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Will the shift from crude oil to natural gas burning for power generation at an oil refinery increase ozone concentrations in the region of Cubatão (SE-Brazil)?

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A B S T R A C T

The ozone (O_3) hypersensitive species *Nicotiana tabacum* Bel W3 was used to assess the impact on O_3 contamination profile by a natural gas-powered thermoelectric plant (TP) that provides power to an oil refinery at Cubatão (SE-Brazil). An increase in O_3 levels would represent an even more harmful effect to the Atlantic Rainforest present in the region. The biomonitoring study was performed along TP pre-operation, transition and TP post-operation phases. Tobacco plants were biweekly exposed at urban, industrial and forest areas at different altitudes. O_3-induced leaf injuries were evaluated at the end of each exposure. *N. tabacum* plants at forest sites at mountain slope were usually more affected by O_3, especially at higher layers. As TP started operating, nitrogen dioxide (O_3 precursor) mean concentrations increased considerably (6 ppb to 16 ppb). The contamination of the Atlantic Rainforest by high levels of N created a favourable scenario for an increase in O_3 concentrations. In fact, F200, F300 and F350 sites (forest sites at 200, 300 and 350 m.a.s.l.) had plants showing a significant increase in O_3-induced leaf injuries. Phytotoxic levels were similar to those found at F700 site (forest site at 700 m.a.s.l.), which were high for the whole study period. The new O_3 contamination profile persisted for F200 and F300 sites during TP post-operation phase. Although slightly lower levels than those seen on transition phase, the intensity of O_3-injuries remained higher compared to the original conditions. The use of *Nicotiana tabacum* Bel W3 allowed to see the negative impact on the air quality after TP started operating, contributing to an increase in O_3 concentrations and phytotoxic levels at forest sites at mountain slope. Plant community were then exposed to an even higher harmful effect compared to the first phase. The stability and fitness of the Atlantic Rainforest influenced by the pollution coming from Cubatão are still under potential risk. However, how the vegetation will behave at this new scenario is unknown and requires time.

1. Introduction

Tropospheric ozone (O_3) is a pollutant with great phytotoxicity whose background concentrations increase continuously all over the world (Royal Society, 2008). O_3 formation in the atmosphere occurs by photochemical reactions involving various O_3-precursors such as methane (CH_4), carbon monoxide (CO), nitrogen oxides (NO_x), and volatile organic compounds (VOCs).

The O_3 enters the leaf through stomatal pores during gas exchanges and reacts on the apoplast generating reactive oxygen species (ROS) that will be counterattacked by the antioxidant defense system (Halliwell and Gutteridge, 2007). When oxidative stress overcomes the capacity of this system, O_3 induces damages at different levels of organization, such as biochemistry (e.g. interference on photosynthesis and respiration processes), cellular (e.g. disruption of cell walls), leaf (e.g. foliar symptoms and leaf senescence) and individual levels (e.g. reduction of plant growth and fitness) (Ashmore, 2005; Fiscus et al., 2005; Gimeno et al., 2004; Guidi et al., 2000; Heath et al., 2009; Krupa et al., 2001). Once the response of the species is heterogeneous, changes in the composition and structure of plant communities and ecosystems may occur (Ainsworth et al., 2012).

Plant responses to O_3-induced stress can be used in air quality biomonitoring to define areas with phytotoxic concentrations, to detect levels of chronic pollution and to assess any potential risks to local species and vegetation (Krupa et al., 2001). The use of indicator species in developing countries is a useful tool for obtaining information on air quality in regions without physical-chemical monitoring networks, which extent is limited due to the high cost of monitors. In addition, the response generated by indicator organisms is a result of the interaction between environmental conditions and biological characteristics of

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each species. Therefore, this approach provides a more valuable information than the simple recording of pollutant concentration in the air only (Pina and Moraes, 2007). According to Manning (2003), this environmental tool gives a biological significance to mechanical monitoring, highlighting the level of the stress that plants and vegetation have been exposed to (Smith et al., 2003).

In a biomonitoring study, sensitive species to the pollutant of interest to be monitored are used. De Temmerman et al. (2004) classify sensitive species as those presenting visible foliar symptoms when exposed to a pollutant. According to Schaub and Calatayud (2013), these are the only specific indicator response of the O_3-induced effects easily detectable in plant species. Unlike expensive and time-consuming laboratory tests, visible foliar symptoms can be assessed in the field and require only training in their identification and quantification. Hence, they are adopted in monitoring programs of O_3-induced risk to forest using standardized O_3 indicator species. *Nicotiana tabacum* Bel W3 is the most widespread species used for ozone biomonitoring studies (Heggestad, 1991; Klumpp et al., 1994; Klumpp et al., 2006; Saitanis, 2003; Saitanis et al., 2004; Sant'Anna et al., 2008; Souza et al., 2009).

In the city of Cubatão, Brazil, there is an industrial complex consisting of 23 large industries including chemical, petrochemical and fertilizer plants, a steel mill and an oil refinery, totaling 260 sources of emission. The city is situated in an area with unfavorable conditions for pollutants dispersion, which are carried by winds towards a mountain range called Serra do Mar that surrounds the city to the north, south and west. (CETESB, 2015). These mountains are covered by the Atlantic Tropical Rainforest. This forest, which originally extended over 3300 km along the Brazilian coast, is now very fragmented, with only 8% of its initial area remaining. The largest fragments are concentrated in southeastern Brazil. The forest holds a great variety of species and a high level of endemism (more than 8000 plant species), being considered a hotspot for the conservation of biodiversity (Brooks et al., 2006).

Several studies have been carried out in the region attesting the harmful effect from Cubatão pollution to the vegetation of the Atlantic forest (Domingos et al., 1998; Esposito et al., 2016; Furlan et al., 2004; Klumpp et al., 1994; Nakazato et al., 2015; Silva et al., 2013; Szabo et al., 2003). Governmental actions to reduce emissions were implemented at the end of the last century (Alonso and Godinho, 1992), but sulphur dioxide (SO_2), nitrogen oxides (NO_x) and particulate matter (PM) concentrations were still high (CETESB, 2009). Most of them are coming from a large oil refinery due to the burning of crude oil in boilers for power generation. Aiming a reduction in all these pollutants emissions (PETROBRAS, 2009), the refinery has compromised to switch its power generation system to a natural gas-powered thermoelectric plant (TP), a less pollutant fuel (Villela and Silveira, 2007).

In a methane-free basis, volatile organic compounds (VOCs) such as ethane, propane and *n*-butane usually account for more than 90% of the natural gas composition (Na et al., 2004; NETL, 2013). These compounds can react with hydroxyl (OH) radicals, naturally present in the atmosphere, and yield different types of peroxy (RO_2) radicals that oxidizes nitrogen monoxide (NO) to nitrogen dioxide (NO_2). This prevents O_3 consumption by NO and provides more NO_2 for O_3 formation reactions (Jacob, 2000). Therefore, there was a concern that the new power generation system could increase VOCs concentration in the region and, thus, may leading to an increase in O_3 levels (PETROBRAS, 2009).

Considering the importance of the conservation of the Atlantic forest and the possibility of O_3 to become an even higher threat to the vegetation, a biomonitoring study was planned in the region of Cubatão aiming to assess if the new power generation system altered the O_3 contamination and phytotoxicity profiles in the region of your surroundings, especially on the slopes covered by the Atlantic Forest. Thus, the O_3 indicator plant species *Nicotiana tabacum* Bel-W3 was used for a previous characterization of each sampling site in respect to their O_3 contamination and phytotoxicity levels, following till after complete shift in the power generation system of the oil refinery.

2. Materials and methods

2.1. Study area and biomonitoring sites

The city of Cubatão is located in the State of São Paulo, SE-Brazil, between 23°45′–23°55′S and 46°21′–46°30′W in a narrow coastal plain surrounded by Serra do Mar, a complex mountain range with pronounced slope all covered by the Atlantic Tropical Rainforest. The climate is tropical super-humid, with high relative humidity and elevated annual rainfall (2600 mm) and the mean annual temperature is 23 °C (Moraes et al., 2002). The oil refinery is situated at 23°52′09″ S and 46°26′09″ W, 19 m above sea level. It has been responsible for, approximately, 40%, 45% and 20% of the total SO_2, NO_x and PM emissions from the industrial complex of Cubatão, respectively (CETESB, 2009). A heavy traffic of vehicles also contributes to local air pollution. Due to the impacts caused by pollution to the vegetation surrounding the industrial complex, this region was intensely studied previously. These studies have shown that relief characteristics and the air mass circulation make some sites more affected by the pollutants than others (Domingos et al., 1998; Furlan et al., 2004; Klumpp et al., 1994; Moraes et al., 2002; Szabo et al., 2003). In addition, they have shown that O_3 concentrations in the mountains increase with altitude. Also, some parts of the mountain are more exposed to the winds that carry the pollutants than others due to the relief features. Based on this, we defined nine study sites with different characteristics (Table 1). Six sites are located at different altitudes along a no longer in use highway that comes down the mountain in locations highly exposed to the winds that pass through the refinery. The other three sites are at the lowland: one in the industrial area; another in the urban area, next to the air quality monitoring station; and the last one in a forest area sheltered from the winds that pass through the industrial complex.

The vegetation of the Atlantic Forest around the six sites in the mountains slope was intensively damaged years ago presenting reduced biodiversity. On the other hand, the physiognomy of the vegetation located in a sheltered area is undamaged, and the trees are more developed with respect to height and diameter of the trunks (Klumpp et al., 1997).

2.2. Monitoring of environmental variables and pollutant concentrations

The data of weather conditions were obtained from a meteorological station located in downtown. Punctual measurements of temperature and relative humidity were also collected in each site, which made possible to observe spatial differences among the biomonitoring sites but not a characterization of the whole study area. Pollutants were continuously monitored by a station of the environmental agency of São Paulo State (CETESB) located in Cubatão. Hourly NO and SO_2 concentrations were used to calculate the daily (24 h) average and

Table 1
Characteristics of the biomonitoring sites situated in Cubatão, Brazil. (single column fitting image).

Site*	Site characteristics	Distance from refinery (m)	Main pollutant source
F100	Forest site	806	Oil refinery
F200	Forest site	1356	Oil refinery
F300	Forest site	1777	Oil refinery
F350	Forest site	2030	Oil refinery
F400	Forest site	1841	Oil refinery
F700	Forest site	2787	Oil refinery
I15	Industrial site	1805	vehicular traffic
U10	Urban site	2102	vehicular traffic
F40	Forest site	6894	vehicular traffic

* letters indicate the site characteristic: F – Forest, I – Industrial, U – Urban; numbers indicate the site altitude (m.a.s.l.).