Black pine (*Pinus nigra*) bark as biomonitors of airborne mercury: sampling and analytical suggestions for minimising methodological biases

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1. Introduction

Tree tissues still have a relatively small niche for heavy metals biomonitoring when compared to mosses and, in particular, lichens ([1] and reference therein). Tree barks are, in principle, excellent adsorbents of airborne pollutants, including toxic metals [2-5]. As emphasized by [6], there are contradictory data and opinions concerning the adequacy of barks as reliable bioindicators of atmospheric pollution (cf. [7]). The skepticism of some researchers is based on: a) the need for a deeper knowledge into mechanisms of bark interaction with air pollutants, and b) limited data regarding variability in bark pollutants, which complicates the assessment of the actual environmental pressure on a given area (see [5] and references therein for a comprehensive review). About b), there is obviously a need for a commonly accepted sampling procedure to make the results more comparable and, hopefully, more reliable. The present study aims to outline some factors that may minimize sampling biases in the analysis of mercury (Hg) in barks. In this work, barks of black Pine (*Pinus nigra* J.F. Arnold) trees from the Abbadia San Salvatore area (Mt. Amiata region, Southern Tuscany, Italy) and the underlying soils were sampled in summer 2016. In this area two industrial activities, past Hg mining and ongoing geothermal energy production, affect local atmospheric Hg levels [8-9].

2. Materials and methods

Thirteen sampling sites, 7 within the mining area of Abbadia San Salvatore (shortly, Abbadia), and 6 in local reference areas not directly affected by mining works, were selected (Fig. 1a, b). For each site, we collected one sample of soil and 8 bark specimens from a single tree. Barks were collected at 2 different heights, 70 and 150 cm, and in the four cardinal directions for each height.

For all bark samples, we selected one slice within the first 1.5 cm. To measure the possible effects of Hg leaching by rainwater, 1 g of crushed bark sample was left for 24h in a MilliQ grade water (50 ml), equilibrated with the atmosphere in an ultra-clean lab for 4 hours. Shredded bark from all 104 samples were re-analyzed for total Hg two years after original sampling.

3. Results and discussion

Total Hg concentration in the soils samples ranged between 2 and 480 mg/kg dw. As expected, the highest concentrations generally occur close to the town of Abbadia, where the principal mines and the metallurgical plants were located [9].

Total Hg concentration in barks ranged between 0.1 and 28.8 mg/kg dw. The overall distribution of the Hg concentration in barks from different sites follows that of soils: the highest values are all centered on the town of effect of prevailing wind directions. Almost systematically, the correlation between sample height and cardinal direction is better for samples collected at a height of 150 cm with respect to those collected at 70 cm. In addition, the equations of the linear model for the samples at 150 cm have a small intercept (less or equal to the detection limit), and a slope close to unity. On the other hand, the correlation between Hg in barks and soils is better for the samples at 70cm that for those at 150 cm. This suggests that samples at 70cm could be more influenced by local soil particle resuspension than samples at a higher height. The Hg concentration at 150 cm is indeed unaffected by the prevailing winds (mostly from 280°), at Mt. Amiata.

A selected set of bark samples were subjected to a preliminary leaching test to evaluate the amount of Hg that could be removed by a rainy event. The results of the test show that the amount of Hg leached is negligible (maximum Hg concentration in the leach solution ~ 0.1 µg/L). As a consequence, it can be assumed that bark sampling is not particularly affected by rain. Re-analysis of bark samples after two years of storage indicate an Hg loss ranging from 5 to 20% with respect to the original concentration, suggesting some Hg re-emission from the sampled barks.

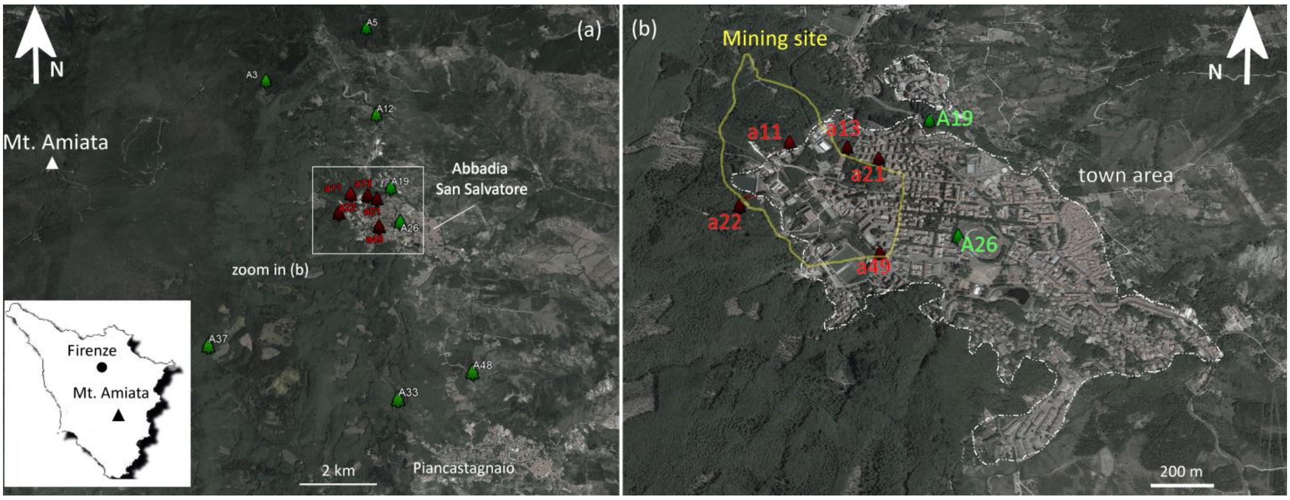

Fig. 1a,b. Satellite image (Google Earth) of the study area with location of sampling points. Symbols: red and green colors refer to sites located inside and outside the mining area, respectively.

4. Conclusions

For *Pinus nigra* species in the Mt. Amiata region, measured concentrations are essentially independent of wind direction. To harmonize results on the employment of tree barks as a biomonitoring substratum, we suggest that a convenient sampling practice for *Pinus nigra* is to collect a 1-2 mm bark slice within the outermost 1.5 cm, at 150 cm from the ground; the occurrence of a rainy event is presumably not critical. Long storage time may affect the Hg content.

5. References

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