Science of the Total Environment 550 (2016) 861–870

Contents lists available at ScienceDirect

Science of the Total Environment

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

Assessing redox potential of a native tree from the Brazilian Atlantic Rainforest: a successful evaluation of oxidative stress associated to a new power generation source of an oil refinery

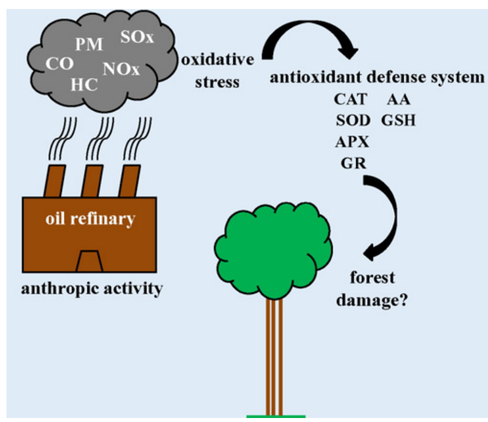
Marisia Pannia Esposito *, Andrea Nunes Vaz Pedroso, Marisa Domingos

Instituto de Botânica, Núcleo de Pesquisa em Ecologia, PO Box 68041, 04045-972 São Paulo, SP, Brazil

HIGHLIGHTS

- The exchange of power generation system would reduce oxidative stress to vegetation.
- *Tibouchina pulchra* would be a promising biosensor plant by changing its redox ability.
- The antioxidant level during the experimental period varied in response to pollutants.
- The gain in environmental quality was not achieved.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 9 November 2015
Received in revised form 28 January 2016
Accepted 28 January 2016
Available online 4 February 2016

Editor: D. Barcelo

Keywords:
Air pollution
Air temperature
Antioxidants
Ascorbate–glutathione cycle
Oil refinery
Redox potential

ABSTRACT

The antioxidant responses in saplings of *Tibouchina pulchra* (a native tree from the Brazilian Atlantic Rainforest) exposed around an oil refinery in the city of Cubatão (SE Brazil), varied during the exchange of its power generation source, from boilers fueled with oil to a thermoelectric fueled with natural gas. The redox potential changed in response to an interaction of air pollution and meteorological parameters, indicating that the pro-oxidant/antioxidant balance was not reached after the exchange of the power generation system. The gain in environmental quality in the region was not achieved as expected due the technological modernization, at least relative to oxidative stressors. These conclusions were based on results of analyses of enzymatic antioxidants: superoxide dismutase (SOD), ascorbate peroxidase (APX), catalase (CAT), glutathione reductase (GR); non-enzymatic antioxidants: reduced, oxidized and total ascorbic acid (AsA, DHA, totAA) and glutathione (GSH, GSSG, totG), their redox state (AsA/totAA and GSH/totG) and an indicator of lipid peroxidation (MDA). We also applied exploratory multivariate statistics in order to verify if the temporal sequence of changes in the plant redox capacity coincided with changes in the profile of air pollution, climatic conditions or with their interactions and if the environmental benefits that would supposedly be promoted by the mentioned exchange of power generation system were achieved in the region.

* Corresponding author.
E-mail address: biompe@yahoo.com.br (M.P. Esposito).

http://dx.doi.org/10.1016/j.scitotenv.2016.01.196
0048-9697/

1. Introduction

Oil refineries are relevant sources of atmospheric emissions, mostly including sulfur compounds (such as sulfur dioxide and hydrogen sulfide), nitrogen oxides, carbon monoxide, organic compounds and particles containing nickel and other heavy metals. Ozone (O_3) formation is other probable consequence due to reactions of hydrocarbons with OH radicals emitted by refinery plants, such as volatile organic compounds (VOCs), in the presence of nitrogen oxides and sunlight (Jenkin and Clemitshaw, 2000; Abdul-Wahab et al., 2002; Lin et al., 2004; Agudelo-Castaneda et al., 2014; Shi et al., 2015, Lyu et al., 2016).

The energy production for supporting the oil refining processes, based on fossil fuel combustion (oil, coal or natural gas), is an additional source of the air pollution emissions associated to refineries. The cleanest energy generally comes from the combustion of natural gas. However, sulfur dioxide (SO_2) and nitrogen oxides (NO_x) emissions from the combustion of all fossil fuels depend on a number of factors, including combustion conditions and emission control procedures (Grauss and Worrel, 2007).

An oil refinery belonged to a large industrial complex in the city of Cubatão (SE-Brazil), in particular, still emits considerable amounts of carbon monoxide (CO), hydrocarbons (HC), NO_x, SO_2 and particulate matter (PM) due to the petroleum refining process itself and the production of power and steam process by burning fuel oil in boilers (CETESB, 2012). Such old system for power generation was substituted by a thermoelectric plant (UTE) fueled by natural gas in 2010, aiming at reducing the environmental problems caused by air pollution. The Atlantic Rainforest that covers the steep slopes of the mountain range found in the region would be one of the beneficiaries of this technological modernization (Domingos et al., 2003).

These gaseous and particulate pollutants may intensify the oxidative stress in plants as a consequence of enhanced formation of reactive oxygen species (ROS). The lifetime of ROS in plants is largely determined by a complex antioxidant network in cells, composed of enzymes (e.g. catalase, ascorbate peroxidase, glutathione reductase, superoxide dismutase) and low molecular weight antioxidants (e.g. ascorbate and glutathione) (Halliwell and Gutteridge, 2007; De Gara et al., 2010; Munné-Bosch et al., 2013; Foyer and Noctor, 2013). The equilibrium between the ROS production and scavenging processes may be disturbed by various biotic and abiotic stress factors, including climatic oscillations and air pollutants (Gill and Tuteja, 2010). Therefore, the reduction/oxidation (redox) metabolism and associated signals of oxidative disturbances at cell level, such as lipid peroxidation, are key indicators plant tolerance against environmental oxidative stressors (Munné-Bosch et al., 2013).

A number of studies revealed that *Tibouchina pulchra* (Cham.) Cogn. (Melastomataceae), a native tree species from this forest, is an adequate biosensor tree species (Falla et al., 2000; De Temmermam et al., 2004) of environmental oxidative stressors, by showing biochemical and physiological alterations (Klumpp et al., 2000; Moraes et al., 2003; Moraes et al., 2004; Furlan et al., 2004; Furlan et al., 2008; Silva and Moraes, 2013; Esposito and Domingos, 2014). Based on these findings, we assumed that *T. pulchra* would be a promising biosensor species to check the hypothesis that the mentioned exchange of the power generation and steam system would reduce the stress posed by oxidative air pollutants to the Atlantic Rainforest around the oil refinery, by following changes in its redox potential.

So, the aim of this study was to verify if the expected environmental benefits were achieved in the region, by evaluating together the changes in air quality, redox potential and oxidative damage in this native biosensor species. Both hypothesis and aim were checked by determining the spatial and temporal changes in the redox potential of *T. pulchra* saplings exposed around the oil refinery, prior, during and after the UTE installation and establishing if the temporal sequence of changes in the redox potential coincided with changes in the profile of air pollution, climatic conditions or with their interactions.

2. Materials and methods

2.1. Description of the study area and plant exposure

The field experiments were conducted in the city of Cubatão, which is located in the Atlantic coast in São Paulo state, southeastern Brazil (23°45′–23°55′S, 46°15′–46°30′W), at the base of a mountain range named as Serra do Mar and covered by the Atlantic Rainforest. Cubatão is approximately 16 km far from the city of Santos, which has an important port that facilitates the trade of industrial products. The most significant development of the industrial pole in Cubatão occurred from 1950 to 1970 and is currently composed of more than 20 industrial sources, including petrochemical, steel and chemical companies. The regional climate is Af (tropical, without dry season), following the Koeppen's classification (Alvares et al., 2013). The opposing wind circulation during the day (from S/SW to NE) and night (from NE to SW) promotes a mixture of air pollutants, so that both the Atlantic Rainforest and the human population in the urban areas are affected. The field exposure experiments with potted saplings of *T. pulchra* were performed in: 1) two sites situated near the refinery and located along an old road that linked formerly the cities of São Paulo and Santos, whose course follows the slopes of Serra do Mar. mountains: *Atlantic Forest 1 and 2* (AF1 and AF2); 2) one site located in the center of Cubatão, named *downtown* (DA), where a continuous monitoring station of air quality and meteorological conditions has been operated by the Environmental Company of São Paulo State (CETESB) and is under the influence of pollutants from refinery and vehicular emissions; 3) a reference site relative to the distance from the emissions of the refinery, located in the Pilões river valley (VP). The study area and biomonitoring sites are described in more details in Nakazato et al. (2015).

The *T. pulchra* saplings for all experiments were acquired from the same nursery and were similar in age and development stage. On average, they were 20 cm high and contained at least six leaves on the main stem. Before each experiment, the saplings were transplanted into 3-liter pots containing a mixture of standardized substrate that consisted predominantly of pine bark and fine vermiculite in a ratio of 3:1. The saplings were fertilized weekly with 100 mL of Hoagland solution and maintained for one month inside a greenhouse under filtered air and ideal meteorological conditions for plant growth (temperature = 20 °C, relative humidity = 80% and photosynthetic active radiation = 443 $\mu mol\ m^{-2}\ s^{-1}$ on average).

The apparatus for *T. pulchra* exposure in the field followed the model proposed by Arndt and Schweizer (1991). In each site, the potted plants were kept on boxes containing water and covered by galvanized wire grids. This apparatus was covered by a shadow screen (50% brightness reduction). Strings inserted into the base of the pots remained immersed in the water stored in the boxes to ensure a suitable water supply to the plants.

A total of 11 field experiments of 90 days each were conducted in all sites, covering a period of 33 months. This experimental design coincided with the exchange schedule of power generation and steam source to the refinery, from oil burning in boilers to natural gas-powered thermoelectric (UTE). It consisted of three distinct phases: 1) Four exposure experiments were held throughout the *Pre-UTE phase*, covering the period from April 2009 to March/2010 (*1st exposure*: April–June/2009; *2nd exposure*: July–September/2009, *3rd exposure*: October–December/2009, *4th exposure*: January–March/2010). During this first phase, the energy was generated by two high-pressure boilers (moved with an equal mixture of oil and natural gas) and two medium-pressure boilers (moved only with oil), prevailing the emission of pollutants from the oil combustion; 2) The 5th to 8th field experiments were performed during *Transition phase*, covering the period from April/2010 to March/2011 (*5th exposure*: April–June/2010, *6th exposure*: July–September/2010, *7th exposure*: October–December/2010 and *8th exposure*: January–March/2011). The UTE came into operation during this phase, in association with one medium pressure boiler and other high pressure boiler,