

## Vegetation damage in the vicinity of an aluminum smelter in Brazil



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### ABSTRACT

A primary aluminum smelter, which is responsible for releasing fluoride and other pollutants to atmosphere, is located at the vicinities of rocky field ecosystem in Brazil. We aimed to evaluate the biological effects of the smelter emissions using *Spondias dulcis* as a bioindicator organism. Evaluations of rainwater quality, atmospheric oxidants and toxicity visual symptomatology were performed in 4 different sites. We also collected leaflets with and without visual toxicity symptoms for anatomical studies under light and scanning electron microscopes, histochemistry, X-ray microanalysis, and fluoride quantification. The fluoride detected on leaves was present in plants at all studied sites, principally at Site 1 (park entrance) and less detected at Site 3 (forest area). However, the fluoride quantity was not the main cause of damage, but the large amount of oxidants which was detected at the atmosphere. This amount of oxidants was increased with the distance from the emission source. It was noticed two types of visual symptoms on the leaflets: a darkening at the adaxial face and a wide brownish necrosis. The anatomical studies showed three damage patterns: superficial necrosis, reaching just the palisade and spongy parenchyma, deep necrosis, reaching the entire mesophyll and a punctual necrosis perceived only at the central veins. With scanning electron microscopy it was detected a turgor loss and a flattening of the cell's external periclinal wall. In the areas where the damage was more noticeable, there was an erosion of the epicuticular wax that lead to delayering, resulting on the epidermis rupture and internal tissue exposure. *S. dulcis* showed visual symptoms after few days of exposure, which culminated in structural alterations, thus indicating that these pollutants are impacting this important vegetation type from a rocky field ecosystem.

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### 1. Introduction

The primary aluminum is the aluminum produced directly from bauxite ore, which is refined and electrolytically reduced to elemental aluminum (USEPA, 1998). Primary aluminum smelters are the main source of fluoride in atmosphere (Weinstein and Davison, 2004) in form of aluminum fluoride (AlF<sub>3</sub>), calcium fluoride (CaF<sub>2</sub>), tetrafluoromethane (CF<sub>4</sub>) and hexafluoroethane (C<sub>2</sub>F<sub>6</sub>) (USEPA, 1998). Fluoride levels can vary according to industrial activities, topography of the area and atmospheric processes. The fluoride concentration is low in the urban atmosphere but it can increase remarkable around emissions sources (Divan Junior et al., 2008).

Fluoride is regarded as the most phytotoxic pollutant, causing important injuries in susceptible species (Weinstein and Davison, 2004). Some studies report atmospheric contamination in leaf

concentrations above 20 µg g<sup>-1</sup> (Divan Junior et al., 2008). Fluoride is absorbed by plants mainly in leaves. When in gaseous state, it penetrates the tissues especially through stomata, and in minor proportion through cuticle (Miller, 1993). In aqueous solution, fluoride is absorbed through the entire leaf surface (Chaves et al., 2002), and moves via apoplastic way inside the leaf, reaching margins and apex through transpiratory stream, where it is accumulated and causes injuries (Miller, 1993).

Chlorosis is usually the first noticeable leaf symptom in response to fluoride, and an increase in the concentration and the exposure time to this element are primarily responsible to the appearance of apical and marginal necrosis (Arndt et al., 1995; Fornasiero, 2001; Divan Junior et al., 2007).

Minas Gerais state is among the largest aluminum producers in Brazil, producing more than 135,000 t of primary aluminum a year (ABAL, 2011). According to the World Health Organization, fluoride levels in atmosphere should be less than 1 µg m<sup>-3</sup> to prevent effects in plants, livestock and also to protect human health (WHO, 2000), yet there has been reports of visual symptoms in extremely

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sensitive plants with fluoride concentrations near  $0.3 \mu\text{g m}^{-3}$  (Cape et al., 2003).

Studies conducted in this area in Brazil showed that fluoride has been causing damages to the nearby vegetation. In a passive biomonitoring study with the purpose of evaluating the fluoride dispersion pattern in atmosphere, Divan Junior et al. (2008) found in all studied species that fluoride accumulation decreased exponentially as the distance from the emission source increased, reaching values, for example, above  $1500 \mu\text{g g}^{-1}$  near to emission source and below  $2.5 \mu\text{g g}^{-1}$  away from the source with the species *Bidens pilosa*. To evaluate the feasibility of consumption of cultivated vegetables near this area, Sant'Anna-Santos and Azevedo (2010) found that even after the vegetables being washed, there were high levels of fluoride in their leaves, much above the levels recommended by sanitary agencies that allow concentrations less than  $1 \mu\text{g m}^{-3}$  in atmosphere (WHO, 2000). Visible signs of contamination by fluoride exposure were reported in the vegetation surrounding the smelter in this same area, yet those species belonging to areas of difficult access were not evaluated (Divan Junior et al., 2007). That vegetation constitutes an ecosystem known as “rocky fields”, with many endemic species, since it occurs in places of very particular ecological conditions (Romero and Nakajima, 1999).

One of the key features in plants to be used in biomonitoring studies is the sensitivity of the species to a given pollutant. In studies performed by Silva et al. (2000) and Sant'Anna-Santos and Azevedo (2007) with several tropical tree species exposed to fluoride-enriched acid rain, *Spondias dulcis* showed higher sensitivity comparing to other species, which highlights its bioindicator potential for environmental biomonitoring. An active biomonitoring study was conducted by Sant'Anna-Santos et al. (2014), using this species for the first time as a bioindicator organism nearby in this area. Those authors observed in three days a rapid fluoride accumulation in the plant tissues, resulting in conspicuous leaf necrosis.

*S. dulcis* Parkinson (Anacardiaceae), popularly known as “cajá-mirim”, is a marketable species in Brazil and its fruits are used for making high quality fruit concentrates, juices, popsicles, ice creams, nectars and jams, all with high nutritional and commercial value (Sacramento and Souza, 2009).

Therefore, we used this species in our biomonitoring study, aiming to answer whether the pollution released by the aluminum smelter reaches the altitudinal gradient of the “rocky fields” vegetation found in the nearby areas.

## 2. Materials and methods

### 2.1. Study area

The study was conducted in Ouro Preto, Minas Gerais, Brazil. Where is located the Itacolomi State Park (Parque Estadual do Itacolomi – PEI) ( $43^{\circ}32'30''$ – $43^{\circ}22'30''$  W;  $20^{\circ}22'30''$ – $20^{\circ}30'00''$  S) (Fig. 1). The park extends throughout 7000 ha and its highest point is the “Itacolomi Peak”, reaching 1772 m (Messias et al., 1997). In this area, five basic types of plant formations can be identified: vegetation on quartzitic rocky outcrops (rocky fields – “campo rupestre”), grasslands, marshy fields, capon forests and capon gallery (Peron, 1989). This area presents high levels of endemism, as it occurs in places of very singular ecological conditions (Romero and Nakajima, 1999).

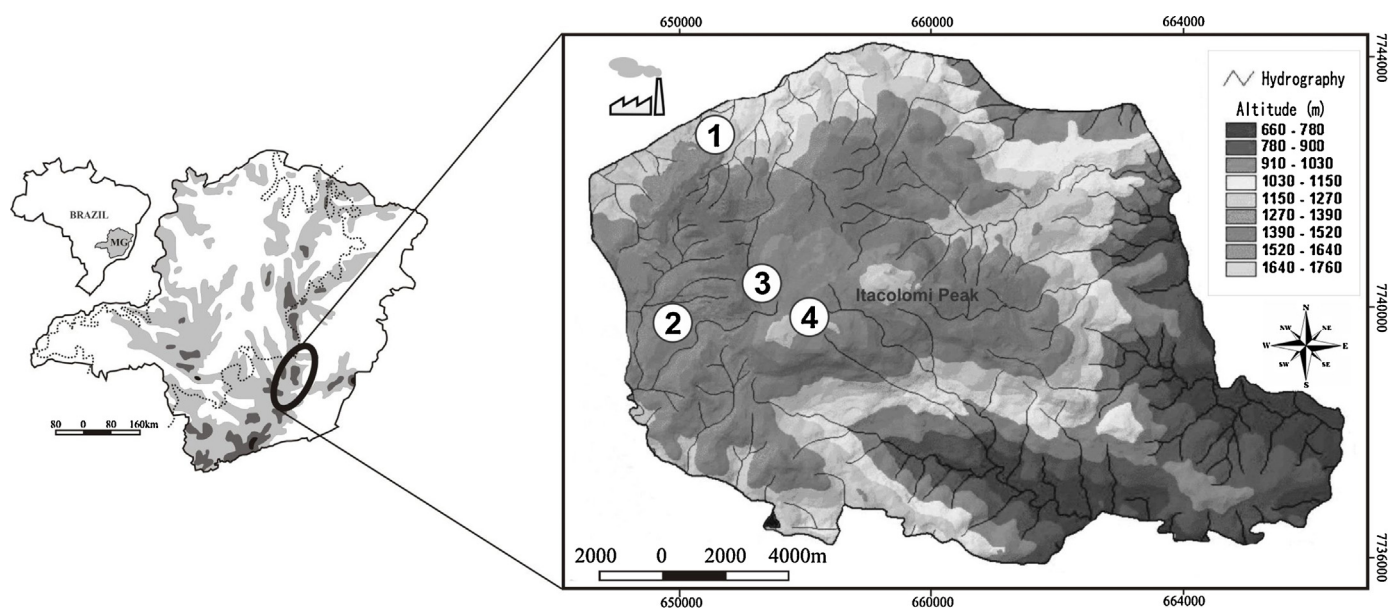
### 2.2. Botanical material

Individuals of *S. dulcis* Parkinson (Anacardiaceae) were obtained through seed propagation from a single adult individual located at Sítio Palmital, Viçosa city, Minas Gerais state, Brazil. Voucher specimens were deposited at the VIC herbarium of Universidade Federal de Viçosa under number 19840.

Plantlets with approximately 3 nodes (6 leaves) were transferred to 1 L plastic pots containing the commercial substrate Plantmax®. After one week of transplantation, 250 mL of Hoagland solution  $\frac{1}{4}$  ionic strength (Hoagland and Arnon, 1950) was added to the plants on a five-day basis, until they reached 40 cm height and had ca. 8 nodes per plant (16 leaves). The seedlings were cultivated in a greenhouse located in “Unidade de Crescimento de Plantas” at Universidade Federal de Viçosa (UFV).

### 2.3. Plant exposure

The experiments consisted in the active exposure of acclimated *S. dulcis* individuals in four sites at PEI, all distant from the emission



**Fig. 1.** Location of Itacolomi State Park (PEI) and the sites where individuals of *Spondias dulcis* were exposed. Sites 1, 2, 3 and 4; including outside the park, the emission source.

Modified from Coser et al. (2010).

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