Chemistry, Atomic and Mass Spectrometry Research Group, Campus Sterre, Krijgslaan 281 – S12, B-9000 Ghent, Belgium.

G Corresponding author. Email: montserrat.filella@unige.ch

Environmental context. Tellurium, a chemical element increasingly being used in new technologies, is an emerging contaminant. Our understanding of tellurium’s environmental behaviour, however, is poor, with critical knowledge gaps such as its distribution in the various environmental compartments and the environmental fluxes associated with mining, usage and disposal. Significant progress in these areas requires the development of robust analytical methods that are sufficiently sensitive to provide data at environmentally relevant concentrations.

Abstract. Tellurium has recently become a ‘technology-critical element’ increasingly used in new applications. Thus, potential environmental impacts need to be evaluated. This, in turn, requires knowledge of its typical concentrations in the environment along with better understanding of the chemical processes governing its environmental behaviour. We evaluate the current situation of our understanding of tellurium in the environment and identify the areas where improvements in measurement technology are most needed. The comprehensive evaluation of published data described in this study shows that values for tellurium concentrations in the different environmental compartments are scarce, particularly in the case of natural waters where reliable estimates of tellurium concentrations in seawater and freshwater cannot even be produced. Data in air are even less abundant than for natural water. Concentration data do exist for soils suggesting a predominant geological origin. Some urban soil surveys and lake sediment data close to tellurium contamination sources point to possible effects on the element’s distribution as a result of human activity; long-range atmospheric transport remains to be proved. Current knowledge about tellurium behaviour in the environment is strongly hindered by analytical difficulties, with insufficiently low analytical detection limits being the main limitation. For instance, ‘dissolved’ concentrations are well below current analytical capabilities in natural water and often require pre-concentration procedures that, for the moment, do not provide consistent results; solid samples require complex mineralisation procedures that often exclude tellurium from routine multielement studies. In general, the use of available measuring techniques is far from straightforward and needs particular expertise. Overcoming the current analytical limitations is essential to be able to progress in the field.

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Introduction

Tellurium belongs to group 16 of the Periodic Table of elements. It can exist in a variety of oxidation states (VI, IV, 0, –II) in environmental and biological conditions. The environmental behaviour of tellurium is largely unknown. As is the case for other technology-critical elements, two reasons may explain why this element has been largely neglected: its low concentration in environmental compartments and, until recently, its limited number of uses. The current increased interest in the study of tellurium is caused by its use in new technological applications. Tellurium has been included in some lists of critical elements (table 1 in Filella and Rodrıíguez-Murillo 2017) and it is currently considered as a critical material in the US (Fortier et al. 2018) but not in the European Union (European Commission 2017).

The first step in the understanding of the environmental behaviour of any chemical element is knowledge of its concentration in different environmental compartments. Based on
this information, it is possible to study biogeochemical cycles (i.e. establish fluxes among the compartments), evaluate the effect of the use of the element – including evidence of anthropogenic impact and (eco)toxicological effects – and progress in the understanding of the underlying chemical and biological processes at play. For this reason, the first aim of the present study is to answer the question ‘how much tellurium is there?’ This is mainly achieved through tracing original concentration data sources for different environmental compartments (i.e. matrices) and critically assessing their soundness. The result of our inquiry is neither a critical compilation of published data nor a traditional ‘narrative’ review. We have paid special attention to the identification of the main current deadlocks in tellurium measurement. Some areas of research on tellurium have been reviewed a few times in recent decades, particularly tellurium uses, biology and toxicology. Reviews published during the last 25 years are compiled in Table S1 (Supplementary Material). They contain useful information and should be consulted where appropriate, particularly in relation to toxicity and biological aspects not touched on in this study.

**Methodology**

The type of information collected in this study differs depending on the environmental compartment considered. Whereas for water and the atmosphere, we have entirely relied on the comprehensive compilation of data published in individual studies, the discussion on soils is based on data from extensive soil surveys. The reason is that soil surveys exist whereas, particularly in soils, the information-value of sparse concentration measurements is very limited. In the case of biological media, only limited sets of analytically traceable data are presented and discussed. Some discussions are based on personal experience accumulated by the different authors over years of analytical method development and application.

References have been collected mainly by searching Web of Science™. In addition, the tables of contents of several journals have been reviewed manually to identify potentially relevant articles. In many cases, reading of these papers led to new references. Only original and review articles have been considered. Articles published in predatory journals have been avoided. Patents, conference proceedings or abstracts and reports, and, as a rule, non-peer-reviewed publications have not been included. An exception concerns reports when one of the coauthors was involved in their authorship. Blind copying of published values in secondary references has been avoided. Where secondary sources are needed (e.g. in some parts of the Tellurium in a nutshell section), special care has been taken to use updated and adequately referenced sources only.
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Tellurium in a nutshell

Uses, sources and world resources

Tellurium is used in the production of cadmium telluride (CdTe) solar cells; this is the major end use for tellurium nowadays. Estimates of global consumption of tellurium by end use are (USGS 2018): solar, 40%; thermoelectric production, 30%; metallurgy, 15%; rubber applications, 5%; and other, 10%. Other sources may give slightly different percentages (Ciaucci et al. 2015). Interestingly, in 1999, the estimated distribution of uses (USGS 2018) was as follows: iron and steel products, 50%; catalysts and chemicals, 25%; additives to non-ferrous alloys, 10%; photoreceptors and thermoelectric devices, 8%; and other uses, 7%. Thus, tellurium demand for most of these uses has remained largely constant over the last 20 years, but has now been overtaken by the demand for photovoltaic and thermoelectric applications. A more detailed list of tellurium uses can be found in Table S2 (Supplementary Material).

Updated data on tellurium world production are not available. According to the USGS, the world production (exclusive of the US, whose production figures were withheld in order to avoid disclosing company proprietary data) in 2017 amounted to 410 and 124 tonnes in 1999, according to the same source. Thus, the new uses of tellurium imply a 3–4× production increase. However, production figures remain very low when compared with those of the main base metals (e.g. copper production in 2010 was estimated at 15.9 million tonnes).

More than 90% of tellurium is produced from anode slimes collected from electrolytic copper refining, and the remainder is derived from skimming at lead refineries and from flue ashes (Talens-Peiró et al. 2013), less than 1% of tellurium is recycled. Traditional metallurgical and chemical uses are dissipative per se (metallurgical additives, chemicals, rubber manufacture). Thermoelectric devices could be recycled but are not collected. The amount recycled from CdTe solar cells is limited because most CdTe solar cells are fairly new and have not yet reached the end of their useful life. There is little or no old scrap from which to extract secondary tellurium.

Reserves of tellurium are difficult to assess because of uncertainty concerning the tellurium content in the copper or other ores from which it is recovered as well as the yields of the process. Kavlak and Graedel (2013) give an estimated value of 2–10% (by mass) of tellurium in anode slimes, citing a secondary source. Published recovery efficiencies range from 4.5% (Kavlak and Graedel 2013) to 7% (Andersson 2000) of tellurium extracted from the ground when mining copper, but not every copper refinery recovers tellurium. Upward revisions are possible if there is an improvement in recovery factors – but this is unlikely owing to the low economic return from tellurium – or if other potential sources, such as gold telluride or other ores from which it is recovered, are exploited.

Main element characteristics and chemistry

The main characteristics of tellurium as a chemical element are given in Table S3 (Supplementary Material).

Natural tellurium has eight isotopes, four of which are stable (120Te, 124Te, 125Te and 126Te) and only account for 33.2% of naturally occurring tellurium. This is owing to the long half-lives of the unstable isotopes. For instance, 130Te has a half-life of 6.9(1.3) × 10^{20} years whereas 128Te, with a half-life of 2.0(3) × 10^{24} years, is the isotope with the longest half-life among all radionuclides (Audi et al. 2017).

Tellurium is a member of the chalcogen group, which also includes oxygen, sulfur and selenium. Tellurium can exist in various redox states: telluride (−II), elemental tellurium (0), tellurite (IV) and tellurate (VI).

Several more or less consistent values for the redox potential of the couple TeIV/TeVI are available (Filella and May 2019) and there seems to be agreement that under ordinary environmental conditions (oxic systems, circumneutral pH, absence of ligands other than those derived from water), the dominant species should be those of TeIV, while TeVI species will be potent oxidants. TeIV behaves as a triprotic acid, with pK values of approximately 2.4, 6.4 and 10 at 25°C while TeVI is a diprotic acid with pK values at 7.7 and 10.8 at the same temperature.

A puzzling aspect in tellurium literature is the lack of agreement about the identity of the main TeIV and TeVI species, in particular the tellurate. Sometimes, it is considered as an oxyanion (i.e. H2TeO4), sometimes as a hydroxide (i.e. Te(OH)6, also written as H3TeO3). This leads to statements like: ‘Tellurium can occur in diverse forms: TeO2, HTeO3, H2TeO4, Te(OH)6, Te(OH)2O, and Te(OH)5’ (Baturin et al. 2007) or ‘Aqueous Te species are suggested to be oxyanions (e.g. TeO2^2-, TeO3^2-) or hydroxide ions (e.g. Te(OH)5^-, TeO(OH)4^-) but this process is not completely understood’ (Harada and Takahashi 2008). In fact, it is well established that, in the solid state, telluric acid contains discrete Te(OH)6 octahedra and that the same structure exists in aqueous solution (Andersson et al. 1981). Even though this has been known for more than 100 years now (Gutbier 1902), the oxyanion formula has persisted in the literature until now. Recommended formulae are: TeO2^2-, HTeO3^-, H2TeO4^-, Te(OH)5^- and TeO(OH)4^- for TeIV and TeO2(OH)2^2-, TeO(OH)3^- and Te(OH)4^- for TeVI.

Tellurium forms alkyl derivatives (Wallschlager and Feldmann 2010) but they tend to decompose under heat and light radiation. Tellurium has a lower electronegativity than sulfur and selenium and for this reason, Te–C bonds are weaker than Se–C and S–C ones.

Terrestrial abundance

Values of tellurium terrestrial abundance given in secondary sources are rather variable and sometimes imprecise (e.g. 0.36–10 μg kg⁻¹ (Hein et al. 2003), <10 μg kg⁻¹ (Olliveliv et al. 2008); ~2 μg kg⁻¹ (Baeseman et al. 2009), 1–5 μg kg⁻¹ (Belzile and Chen 2015)). They often lack the original data source or refer to other secondary sources. Classical publications on elemental crustal abundances (Taylor and McLennan 1985, 1995; Condie 1993; Wedepohl 1995; Gao et al. 1998; Plank and Langmuir 1998; McLennan 2001; Rudnick and Gao 2003, 2014) do not provide any value for tellurium. Because tellurium is present at very low concentrations in most geological materials, the analytical difficulties in determining it at nanogram levels largely explain the lack of crustal abundance data. Hu and Gao in their authoritative work published in 2008 give 27 ± 3 μg kg⁻¹ as the concentration of tellurium in the upper continental crust (UCC) (Hu and Gao 2008). This value is based on a positive correlation with boron in sedimentary rocks and loess and upper crustal boron abundance, and can be considered as the best available estimate for the moment. Much lower values have usually been used in enrichment factor (EF) calculations (Hein et al. 2003), leading to very high EF values, often considered exceptional.

The extreme rarity of tellurium in the Earth’s crust is not a reflection of its cosmic abundance (Anders and Grevesse 1989;
the study of Lee and Edmond (1985) published more than Table S6 (Supplementary Material) shows data for rain and snow. in Tables S4 and S5 (Supplementary Material) respectively. Values published for marine waters and freshwaters are collated How much tellurium in surface waters? 

Minerals 

There are 134 International Mineralogical Association (IMA)-recognised minerals that contain tellurium (www.mindat.org; accessed 6 March 2019). They are distributed as follows: sulfides and sulfosalts (70), oxides (45), sulfates (12), halides (2), phosphates (1), arsenates (1), vanadates (1), silicates (1), native element (1). Tellurium is well known for its association with gold (15 minerals among which nargayite, calaverite, krennerite, petzite, sylvanite). Tellurium compounds are the most common naturally occurring chemical compounds of gold. Tellurium is also most commonly associated with lead (50 minerals), copper (47) bismuth (38), silver (24), iron (22), palladium (18). The reader is advised to consult www.mindat.org if interested in detailed information about tellurium minerals and their distribution, while keeping in mind that information from Mindat does not allow inferences as to the abundance of a particular species, because Mindat ‘abundances’ reflect the number of localities entered for a particular species and they are therefore skewed towards minerals of interest to collectors and may give a biased view where rare species are over-represented compared with common ones.

How much tellurium in surface waters? 

Values published for marine waters and freshwaters are collated in Tables S4 and S5 (Supplementary Material) respectively. Table S5 includes values for groundwater and drinking waters. Table S6 (Supplementary Material) shows data for rain and snow. The most widely cited, and used, seawater data come from the study of Lee and Edmond (1985) published more than 30 years ago. These concentration values, and others published before 1990, are of the order of tenths of nanograms per litre. More recent values (not very abundant) do not confirm these initial results, with concentrations in the tens of nanograms per litre, a 2–3 orders of magnitude difference. Unfortunately, the lack of certified reference materials with certified values for tellurium in natural waters makes it impossible to assess the accuracy of the results obtained. As discussed later, the use of the values of Lee and Edmond as a reference is widespread and they serve as the basis of many assumptions concerning tellurium behaviour in the environment.

It is always more difficult to evaluate the reliability of concentrations in freshwater than in seawater because of the more direct influence of the local geological background and anthropogenic contamination on the concentrations measured as compared with seawater (i.e. there is a difficulty in knowing whether differences are ‘real’). It is easy to notice, however, that authors who reported very low concentrations in seawater reported similar levels in freshwaters (Yoon et al. 1990), probably pointing to some systematic analytical artefact. However, some published values are positively absurd, with values exceeding 100 or even 1000 ng L\(^{-1}\) (e.g. Urbánková et al. 2011, to cite only one recent article) and such results have not been included in our compilation. Tellurium literature is also plagued with studies where the authors develop methods intended for aqueous samples with insufficiently low detection limits. Unfortunately, large geochemical surveys, like FOREGS (Forum of European Geological Surveys) (Salminen et al. 2005) that usually allow the evaluation of the influence of geological factors suffer from insufficient detection limits and have high proportions of below detection limit (BDL) values (60%, detection limit (DL): 5 ng L\(^{-1}\)).

Most recent values in surface waters point to concentrations in the few to low tens of nanograms per litre range (Tables S4 and S5). These values have been obtained with different methods and, in the case of a voltammetric determination, without any preconcentration procedure (Biver et al. 2015). However, it is at present impossible to suggest a reliable reference value because of the many analytical difficulties involved. The major limitation is inadequate limits of detection for tellurium of routinely available, modern spectrometric instrumentation, preventing accurate quantification of the element in uncontaminated natural matrices. This has called for the use of preconcentration techniques with the concomitant risks of analytic loss. The different behaviour of Te\(^{4+}\) and Te\(^{6+}\) during preconcentration and, in some cases, at measurement stage often requiring Te\(^{4+}\) prereduction, add to the analytical difficulties. These aspects, together with the intricacies of tellurium measurement by inductively coupled plasma mass spectrometry (ICP-MS), are discussed in the section Measuring tellurium.

Tellurium in the atmosphere 

For many elements, initial data in atmospheric samples come from neutron activation analysis (NAA) multielement studies. This is not the case for tellurium. This concords with Dams’ view, who does not deem tellurium an environmentally relevant element in his IUPAC critical review on the application of nuclear activation techniques to environmental samples (Dams 1992). Most of the existing data (Table S7, Supplementary Material) come only from the work of two research groups in the late 80s and early 90s: a group in the University of Missouri (Chiou and Manuel 1984, 1986; 1988; Muangnoicharoen et al. 1986, 1988) and a Japanese group at Keio University, Yokohama (Hashimoto et al. 1989; Watanabe et al. 1989; Sekine and Hashimoto 1991; Sekine et al. 1992). No more recent values appear to exist; deposition calculations in a recent study on Canadian lakes (Wiklund et al. 2018) use these old values.

It had been speculated that significant amounts of tellurium may accompany the release of SO\(_2\) into the atmosphere from fossil fuel-burning electrical power stations, industrial combustion operations, etc., but primary data are lacking. For instance, following Chiou and Manuel (1986), who suggested that coal combustion could be the major source of telluric gases in the atmosphere, a very recent study by Wiklund et al. (2018) stated, as if it were a well-established fact, that tellurium is ‘highly enriched in coal combustion aerosols’. In the second reference cited by these authors (Sen and Peucker-Ehrenbrink 2012), coal burning appears as the only significant anthropogenic flux of tellurium but only a report (US Energy Information Administration) that is not available is given as the data source. Interestingly, Chiou and Manuel (1988) attributed observed decreasing
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Se/S ratios in snow since the start of the Industrial Revolution to the ‘increased usage of fossil fuels’. No similar ratios were reported for tellurium because of the lack of historical data but the authors extended these conclusions to this element also. Following this reasoning, fossil fuel contribution would not increase tellurium release. At least, not to the same extent as sulfur.

Tellurium has not been included in deposition surveys (e.g. moss contents, Harmens et al. (2010), Harmens et al. (2015)). It is thus not possible to know whether reductions in industrial and energy-related dust emissions from fossil fuel combustion have had any effect on tellurium concentrations in the atmosphere. This would have been an indirect proof of the role of coal combustion as a source of atmospheric tellurium. Sediments have often also been used as tracers of contamination and atmospheric transport. This subject is discussed in the section Sediments as tracers of pollution and atmospheric transport.

Natural atmospheric sources of tellurium are volcanism and biomethylation. Trace metals that are geochemically very rare may be abundant in the plumes of quiescently degassing volcanoes. Volcanic emissions of such metals may influence or control the levels of these metals in the atmosphere, or at least may have done so in the pre-industrial past. In strong contrast with selenium (Floor and Román-Ross 2012), there is a paucity of tellurium data in volcanic systems. Hinkley et al. (1999) estimated the worldwide volcanic emission of tellurium at 270 tonnes per year based on measurements in the Kiluaea volcano. This seems to be the only published estimation of this type. Fumarole emissions from the Ertä Ale volcano in Ethiopia were highly enriched in tellurium compared with local basalts (Zelenški et al. 2013). The element was considered in the ‘highly volatile’ category in a study on the gaseous plume released during a highly explosive eruption of the Hekla volcano, Iceland (Moune et al. 2006).

Volatile alkyl species of tellurium have been reported to be produced in the anaerobic digestion of sewage sludge (Michalke et al. 2000), the laboratory incubation of alluvial soil (Meyer et al. 2007), the intestines of humans and mice (Michalke et al. 2008) and when composting duck manure (Pelín-Raffaitin et al. 2008). However, at the current level of knowledge, it is doubtful that these small fluxes of organic tellurium compounds have a notable effect on total tellurium concentrations in the air far from immediate sources.

Tellurium in soils

Owing to analytical problems, tellurium is rarely included in regional geochemical soil surveys and, even when it is reported, the majority of the results are BDL. Publications on tellurium in soil are most often focussed on analytical method development. Even results from the near surroundings of contaminated sites are rare. One such example is the case of the Ni refinery in the Swansea valley (UK) presented by Perkins (2011), who reports values up to 11 mg kg$^{-1}$ tellurium in topsoil (0–5 cm). During the last 20 years, several large soil surveys covering substantial and thus quite representative areas (from 2.0 $\times$ 10$^5$ to 5.6 $\times$ 10$^7$ km$^2$) have been carried out by the Geological Surveys of Europe: Kola, Baltic Soil Survey (BSS), FOREGS and GEMAS (Geochemical Mapping of Agricultural and grazing land Soil) projects (Reimann et al. 1998; Reimann et al. 2003; Salminen et al. 2005; Reimann et al. 2014). Information is gathered in Table S8 (Supplementary Material). In all these surveys, tellurium was part of the analysed suite, usually totalling 50+ chemical elements. In all of these surveys, standard multielement packages, including tellurium, were used for analysis. Though none of these surveys was optimised for tellurium, the results provide a first indication of the concentration levels expected to be in soil samples, the required detection limit needed for providing a representative regional-scale dataset, and geological settings and processes that may lead to enhanced tellurium concentrations in soil.

An extensive external quality control (QC) program was part of all these surveys (for a detailed description, see Reimann et al. 2014). However, with on average ~30% of all results being BDL and no international reference material with certified tellurium values included in the analytical batches, proper assessment of data quality is challenging. This fact, combined with slight differences in the extraction and dissolution methods used, may explain the substantial differences in the median values provided in Table S8. Only for the FOREGS project, a near total four-acid (including HF and HClO$_4$) dissolution was used and this resulted in the highest median values (Table S8), in fact a median that is close to the UCC value (Terrestrial abundance section). The other three projects used an aqua regia extraction and it appears that the extraction used for the GEMAS samples was an especially mild variant (or that tellurium was partly lost during the open-vessel extraction procedure). The other two surveys provide a median value that is close to the world average as provided by Koljonen (1992) (0.006 mg kg$^{-1}$).

Regardless of the potential issues with accuracy of the analytical results, the QC used demonstrated sufficient precision of the tellurium analyses to construct geochemical maps. Unfortunately, for the Kola project (Reimann et al. 1998), only the deeper mineral soil horizon samples (soil B and C horizons) were analysed for tellurium (Fig. 1). Both maps show a clear relationship between tellurium content and the underlying geology. High concentration values mark the occurrence of Caledonian and Proterozoic sedimentary rocks along the coast of the Barents Sea. Furthermore, the granulite belt in northern Finland is quite clearly characterised by high tellurium values. The anomaly in the centre of the Finish project area is related to mineralisation and is visible for many additional elements. The vicinity of copper and nickel smelters (Zapoljarniy/Nikel and Monchegorsk) is also marked by some high values, and here it is difficult to decide whether this is due to surface contamination reaching the B horizon, or due to copper mineralisation (Fig. 1). The anomalies are less pronounced in the soil C horizon, which may provide some evidence that anthropogenic influence contributes to these anomalies.

For the Baltic Soil Survey, the maps again show indications of both geological processes and possibly contamination (Fig. 2). The major anomaly in central Sweden, particularly visible for the bottom soil samples, marks a major mineralised area in Sweden and is possibly related to the occurrence of a geothermal anomaly at depth (Reimann et al. 2003). A major arsenic anomaly was observed at the same location. The anomaly in Russia is related to the occurrence of black shales and accompanied by a selenium anomaly. The enhanced values along the Polish–Czech–Slovakian border may be due to anthropogenic activities in this highly industrialised area (Fig. 2).

Both FOREGS and GEMAS maps (not shown here, see Salminen et al. (2005) and Reimann et al. (2014)) show a clear north–south gradient; practically all the highest tellurium concentrations are observed in southern Europe, south of the maximum extension of the last Ice Age, which is marked by a clear concentration break. This points at soil age and weathering playing an important role in enriching tellurium in soil over
Fig. 1. Tellurium in soil B horizon samples of the Kola Project area (modified from Reimann et al. 1998). GF-AAS: graphite furnace-atomic absorption spectroscopy.

Fig. 2. Tellurium in topsoil (TOP, 0–25 cm) and bottom soil (BOT, 50–75 cm) samples from the Baltic Soil Survey (BSS project) (modified from Reimann et al. 2003).
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time. Many other elements show this pattern (Reimann et al. 2014), arsenic and antimony being two prominent examples. In terms of rock types, it appears that soils developed on karst (terra rossa) often contain enhanced tellurium concentrations. Areas underlain by alkaline volcanics (e.g. the Roman–Neapolitan volcanic province) are also often marked by enhanced tellurium concentrations.

The British Geological Survey (BGS) has carried out an urban geochemical study of London and surroundings, the ‘London Earth Project’ (BGS 2011), based on 7189 topsoil samples (0–20 cm). Here, the reported median value for tellurium was <0.5 mg kg\(^{-1}\) and the maximum concentration observed 1.9 mg kg\(^{-1}\). This and other recent urban geochemistry studies where tellurium has been measured are shown in Table S9 (Supplementary Material).

Results presented show that a detection limit one to two orders of magnitude lower (probably ~0.0001 mg kg\(^{-1}\)) than those reached for the above surveys would be desirable for a reliable measurements of tellurium concentrations in soil samples. These can hardly be reached using standard multielement analytical packages as provided by many commercial laboratories. Rather, it may require extra attention and a tellurium-specific analytical method, thus increasing costs for analyses beyond the financial possibilities of standard geochemical mapping programs.

Sediments as tracers of pollution and atmospheric transport

Natural environment archives, such as ice, ombrotrophic peat bogs and lake sediments offer a useful means of tracing the use of chemical elements and their dispersion provided that they are geomorphically stable. In the case of tellurium, until very recently, the number of such studies was very low (Table S10, Supplementary Material) (Dolor et al. 2009; Reynolds et al. 2010; Duan et al. 2014; Wiklund et al. 2018) with a few cores studied and with all studied sites under the direct influence of sources of contamination. Thus, any trends observed corresponded to local or regional input conditions and did not provide any evidence of long-range atmospheric transport. The only exception is the recent study on Canadian lakes (Wiklund et al. 2018), where tellurium was measured in a larger number of lakes. Most results confirm the effect of local sources in sediment concentrations but these authors also claim that observed profiles in the sediments of some of the lakes prove the transport of tellurium over long distances.

Tellurium hotspots

Hotspots are interesting from the scientific point of view, particularly in the case of an element usually present in very low concentrations, as is the case for tellurium. Hotspot samples allow studies to be carried out by applying techniques not sensitive enough at natural levels. This is the case, for instance, in the extended X-ray absorption fine structure (EXAFS) study of Japanese soils contaminated by tailings from an abandoned Au–Ag mine by Qin et al. (2017). However, even hotspots seem to be scarce in the case of tellurium. Tellurium has only been reported in high concentrations in a few abandoned mine tailings (Wray 1998; Moreno et al. 2007; Qin et al. 2017), around one non-metal smelter and refinery (Perkins 2011) and in ferromanganese crusts (Hein et al. 2003). Even sludge, which usually contains high trace element concentrations, showed fairly low concentrations in the case of tellurium in a recent survey of sludges and effluents of Swiss wastewater treatment plants. The median value in sludges was 0.2 mg kg\(^{-1}\) (with a maximum of 0.5 mg kg\(^{-1}\), DL: 0.09 mg kg\(^{-1}\)) but samples were BDL in 43 effluents (total number of samples: 64) (Vriens et al. 2017).

Ferromanganese crusts deserve a comment because of their importance in the tellurium literature. The presence of tellurium in oceanic sediments was first reported in 1963 (Lakin et al. 1963). Since then, tellurium in ferromanganese crusts has been the object of renewed attention (Hein et al. 2003; Baturin 2007), either to explain ocean concentration levels and element speciation or as a potential mining source. The high enrichment of tellurium in these crusts is often cited as a proof of the unusual behaviour of this element in the environment. However, as Kashiwabara et al. (2014) adequately pointed out, the extremely large values of tellurium enrichment in crusts may be partly attributed to the use of low abundance values for tellurium in the Earth’s crusts in the calculations. According to these authors, it would be more judicious to calculate the EFs relative to seawater concentrations. These authors noted that, following this method, the EF was still higher (~10\(^5\)) than for similar elements (i.e. oxyanions (~10\(^4\)) but less spectacular. Unfortunately, they used as water concentrations the values reported by Lee and Edmond (1985)! If values in seawater are 100 times higher, then tellurium’s behaviour is closer to that of other similar elements. According to Hein, the crusts extract Te\(^{VI}\) from seawater and these ions are oxidised into Te\(^{IV}\), a process that explains the high concentrations of Te\(^{VI}\) compared with Te\(^{IV}\). This mechanism has been questioned in later studies (see Tellurium (redox) speciation section). Baturin et al. (2007) observed, along with sorbed forms, the presence of tellurium as tellurium oxide in crusts.

Tellurium in biological systems

The first report of a biological interaction with inorganic tellurium is attributed to Gmelin, who described the olfactory detection of `odorous compounds’ in the breath of animals exposed to this element (Gmelin 1824). Curious historical aspects of the characteristic garlic-like odour associated with tellurium intake in mammals are described in Chasteen et al. (2009).

Tellurium is not an essential element. However, some authors have maintained the idea that it is found in substantial amounts in biological systems, in particular in the human body. For instance, Hein et al. (2003) wrote ‘tellurium is abundant in plants and primary consumers, such as humans, even if it occurs at extremely low concentrations in soils’. It has also been stated that most of the body burden of tellurium in humans is found in bones to the point that tellurium ‘is one of the most abundant trace elements in human bone’ (Ottosson et al. 2010). All these statements seem to be based on only one study that is now 50 years old (Schröder et al. 1967) and where a concentration of 1 µg mL\(^{-1}\) is given for tellurium in serum: in light of current knowledge, this is a clearly doubtful figure.

Data on tellurium concentrations in biological matrices are scarce, dispersed in the literature and probably very often affected by analytical challenges. For example, in human biomonitoring, hair, nails and urine are considered useful pollution biomarkers and determination of the concentration of many chemical elements in these matrices has become very popular. However, establishing reliable baseline values for healthy, unexposed individuals for ultratrace elements is far from straightforward, as the study on antimony, an element in some aspects similar to tellurium but much easier to measure, has shown (Filel la et al. 2012, 2013a). Similarly, finding reliable data for whole blood, plasma or serum, cerebrospinal fluid,
saliva, etc. for unexposed humans is rather complex (Filella et al. 2013b). Rather than compiling isolated values from many different sources whose reliability is impossible to assess, we have favoured the summary of one of the coauthors’ data, as its quality reflects optimised conditions offered by modern analytical instrumentation and particular care to avoid biases at the measurement stages (Table S11, Supplementary Material). For body fluids, typical tellurium concentrations are in the low nanogram per litre range, with highest values found in urine (up to 260 ng L$^{-1}$). Scalp hair and fingernails have rather broad concentration ranges, probably reflecting strongly bound exogenous contamination of these matrices, with high extremes at single nanogram per gram levels. In soft tissues, tellurium is present at similar levels with lowest concentrations in muscle, brain and lung and highest in kidney and liver.

The same analytical procedure gave mean tellurium concentrations in the range $<0.02$ to $1.4 \mu g\ kg^{-1}$ among 13 nut and seed varieties tested, with the lowest concentrations in pumpkin seeds and the highest in Brazil nuts (Rodushkin et al. 2008). These concentration levels probably explain why Reimann et al. (2015) and Reimann et al. (2018) found all median concentrations BDL for tellurium (DL: 20 mg L$^{-1}$) from the same survey area as Reimann et al. (2018) and found a median value of 26.5 $\mu g\ kg^{-1}$ (DL: 20 $\mu g\ kg^{-1}$, $n = 40$) with a maximum concentration of 110 $\mu g\ kg^{-1}$. Interest in the soil–plant transfer and in human accumulation of tellurium has revived in the wake of the Fukushima Daiichi nuclear incident, power plant transfer accident in March 2011, which released large amounts of radioactive tellurium into the environment (Yang et al. 2013; Fujiwara et al. 2017). This has led to the extensive collection of data in Japanese soils and plants.

In the last decade, many anaerobic bacteria capable of tellurium reduction have been isolated from extreme environments such as ocean hydrothermal vents (Rathgeber et al. 2002; Csonthy et al. 2006) or the highly alkaline waters of Mono Lake, California (Baesman et al. 2007, 2009). The driving force behind this active research field is that one of these organism’s resistance mechanisms is the reduction of tellurite to elemental tellurium, a process that generates nanometric tellurium crystals of possible technological interest. It is interesting to note that a few bacteria are even able to use tellurium (e.g. Te$^{IV}$ or Te$^{V}$) as respiratory electron acceptors (Baesman et al. 2007, 2009). However, it is unclear whether microorganisms play a significant role in the biogeochemistry of tellurium in soils and sediments of less extreme environments, either through the production of Te$^{0}$ or of alkyl compounds (Wallschlager and Feldmann 2010).

**Tellurium (redox) speciation**

**Surface waters**

As far as the redox speciation of tellurium in natural waters is concerned, current knowledge is largely restricted to purely empirical findings: in circumneutral, oxic waters, both Te$^{IV}$ and Te$^{VI}$ are known to occur (Table S12, Supplementary Material), and the proportions in which they do still escape rationalisation. As mentioned in the section *Main element characteristics and chemistry*, according to thermodynamic considerations, the dominant species in aqueous solution should be those of Te$^{IV}$, whereas Te$^{VI}$ species will act as potent oxidants.

On the one hand, the natural occurrence of substantial proportions of Te$^{VI}$ in waters, even in the absence of strong oxidants, suggests that the reduction of Te$^{VI}$ is kinetically extremely slow. In the course of our own investigations (Biver et al. 2015, see below), we found it surprisingly difficult to reduce Te$^{VI}$ quickly and reliably for analytical purposes; with most commonly used strong reductants, no reaction occurred in any reasonable lapse of time, even though thermodynamically, Te$^{IV}$ was by far the favoured oxidation state. We further observed that two near-neutral 0.01 M aqueous solutions of telluric acid stored in polyethylene bottles under ambient conditions and without any special precautions did not show any signs of reduction after 4 years.

However, it is noteworthy that Te$^{IV}$ seems equally inert, both towards further reduction to Te$^{0}$, as well as towards oxidation to Te$^{VI}$. The older analytical literature abounds with complaints that the reduction may only be achieved by extremely strong reductants, which are unstable in air (such as Ti$^{3+}$ or Cr$^{2+}$) or under especially vigorous conditions (protracted boiling, combination of reagents), and even then the reactions are slow. This may point to a particular inertness of the (hydroxo-)tellurite ion – Johnson and Fredrickson (1952) report that after conversion to the hexaiodotellurite complex, the reduction can be brought about, quite mildly, by thioulate at a rate sufficient for the purposes of direct titration. Conversely, titrations of Te$^{IV}$ by ceric ion, dichromate or permanganate are invariably carried out as back-titrations, and are best sped up by the use of catalysts, typically cations of multivalent transition metals, e.g. Cr or Ru (Vogel 1961; Dindi and Reddy 1993).

We therefore consider it likely that any given Te$^{IV}$/Te$^{VI}$ ratio in a water sample, however removed from equilibrium it may happen to be, will persist for kinetic reasons.

Information at a mechanistic level is scarce. By analogy with other elements, Hein et al. (2003) proposed that oxidation processes control tellurium concentrations with Te$^{IV}$ in seawater being preferentially adsorbed onto iron oxyhydroxides and subsequently oxidised to Te$^{VI}$, but they did not provide any proof that this actually occurs. Kashiwabara et al. (2014), however, presented experimental evidence for the sorption of both Te$^{IV}$ and Te$^{VI}$ onto ferrihydrite, but according to their work, only $\delta$-MnO$_2$ oxidises Te$^{IV}$ to Te$^{VI}$. Obviously, this type of study needs to be considerably extended before it can provide a clear answer to the observed redox distributions.

**Speciation in the atmosphere**

Tellurium seems to be mainly present in the fine particulate fraction, but only a single measurement seems to have been performed (Chiou and Manuel 1986). Concerning redox species, Muangnoicharoen et al. (1988) analysed tellurium in indoor and outdoor air and found most of the tellurium present as Te$^{VI}$ in outdoor samples, but Te$^{0}$ was the main species, with Te$^{IV}$ and Te$^{VI}$ in similar amounts in indoor samples. According to Chiou and Manuel (1988), tellurium exists as Te$^{0}$ in fly ash, because excess SO$_2$ produced in the combustion process acts as a reducing agent of the initially generated tellurium oxides. Conversion of Te$^{VI}$ and Te$^{IV}$ in dilute HCl solution to black elemental tellurium when the solution is sparged with SO$_2$ used to be a common method of tellurium detection (Cooper 1971).

**Speciation in solid phases**

Tellurium content in common solid phases (e.g. soils, sediments, air particulates) is too low to be studied by X-ray

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The low concentrations of tellurium in natural waters have led to the extended use of preconcentration methods, with usual techniques including coprecipitation and solid-phase extraction on a chelating adsorbent. The studies before 1990, where lower concentrations were obtained, used either sulfhydryl cotton and that it is necessary to reduce it first to TeVI. This observation is consistent with the results of a study on tellurium binding by cysteine, where no binding was observed for TeVI (Albeck et al. 1998). Without further evidence, it is difficult to ascertain whether incomplete preconcentration is to be blamed for the low results found before 1990.

Hydride generation (HG) systems for sample introduction have also been employed (Dédina 1995). The advantages lie in improved sensitivity of the technique and the elimination of many other, potentially interfering elements. However, TeVI neither forms a volatile hydride with the most commonly used reagent for HG (NaBH4) nor does it undergo reduction to TeIV in its presence. This has both advantages and disadvantages: measuring total tellurium requires the previous reduction of TeVI, but, at the same time, it allows the selective determination of TeIV in the presence of the element in the higher oxidation state.

**TeVI reduction**

On the basis of the high electrode potential of the TeVI/TeIV couple (Latimer 1953), one might expect an extensive suite of alternative reductants from which to choose. This is, unfortunately, not the case, and the kinetic inertness of the TeVI appears to be the principal explanation, along with the additional requirement that the reduction not proceed to the elemental state. The few reductants known to work in the desired fashion appear to be limited to TiCl3, fairly concentrated hydrochloric acid solutions, L-cysteine, and KI (prior to liquid chromatography–hydride generation–atomic fluorescence spectroscopy (LC-HG-AFS)). Reduction has been claimed to be possible with hydroxylamine in concentrated perchloric acid at high temperature (Nicolas 1976).

In the case of HG, boiling in the presence of HCl is the method of choice (D’Ulivo 1997). However, the application of an HG technique is not the only case when TeVI reduction is required. For instance, the separation of tellurium and selenium also requires tellurium to be present as TeIV. In this case, treatment with HCl has also been used (Chiou and Manuel 1984). A further case is the use of electroanalytical methods. A common characteristic of all voltammetric methods is their limitation to tellurium in the +IV oxidation state, with the exception of the direct polarographic technique of Norton et al. (1953). The reduction of TeVI to TeIV has been examined with cathodic stripping voltammetry in mind, because this is the only electrochemical method applicable to the environmental concentrations of Te. Reductions with HCl and KBr or KI, known to work when combined with spectroscope techniques, have been found unsuitable for electrochemical work, because the high acid and/or salt concentrations require substantial dilution before the voltammetric analysis may be carried out. Several voltammetrically compatible alternatives, known to work for other elements, have therefore been evaluated: hydrazine (Holak 1980; Sadana 1983), UV photolysis of glucose (Mattsson et al. 1995), cysteine, methionine (Huang and Hu 2008; Liu et al. 2015) and TiCl3 (Jin et al. 1979). Only TiCl3 could be retained for practical work, because it reliably reduces TeVI under fairly mild conditions (i.e. moderately acidic pH, ambient temperature, and tolerably fast kinetics) and excess reagent can be rendered innocuous by simple means (chelation with EDTA) before voltammetry (Biver et al. 2015).

**Digestion of solid matrices**

A very broad variety of treatments has been often described for the digestion of solid samples before the determination of tellurium with no apparent problems. One aspect, however, deserves attention: lower concentrations have been reported after aqua regia digests compared with HF-based attacks (Hall and Pelchat 1997; Yang et al. 2013). It is difficult to know
whether this is due to incomplete analyte recovery or to tellurium losses during sample digestion. Yang et al. (2013) explicitly mentioned that they sealed their vessels when digesting with aqua regia ‘to avoid leakage of chlorides of tellurium’ but aqua regia digestions or evaporation to dryness procedures are often performed in open vessels. Mentions of possible loss of tellurium when HCl is used can be found in the literature (Shimoiishi 1976; Chiou and Manuel 1984). Warnings about the volatilisation of tellurium if halogenated reagents are used for sample dissolution (e.g. working at sub-boiling temperatures) are issued in classical analytical texts (Cooper 1971). A recent study by Chen et al. (2016) concludes that, on the one hand, losses become inevitable in 3.0 mol L\(^{-1}\) HCl, and that these losses increase with temperature. Similarly, sample treatments with HF lead to losses (Nicolas 1976), which might be due to the formation of gaseous TeF\(_6\). On the other hand, in mixed acidic systems (HNO\(_3\), HF with HCl), HCl seemingly does no harm, even on protracted heating. No losses were observed following digestions with concentrated HNO\(_3\)–HClO\(_4\) mixtures (Chen et al. 2016), an observation made earlier by Nicolas (1976) and Nazarenko and Ermakov (1972). Similarly, in the older literature, evaporation to dryness with concentrated HNO\(_3\) is often used for the preparation of standards or sample digestions (Watterson and Neuberger 1975), apparently without loss. Our own work (unpubl. data) suggests that attack of elemental arsenic with coprecipitated tellurium by evaporation with concentrated HNO\(_3\) does not lead to tellurium losses either. Digestion with boiling, concentrated H\(_2\)SO\(_4\) is recommended for the digestion of minerals and sulfidic ores (Jankovsky and Ksir 1960), without losses.

Measuring tellurium

Tellurium has often been measured by atomic absorption spectroscopy (AAS) or AFS, usually coupled to HG. The main limitation of these methods is the insufficiently low detection limit that, as discussed above, makes it necessary to use preconcentration procedures. ICP-MS has become the technique of choice for measuring trace element concentrations and, as such, is increasingly used for measuring tellurium. However, tellurium is a difficult element for ICP-MS measurements because of poor sensitivity caused by its high ionisation energy and it having many isotopes, nearly all suffering from isobaric Xe interference originating from plasma gas impurities. The most abundant isotope, \(^{125}\)Te, is also affected by \(^{130}\)Ba isobaric interference. Fortunately though, accurate results can be obtained in the majority of matrices using both \(^{125}\)Te and \(^{126}\)Te (Filhella and Rodushkin 2018). Probably the best analytical option in many matrices is the \(^{126}\)Te isotope with 19 % abundance analysed in low-resolution mode with methane addition to the plasma, thus ensuring more efficient ionisation of the element. Though affected by very minor \(^{126}\)Xe interference, this isotope returns more accurate values than \(^{125}\)Te (commonly recommended or suggested by instrumental software), as \(^{40}\)Ar\(^{85}\)Rb and \(^{40}\)Ca\(^{85}\)Rb interferences may affect mass 125. The generalised use in the near future of tandem quadrupole ICP-MS/MS, with an efficient elimination of spectral interferences, may be particularly interesting in the case of tellurium.

Although voltammetry is not a very popular technique nowadays, the possibility of using it for total or speciation measurements needs to be mentioned. Voltammetry has low running costs and offers speciation capabilities. Biver et al. (2015) recently reported a limit of detection of \(\sim 5\) ng L\(^{-1}\) in natural waters by means of catalytic cathodic stripping voltammetry (CSV) at the hanging mercury drop electrode (HMDE); such a low detection limit allows tellurium to be determined in mineral, river and coastal sea waters at ambient levels without preconcentration needed. Therefore, voltammetry seems to be a plausible alternative to ICP-MS for the analysis of tellurium in environmental matrices.

Certified reference materials (CRMs)

Tellurium is rarely a part of certification campaigns for CRMs intended to aid quality assurance/quality control in environmental studies (Zeisler et al. 2006). Published values of tellurium concentrations in CRMs used in reviewed studies, usually with no information or certified values for tellurium, are collated in Table S13 (Supplementary Material). Table S14 (Supplementary Material) contains a summary of previously unpublished tellurium concentrations found in a variety of commercially available reference materials used for method development and daily quality control in a single laboratory. Data were obtained using closed-vessel microwave-assisted digestion with an HNO\(_3\)/HF acid mixture and ICP-sector field MS analysis, with the number of individual analyses per material in the range of 20 to \(\geq 200\) replicates. These compilations may aid QA/QC in future studies. Certified reference materials do, however, exist for rock analysis (see GEOREM database: http://georem.mpch-mainz.gwdg.de for details; accessed 6 March 2019).

Conclusions

Although, at first sight, only negative conclusions derive from our study:

- No information is available on the transformation and transport of tellurium in the different environmental compartments and even information on total tellurium content in the various environmental media is scarce and often contradictory.
- Available analytical methods and lack of adequate CRMs strongly limit the value of existing information.
- Current thinking about tellurium in the environment is marked by the scarcity of data but also by the burden of being built on excessive use of secondary sources, in particular in seawater,

it lays the necessary foundations to progress in the understanding of the behaviour of the element in the environment by:

- Providing updated background information (chemical characteristics of the element, production, uses, UCCs, etc.),
- Identifying the main contradictions in published data, information essential for the evaluation of new data in future studies,
- Discussing published results in the light of what is known about the chemistry of the element,
- Explaining where the analytical limitations are and why they need to be solved,
- Emphasising the absolute need for CRMs and compiling published concentrations of tellurium in CRMs certified for other elements.

Supplementary material

The Supplementary Material includes: Table S1. Reviews on tellurium, or reviews that contain a significant part on this element, published in the last 25 years; Table S2. Tellurium uses; Table S3. Properties of tellurium relevant to understanding its environmental chemistry; Table S4. Published ‘dissolved’
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tellurium concentrations in seawater; Table S5. Published ‘dissolved’ tellurium concentrations in freshwater systems, including groundwater; Table S6. Published ‘dissolved’ tellurium concentrations in rainwater and snow; Table S7. Published tellurium concentrations in air samples; Table S8. Detection limit and tellurium median and maximum concentrations as reported from several low-density regional geochemical soil surveys in Europe; Table S9. Tellurium in recent urban geochemistry studies; Table S10. Tellurium concentrations in dated sediment cores; Table S11. Biological samples analysed at the ALS Luleå laboratory; Table S12. Published tellurium (redox) speciation in surface water, air and soils; Table S13. Published values of tellurium concentrations in Certified Reference Materials.

Conflicts of interest
The authors declare no conflicts of interest.

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