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ScienceDirect

Environmental Pollution 148 (2007) 48–61

ENVIRONMENTAL POLLUTION

www.elsevier.com/locate/envpol

The use of tree-rings and foliage as an archive of volcanogenic cation deposition

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Received 1 April 2006; received in revised form 30 October 2006; accepted 3 November 2006

Dendrochemistry does not provide an archive of persistent volcanic activity.

Abstract

Tree cores (*Pinus nigra* ssp. *laricio*) and leaves (*Castanea sativa*) from the flanks of Mount Etna, Sicily were analysed by ICP-MS to investigate whether volcanogenic cations within plant material provide an archive of a volcano's temporal and spatial depositional influence. There is significant compositional variability both within and between trees, but no systematic dendrochemical correlation with periods of effusive, explosive or increased degassing activity. Dendrochemistry does not provide a record of persistent but fluctuating volcanic activity. Foliar levels of bioaccumulated cations correspond to modelled plume transport patterns, and map short-term volcanic fumigation. Around the flanks of the volcano foliar variation is greater for volatile cations (Cs, Cd, Pb) than for lithophilic cations (Ba, Sr), consistent with trace-metal supply from volcanic aerosol during quiescent periods.

Keywords: Mount Etna; Volcanogenic cations; Tree-rings; *Pinus nigra*; *Castanea sativa*

1. Introduction

Volcanic activity can affect vegetation in numerous direct and indirect ways, from local fumigation (Delmelle, 2003) to perturbations of radiation budgets and climate (Briffa et al., 1998; Gu et al., 2003). Understanding the environmental fate of volcanogenic trace elements may allow the development of reliable proxies for volcanic activity. For example, if a diagnostic chemical signature could be found in tree-rings linked to a causal volcanic event, this would be of great value for reconstructing records of past eruptions.

Multi-elemental dendrochemical analysis (investigation of the composition of tree-rings) has been used extensively to study anthropogenic pollution, commonly using laser-ablation or solution inductively-coupled-plasma mass-spectrometry (ICP-MS) on individual or composited tree-rings (e.g., Hall et al., 1990; Hoffmann et al., 1994). Some authors have argued that dendrochemistry is unsuitable as a pollution archive (e.g., Bindler et al., 2004; Garbe-Schönberg et al., 1997; Zhang et al., 1995), while others conclude it has potential (e.g., Eklund, 1995; McClenahan et al., 1989) though perhaps only qualitatively (Bondietti et al., 1989). Dendrochemical methods have successfully recorded changing pollution levels on decadal to centennial timescales, and across large spatial scales (e.g., Padilla and Anderson, 2002; Tommasini et al., 2000; Watmough, 1999).

If dendrochemistry may be used to investigate anthropogenic pollution sources, then the method may reasonably be

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doi:10.1016/j.envpol.2006.11.007

applied to active volcanic areas, since volcanoes emit many of the same trace constituents, such as Cu, Zn, Hg and Pb. Dendrochemical methods have been applied to large individual volcanic eruptions (e.g., Laki, 1783 AD and Tambora, 1815 AD; Padilla and Anderson, 2002; Pearson et al., 2005). While these studies demonstrate the potential of tree-rings to record macroenvironmental volcanic impacts, their potential as local archives of persistent but fluctuating volcanic activity remains uncertain. Here, we evaluate the potential of tree-ring and foliar chemistry to record the temporal and spatial influence around a persistently active volcano (Mount Etna, Sicily) in terms of cation signatures preserved in vegetation on sub-annual (foliage) and annual to supra-annual (tree-rings) timescales. This work, especially the leaf cation measurements, complements similar work on volcanogenic fluorine deposition (Bellomo, 2005).

1.1. Volcanic emissions

Active volcanoes display a spectrum of behaviour, with persistent non-eruptive degassing common at many systems. This is characterised by the emission of gases (including SO_2, HCl and HF), which increase depositional fluxes of anions (e.g., SO_4^{2-}, Cl^- and F^-) to local ecosystems. Other trace elements are also released during both eruptive and non-eruptive degassing, and volcanoes may be the major global natural emission source for some key elements (e.g., As, Cd, Cu, Pb; Mather et al., 2003). Trace cations are generally (with some exceptions, e.g., Hg; Pyle and Mather, 2003) carried in the solid phase (Hinkley, 1991), either predominantly in the silicate ash phase (lithophilic elements) or the non-silicate aerosol phase (volatile elements). Volatile cations may be conveniently categorised by their affinity for certain complexing anions as chalcophilic (sulphide-forming) or halide-forming (see Table 1). During eruptions, activity including explosions, fire-fountaining and ashfall (Fig. 1) may introduce large quantities of fresh material rich in lithophilic cations to the environment; during non-eruptive periods, emissions will be dominated more by volatile cations (e.g., Aiuppa et al., 2003b). Such signals might potentially be recorded in dendrochemical archives.

Volcanic cation emission rates are difficult to quantify, but may be estimated using gaseous SO_2 fluxes, if cation:SO_2 ratios are known (although large variation may occur in these ratios; Mather et al., 2003). Detailed SO_2 flux records such as that for Etna since 1987 (Caltabiano et al., 2004) are the best rough proxies for volcanogenic cation release.

Volcanic plumes aid cloud formation, causing acidic rain and fog (Fig. 1). Rainfall is an important controlling factor in the enhanced deposition of cations scavenged from the plume (Aiuppa et al., 2006; Gauthier and Le Cloarec, 1998).

1.2. Vegetation response to cation deposition

Within a plant, elemental uptake from the environment may occur via the roots, foliage and stem (Lepp, 1975), with subsequent transport through the phloem and into the xylem. Rates of cation absorption and transport, and the degree to which cations move between tree-rings, are determined by element mobility, which varies widely between tree species and over which there is some disagreement (e.g., Bondietti et al., 1989; Prohaska et al., 1998).

Table 1
Categorisation of selected elements found in Etnean lava and aerosol

Element	Category[a, b]	Weight ash fraction[b], %	Mean total Etnean flux[c] (kg day^{-1})	Notes
Na	Halide-forming	67	210 000[d], 35 000[e]	
K	Halide-forming	35	155 000[d], 30 000[e]	
Mg	Lithophile	100		
Sr	Lithophile	100		
Ba	Lithophile	100		
Al	Lithophile	38		Intermediate, also forms sulphates
Zn	Chalcophile	23	4000[d], 440[e]	Intermediate, can act as lithophile
Cu	Chalcophile	6	5600[d], 560[e]	Intermediate, also forms halides
Cd	Chalcophile	3	100[d], 20[e]	
Hg	Chalcophile	3		Probably highly enriched in plume[f]
Pb	Chalcophile	3	900[d], 160[e]	
As	Unclear	2		No clear behaviour

[a] Volatile trace elements are predominantly transported in the non-silicate aerosol as cations and dominate the volcanic output during passive magmatic degassing. They may be categorised by their complexing anions, as chalcophilic (affinity for reduced sulphur) or halide-forming (commonly chlorides or fluorides; e.g., Aiuppa et al. (2003b)). Lithophilic elements have an affinity for the magmatic rather than the gas phase. Cations within each category are expected to have a similar pattern of introduction to the environment.

[b] Aiuppa et al. (2003b); 100% shows entirely associated with ash (lithophilic), 0% entirely volatile.

[c] Gauthier and Le Cloarec (1998).

[d] In eruptive period.

[e] In non-eruptive period.

[f] Pyle and Mather (2003).

The dominant plant-cation uptake route is through the soil (Martin and Coughtrey, 1982), although this may be reduced in nutrient poor, shallow or acidic soil (Cutter and Guyette, 1993). Soil processes are highly important in terms of cation transport and uptake to the plant (Fig. 1, Kapusta et al., 2006). Etnean soils are derived from volcanic ash, and have a high cation exchange capacity and are able to receive large amounts of volcanogenic cations. However, intense soil leaching may cause the release of these cations to groundwater (Guicharnaud and Paton, 2005). Acid deposition (e.g., from volcanic sulphate and chloride) increases soil cation leaching and may decrease levels of exchangeable cations such as Ca and Mg (Delmelle et al., 2003; Tendel and Wolf, 1988). Low pH soil solutions may also increase mobility of elements including Zn, Al and Cd (Bondietti et al., 1989; Smolders, 2001). Solute flow rate and contact time between plant roots and soil solution are other important factors determining cation uptake by plant roots.

Trees in poor soils may favour stem or foliar uptake, and show greater sensitivity to environmental changes (Ragsdale