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Internal tree cycling and atmospheric archiving of mercury: examination with concentration and stable isotope analyses.

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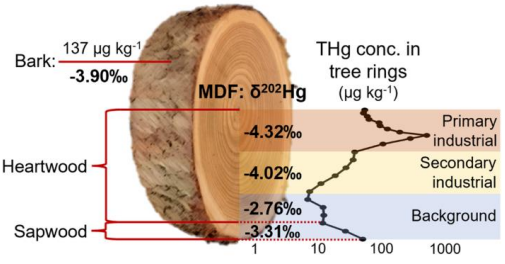

Abstract. Trees predominantly take up mercury (Hg) from the atmosphere via stomatal assimilation of gaseous elemental Hg (GEM). Hg is oxidised in leaves/needles and transported to other tree anatomy including bole wood where it can be stored long-term. Using Hg associated with growth rings facilitates archiving of historical GEM concentrations. Nonetheless, there are significant knowledge gaps on the cycling of Hg within trees. We investigate Hg archived in tree rings, internal tree Hg cycling, and differences in Hg uptake mechanisms in Norway spruce and European larch sampled within 1 km of a $HgCl_2$ contaminated site using total Hg (THg) and Hg stable isotope

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analyses. Tree ring samples are indicative of significant increases in THg concentrations (up to 521µg·kg^{-1}) from *background period* (*BGP*; facility closed; 1992—present) to *secondary industrial period* (*2ndIP*; no $HgCl_2$ wood treatment; 1962–1992) to *primary industrial period* (*1stIP*; active $HgCl_2$ wood treatment; ≈1900–1962). Mass dependent fractionation (MDF) Hg stable isotope data are shifted negative during industrial periods (δ^{202}Hg: *1stIP*: -4.32±0.15‰; *2ndIP*: -4.04±0.32‰; *BGP:* -2.83±0.74‰; 1SD). Even accounting for a ≈-2.6‰ MDF shift associated with stomatal uptake, these data are indicative of emissions derived from industrial activity being enriched in lighter isotopes associated with $HgCl_2$ reduction and Hg^0 volatilisation. Similar MDF (δ^{202}Hg: -3.90±0.30‰; 1SD) in bark Hg (137±105µg·kg^{-1}) suggests that stomatal assimilation and downward transport is also the dominant uptake mechanism for bark Hg (reflective of negative stomatal uptake MDF shift) rather than deposition to bark. THg was enriched in sapwood of all sampled trees across both tree species. This may indicate long-term storage of a fraction of Hg in sapwood or xylem solution. These data advance our understanding of the physiological processing of Hg within trees and provide critical direction to future research into the use of trees as archives for historical atmospheric Hg.

Key words

Mercury biogeochemistry, tree rings, sapwood (hydroactive xylem), heartwood, phloem, bark, process and source tracing.

1. Introduction

Until the last 10—15 years, it was hypothesised that the major transfer pathway of mercury (Hg) from the atmospheric to terrestrial and aquatic matrices was the wet and dry deposition of Hg(II) as either gaseous oxidised Hg (GOM) or particulate bound-Hg (PBM) (Lin and Pehkonen, 1999; Lindberg et al., 2007; Selin, 2009). However, studies began to suggest that dry deposition of gaseous elemental Hg (GEM) had to be more important than was thought because of inconsistencies between measurement data of atmospheric Hg species and modelling predictions (Selin et al., 2008; Zhang et al., 2009; Mao and Talbot, 2009). A major mechanism for dry deposition of GEM is uptake and assimilation to flora via stomata during plant respiration, an idea that was posited by scientists as far back as the late 1970s (Browne and Fang, 1978; Lindberg et al., 1979). The rate of GEM uptake correlates to photosynthetic activity of the plants (Laacouri et al., 2013), but is also species dependent since it is related to stomatal conductance and the number of stomata per leaf (Laacouri et al., 2013; Millhollen et al., 2006). Recent work has provided evidence that dry deposition of GEM to vegetation via stomatal uptake and subsequent transfer via leaf/needle senescence, abscission, and litterfall is

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likely to be the dominant mechanism for Hg deposition from the atmosphere to terrestrial matrices (Obrist et al., 2017; 2018; Jiskra et al., 2018).

Similarly, there is strong evidence that GEM is also the major source of Hg in bole wood (Scanlon et al, 2020, Wang et al., 2020; 2021). Using Hg stable isotope measurements, GEM deposition has been estimated to supply 57—94 % of total Hg (THg) in vegetated terrestrial systems (Khan et al., 2019 and references therein). A major loss mechanism of Hg from forest ecosystems is during biomass burning (Friedli et al., 2009; McLagan et al., 2021a; Dastoor et al., 2022).

To assess Hg cycling within trees we must also reflect on alterative uptake mechanisms: (i) uptake from roots and (ii) deposition to above ground tree surfaces (stems, leaves, and bark) and potential sorption to and translocation into tree tissue. Hg uptake from roots has been studied for decades. Data overwhelmingly show minimal transport of Hg from the root zone to aerial mass of trees (Beauford et al., 1977; Lindberg et al., 1979; Bishop et al., 1998; Moreno et al., 2005; Graydon et al. 2009; Cui et al., 2014; Cozzolino et al., 2016; Peckham et al., 2019a). Even in soils with elevated THg concentrations, upward transfer from roots is low in relative terms (Beauford et al., 1977; Lindberg et al., 1979; Graydon et al. 2009). Limited uptake of Hg and other metals via the roots has been attributed to restrictive barriers in the roots such as that provided by the endodermis (Kahle, 1993). Alternatively, Hg can also be deposited to surfaces of the aerial anatomy of trees, predominantly as GOM and PBM (Rea et al., 2002; Mowat et al., 2011; Laacouri et al., 2013). Hg on leaf surfaces contributes only a minor fraction of THg in foliage and accumulation rates are low due to both precipitation wash-off (Rea et al., 2000; 2001; Laccouri et al., 2013) and photoreduction and subsequent evasion of GEM (Graydon et al., 2006; Mowat et al., 2011). Several studies have demonstrated elevated bark THg concentrations relative to branch and bole wood (Siwik et al., 2010; Zhou et al., 2017; Liu et al., 2020). Therefore, it has been suggested that Hg in bark is chiefly derived from atmospheric deposition (Chiarantini et al., 2016; 2017) potentially with a greater proportion of GOM and PBM rather than GEM (Peckham et al., 2019a).

Trees make up a large sink for atmospheric Hg and therefore play an important role in the global Hg cycle. Hg has no known biological function in plants (Moreno-Jiménez et al., 2006; Peralta-Videa et al., 2009; Cozzolino et al., 2016); thus, it is important to understand the physiological processing of Hg within trees from a phytotoxicological standpoint. After assimilation through leaf/needle stoma GEM is assumed to be oxidised to form Hg(II) compounds and integrate with internal leaf tissue (Laacouri et a., 2013; Demers et al., 2013). A recent study examining three evergreen species used Hg stable isotopes to show that reduction and re-release can occur (Yuan et al., 2018). Although the bole wood of trees has lower THg concentrations than bark and needles/leaves in both deciduous and

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evergreen species (Navrátil et al., 2017; Zhou et al., 2017; Liu et al., 2020), the overall Hg loading of the tree is the reverse: wood carries the largest total mass of Hg due to much greater overall biomass (Liu et al., 2020).

Hg is transported from the foliage to bole wood via the phloem, which is the conduit for nutrient and photosynthetic product transfer from leaves/needles to the rest of the trees (Cutter and Guyette, 1993). Phloem lies between the cambium (tissue that promotes new xylem and phloem growth) and the inner bark. Once oxidised to Hg(II) species in the leaves/needles, it likely associates with phytochelatin, cysteine compounds for phloem transport (O'Connor et al., 2019; Dennis et al., 2019). Phloem-to-xylem translocation (new xylem makes up sapwood and forms tree rings) is expected to occur throughout this downward transport (Arnold et al., 2018; Yanai et al., 2020; Nováková et al., 2021; 2022). This translocation likely proceeds via *rays*, parenchyma cells that radially connect xylem and phloem conductive tissues and mediate water and nutrient transport, tree growth, and biotic and abiotic stressors (Nagy et al., 2014; Pfautsch et al., 2015; Gustin et al., 2022). THg is expected to be preserved in the newly forming xylem tree rings; and hence, THg concentrations in tree rings have been used as a proxy for historical atmospheric GEM concentration (Siwik et al., 2010; Wright et al., 2014; Clackett et al., 2018). This includes identification of elevated GEM concentrations, past and present, associated with atmospheric Hg emissions from industrial activities located near sampled trees (Odabasi et al., 2016; Navrátil et al., 2017; Scanlon et al., 2020; Nováková et al., 2022). A potential caveat to this method of chronicling historical atmospheric GEM concentrations is the translocation of Hg between tree rings that has been reported in certain studies; tree ring concentrations do not reflect reported industrial activity (Nováková et al., 2021; Wang et al., 2021). However, there are a number of studies that demonstrate this inter-ring translocation does not significantly influence results; tree ring Hg concentrations reflect reported industrial (Clackett et al., 2018; Navrátil et al., 2018; Peckham et al., 2019b). Tree species may be a factor affecting inter-ring Hg translocation (Scanlon et al., 2020; Nováková et al., 2021).

Hg stable isotopes represent a powerful and relatively new technique that can provide information relating to the biogeochemical cycling history and potentially source information of sampled Hg (Bergquist and Bloom 2007; 2009). This premise assumes distinct "signature" ratios of different sources, and mass-dependant (MDF) and mass-independent (MIF) fractionations of the seven stable Hg isotopes that can be imparted by environmental transformation processes (Bergquist and Bloom 2007; 2009). Forest ecosystems are no exception to this. For instance, Hg stable isotopes added substantial evidence to the argument that GEM stomatal assimilation and eventual litterfall (or vegetation death) was the dominant mechanism for Hg deposition to soils in vegetated ecosystems

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(Wang et al., 2017; Jiskra et al., 2018; Yuan et al., 2018). Studies examining Hg stable isotopes in tree-rings are limited (Scanlon et al., 2020; Wang et al., 2021). Both studies associated differences in MIF (Δ^{199}Hg) with varying sources over time, but Wang et al. (2021) suggested there were limitations to this interpretation due to inter-ring translocation of Hg. They also attribute differences in MDF (δ^{202}Hg) with physiological differences (i.e., inter-ring translocation, stomatal conductance, and canopy dynamics), particularly as they relate to tree species, and environmental factors (i.e., soil conditions, slope, and winds) (Wang et al., 2021).

In this study, we examine THg concentrations and stable isotopes in two coniferous tree species, Norway spruce (*Picea abies*) and European larch (*Larix decidua*), surrounding a legacy Hg contaminated site in the German Black Forest. We aim to investigate if historical records of the industrial activities correlate with elevated THg concentrations in tree rings of sampled trees. There are no records of historical atmospheric Hg emissions or concentrations at this site, which was subject primarily to soil and water contamination (application of low-volatility $HgCl_2$ solution) rather than combustion emissions to the atmosphere. Thus, we compliment tree-ring data with deployments of GEM passive air samplers (PASs) at the site to assess atmospheric GEM conditions at the former industrial site past (tree rings) and present (PASs). Using Hg stable isotopes, we aim to examine potential source related variations in MDF and MIF across the tree ring records and physiological processes that may separate pools of Hg in the transport mechanism from atmosphere to foliage to phloem to tree-ring/bole wood. Additionally, we aim to investigate if deposition and sorption of Hg to tree bark is the dominant mechanism for bark Hg (isotopically distinct from bole wood).

2. Methods

2.1. Study site

The study area is in the High Black Forest (≈850 m a.s.l.) in Baden-Württemberg, Germany. Trees were sampled within a 1 km radius of a former kyanisation facility that treated timber with ≈0.66% $HgCl_2$ solution for preservation with substantial losses of this contaminated solution to soils, groundwater, and stream water (Eisele, 2004, Richard et al., 2016; McLagan et al., 2022). Although the trees were sampled within a 1 km radius of the contaminated site, all trees were outside, and upslope of the area directly affected by Hg contamination to soils and groundwater. The location of the sampled trees, former industrial buildings, wood drying areas, and passive sampling locations are shown in Fig. 1. The history of the industrial activities at the site can be divided into three distinct periods:

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1. *Primary (first) industrial period (1stIP; 1892-1961):* Reports on this contaminated site describe the operation of the kyanisation facilities (wood treatment with 0.66 % $HgCl_2$) from 1892 until site owners went bankrupt in 1961 (Weis, 2020; Eisele, 2004; Schrenk and Hiester, 2007).
2. *Secondary industrial period (2ndIP; 1962-1992):* The site was acquired by another company and wood use and timber production as well as storage of timber treated with $HgCl_2$ is reported to have continued at the site until 1992 (Eisele, 2004; Schrenk and Hiester, 2007).
3. *Background period (BGP; 1992-present):* The site lay fallow between 1992 and 2002 before site remediation (2002—2004) and conversion of the area to a commercial space (Eisele, 2004; Schrenk and Hiester, 2007).

These three periods will be referred to throughout the study under the descriptors of *1stIP*, *2ndIP*, and *BGP*, respectively.

2.2. Sampling and sample preparation

Bole wood (tree ring) samples were collected via two methods. The first was using a 450 mm long, 5.15 mm diameter increment borer (Haglöf Sweden). The tree core was sampled at breast height (≈1.2—1.5 m above ground). Whole tree core samples were placed in lab grade sampling straws and double zip-seal bags for transport back to the lab. Spruce 1—3, spruce BG, and larch 1—3 were all sampled by this method. Samples were counted for the visibly defined rings and cut with a disposable scalpel.

The second method involved the collection of freshly cut (collected on day of tree felling) tree slices or "cookies" (see TOC art; Section S1) from ≈0.5 m above the ground. A ≈50 mm slice was cut from the middle of each tree cookie with a large table saw. Tree ring samples were cut from this slice with a plain edge chisel. All exposed sides we cut away and discarded. Spruce ISO4—6 were sampled by this method.

The number of tree rings (temporal resolution) in any given sample was typically 5 years but varied somewhat with higher resolution in samples from some trees during *1stIP* and *2ndIP*, and lower in some samples from spruce ISO trees that required higher THg concentrations per sample for Hg stable isotope analyses. Samples were counted for rings, cut with a lab scalpel, weighed into nickel boats and then combusted at 750 °C for 300 seconds. Care was taken to remove bark and phloem from wood, but there may have been instances where some phloem remained attached to the newest tree ring sample. Bark was sampled from spruce ISO4—6. Bark from spruce ISO4 and Spruce ISO5 were divided into inner and outer bark (estimated as the middle of the bark) using a disposable scalpel.

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After sample preparation samples were frozen (-20 °C), then freeze dried (-80 °C and 7 pa), and subsequently stored at room temperature until analysis. Cleaning methods for equipment and surfaces is detailed in Section S1. As these samples are from living (or freshly cut) trees no cross dating methods were necessary; ring counting represents the most accurate method of dating. Sapwood was visually identified by colour changes (Bertaud and Holmbom, 2004). However, any uncertainty associated with identification of the exact number of sapwood rings is of little consequence to the study as the greatest THg enrichment in sapwood was in the youngest tree rings, which, we can state with certainty, were sapwood.

2.3. Total Hg analyses

THg concentration of samples collected with the increment borer were made using a thermal desorption, amalgamation and atomic adsorption spectrometry (DMA80, Milestone Instruments). Samples were counted for rings, cut with a lab scalpel (see borer cleaning methods), weighed into nickel boats and then combusted at 750 °C for 300 seconds. Reference materials, Apple leaves (SRM 1515, NIST) and China Soil (NCS-DC73030; China National Analysis Centre for Iron and Steel), were measured throughout the analyses and the recoveries were 103 ± 3 % (n = 30) and 99 ± 5 % (n = 11), respectively. Details of the GEM passive air sampler methods and data can be found in Section S2. THg concentration for the ISO trees were calculated from the analysis of traps after the pre-concentration for isotope analysis (DMA-80L). All samples were considered on a dry-weight basis (after freeze-drying) to remove any potential bias associated with moisture loss during transport and storage before freezing.

2.4. Hg stable isotope analyses

Hg stable isotope analyses were performed on tree slice samples from trees: spruce ISO4—6. No larch trees could be analysed for Hg stable isotopes as no larch tree slices could be collected. The low THg concentration in many sections of the wood is a challenge for Hg stable isotope analyses. Low concentration samples required pre-concentration and trapping by combusting samples in a DMA80 and then purging the released Hg from multiple boats of the same sample into 5 mL traps consisting of 40 % (v/v) inverse aqua regia that replaced HCl with BrCl. Further method details (see also McLagan et al. (2022)) and quality control/assurance of these analyses are provided in Section S4. Traps with insufficient concentrations for isotope analysis were pool using the purge and trap method detailed in Section S5. Hg stable isotope measurements were made using a Nu Plasma II (Nu Instruments) inductively coupled plasma mass spectrometer (MC-ICP-MS) connected to an HGX-200 cold vapour generator for Hg introduction (Teledyne Cetac) and a desolvating nebulizer

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for external mass bias correction by Tl doping using NIST-997 (Aridus 2, Teledyne Cetac) following a method previously established in our laboratory (see McLagan et al. (2022) and Wiederhold et al. (2010) for method details). All samples and standards were diluted to match concentrations within each session and samples were measured using standard bracketing with NIST-3133. Analytical precision (2SD) and accuracy (using repeated measurements of "in-house" *ETH Fluka* standard and NIST-3133 standards) for these analyses are reported in Section S6 along with full Hg stable isotope datasets. Isotope ratios are reported as the deviation from the isotopic composition of the NIST-3133 standard using delta notation and expressed in per mil (‰) (details in Section S4).

3. Results and Discussion

3.1. Elevated tree ring total Hg concentrations during industrial activity

Elevated THg concentrations were observed in both Norway spruce (*P. abies*) and European larch (*L. decidua*) tree rings dated before the mid-1990s compared to tree rings from the background Norway spruce (spruce BG), which was situated ≈5.5km west (upwind based on dominant westerly winds in the area) of the former industrial facility (Fig. 2; THg data in Section S4). These species were chosen due to suggested suitability for Hg archiving in previous studies (Hojdová et al., 2011; Nováková et al., 2021) and there was a distinct pattern in tree ring THg concentrations in across all sampled trees near the legacy contaminated site regardless of species. This resulted in four distinct periods: (i) slightly elevated THg concentration in sapwood (hydroactive xylem) rings (0—5, 0—10, or 0—15 year tree rings; see Section 3.3.2 for discussion), (ii) low THg concentration in rings from the *BGP* not influenced by any known industrial activity (1992—sapwood), (iii) increasing THg concentrations in rings from what we term the *2ndIP* (1962—1992), and (iv) very elevated THg concentrations during the active kyanising or *1stIP* (before 1962) (Fig. 2). Not all sampled trees were of sufficient age to cover all of these periods (no larch trees reached the *1stIP*, but all trees that were old enough did follow this trend albeit with some distinct inter-tree differences in THg concentrations (Fig. 2).

The THg concentrations ranged from ≈1—10 μg·kg^{-1} from tree rings in the *BGP* up to 521 μg·kg^{-1} in a sample dated from 1951—1953 during the *1stIP* in spruce 1, which is ≈400—500 m northeast of the former kyanisation building and wood drying areas. Additionally, THg concentrations of up to 211 μg·kg^{-1} were measured in a sample dated 1974—1976 (*2ndIP*) in spruce 2, which was the closest tree sampled to the former facility (≈200—300 m south). However, this tree was planted after the *1stIP*. Distance of the tree from the industrial source was a definite factor in the between tree variability in THg concentrations, which has also been documented by Navrátil et al. (2017) and

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Nováková et al. (2022). These THg concentrations are comparable to other studies with the high THg concentrations measured in tree rings such as Becnel et al. (2004) (Loblolly Pine and Red Maple; THg concentrations up to 644 $\mu g \cdot kg^{-1}$), Abreu et al. (2008) (Black Poplar; THg concentrations up to 280 $\mu g \cdot kg^{-1}$), and Nováková et al. (2022) (European Larch; THg concentrations up to 249 $\mu g \cdot kg^{-1}$). However, the THg concentrations in our study are lower than the very high concentrations measured by Wang et al. (2021) (Masson Pine; THg concentrations up to 2140 $\mu g \cdot kg^{-1}$), which is likely associated with the source being a former Hg mine known to have emitted large quantities of elemental Hg (Hg(0)) to the atmosphere.

The THg concentrations in the tree rings generally provide a good representation of the industrial history of the site based on the applied ≈5-year sampling resolution. While the end of the *2nd IP* falls in the middle of the 25—30 year tree ring samples, there is an increase in THg concentrations in all trees in samples 30—35 year and greater (before 1990). This is most apparent in the spruce 1 and spruce 2, which are the two sampled spruce trees closest to the former kyanisation building and wood drying sites. The average THg concentration for spruce 1 and spruce 2 was significantly higher (p = 0.031 and $p < 0.001$, respectively) during the *2nd IP* (1962—1990; Spruce 1: 23.1 ± 12.8 $\mu g \cdot kg^{-1}$; and spruce 2: 134 ± 56 $\mu g \cdot kg^{-1}$) than during the *BGP* (1990—sapwood; spruce 1: 10.8 ± 2.6 $\mu g \cdot kg^{-1}$; and spruce 2: 9.46 ± 3.65 $\mu g \cdot kg^{-1}$). There was a sharp increase in THg concentration in the closest larch tree to the site (larch 1) at this time, but the tree only dated to 1978, which is less than halfway through the *2nd IP*. Spruce 1 was also indicative of significantly higher (p = 0.007) THg concentrations during the *1st IP* (150 ± 141 $\mu g \cdot kg^{-1}$) compared to the elevated THg concentrations of the *2nd IP*. These agrees with other studies that have demonstrated good correlations between industrial activity and tree ring Hg (Clackett et al., 2018; Navrátil et al., 2017; 2018; Nováková et al. 2022). Nonetheless, several studies have suggested that Hg can translocate across tree rings, which results in temporal differences between tree ring Hg and reported industrial activities/inventories (Nováková et al., 2021; Wang et al., 2021). This should continue to be monitored closely in future studies, particularly considering the sapwood enrichment discussed in Section 3.3.2.

Although the exact location of the three Spruce ISO trees (tree slices collected for Hg stable isotope analysis) is unknown, they were from a deforested stand of spruce between 200—500 m further from the wood drying site than spruce 1 on an easterly facing slope (away from the site). Consequently, the mean THg concentrations in the spruce ISO4—6 were generally lower than in spruce 1. Nonetheless, the same trends were observable: mean THg concentrations during the active industrial period (before 1962, THg: 44.2 ± 15.5 $\mu g \cdot kg^{-1}$) were significantly greater (p = 0.006) than during the *2nd IP* (1962—1990, THg: 26.7 ± 15.7 $\mu g \cdot kg^{-1}$), which were significantly greater (p = 0.001) than

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rings from 1990—sapwood (THg: 6.5 ± 4.6 μg·kg^{-1}) based on combined data from all three spruce ISO trees.

3.2. Isotopically fractionated Hg in tree rings associated with industrial emissions

3.2.1. Mass dependant fractionation (MDF)

The THg concentration data from tree rings suggest substantial emissions of Hg to the atmosphere during the industrial period. However, the original Hg contamination at these sites was the treatment of timber with $HgCl_2$ solution, a species that has a high solubility and low volatility compared to Hg(0) (Henry's Law constant: Hg(0): 1.4x10^{-3} mol·m^{-3}·Pa^{-1}; $HgCl_2$: 2.7x10^{4} mol·m^{-3}·Pa^{-1}; Schroeder and Munthe, 1998). Thus, the majority of any Hg releases to the atmosphere must have occurred via reduction of Hg(II) to Hg(0) and subsequent volatilisation as GEM. Kinetic processes such as reduction and evaporation result in the product (Hg released to the atmosphere in this case) becoming enriched in lighter isotopes (more negative δ^{202}Hg; Bergquist and Blum, 2007; 2009). Like the THg concentrations, MDF values reflect a chronological trend: δ^{202}Hg values from the *1stIP* (δ^{202}Hg: -4.32 ± 0.15 ‰, 1SD) were significantly more negative (p = 0.007) than during the *2ndIP* (δ^{202}Hg: -4.02 ± 0.31 ‰; 1SD), which in turn were significantly more negative (p < 0.001) than rings from the *BGP* (δ^{202}Hg: -2.76 ± 0.76 ‰, 1SD; sapwood 0–5 year samples not included, see Section 3.3.2) based on combined data from all three spruce ISO trees (Fig. 3A). Wang et al. (2021) observed similar, although weaker, trends in Masson pines near Hg contaminated sites in China (range: −5.06 ‰ to −2.53 ‰; median: −3.74 ‰). MDF (δ^{202}Hg) has also been examined in oak (-1.82 ± 0.09 ‰) and pitch pine (-2.98 ± 0.76 ‰; North America; Scanlon et al., 2020), conifers (-2.76 ± 0.46 ‰; China; Liu et al., 2021), evergreen trees (-3.15 ± 0.22 ‰; China; Wang et al., 2020), and harvested one-year old Norway spruce saplings (-2.71 ± 0.27 ‰; Germany; Yamakawa et al., 2021). δ^{202}Hg values in these studies were more similar to samples from the *BGP* in our study, which likely relates to their low bole wood THg concentrations associated with the remoteness of their study sites from contamination sources (Scanlon et al., 2020; Wang et al., 2020; Liu et al., 2021; Yamakawa et al., 2021).

McLagan et al. (2022) highlight the difficulties in characterising a specific source signature of Hg stocks used in industrial activities due to the variability in stock δ^{202}Hg values, potential change in Hg supplies during the facility's lifetime, and the possibility that the industrial use of Hg resulted in the Hg emitted to different environmental media being fractionated from the original Hg stock. The highly negative δ^{202}Hg values during both the *1stIP* and *2ndIP* support the hypothesis that there was significant loss of Hg to the atmosphere during the industrial activities, which would result in the

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residual $HgCl_2$ in solution (major source of soil-groundwater contamination) being isotopically heavier than the original Hg stocks used at the site. Indeed, solid phase materials (listed as "SCA1" and "TSA" in McLagan et al., 2022) beneath the former kyanisation plant with THg concentrations >50 µg·kg^{-1} had mean δ^{202}Hg values of 0.06 ± 0.23 ‰ (McLagan et al., 2022). This is at the positive end of the range of δ^{202}Hg values reported for cinnabar ores and commercial liquid Hg^0 stocks (Sun et al., 2016; Grigg et al., 2018).

δ^{202}Hg for GEM in background air is typically in the range of ≈-0.2 to 1.5 ‰ (Szponar et al., 2020 and references therein). Foliar uptake of GEM is reported to cause substantial MDF of between -2.3 and -2.9 ‰ (Demers et al., 2013; Enrico et al., 2016; Wang et al., 2021). If we subtract the middle of the estimated range of MDF caused by foliar uptake (δ^{202}Hg: -2.6 ± 0.3 ‰) from the mean δ^{202}Hg values measured in tree rings during *1stIP* and *2ndIP* we get δ^{202}Hg estimates of -1.7 ± 0.2 ‰ and -1.4 ± 0.2 ‰ (propagated uncertainty), respectively, for GEM during these periods at the approximate location of the southeast facing forest stand where the spruce ISO trees were sampled (see also Fig. 4). This agrees with other studies that suggest industrial sources of Hg are enriched in lighter isotopes compared to background air (Jiskra et al., 2019; Szponar et al., 2020, and references therein). These estimates assume Hg in tree rings is derived from foliar uptake of GEM from the atmosphere, which is suggested to be the dominant uptake pathway of Hg in trees (e.g., Beauford et al., 1977; Graydon et al. 2009; Cozzolino et al., 2016), and no further MDF during downward transport of Hg within the trees (as observed by Liu et al., 2021).

Applying the same correction to the δ^{202}Hg in tree rings from the *BGP* we get a δ^{202}Hg estimate of -0.2 ± 0.3 ‰ for GEM during this time (see also Fig. 4). This is right on the lower end of the reported range for δ^{202}Hg of typical background GEM and suggests there may still be some minor inputs of Hg from the still contaminated soils (McLagan et al., 2022) to the trees during the *BGP*. GEM concentrations were measured with PASs over the areas of the former kyanisation building and wood drying areas (2.9 ± 0.6 ng·m^{-3}) and concentrations were approximately double typical European background concentrations (≈1.5—2.0 ng·m^{-3}) (Sprovieri et al., 2016). Other studies that have observed more elevated GEM concentrations with co-located GEM PAS deployments: up to three orders of magnitude higher concentrations at a former Hg mine (McLagan et al., 2018) and 3—4x higher at a Hg contaminated waste site (McLagan et al., 2021b). Therefore, we can assume the slightly elevated GEM concentrations detected at the site in 2018 are associated with low-level GEM emission from the site. These minor emissions likely cause a small negative shift in δ^{202}Hg values of the tree rings from what might be expected of "true" background values. To our knowledge this is the first study to address elevated GEM concentrations from a former Hg kyanisation facility.

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346 **3.2.2. Mass independent fractionation (MIF)**

347 We also observed small variability in odd isotope-MIF in the spruce ISO tree rings (Fig. 3B). The
348 mean Δ^{199}Hg for the *1st IP* (Δ^{199}Hg: 0.00 ± 0.03 ‰, 1SD) was significantly greater ($p < 0.001$) than
349 for the *2nd IP* (Δ^{199}Hg: -0.06 ± 0.04 ‰, 1SD), which in turn was significantly greater ($p < 0.001$) than
350 the *BGP* (Δ^{199}Hg: -0.13 ± 0.03 ‰, 1SD). The Δ^{199}Hg of the *1st IP* is right at the mean values for
351 cinnabar ores (Δ^{199}Hg: 0.01 ± 0.10 ‰, 1SD) and liquid Hg(0) stocks (Δ^{199}Hg: -0.01 ± 0.03 ‰, 1SD)
352 (Sun et al., 2016; Grigg et al., 2018). Additionally, the mean Δ^{199}Hg values from the solid phase
353 materials at this contaminated site were -0.01 ± 0.06 ‰ (McLagan et al., 2022). Hence, we suggest
354 Δ^{199}Hg values in the tree rings during *1st IP* are conserved from the industrial activities.

355 Wang et al. (2021) made similar observations in Masson Pine tree rings near a former Hg mine in
356 Guizhou Province of China: more positive Δ^{199}Hg values during periods of more intense industrial
357 activity. The more negative Δ^{199}Hg values in tree rings from the *BGP* are similar to the more negative
358 background GEM values (typical range: -0.4 to 0.0 ‰; Szponar et al., 2020 and references therein).
359 Scanlon et al. (2020) measured low THg concentration (<4.5 $\mu g \cdot kg^{-1}$) in red oak, white oak, and pitch
360 pine tree rings and negative Δ^{199}Hg values (-0.39 to -0.14 ‰) and also associated this with the
361 characteristic GEM signature of background air. The difference in Δ^{199}Hg between the *1st IP*, *2nd IP*,
362 and *BGP* is likely related to the atmospheric mixing of background GEM with industrially derived
363 Hg. Foliar uptake has been reported to impart a small negative Δ^{199}Hg shift (≈-0.1 to -0.2 ‰; Demers
364 et al., 2013; Yuan et al., 2018). Yet, our data were more indicative of sources (industrial or
365 background); thus, any negative Δ^{199}Hg shift may be small in Norway spruce and/or differences fall
366 within the range of variability of the sources.

367 Information on the specific processes driving odd-MIF (nuclear volume effect (NVE) vs magnetic
368 isotope effect (MIE)) in the measured Hg can be derived from the ratio of Δ^{199}Hg to Δ^{201}Hg (Bergquist
369 and Blum, 2007; Blum et al., 2014). We derived a slope of 1.25 ± 0.13 (1SE) for bole wood using
370 York orthogonal regression (Fig. S8.1; York et al., 2004), which is higher than other studies (1.04 in
371 Wang et al., 2021; and 1.05 in Scanlon et al., 2020 and Liu et al., 2021), but still lies in the range of
372 the expected slope (1.0—1.3) for MIE related photochemical reduction of Hg(II) to Hg(0) (Bergquist
373 and Blum, 2007; Zheng et al., 2009). The observed MIF data suggest MIE related photochemical
374 reduction and subsequent Hg(0) evasion is likely the dominant pathway of Hg(0) to the atmosphere.
375 However, we caution against the over interpretation of these data as there was a large difference in
376 the slope using a different orthogonal regression method (Fig. S8.1; Deming 1943). This difference
377 in methods can largely be explained by the limited extent of odd-MIF observed in the tree ring data.

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Both, Δ^{200}Hg and Δ^{204}Hg values show there was no significant even isotope-MIF in the bole wood samples (Section S8). Δ^{200}Hg anomalies have been reported for Hg in precipitation samples and related to upper atmosphere oxidation of Hg(0) (Gratz et al., 2010; Chen et al., 2012). Thus, the near zero even-MIF supports the hypothesis that the Hg in tree rings relates to foliar uptake of atmospheric GEM (unaffected by even-MIF) rather than root uptake of Hg deposited to soils via wet deposition of Hg(II).

3.3. Physiological and species related factors impacting within tree Hg cycling

3.3.1. THg concentration and stable Hg isotopes in bark

THg concentrations in the bark of three spruce ISO trees (137 ± 105 µg·kg^{-1}) were significantly higher than THg in bole wood of *BGP* (p = 0.014), *2ndIP* (p = 0.025), and *1stIP* (p = 0.042). Furthermore, the bark was divided into inner (younger) and outer (older) bark of spruce ISO4 and ISO5 trees and the outer bark was 2.0 and 2.7x higher in THg concentrations, respectively. This is similar to the observations made by Chiarantini et al. (2016) for black pine and could be related to longer and more exposure of the outer bark to elevated atmospheric Hg concentrations leading to more Hg deposited to these layers. Nonetheless, the older, outer bark would have been closer to the phloem (inner most bark layer; likely pathway for downward transport of Hg in trees) during the *1stIP* and *2ndIP* when we expect GEM concentrations were much higher than they are presently. Moreover, the inner bark concentrations (spruce ISO4: 57.7 µg·kg^{-1}; spruce ISO5: 163.1 µg·kg^{-1}) were still elevated with reference to the *BGP* in particular. Arnold et al. (2018) and Peckham et al. (2019a) suggest that translocation of Hg from the phloem into the inactive inner bark layers may be an important source of Hg stored within bark, which they further suggest supports findings by Chiarantini et al. (2016) that inner bark layers have a higher proportion of "organic Hg" than the outer layers in black pine.

If the predominant source of Hg in bark was via deposition of either GEM or GOM/PBM then we would expect to observe more positive δ^{202}Hg values in the bark samples as this pathway is unaffected by the large negative MDF (≈-2.6 ‰) associated with stomatal uptake. However, the δ^{202}Hg values for the bark samples were all highly negative (δ^{202}Hg: -3.90 ± 0.30 ‰, 1SD) and similar to the highly negative values in tree ring samples from the *1stIP* and *2ndIP*. Furthermore, GOM/PBM is reported to have more positive Δ^{199}Hg values than GEM (Szponar et al., 2020), but the bark samples (Δ^{199}Hg: -0.14 ± 0.06 ‰, 1SD) were similar if not slightly more negative than the bole wood from these industrial periods (Fig. 4). There was very little difference in δ^{202}Hg or Δ^{199}Hg between the inner and outer bark of either spruce ISO4 or ISO5 tree (Table S4.1). In summary, our Hg stable isotope data

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suggests the stomatal uptake, internal transport, and translocation from phloem to inner bark is likely the dominant uptake pathway for Hg stored in bark. Liu et al. (2021) posited the same foliage assimilation pathway for bark Hg uptake based on similar δ^{202}Hg and Δ^{199}Hg values in both their bark and bole wood samples from subtropical evergreen species at a background site. Considering *rays* that connect xylem and phloem reach as far as the inner bark (Nagy et al., 2014; Pfautsch et al., 2015), this mechanism of bark Hg enrichment is a distinct possibility. More data across a range of species, particularly using Hg stable isotopes, would be beneficial to determine the robustness of this conclusion.

3.3.2. Sapwood (hydroactive xylem) rings enriched in Hg

THg concentrations were elevated in sapwood tree ring samples of all trees from both species, including spruce BG, compared to tree rings from the *BGP*. The 0—5 year samples were elevated in all trees and the 5—10 and 10—15 year samples were also higher in THg concentrations in some trees (Fig. 2). Although part of the phloem (first layer of bark) may have been included in some 0—5 year samples and contributed to enrichment of these samples, elevated THg concentrations in certain 5—10 and 10—15 year samples indicate this is not the sole determinant. Sapwood enrichment has also been observed in both Norway spruce (Hojdová et al., 2011) and European larch (Navrátil et al., 2018; Nováková et al., 2021; 2022) and various species of oak and pine (Wright et al., 2014; Navrátil et al., 2017; Scanlon et al., 2020; Wang et al., 2021). Our study represents perhaps the most pronounced and consistent (across all trees) example of this sapwood enrichment. Nováková et al. (2021) suggest the tree coring sampling method could be a potential source of this enrichment. However, we observe this in the spruce ISO trees that were sampled by breaking up tree "cookies" rather than coring, which would rule out this possibility.

We examine three alternate scenarios to explain this. The first is that GEM concentrations in the area have been elevated during the last decade compared to the *BGP*. While the PAS measured GEM concentrations were slightly elevated (≈2x European background concentrations) likely associated with minor on-going releases from contaminated topsoils, there is no evidence to suggest why GEM concentrations in the most recent 5—10 years would be higher than the earlier *BGP*. Additionally, the spruce BG tree also had elevated THg concentrations in all samples under 15 years, which had little-to-no impact in tree ring Hg by the industrial facility during *1stIP* or *2ndIP*. The European Monitoring and Evaluation Programme (EMEP) has a long-term monitoring station ≈22km to the west of the former industrial site (≈16.5 km west of spruce BG) and reports a mean total gaseous Hg (predominantly GEM) concentration of 1.49 ng·m^{-3} over the last decade (EMEP, 2022), which is a

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typical background concentration for Europe (Sprovieri et al., 2016). Hence, recently elevated GEM concentrations cannot explain the elevated sapwood THg concentrations.

The second would relate to uptake of Hg from tree roots. The conductive or actively transporting component of xylem (hydroactive xylem) exists within the sapwood of trees. Its primary role is the upward transport of water and nutrients from tree roots to the aerial components and particularly leaves/needles. We have already discussed how this pathway has been shown to be a minor mechanism of Hg uptake in many studies (e.g., Beauford et al., 1977; Graydon et al. 2009; Cozzolino et al., 2016). Also, the sampled trees are outside the area in which surface contamination from the industrial activity occurred (particularly spruce BG); any soil contamination must have come from atmospheric Hg emissions and subsequent deposition, of which stomatal uptake of GEM is the dominant conduit in forest ecosystems (Obrist et al., 2017; 2018; Jiskra et al., 2018). We consider this mechanism highly unlikely to be driving sapwood enrichment.

The third scenario relates to tree physiology. Hg is transported downwards in trees via the phloem and has been reported to translocate from phloem to xylem (sapwood) throughout this process (Arnold et al., 2018; Yanai et al., 2020; Nováková et al., 2021). As sapwood ages it undergoes a physiological transition to heartwood, which is drier, contains predominantly dead cells, and is used for structure rather than transport (Bertaud and Holmbom, 2004; Metsä-Kortelainen et al., 2006). Hg that remains in the tree rings after the transition to heartwood likely binds to components that endure this change, but there is a caveat in our knowledge of this process (Yanai et al., 2020; Nováková et al., 2021). Since we use dry weight THg concentrations, if all the Hg translocated from phloem to xylem was conserved in the wood during the transition from sapwood to heartwood, then we would not expect to see any sapwood enrichment. Thus, we deem it likely that some fraction of Hg is retained in the xylem solution or structures/chemicals enhanced in sapwood (compared to heartwood) of these species. Although we only have two samples from the 0—5 year tree rings analysed for stable isotopes, the δ^{202}Hg data from spruce ISO5 and ISO 6 are shifted negative (-0.41 and -0.33 ‰, respectively) in these samples compared to the adjacent composite sample of tree rings in each respective tree (Fig. 3A; Section S6). Hence, the process controlling retention of this Hg in sapwood would seem to favour lighter isotopes, implying there could be either preferential retention of specific Hg-compounds or a change in binding form during the retention process.

Any upwards transport of xylem solution Hg may contribute to the slightly elevated THg concentrations that Yanai et al. (2020) observed in tree rings at higher elevations above the ground. Sapwood is also a storage reserve for energy (starch) and water (Taylor et al., 2002); therefore, some

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of the Hg in xylem solution may be stored long-term in the hydroactive xylem without being transferred as the sapwood rings transition to heartwood. While long-term storage of some Hg in sapwood could be a factor driving temporal differences between tree ring THg concentrations and reported industrial activity in the literature (Arnold et al., 2018; Wang et al., 2021), our data do not reflect such Hg translocation. Ultimately, further research will be needed, particularly using Hg stable isotopes, to further explore this hypothesis and the physiological mechanisms behind this enrichment.

3.3.3. The impact of species on uptake and storage of Hg in tree rings

There is extensive discussion in the literature on species specific differences in THg concentrations of tree rings, particularly as they relate to foliar uptake rates (Wohlgemuth et al., 2020) and inter-ring translocation (Arnold et al., 2018; O'Connor et al., 2019). Inter-ring translocation has led some studies to question the overall effectiveness using tree rings as an archive for atmospheric GEM, but many of these studies have utilised oak (Scanlon et al., 2020), some pine species (Wang et al., 2021; Nováková et al., 2021), and Populus (Arnold et al., 2018). Certain physiological characteristics of these species (i.e., more radially conductive xylem) that enhance this translocation may limit their applicability to tree ring atmospheric archiving (Arnold et al., 2018; Nováková et al., 2021; Gustine et al., 2022). Several studies have observed strong correlations between THg concentrations in spruce (Hojdová et al., 2011) and larch (Navrátil et al., 2018; Nováková et al., 2021) tree rings and reported industrial activities and suggest these to be appropriate species for archiving atmospheric GEM concentrations.

Despite the quite apparent physiological differences between European larch (deciduous conifer) and Norway spruce (evergreen conifer), trends in THg concentrations varied little between the sampled trees of either species. Sapwood was enriched, *BGP* THg was low, and concentrations increased into the $2^{nd}IP$ at the same time (early 1990s) in both larch and spruce trees (all sampled larch were planted after the $1^{st}IP$) (Fig. 2). Additionally, the good correlation between changes in THg concentrations and the timelines of the $1^{st}IP$, $2^{nd}IP$, and *BGP* suggest the process driving sapwood Hg enrichment results in limited inter-ring Hg translocation in Norway spruce and European larch; the fraction of Hg transferred to heartwood must be relatively consistent under this scenario. Thus, our data too suggest Norway spruce and European larch are effective species for the chronicling of historic GEM concentrations.

3.3.4. Between and within tree variability in tree ring Hg

Heterogeneity in the radial distribution of Hg has been observed in other studies and authors suggest sampling of multiple trees in each stand and different radial sections of trees provides more

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representative assessments (Wright et al., 2014; Peckham et al., 2019b). The sampling direction of the bole or height of the sampling can cause differences within replicate samples from the same tree. Factors affecting between tree variability include microtopography, tree age or species and related specific physiological differences such as photosynthesis rate, stomatal conductance and transpiration (Binda et al., 2021). No correlation between Hg concentration and tree core mass was reported by Scanlon et al. (2020) and they concluded that differences in radial growth do not dilute or concentrate Hg in tree rings. These authors therefore concluded that Hg concentrations are a suitable proxy to evaluate trends of GEM. We detected some variability in THg concentrations between spruce ISO4, ISO5, and ISO6 from the same stand of trees (Fig. 2) and in "replicated" tree rings from different sides of the spruce ISO tree slices (mean relative difference: 78 ± 35 %; mean absolute difference: 5 ± 5 $\mu g \cdot kg^{-1}$; n = 10; Table S3.1). Yet, variability in the ratios of Hg stable isotopes within the bole wood was low (mean absolute difference: δ^{202}Hg: 0.11 ± 0.08 ‰ 1SD; Δ^{199}Hg: 0.08 ± 0.02 ‰ 1SD; n = 4; Table S4.2). This suggests factors influencing radial Hg heterogeneity cause little impact of Hg stable isotopes. We considered the stable isotopes analyses based on combined data from all three trees, but individual trees also followed these trends (Section S6).

Data availability

All data are available within the paper and supplementary information. If there are any additional requests, please contact the authors.

Supplementary information

The Supporting Information is available free of charge at DOI: XXX.

Author Contribution

The project design and planning were made by DSM and LS, with inputs from TN. The manuscript was written predominantly by DSM with inputs from LS. Figures were prepared by DSM and LS. Supplemental information was prepared predominantly by LS with inputs from DSM. Tree core sampling was performed by DSM and LS, HB collected tree slices/"cookies". THg analyses were performed by LS and DSM, passive samplers were analysed by DSM, pre-concentration and isotope analysis was performed by LS. Lab space provided by HB and SMK. DSM, LS, HB, and TN contributed to manuscript reviews. DSM and LS contributed equally to this work.

Conflicts of Interest

The authors declare no competing financial interest.

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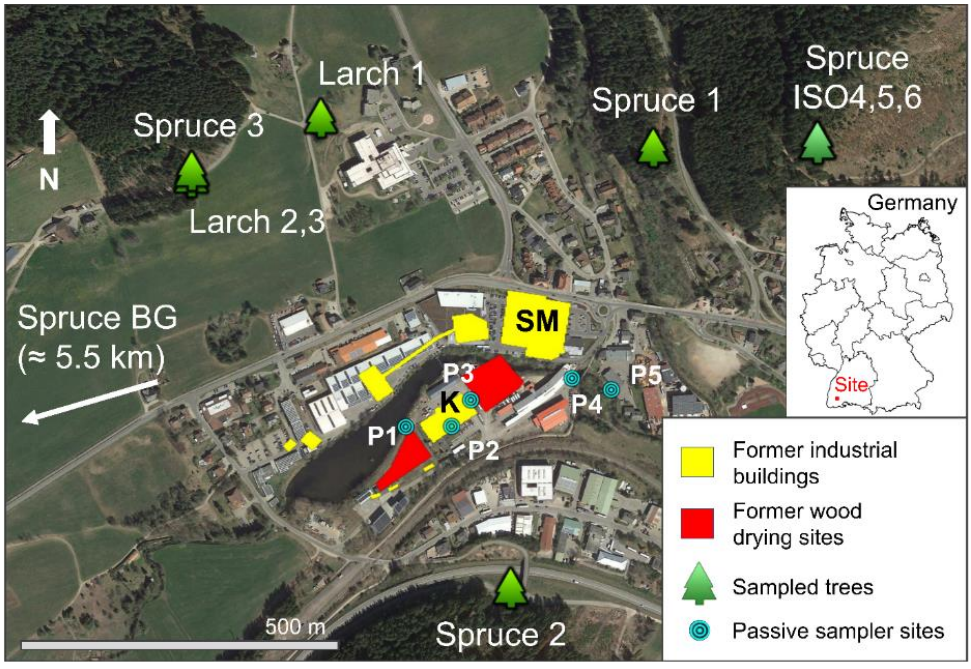

838

839 *Figure 1: Map showing the location of sampled trees, former industrial buildings and wood drying*
840 *sites (before 1968), and passive sampler locations (labelled P1—P5). The location of spruce*
841 *background tree (spruce BG) is ≈5.5 kilometres west southwest of the study site (direction indicated*
842 *on map). SM – Former sawmill; K – former kyanisation hall/wood treatment area. The three spruce*
843 *ISO trees are from the deforested stand in the northwest of Fig. 1; exact location of each of these*
844 *trees within this stand is unknown (trees felled by forest workers). ©Google Earth 2019.*

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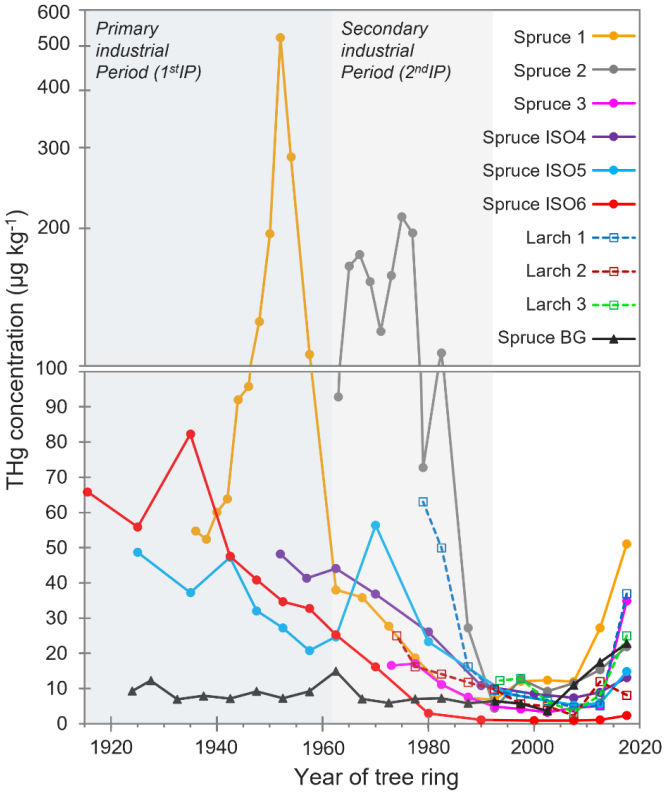

846

847 ***Figure 2**: THg concentrations in tree rings dated by year. Years of tree rings correspond to the*
848 *middle point of samples of combined adjacent rings (i.e., 0—5 year = 2.5 years). Y-axis is split at 100*
849 *µg·kg-1 changing from normal- to log-scale due to the very high concentrations measured in Spruce*
850 *1 and Spruce 2. 1stIP (before 1962) and 2ndIP (1962—1992) are highlighted.*

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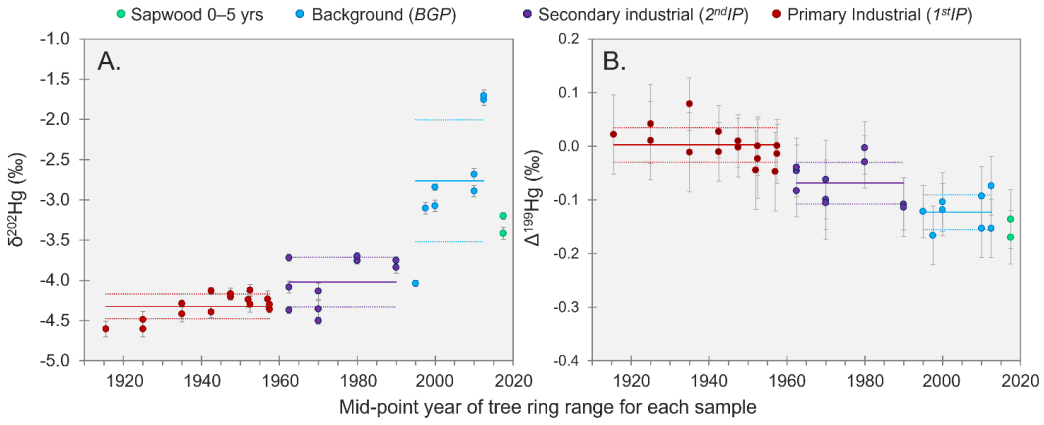

852

853 ***Figure 3**: δ^{202}Hg (Panel A) and Δ^{199}Hg (Panel B) in tree rings dated by year for samples from*
854 *spruce ISO4—6 trees. Solid and dotted lines for each period represent the mean and standard*
855 *deviation, respectively. Data displayed are the composite of all three trees (figures for individual*
856 *trees are shown in Section S6). Data for THg plotted against MDF and THg against MIF are shown*
857 *in Section S7. Error bars for individual datapoints represent session 2SD for secondary standard*
858 *"ETH Fluka".*

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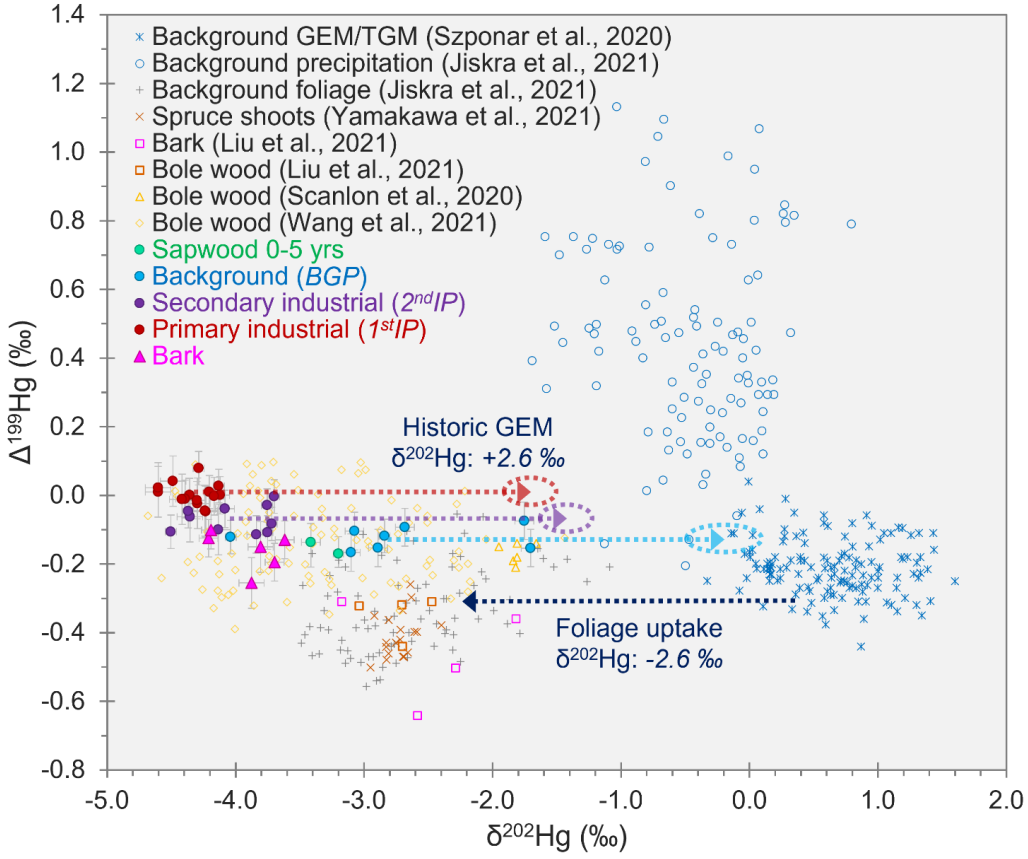

860

861 ***Figure 4***: *Relationships between Δ^{199}Hg and δ^{202}Hg for tree rings samples from spruce ISO4—6*
862 *trees analysed for Hg stable isotopes (data with solid markers). Figure includes the Δ^{199}Hg and*
863 *δ^{202}Hg values for tree samples (bole wood, bark, foliage, and shoots) from other studies. Additionally,*
864 *background TGM/GEM data were included to show the ≈-2.6 ‰ MDF associated with stomatal*
865 *uptake of GEM (dark blue dotted line), and background precipitation samples were included to*
866 *demonstrate that there was little influence from precipitation on found Hg in within trees. The red,*
867 *purple, and light-blue dotted lines indicate the predicted GEM values in air at the site during the*
868 *1st IP, 2nd IP, and BGP, respectively, based off the mean measured δ^{202}Hg values in tree rings for these*
869 *respective periods (MIF was assumed to be zero for stomatal uptake in these calculations).*

870