Ecological Indicators 14 (2012) 170–177

Contents lists available at ScienceDirect

Ecological Indicators

journal homepage: www.elsevier.com/locate/ecolind

# Atmospheric element deposit on tree barks: The opposite effects of rain and transpiration

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ARTICLE INFO

*Article history:*
Received 16 February 2011
Received in revised form 1 July 2011
Accepted 10 July 2011

*Keywords:*
Bark
Air pollution
Stemflow
Transpiration
SEM-EDX
ICP-MS

ABSTRACT

The elemental composition of the deposit formed on the bark of ash-trees was studied over several months on stems ranging from 3 months to 10 years. For this purpose (1) the total elemental composition of the deposit, (2) the structure and composition of the solid particles and (3) the deposit dry weight per $dm^2$ were studied. Concurrently the part of this superficial deposit washed out by rain during 3.5 months was sampled at each rain event and its elemental composition analyzed. This study shows that the deposit was submitted to an intense turnover, with an average leaching-out flux reaching approximately 27 mg $dm^{-2}$ $month^{-1}$ and a very low increase of the deposit weight per $dm^2$ during the first five years and almost null afterwards. The origin of this superficial deposit was investigated. The main part (78 ± 10%) was organic matter originating from the atmospheric deposition or from the tree. The inorganic content originated partly from the atmosphere, with geogenic and anthropogenic particles, and also from the tree, in which it was demonstrated by scanning electron microscopy – energy dispersive X-ray that a non-negligible part was obtained from bark transpiration, inducing a superficial deposit, mainly of Ca or K in the area surrounding the lenticels. All those results demonstrate that this bark superficial deposit is a complex matrix which must not be considered as a simple cumulative archive but which seems to be the source of interesting information targeting mostly recent atmospheric pollution pressures, when compared to the bulk of suber integrated particles.



## 1. Introduction

The deposition of atmospheric components on tree barks has been supposed for a long time to be representative of the atmospheric content and of its changes over long periods of time (Ballach et al., 2002; Purvis et al., 2007; Schulz et al., 1999). As trees are very common in countries with a temperate climate, they were chosen by numerous scientific teams for several decades to study the nature of atmospheric deposition on their barks, its changes as a function of time and to carry out quantitative measurements of deposition rate (Al-Shayeb et al., 1995; Askoy and Öztürk, 1997; Böhm et al., 1998; El-Hasan et al., 2002; Freitas et al., 1997).

Concurrently, the numerous direct measurements of the elemental composition of atmospheric gazes and particles suspended in the air column (Freitas et al., 2004; Geagea et al., 2008; Salma and Maenhaut, 2006) allowed to understand that the deposits found on tree barks (1) were far more complex than a simple representation of the atmospheric mixture (Catinon et al., 2009a) and (2) were therefore not a true faithful record of the atmospheric composition changes over periods of time corresponding to the tree's age.

However, the numerous interesting results previously obtained on tree bark, especially in typical situations (heavily polluted areas, surroundings of mines or large towns (Ballach et al., 2002; Bellis et al., 2001; Kuang et al., 2007; Palma et al., 2003)) suggested that fruitful information about air contaminations was registered in such deposits but there was yet no way of reading and understanding it, as was the case for hieroglyphs before Champollion's discovery. For a better use, it was consequently necessary to know the numerous events and mechanisms involved in the formation and fate of this superficial deposit. For this purpose, in a first attempt we measured the bark deposit accumulation kinetics from year to year through a comparison of the deposits per $dm^2$ bark area coming from the stem segments corresponding to each year (Catinon et al., 2008). In a second attempt, the deposit on bark was compared to the part integrated inside suber (Catinon et al., 2009b). It showed that solid particles integrated inside the suber tissue

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doi:10.1016/j.ecolind.2011.07.013

were a significant archive corresponding to fairly well-known ages (Catinon et al., 2009b).

The present report is an attempt to show whether the bark superficial deposit was submitted or not to a non-negligible turn over. For this purpose, the two different possible origins of the deposit were considered, either endogenous (through an externalization of xylem sap) or exogenous (corresponding to the atmospheric deposition with two different sources, either geogenic or anthropogenic). It was supposed that the main leaching-out agent was rain. A simple experimental device was consequently conceived to obtain the leachates and study their compositions and amounts. Concurrently, measurements of stem transpiration rates were carried out in atmospheres with a low relative humidity, using potometers. This experiment allowed to estimate whether the amount of minerals deposited by transpiration on the bark surface was negligible or not.

## 2. Materials and methods

### 2.1. Sampling

#### 2.1.1. Site

The experimental site chosen for this study was the botanical garden of the LECA Laboratory in the University Campus (University Joseph Fourier, Saint Martin d'Hères, Isère, France) where numerous *Fraxinus excelsior* aged from 1 to 40 years were available for study. This site stands 800 m away from the A41 highway Grenoble-Chambéry with a 50,000 vehicles/day traffic and 4 km away from the centre of the town at an altitude of 200 m, in the Isère valley, surrounded by mountains reaching as high as 1500 m and even over 2000 m.

#### 2.1.2. Sampling the whole deposit on the bark

The *in situ* bark superficial deposit was sampled as explained in Catinon et al. (2009a).

### 2.2. Sap harvesting in the ash-tree xylem vessels

Thirty 4-year-old ash-tree stem internode segments (between 30 and 50 cm-long) were sampled in order to force water inside the xylem vessels. A pipe was connected to the stem section at one end and to a compressed air supply (3.7 bar) at the other. One hundred milliliters of distilled water were introduced into the pipe before opening the pressured air tap. Water having leached the stem vessels was harvested and then dried in an oven. The dry mass harvested was analyzed by inductively coupled plasma-mass spectrometry (ICP-MS).

### 2.3. Potometers

The basis of short cut stems (with or without leaves) was connected to a graduated glass tube full of water. The loss of water was concurrently measured from the loss of weight and from the decrease of the water content inside the graduated tube.

### 2.4. Harvesting runoff rainwater from the trunk

The device shown in Fig. 1 was conceived in order to collect the rainwater running down the stem surface. Two 10-year-old ash-trees were equipped with such a device at a height of 1.5 m on the trunk with a maximum capacity of water harvesting of 10 L. Concurrently, a 40 cm in diameter pluviometer collected rain at 2.50 m above open ground. The harvest of water was carried out over a period of 3.5 months (February 27 to June 07, 2007) with 15 rain events.

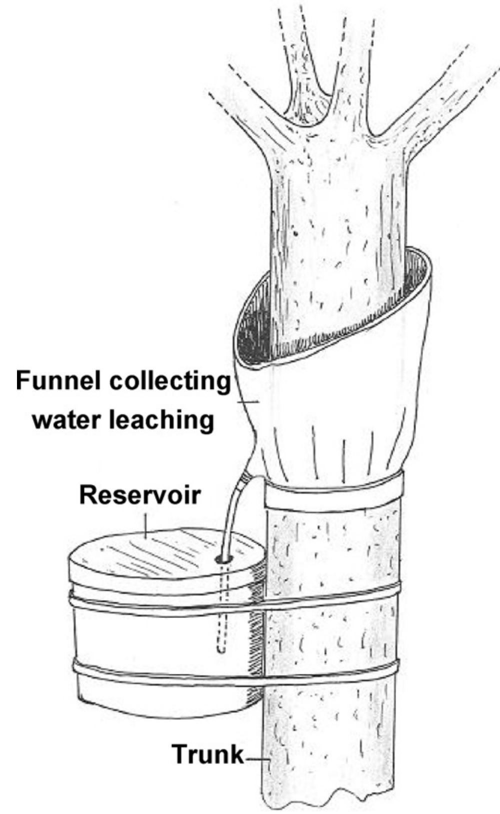


**Fig. 1.** Scheme illustrating the device for leachate collection on tree trunks.

### 2.5. SEM-EDX studies

Sample characterisation was performed using a ZEISS SUPRA 55 VP Scanning Electron Microscope (SEM) (3rd generation of GEMINI field emission column), allowing a spatial resolution down to 1.0 nm, coupled to an energy dispersive X-ray (EDX) microanalysis system (SAHARA Silicon Drift Detector with Spirit Software of PGT) allowing high counting rates.

Samples were studied using electronic imaging (secondary electrons [SE] and back scattered electrons [BSE]), X-ray qualitative analysis and X-ray elemental mapping.

Analytical conditions were as below:

- Accelerating voltage: 15 kV.
- Working distance was about 7 mm (optimal distance for EDX analysis).
- Samples were carbon-coated to reduce charging effects.

### 2.6. Determination of the organic matter content and ICP-MS element analysis

The organic matter content was estimated through the measurement of the dry weight loss after 24 h at 550 °C in a muffle furnace.

For ICP-MS analysis, the total digestion step was conducted in PTFE closed flasks, on a digestion plate (Digiprep, SCP Science) as previously described (Catinon et al., 2008). The elemental content was analyzed by inductively coupled plasma-mass spectrometry ICP-MS (XII CCT series, Thermo Electron), according to the procedure described by Ayrault et al. (2001), modified by the use of a collision cell technique (CCT) to reduce the isobaric interferences of the Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As. The data quality was controlled with reference materials (lichen-336 and sediment-SL1,