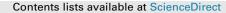
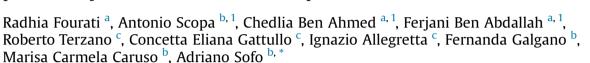
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Leaf biochemical responses and fruit oil quality parameters in olive plants subjected to airborne metal pollution



^a Faculty of Sciences, University of Sfax, Road of Soukra km 4 – BP n° 802, 3038 Sfax, Tunisia

b School of Agricultural, Forestry, Food and Environmental Sciences, University of Basilicata, Viale dell'Ateneo Lucano, 10, 85100 Potenza, Italy

^c Department of Soil, Plant and Food Sciences, University of Bari, Via Amendola 165/A, 70126, Bari, Italy

Department of son, Plant and Pood Sciences, Oniversity of Bari, via Amenaola 165/A, 70126,

HIGHLIGHTS

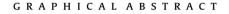
- Olive trees and fruits exposed to airborne metal pollution were studied for two years.
- High levels of Cd, Cu, Fe, Mn, Ni and Pb were found on the fruits but not in the oil.
- A depression of the antioxidant system and changes in hormone levels occurred.
- Atmospheric metals negatively affected olive oil chemical and sensory quality.
- Airborne metal pollution could indirectly have negative effects on oil consumers.

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ABSTRACT

This study was carried out in two olive orchards (*Olea europaea* L, cv. Chemlali) located in a polluted area near a fertilizers factory and in a control unpolluted site, managed with similar cultivation techniques. The aim was to investigate the physiological and biochemical responses of polluted plants (PP), exposed to atmospheric metal contamination (Cd, Cu, Fe, Mn, Ni and Pb) as compared to control plants (CP). Leaves, roots and fruits of PP showed a depression of their non-enzymatic and enzymatic antioxidant defences and a disruption of their hormonal homeostasis. The anomalous physiological status of PP was also demonstrated by the lower values of pigments in leaves and fruits, as compared to CP. Atmospheric metals negatively affected olive oil chemical and sensory quality. However, despite metal deposition on fruit surfaces, the accumulation of potentially toxic metals in olive oil was negligible. Considering that olive oil is an important food product worldwide and that many productive olive orchards are exposed to several sources of pollution, this work could contribute to clarify the effects of atmospheric metal pollution on olive oil quality and its potential toxicity for humans.

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1. Introduction

- * Corresponding author.
- E-mail address: adriano.sofo@unibas.it (A. Sofo).
- ¹ The second, third and fourth authors have contributed equally into the work.

http://dx.doi.org/10.1016/j.chemosphere.2016.11.041 0045-6535/© 2016 Elsevier Ltd. All rights reserved. Environmental abiotic stresses, such as extreme temperature, salinity, drought, flooding, metal exposure and air pollutants,



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greatly affect plant metabolism and productivity. The plant surfaces are a major sink for aerosol and airborne particles, which may negatively influence vegetation health (Pariyar et al., 2013; Yan et al., 2014). Airborne particles are important metal carriers, especially in polluted areas such as in urbanized and industrialized regions. Particularly, fertilizers production is one the major sources of anthropogenic atmospheric particles and metal pollution (Wang et al., 2011).

Nowadays, in Tunisia, due to the intensive increase of the industrial productions, the olive cultivation, which is one of the main agricultural activities in the country, is facing the combined effects of arid climate and air pollution. In Sfax city, the main industrial area in Tunisia, it has been recently observed that the landscape around the factory called 'Société Industrielle d'Acide Phosphorique et d'Engrais' (SIAPE) ('Industrial Society of Phosphoric Acid and Fertilizers') is characterized by the progressive degradation of surrounding vegetation. Metals (particularly Cd, Cu, Fe, Mn, Ni, Pb and Zn) are among the most phytotoxic air pollutants emitted from this industry (Ben Abdallah and Boukhris, 1990; Azri et al., 2002; Mezghani et al., 2005).

Regarding their relation with plants, metals can be classified into two categories: essential metals, which are necessary in many physiological processes and whose deficiency or excess may cause harmful effects in plant cells (e.g., Cu, Fe, Mn, Ni), and non-essential metals, which can be toxic even at relatively low concentrations (e.g., Cd, Pb) (Appenroth, 2010; Krzeslowska, 2011). Usually, metals are loosely bound to the surface of dust particles, thus they might be highly mobile and potentially bioavailable (Marx et al., 2008). Their residence time in the atmosphere varies according to the size of metal-bearing particles. Coarse particles settle rapidly and near the pollution source, whereas fine particles settle very slowly and are usually dispersed to higher distances by the wind (Candeias et al., 2014). Thus, deposition is a significant pathway for the transfer of metals from the atmosphere to plants and soils. Metals can be absorbed by plants via root uptake and/or via direct foliar contact, and exert detrimental effects on plant physiology.

A great deal of research has been performed to evaluate the effects of metal pollution on plant productivity and/or to determine metal accumulation in the different plant parts. However, few works have focussed on the changes in plant biochemical traits induced by plant exposure to metals. Moreover, the effects of metal pollution on plants have been mainly studied in annual or forest species, while information on the response of tree crops is scarce. Indeed, to our knowledge, no study has addressed the effect of airborne metal pollution on both plant biochemical responses and oil quality of olive trees. Olive tree (Olea europaea L.) is one of the most important commercially valuable crops in Tunisia, particularly in Sfax region, not only for its socio-economic importance, but also for the benefits of olive fruits in limiting several cardiovascular diseases, certain types of cancers and artherosclerosis (Romero et al., 2002; Somova et al., 2003). Recently, it has been shown that olive leaves possess interesting antimicrobial and antioxidant activities and can be used as a natural and functional ingredient in food technology (Lee and Lee, 2010; Taamalli et al., 2012). Moreover, local populations used decoction of olive leaves in folk medicine for its beneficial effects against several diseases, as described by Japon-Lujan and Luque De Castro (2007). For this reason, the consumption of olive oil and table olives has steadily increased in recent years, even in countries that do not have a tradition (International Olive Council, 2015). To the best of our knowledge, most papers dealing with responses of olive trees grown around industrial activity have focused only on gaseous pollution and its effects on some morphological and biochemical effects on leaves (Mezghani et al., 2005; Nanos and Ilias, 2007; Dilek et al., 2011).

In this study, the biochemical responses of olive plants exposed to atmospheric metal pollution in an area near a fertilizer factory have been investigated. The results were compared with those of olive trees growing in a relatively clean area, not directly exposed to metal pollution. For this purpose, the following determinations were carried out: (a) accumulation of metals on olive fruits and into the oils extracted from the same fruits; (b) levels of plant growth regulators, pigments, and enzymatic and non-enzymatic antioxidants in olive organs exposed to metal-bearing aerosol; and (c) chemical and sensory quality indices of the extracted oils.

2. Materials and methods

2.1. Plant material, experimental design and oil extraction

The region of Sfax is located in the south east of Tunisia on the Mediterranean Sea ($34^{\circ}43'N$; $10^{\circ}46'E$, area of 7086 km²). It is characterized by an arid Mediterranean climate largely influenced by its mild and gentle topography, and its maritime exposure. The region is well ventilated with low to moderate wind velocities rarely exceeding 5 m s⁻¹ (Bahloul et al., 2015). Over a 52 year-period, the average total year rainfall is 210 mm, the average minimum air temperature of the coldest month (January) is 6.5 °C and the average maximum air temperature of the hottest month (August) is 31 °C, with a yearly mean of 23 °C. Most of the total annual rainfall is mostly occurring from October to December; the dry period is during June–September (data provided by the Meteorological Station of Sfax city).

The studied polluted region is a low plain along the Mediterranean sea-side lined up with series of 100-m-high hills and situated about 20 km along the coast. It is submitted both to continental dry winds and to highly humid sea coastal winds. The prevailing winds from the southeastern sector have a frequency of 25.5%, and those of the southwestern sector appear with a frequency of about 16.3%. However, northwest and north-east winds occur with intermediate frequencies. The studied olive trees (*Olea europaea* L, cv. Chemlali) were located in a land plot located at 0.7 km from the "Société Industrielle d'Acide Phosphorique et d'Engrais" (SIAPE) factory, close to Sfax city. They consist of 35-yearold trees planted on a loamy sand soil and are referred to as polluted plants (PP).

The SIAPE is the main pollution source in Sfax city. It is a phosphate fertilizer producing factory, located in the southern suburb of Sfax, that converts crude phosphate with a high fluoroapatite [Ca₅(PO₄)₃F] content into a granule phosphate fertilizer easily assimilated by plants. During the phosphate attack by sulphuric and phosphoric acids, metals (particularly Cd, Cu, Fe, Mn, Ni, Pb and Zn) are released from the industry chimney in the form of inorganic particulate (dust emission at source = 160 kg h^{-1}). The factory emissions of metal in the particulate were found at concentrations of 2.0 (Cd), 3.2 (Cu), 7.4 (Fe), 2.4 (Mn), 3.1 (Ni), 0.3 (Pb), and 9.4 (Zn) g t^{-1} of raw material (Ben Abdallah and Boukhris, 1990; Azri et al., 2002; Mezghani et al., 2005). Generally, wet deposition dominates during winter (in coincidence with high precipitation). It may occur as washout from smoke below clouds or rainout of particulates taken up by clouds. Whereas, dry deposition would dominate in summer period (in association with low precipitation). Therefore, vegetation developed around the SIAPE Society is continuously exposed to air metal pollution. On the other side, the control plot (with control plants, CP) was located in El Hencha region, 40 km north of SIAPE, in an inland rural area, without any industries, where winds occur with scarce frequencies. In the control plot, the same atmospheric metals examined for PP were found at concentrations below the instrument detection limits.

The olive plants of the two sites (PP and CP) were similar in age,

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