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Black pine (*Pinus nigra*) barks as biomonitors of airborne mercury pollution



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HIGHLIGHTS

- At the Mt. Amiata Hg district, *Pinus nigra* barks show high Hg concentrations.
- *Pinus nigra* barks showed the highest Hg concentration ever reported in literature.
- Tree bark is a reliable, diffuse, practical and low-cost candidate as biomonitor.

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ABSTRACT

Tree barks are relevant interfaces between plants and the external environment, and can effectively retain airborne particles and elements at their surface. In this paper we have studied the distribution of mercury (Hg) in soils and in black pine (*Pinus nigra*) barks from the Mt. Amiata Hg district in southern Tuscany (Italy), where past Hg mining and present-day geothermal power plants affect local atmospheric Hg concentration, posing serious environmental concerns. Barks collected in heavily Hg-polluted areas of the district display the highest Hg concentration ever reported in literature (8.6 mg/kg). In comparison, barks of the same species collected in local reference areas and near geothermal power plants show much lower (range 19–803 µg/kg) concentrations; even lower concentrations are observed at a “blank” site near the city of Florence (5–98 µg/kg). Results show a general decrease of Hg concentration from bark surface inwards, in accordance with a deposition of airborne Hg, with minor contribution from systemic uptake from soils. Preliminary results indicate that bark Hg concentrations are comparable with values reported for lichens in the same areas, suggesting that tree barks may represent an additional useful tool for biomonitoring of airborne Hg.

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1. Introduction

Mercury (Hg) is a widespread contaminant of much concern due to its high toxicity, persistence and accumulating behavior in the environment. Moreover, Hg displays long residence times in the atmosphere, and a corresponding ability to be transported over long distances. For this reason, Hg is unanimously considered a global pollutant (Selin, 2009). Many models of Hg transport and deposition are based on monitoring networks at variable scale (Brown et al., 2015, and references therein). Blackwell and Driscoll (2015) recently pointed out that, while these estimates have advanced our understanding of global Hg cycling,

they are not capable of accurately resolving deposition patterns at a regional scale. Moreover, the biogeochemical cycle of Hg is particularly susceptible to modification in the future because of global climate variability and change (e.g., Stern et al., 2012). Thus, something of what we have learned up to now regarding Hg cycling may be obsolete. As noted by Blackwell and Driscoll (2015), without an increase in monitoring sites it is unlikely that models developed in the future will be capable of capturing fine-scale Hg deposition patterns at a regional scale. According to Pirrone et al. (2013), to expand monitoring beyond a limited number of sites it is necessary to develop simple, low cost, and reliable techniques. Biomonitoring methods may satisfy these requirements, but with some limitations, as clearly described by Lodenius (2013). For instance, the widely used Hg biomonitoring technique based on lichens and mosses (Bargagli et al., 2002; De Bruin and Hackeniz, 1986; Garrec and Van

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Haluwyn, 2002; Grangeon et al., 2012; Szczepaniak and Biziuk, 2003) has some disadvantages, including patchy distribution, slow regeneration rates, and difficulty in differentiating between similar species (Pacheco et al., 2002). Accumulation in foliage (Blackwell and Driscoll, 2015; Obrist et al., in press; and references therein) and peat bogs (Enrico et al., 2016) were recently used in biomonitoring campaigns of Hg deposition, but they suffer of similar limitations. For example, even if a linear relationship between atmospheric Hg concentrations and leaf concentration has been frequently reported (Chen and Yang, 2012), the length of Hg exposure may be limited to a restricted time by factors such as: the seasonal senescence of leaves in deciduous species and the leaf retention time in evergreen species. In the case of peat bogs, their scarce distribution may lead to significant sampling restrictions. In this context, the use of tree tissues for biomonitoring could offer key advantages, including year-round and ubiquitous availability, simple species identification, and easy sampling. In living plant tissues, metallic Hg in vapor form is quickly oxidized to Hg^{2+} by catalases (Du and Fang, 1983) located in leaf peroxisomes, and it is trapped to biological matters. The Hg uptake is controlled by the number of stomata per samples and it is higher during periods of higher photosynthetic activity (Laacouri et al., 2013). In dead plant tissues, like tree barks, the mechanism of Hg sorption in natural environments is largely unknown. Laboratory experiments on *Pinus pinaster* barks suggest that Hg^{2+} could be sorbed by a mechanism involving an ion exchange with the tannins in the bark (Vázquez et al., 2002).

In the past decade, researchers have started to comprehensively investigate interactions between airborne pollution and tree bark (Berlizov et al., 2007; Freer-Smith et al., 2005; Harju et al., 2002; Mandiwana et al., 2006; Narewski et al., 2000; Pacheco et al., 2001, 2002, 2003, 2008; Panichev and McCrindle, 2004; Saarela et al., 2005; Santitoro et al., 2004; Shin et al., 2007; Suzuki, 2006; Tye et al., 2006). Tree bark, with its porous morphology and lack of metabolic activity, can be an effective adsorbent of airborne pollutants, including Hg (Siwik et al., 2010). Due to its generally low bioavailability in soils, Hg may not be taken up through plant roots in substantial quantities (Boszke et al., 2008; Rasmussen et al., 2000). Moreover, the portion of Hg translocated to the shoots was reported to be negligible, making the roots the main site for the accumulation of the element (Chen and Yang, 2012). In fact, Siwik et al. (2010) showed that Hg reaches tree core through leaves and possibly bark, but not through roots, suggesting that the systemic uptake from soils can be considered marginal (Fleck et al., 1999; Frescholtz et al., 2003; Poissant et al., 2008; Reimann et al., 2007). Thus, bark appears to be a simple, inexpensive, passive and integrative biomonitor particularly suitable for airborne Hg pollution surveys. However, scientific literature reports few examples of such use, probably because its actual reliability is still unclear. For instance, in his comprehensive review of Hg biomonitoring methods, Lodenius (2013) reports that bark has been used in airborne Hg surveys, but some researchers (e.g., Lippo et al., 1995) consider tree bark less suitable, due to small variations in Hg concentration, which discourages its use for regional surveys. Indeed this latter aspect, the amount of Hg that may be retained by barks, appears of paramount relevance for the use of bark in future Hg biomonitoring studies.

As a first contribution in this direction, the present study aims to establish the amount of Hg that can be retained by barks in a highly contaminated area, and how this metal is distributed from the outer to the inner bark. The study was realized in tree barks from the Mt. Amiata region in southern Tuscany, Italy, where two industrial activities, Hg mining and geothermal energy production, affect local atmospheric Hg levels (Loppi, 2001; Rimondi et al., 2015). This study assessed Hg levels in bark from black pine (*Pinus nigra* J.F. Arnold), a large coniferous evergreen tree common throughout the Mediterranean area. This species was planted in the Mt. Amiata region at the beginning of the past century and during the 1950–1970 decades (Unione Comuni Amiata Val d'Orcia, Forestry Management Office, oral communication). *Pinus nigra* species was selected for the present study because of its wide

distribution in the region, and because of the distinctive multilayered structure of its barks, which facilitated the investigation of Hg distribution as a function of depth.

2. Study site

The Mt. Amiata Hg mining district (southern Tuscany, Italy; Fig. 1a) was originally exploited by the Etruscans (about 800 BCE) and rediscovered in 1868 (Barghigiani and Ristori, 1995; Ferrara et al., 1991; Pattelli et al., 2014; Rimondi et al., 2015). About 102,000 t of Hg were produced from the 1860 to 1980, ranking it as the third largest Hg producing district worldwide (Ferrara et al., 1998). Similarly to most Hg deposits, cinnabar is the dominant ore mineral, associated with minor amounts of pyrite, rare stibnite, marcasite, and arsenic-bearing sulphides (Rimondi et al., 2015). During the exploitation period, the recovery of Hg from ores of the whole district was mostly accomplished close to the mining town of Abbadia San Salvatore, which was the largest one of the entire Hg district. As a result, the town is closely interconnected with the mining/roasting plants and with the roasting waste calcines.

The Mt. Amiata Hg district is located in the homonymous volcano-geothermal region (Bacci et al., 2000; Rimondi et al., 2015; Vaselli et al., 2013). At Piancastagnaio and Bagnore (Fig. 1a), two power plants exploit the geothermal fluids for the production of electrical energy by the National Agency for Electric Energy. The geothermal fluids of Mt. Amiata contain Hg (Bacci et al., 2000), at least partly discharged as gaseous Hg^0 to the atmosphere during geothermal energy production. To minimize the environmental impact of the geothermal energy production, the plants were recently equipped with pollution control technology (AMIS, the Italian acronym for Mercury and Hydrogen Sulphide Abatement) to reduce the atmospheric emissions of hydrogen sulphide and Hg from exploited geothermal fluids (Baldacci et al., 2005; Bertani, 2007).

3. Sampling and analytical procedures

3.1. Sample collection

The east flank of Mt. Amiata, where the Abbadia San Salvatore mine is located, has been the subject of much research on Hg distribution in different matrices such as soils, stream sediments and water, fish, air, and vegetation (Bargagli et al., 1986, 1987, 2002; Barghigiani and Ristori, 1995; Ferrara et al., 1991; Rimondi et al., 2012, 2014, 2015; Vaselli et al., 2013). Due to the intense past mining activity, Hg is widely distributed both in abiotic and biotic matrices. The primary aim of the present study was to investigate the feasibility of tree bark as a biomonitor of atmospheric Hg in a well-known contaminated area. The Abbadia San Salvatore surroundings offer the opportunity to collect some preliminary data to test this possibility. Barks of *P. nigra* and nearby soils were collected at a number of representative sites (Fig. 1b), including areas associated with historical mining activity, geothermal power plants, and local and regional reference sites. We emphasize that the Mt. Amiata area was highly impacted by Hg mining activities. The diffusion of Hg was not limited to mining sites, because mine wastes were extensively recycled and dispersed in the area for many different purposes. Moreover, the numerous geothermal manifestations are an additional Hg carrier (Vaselli et al., 2013), that superimpose to the natural and anthropogenic anomaly. For all these reasons, the choice of local reference sampling sites is not straightforward. As a compromise, we considered eligible as local reference areas those located a) as far as possible from sites directly or indirectly affected by mining operations; b) as far as possible from Hg mineral occurrences; and c) where the effects of other natural Hg sources could be considered minor. Mine-affected soils were collected near Abbadia San Salvatore (Laghetto Verde, Abbadia San Salvatore public garden). Another soil was sampled at Acquapassante, which hosts an old mine drilling, and now is a well-

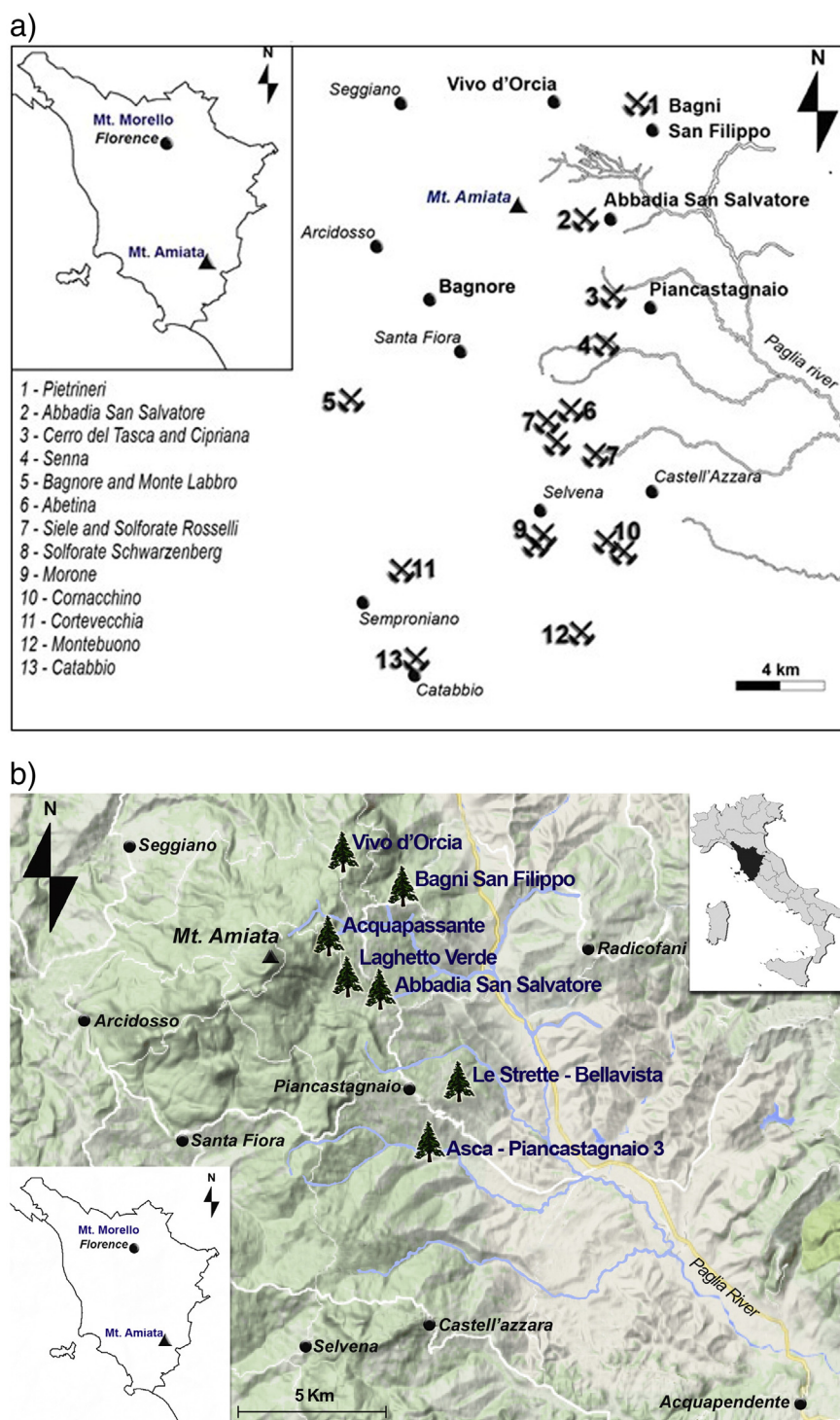


Fig. 1. Map of the Mt. Amiata Hg mining district; a) the exploited Hg mines in the region; the sampling sites (tree symbols) selected for barks of *Pinus nigra* and relative soils. Symbols: black dots = towns; black triangles: mountain peak.

known emission source of CO₂ and H₂S (Nisi et al., 2014; Tretiac and Ganis, 1999). Due to the proximity to the mining area, this site was considered as a mine-affected soil as well. Samples from “geothermal areas” were collected in proximity of the power plants of Asca-Piancastagnaio 3 and Le Strette-Bellavista, both located near the town of Piancastagnaio. To document Hg deposition from the geothermal plants, both tree barks and soil were collected within a 500–600 m. radius from the geothermal installations, where the maximum anomalous concentrations are documented (Bargagli et al., 1997). Two sets of reference samples (“local” and “regional”) were also collected. Local reference

samples were picked up at two sites (Bagni San Filippo and Vivo d'Orcia) north of Abbadia San Salvatore, far from mining sites (about 6 km) and geothermal power plants. At Bagni San Filippo village, the wide presence of CO₂ gas-rich manifestations and active travertine deposition give rise a significant increase of airborne Hg⁰ with respect to the background levels (Vaselli et al., 2013). However, such an increase is insignificant if compared with the Hg⁰ values detected in the Abbadia San Salvatore urban and mining areas (Vaselli et al., 2013).

Regional reference samples were collected at a non-impacted site near Florence (Fonte dei Seppi at Mt. Morello), more than 100 km far

from the Hg mining region. The Mt. Morello site was recently selected as an ideal station for the measurement of background levels in studies devoted to aerosol pollution (Udisti et al., 2009). In all sites, soils were collected outside the tree canopy protection.

Bark sampling was carried out in July 2014 by core drilling (Fig. 2) at least three trees at each site at a height of about 1.5 m above the ground. Sampled trees from southern Tuscany have almost the same size (trunk diameter, measured at a height of 60 cm above the ground level, is about 35 cm) and age (around 60 years old: S. Visconti, personal comm.). Trees from Monte Morello are smaller in diameter (about 25 cm at a height of 60 cm above the ground level), and relatively younger (approximately 40 years old).

With few exceptions (Sanjo et al., 2004), in literature the metal concentrations of barks are usually reported for the bulk sample, assuming that concentration is homogeneous across the sample thickness. Barks of the *Pinus* genus, in particular the *P. nigra* species, usually consist of stratified bark sheets, each having a thickness of 1–2 mm. Bark layers grow outward from the interior of the tree, thus bark layer age decreases moving from the outer bark surface to interior bark sheets. These sheets can be easily separated from one another (Fig. 2a). In this study, we determined Hg concentrations separately for different layers (Fig. 2 b-c). For each sampling site at least two samples of barks were segregated into slices using a ceramic knife, trying to avoid any contamination among different layers. The position of a given slice within the bark core was identified, measuring the distance from the external surface exposed to the atmosphere. At least three portions of each sample (external, middle and internal) across the bark thickness were selected. For samples expected to have high Hg concentrations, we increased the number of bark slices to better describe the Hg distribution throughout the bark.

There is no established method for sampling and analyzing barks for Hg. Usually, analytical results are presented on dry weight basis.

Concerning the drying procedure, Siwik et al. (2010) air dried barks before acid digestion. Kuang et al. (2007) and El Khoukhi et al. (2005) oven dried barks at 60 °C prior to metal analysis, but they were not specifically interested in analyzing for Hg. To avoid the risk of Hg volatilization, each bark sample was divided into two subsamples. One subsample was oven dried at 110 °C until a stable weight was achieved, thus allowing calculation of the water loss. This heated subsample most probably suffered a partial loss of Hg due to volatilization, therefore this aliquot was discarded. Mercury was instead analyzed in the other subsample; the obtained value of Hg concentration was then corrected for water loss as determined for the other subsample, and reported on a dry weight basis.

Soils were sampled outside the tree canopy projection, but at a distance from the trunk never exceeding a few meters. They were subsequently transported in the lab, air dried, sieved, selecting the fraction <2 mm, and ground. In order to avoid any contamination, all the equipment used for sampling (Teflon scoops) and sample preparation (sieves and mortars) were adequately cleaned up and rinsed before their use.

3.2. Mercury analysis

Mercury was measured in bark and soil (see also in the following) by means of a direct Hg analyzer (Milestone DMA-80), based on EPA method 7473 combining thermal decomposition, amalgamation, and atomic absorption spectrophotometry. For each bark slice, a portion of about 1 cm³ was finely minced for subsequent DMA analysis. The final weight of each sample ranged between 60 and 150 mg. To estimate the analytical precision, replicate analyses of the same slice were routinely performed; results were reproduced within 10% of the average value. A slightly higher error (up to about 15%) was observed in very few cases, indicating small-scale spatial heterogeneity of the samples. Long-term accuracy was evaluated using international standards for

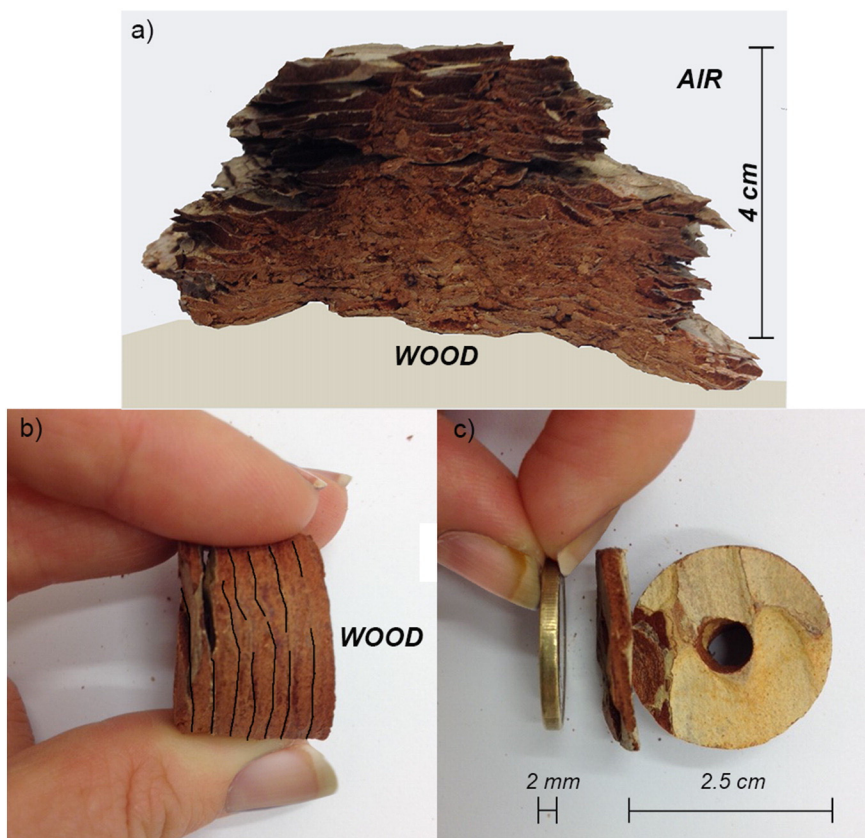


Fig. 2. Images of sampled barks; a) bark cross section from external surface exposed to the atmosphere (up), into the tree core near the phloem (down); b) bark core drill with evidenced the stratified bark sheets; c) bark sheet sliced during sample preparation and employed for Hg analysis.

soils, sediments and leaves (NIST SRM 2711; NIST SRM 1573a; NRC-CNRC MESS-3; CCRMP STSD-1). Estimated accuracy was within 10%.

Soils with high Hg concentration (>10 mg/kg) exhibited high analytical variability using the direct Hg analyzer, likely due to the well known “nugget effect” associated with the analysis of small sample masses of highly contaminated soils (Kocman et al., 2006). To minimize this effect, a higher mass of sample was analyzed by ICP-OES (Perkin Elmer Optima 8000 instrument) equipped with a hydride generator (Perkin Elmer B0507957), following the procedure of Hineman (2011–2012): after drying, sieving and grinding, samples were leached with aqua regia (US EPA 3051) in Teflon bombs in a microwave oven (Techno Fisher MARS 6). The solutions were injected in the ICP-OES plasma torch either by a Miramist™ nebulizer (Burgener Research Inc.) and a cyclonic chamber, or as argon-stripped Hg cold vapor obtained by SnCl₂ reduction in the hydride/Hg generation apparatus, depending on Hg concentrations. In the case of Hg cold vapor, the most sensitive wavelength of 253.652 nm was chosen; otherwise for the nebulizer the wavelength of 194.168 nm was preferred, to avoid iron interference. The analytical accuracy, checked against NIST SRM 2711 and CCRMP STSD-1 standards, was about 10%.

4. Results

Mercury concentrations in soils and barks (corrected for water loss) are presented as electronic supporting information (Tables A1a and A1b). Mercury soil concentrations are highly variable. The Abbadia San Salvatore mining area presents the highest concentrations, reaching values of about 70 mg/kg (range 2.4–68 mg/kg), whereas the minimum concentrations are observed at Mt. Morello, the regional reference site (121 µg/kg). High and variable Hg concentrations are measured also in the Asca - Piancastagnaio area, close to the geothermal plants, with values covering the range between 1 and 2.2 mg/kg. Lower, and more homogeneous, concentrations are recorded in the Mt. Amiata local reference areas (Bagni San Filippo, Vivo d'Orcia), with values in the range of 432–459 µg/kg.

Barks have water content falling between 9.1 and 25.1% by weight (Table A1b). With some exceptions, the highest water content in each sample was observed in the innermost bark layer, at the contact with the phloem.

Mercury in analyzed barks varies from 5 to 8651 µg/kg. We found the lowest concentrations (range 5–98 µg/kg; average 26 µg/kg) at the regional reference site Mt. Morello, and the highest in the Abbadia San Salvatore mining area. The two local reference areas (Bagni San Filippo, Vivo d'Orcia) in the Mt. Amiata district show similar Hg concentrations (in the range of 19–803 µg/kg; mean 207 µg/kg), definitely lower compared to the Abbadia San Salvatore mining area, but distinctly higher than at Mt. Morello. Barks sampled in the surroundings of the two power plants (Asca - Piancastagnaio 3, Le Strette - Bellavista) show slightly different Hg concentrations, but within the range of 32–117 µg/kg. These values are the lowest detected in the Mt. Amiata area (Fig. 3).

In general, the highest Hg values occur at the external bark surface, and the minimum concentrations in the innermost layer, near to the phloem (Fig. 3). This pattern is observed in most bark samples, particularly in all those collected in the local reference sites (Bagni San Filippo, Vivo d'Orcia) and the regional reference site (Mt. Morello). However, in a small number of samples from highly polluted sites of the Mt. Amiata mine district (e.g. Laghetto Verde, Acquapassante and Abbadia San Salvatore public garden), the highest Hg values are not found at the bark surface, but at some depth below (generally between 1 and 2.5 cm).

Fig. 4 shows the comparison between the Hg concentration in soils and in the external bark portion, reported as the mean of the three different trees for each site. The external bark portion was chosen since it represents the direct interface with the atmosphere. Fig. 4 shows that, at least for the sites of Bagni San Filippo, Vivo d'Orcia, Acquapassante,

Abbadia San Salvatore, and Laghetto Verde, the Hg bark concentration increases with increasing soil Hg ($R^2 = 0.95$, $p = 0.003$). On the other hand, we did not observe any significant correlation for the barks located at Mt. Morello and near the power plants of Piancastagnaio and Bellavista. Notably, in these geothermal areas the comparatively high Hg concentrations in soils are not matched by the tree barks.

5. Discussion

5.1. Mercury in soils

According to Rudnick and Gao (2003) the average concentration of Hg in the upper continental crust is approximately 50 µg/kg; higher values (up to 400 µg/kg) are proposed by Fitzgerald and Lamborg (2003). Soils of the Mt. Amiata district (at Abbadia San Salvatore mine, but also in the reference sites of Bagni San Filippo and Vivo d'Orcia) usually show Hg contents higher than 400 µg/kg, confirming the existence of a broad geogenic and anthropogenic Hg anomaly in this area (Rimondi et al., 2014). Furthermore, in proximity to the calcine wastes and roasting plants at Abbadia, soils can contain up to 68 mg/kg of Hg. In comparison, soils from the Mt. Morello area, the regional reference site, display, as expected, much lower Hg concentrations (121 µg/kg).

5.2. Bulk Hg in barks

According to Schulz et al. (1999) tree barks, especially those belonging to the *Pinus* genus, may adsorb high amounts of airborne pollutants, including heavy metals, with no metabolic transformation, since they behave as almost inert sorbents. To standardize the use of bark in environmental studies, it is necessary to understand more deeply the influence of parameters like the sample height (above ground level), the geographical orientation and exposure to prevailing wind directions, the bark age, the chemical speciation of airborne Hg, and the efficiency of barks in trapping and retaining Hg. In any case, the starting point is the measurement of Hg concentration across bark thickness. The relatively few studies on Hg concentration in tree barks indicate rather wide compositional ranges. Not surprisingly, the highest concentrations have been observed in highly anthropized areas. In a study conducted in Germany on barks of *P. sylvestris*, Schulz et al. (1999) detected up to 1180 µg/kg Hg, to our knowledge the highest value reported in the literature before our study. Reimann et al. (2007) and Siwik et al. (2010) measured Hg concentrations ranging from 11.5 to 26 µg/kg in barks of different tree species from contaminated areas. Higher values (320 µg/kg) have been recorded by Sanjo et al. (2004) on *Ginkgo biloba* barks in the urban area of Tokyo. Anyway, none of these studies (with the exception of Sanjo et al., 2004) clearly reports which bark portion was analyzed.

Our survey was conducted on barks from only one tree species (*P. nigra*), in order to make results more internally consistent. Consequently, any comparison with results obtained by other authors for tree barks of different plant species should be taken cautiously. The maximum Hg concentrations displayed by pine barks in this study (up to about 8.6 mg/kg) are apparently the highest ever reported, and extend beyond previously reported ranges of Hg concentration accumulated by barks (Schulz et al., 1999). This result is not unexpected, considering the very high atmospheric Hg⁰ values observed in the town of Abbadia San Salvatore (Vaselli et al., 2013).

Considering the total bark mass for each tree of *P. nigra* (the order of magnitude is of some tens of kg), and the highest Hg concentration observed, the total mass of Hg stored in tree barks may be very significant. In other words, barks may represent an important Hg reservoir that could influence the cycling of Hg through the surrounding environment.

We further notice that in the “clean” regional reference area of Mt. Morello, near Florence, the barks of *P. nigra* show average Hg concentrations of about 26 µg/kg, i.e. lower than in the Mt. Amiata district, but higher than in polluted areas elsewhere (cf. Reimann et al., 2007 and

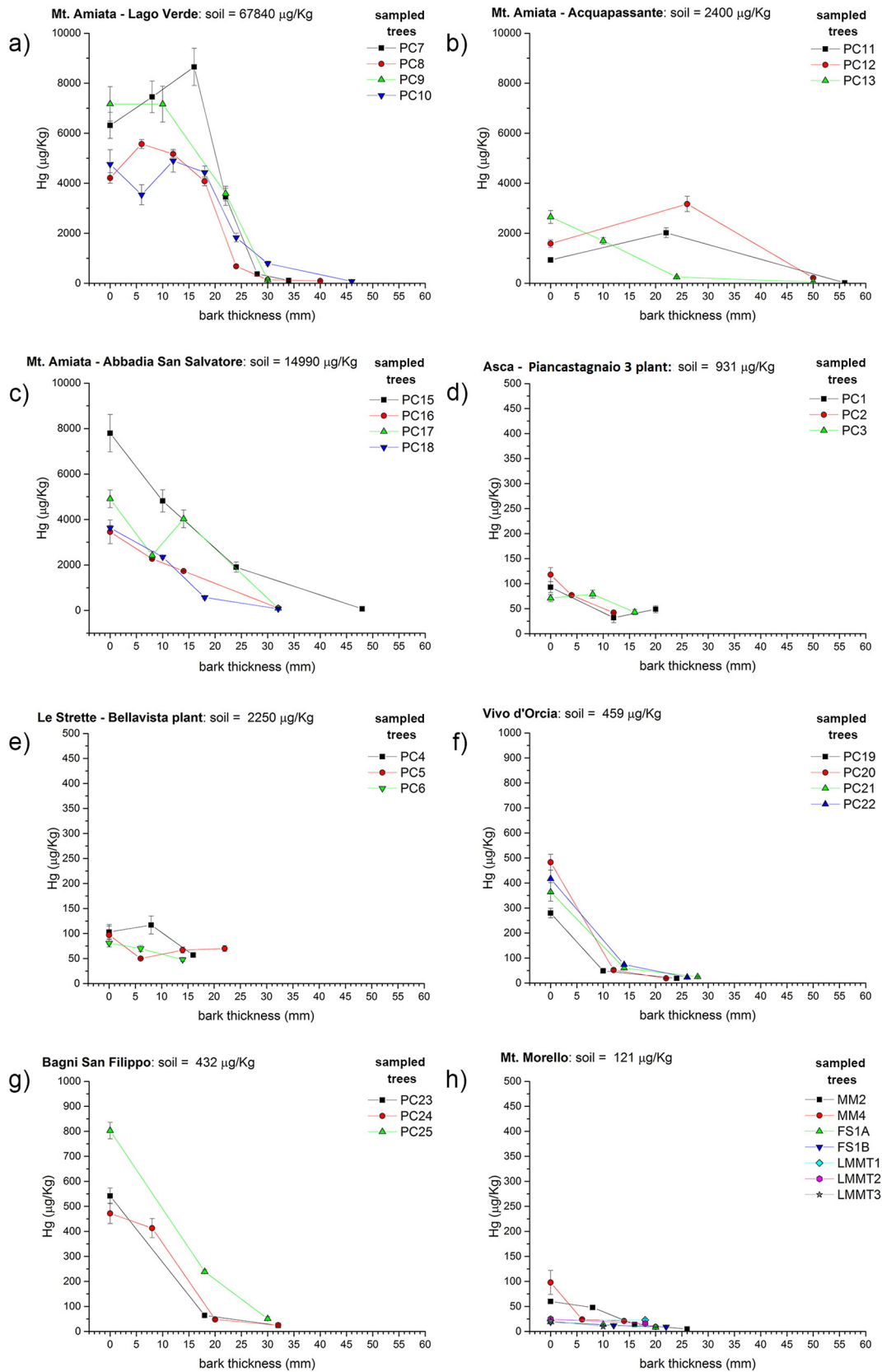


Fig. 3. Mercury concentration in barks (mean value and standard deviation) versus bark depth measured as the distance from the external surface; each set of data represents a sampled tree; a) Amiata-Lago Verde barks; b) Amiata-Acquapassante; c) Amiata-Abbadia San Salvatore; d) Asca-Piancastagnaio 3 plant; e) Le Strette-Bellavista plant; f) Vivo d'Orcia; g) Bagni San Filippo; and h) Monte Morello.

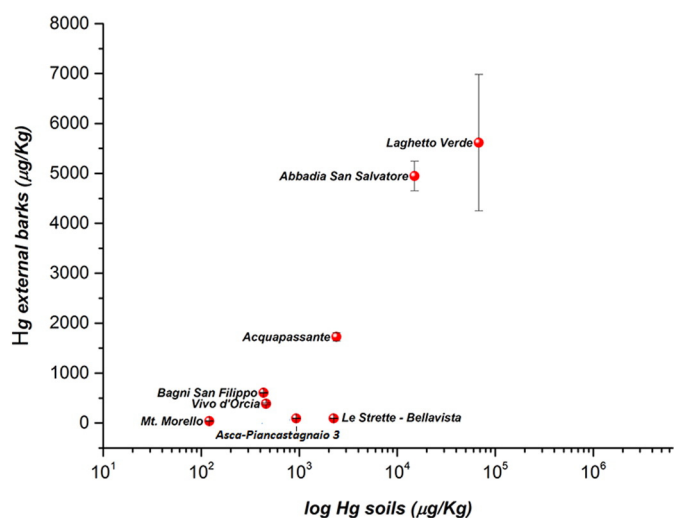


Fig. 4. Mercury concentration in the external portion of the barks (as average of the samples in their external portion) versus Log Hg contents in relative soils; at least for the sample sites of Bagni San Filippo, Vivo d'Orcia, Acquapassante, Abbadia San Salvatore, and Lago Verde, the Hg bark concentration is positively correlated with the Log Hg in soils.

Siwik et al., 2010). It is interesting that, according to Sanjo et al. (2004), the barks of *Ginkgo biloba* from rural and suburban sites in the Tokyo region contain Hg concentrations close to those measured at Mt. Morello.

5.3. Distribution pattern of Hg in barks

A number of studies on Hg distribution in plant tissues point out that roots play a minor role in taking up and translocating Hg from the soil to the higher portions of the plant (Greger et al., 2005; Millhollen et al., 2006; Wang et al., 2005). In a recent and comprehensive study on the distribution of Hg in tree tissues, Siwik et al. (2010) illustrated that Hg mainly accumulates in the phloem of common deciduous trees either through the bark or the leaves, but not through the roots. Similar mechanisms of Hg accumulation have been highlighted in many other studies (Lepp and Dollard, 1974; Sanjo et al., 2004; Watmough and Hutchinson, 2003; Zhang et al., 1995). Accordingly, plants tend to accumulate Hg from the atmosphere rather than from soils, even in the case of severe Hg pollution, chiefly due to the low bioavailability of this metal in soils (Boszke et al., 2008). In any case, since pine needles have been reported to accumulate Hg from the atmosphere (Hutnik et al., 2014), a possible transfer of the element to other plant organs and tissues cannot be neglected, even if the possibility of its reaching ultimately the bark appears remote.

Rimondi et al. (2014) recently studied the speciation of Hg in the Abbadia San Salvatore area using chemical extraction techniques coupled with X-ray absorption spectroscopy. Results indicate that Hg geoavailability in the Mt. Amiata region is rather low, since the metal is mostly incorporated in highly insoluble sulphides like cinnabar and metacinnabar. The general decrease of Hg concentration from the surface inwards shown by *P. nigra* barks at Abbadia is in accordance with deposition (and in-depth penetration) of airborne Hg. This finding substantially excludes a systemic uptake of Hg from roots. The positive correlation of Hg in soils and barks from Abbadia San Salvatore, Bagni San Filippo and Vivo d'Orcia can be interpreted as an uptake of Hg by barks from resuspended local soil dust or from Hg⁰ soil degassing. Actually, it cannot be excluded that some amount of Hg, originally deposited on leaves, could be leached by rainfall and redeposited onto barks.

At Bagni San Filippo, Vaselli et al. (2013) found a positive anomaly of Hg in air. Here, CO₂-rich dry gas vents, thermal waters, and fossil and active travertine deposition are surface manifestations of the Bagnore-Piancastagnaio geothermal field (Froncini et al., 2009; Rimondi et al.,

2015). Therefore, we can envisage that the significant amount of Hg observed in bark at this site is due to the presence of thermal manifestations.

The town of Abbadia San Salvatore is so closely interconnected with the mining and roasting plants that the waste calcines are located next to the urban center (Rimondi et al., 2014). Moreno et al. (2005) pointed out that the airborne particulate at Almadén (Spain) may contain Hg concentration as high as 6000 mg/kg in the form of Hg sulphides, chlorides and oxides. Similar results, concerning Hg speciation in soils close to retorting plants, were recently obtained by Rimondi et al. (2014) at Abbadia San Salvatore. Here, in addition, a diffuse presence of Hg⁰ was also observed. Since all these Hg species contribute to total gaseous and airborne particulate, it is not unexpected that the highest concentrations of Hg in barks were observed at Abbadia San Salvatore, where the highest Hg concentrations in the atmosphere also occur (Vaselli et al., 2013).

It is unclear how permanently Hg, once deposited, can reside in barks. The efficiency of *P. nigra* barks in scavenging and retaining Hg depends on a number of factors, among which the Hg chemical speciation and the bark structure and composition are probably the most relevant (Sen et al., 2015). For example, Vázquez et al., 2002 found that tannins (procyandinin) in barks can act as ion-exchangers by chelating bivalent cations such as Hg²⁺. Within Hg mining and retorting areas, the speciation of airborne Hg should encompass soluble Hg species (soluble Hg ionic species and reactive gaseous Hg species; Gray et al., 2004; Lindberg and Stratton, 1998; Nacht and Gustin, 2004), Hg sulphides (Moreno et al., 2005), and gaseous Hg⁰. This latter species is expected to become dominant moving to long distances away from the mining area (Weiss-Penzias et al., 2003). As previously described, we observed a different Hg distribution in some barks from highly polluted sites within the Mt. Amiata mining district (e.g. Laghetto Verde, Acquapassante and Abbadia San Salvatore public garden), where Hg reaches its maximum concentration at 1–2 cm below the bark surface (Table A1b and Fig. 4) rather than at the bark-air interface. Although this unusual Hg distribution along bark thickness needs to be better investigated, some hypotheses may be preliminarily formulated to explain this evidence, including: a) Hg loss from the very external portion of barks due to evaporation, a process that is well documented not only in soils, but also in barks (Hanson et al., 1997; Schlüter, 2000); b) bark ageing, with consequent reduction of adsorption capacity; and c) peculiar Hg speciation which may have influenced the extent of leaching by rainfall.

5.4. Barks versus lichens as environmental biomonitors of Hg contamination

Lodenius (2013), based on the results of Lippo et al. (1995) on a nationwide sampling in Finland, claims that tree barks are less suitable than mosses and lichens for survey studies of airborne heavy metals, since they do not generally reveal regional differences, and have lower Hg concentrations, particularly compared to lichens. These conclusions are not in agreement with the study by Pacheco et al. (2008), that compared the concentration of several elements in barks and lichens in an urbanized and industrialized area in Portugal. They found that these natural matrices show a good correlation with atmospheric deposition. It should be noticed that different tree bark species and different environments of study may be responsible for the opposite conclusions drawn by these authors.

According to our results, albeit preliminary, in the Mt. Amiata area the concentration of Hg in barks is comparable to that found in lichens (from plants grown on Hg polluted soils in the same area; Bargagli et al., 1987). Specifically, Loppi and Bonini (2000) report at Bagni San Filippo a Hg concentration in lichens of 367 µg/kg, which compares well with Hg concentrations we measured in the outer portions of barks at the same site (472–803 µg/kg, see Table A1b). In a subsequent survey, Loppi et al. (2006) measured Hg concentrations of 10–220 µg/kg

(average value = 100 µg/kg) in lichens grown in proximity to the Asca-Piancastagnaio 3 power plant, and much higher concentrations (0.51–1.96 mg/kg Hg) in lichens from the Abbadia San Salvatore mining site. These values are again comparable with bark Hg concentrations we found at corresponding sites. Even if based on a limited data set, our results suggest that the overall Hg concentrations in barks and lichens exposed to the same environment are of the same order of magnitude.

As described above, lichens have also been used as biomonitors of the environmental impact of geothermal exploitation in the Mt. Amiata area (Bacci et al., 2000; Baldi, 1988; Bargagli et al., 1987; Ferrara et al., 1991; Loppi and Bonini, 2000; Loppi et al., 2006). These studies indicated the existence of anomalous Hg concentrations in the surroundings of geothermal plants, including Asca-Piancastagnaio 3 and Le Strette-Bellavista (Loppi and Nascimbene, 1998). Starting from 2002, all geothermal plants were progressively equipped with AMIS® systems to reduce Hg emissions: the Asca-Piancastagnaio 3 power plant was fitted with AMIS® in 2005 (ARPAT, 2009), whereas the Le Strette-Bellavista plant stopped operation in 2002 before introduction of AMIS. Air quality surveys conducted by the regional environmental Agency (ARPAT-Toscana) indicate significant reduction of Hg emissions from the Asca-Piancastagnaio 3 power plant after the AMIS® installation: from about 30 g/h to 4 g/h (mean value of the period 2005–2008) (ARPAT, 2009).

In agreement with these results, the Hg concentrations of tree barks around the two above mentioned geothermal plants are lower than around the Abbadia San Salvatore mine and other areas of the Mt. Amiata region, including the regional reference sites of Bagni San Filippo and Vivo d'Orcia.

6. Conclusions

Barks of *P. nigra* collected in heavily Hg-polluted areas of the Mt. Amiata mine district display Hg concentrations as high as 8.6 mg/kg, the highest ever reported in literature. In comparison, barks of the same species collected in local reference areas and near geothermal power plants in the same region show much lower concentrations (range 19–803 µg/kg), but these levels are generally higher than values (5–98 µg/kg) observed in a regional reference area near the city of Florence. Barks with the highest mercury concentrations (>500 µg/kg) show a positive correlation between Hg content of their external portion and soils as a consequence of soil dust re-suspension. The Hg concentration in our barks samples is rather variable, in contrast with other studies (e.g., Lippo et al., 1995). Noteworthy, Hg in barks from Mt. Amiata and Florence follows a coherent picture, where Hg levels are highest close to the main Hg sources, and are consistent with lichens from the same area. These features potentially make barks a reliable, well distributed, practical and low-cost candidate for biomonitoring studies.

Moreover, we documented that there is an evident concentration gradient of Hg into tree bark. This evidence, while confirming (in agreement with literature) that the Hg uptake by plants directly from soils is minimal, strongly suggests that the use of barks for biomonitoring surveys requires a specific sampling and analytical protocol in order to produce unbiased results. This protocol should encompass additional (yet poorly known) aspects concerning how Hg concentration may be affected by sample position, exposure to prevailing winds, and tree and bark age.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2016.06.029>.

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