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# Antioxidant capacity in urban soils

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#### HIGHLIGHTS

- The antioxidant capacity is one of many possible indicators of soil quality.
- The antioxidant capacity is related to phenol compounds and microbial functional diversity.

• The antioxidant system is useful indicator of the soil biological status.

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#### ABSTRACT

The quality of soils in 31 urban green areas in Pisa was assessed in terms their soil antioxidant systems by measuring antioxidant capacity (TEAC) and phenol substances, soil basal respiration, community level physiological profile (CLPP), expressed as average well color development (AWCD), community metabolic diversity (CMD), the Shannon–Weaver index (*H*), and soil enzyme activities. The urban results were compared to an extra-urban control area (near the S. Rossore-Migliarino-Massaciuccoli Natural Park).

The soils of the greenspaces of Pisa city were mostly sandy, subalkaline, lightly calcareous, with a rather high (mean of  $3.27 \pm 1.24$  gC 100 g<sup>-1</sup> dry soil) and variable (1.32-7.57 gC 100 g<sup>-1</sup> dry soil) organic matter content.

There were little differences in the functional diversity (AWCD) of soil microbial communities. Dehydrogenase, catalase, alkaline phosphatase,  $\beta$ -glucosidase and lipase showed little variability among soils while arylsulphatase, protease and urease activities varied within a fairly wide range of values. Values of the alkali-and water-soluble TEAC of urban soils varied within quite large ranges (2.53–11.45 mM g<sup>-1</sup> soil and 0.11–2.91 mM g<sup>-1</sup> dry soil, respectively) and were generally higher than those of control. TEAC and phenol substances, both in alkaline and water extracts, were closely correlated (r > 0.850,  $P \le 0.01$ ) and were also positively correlated with soil organic C, AWCD, CMD and, *H*. With the exception of dehydrogenase, the soil antioxidant system showed positive correlations with the enzymatic activities and soil basal respiration. The antioxidant system and soil basal respiration can be considered useful indicators of the soil biological status and soil quality in the examined urban soils.

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1. Introduction

Urban areas alter biogeochemical cycles (Kaye, McCulley, & Burke, 2005; Pouyat, Pataki, et al., 2007), air pollution (Noyes et al., 2009) being main sources of CO<sub>2</sub> and other gases (Seto & Satterthwaite, 2010), water contamination (Choqfi et al., 2004), soil accumulation of nutrients (Cao, Zhu, & Chen, 2007) and trace metals (Wei & Yang, 2010). Besides, urban areas are responsible for both global and local climate change (Heisler & Brazel, 2010), for soil consumption, desertification and sealing (Munafò, Salvati, & Zitti, 2013; Scalenghe & Ajmone Marsan, 2009), for the increasing problems of disposal of growing quantities of solid and liquid waste, for the alteration of areas of geographical and historical value (ISPRA, 2011) and for the ever-increasing consumption of more high quality soil types (Salvati, 2013).

The "Thematic Strategy on the Urban Environment" (Commission of the European Communities, 2006) pointed out the importance of the identification of urban environment quality indicators and their monitoring. One of the main indicators of the status of urban greenspaces is soil quality. Many soil enzymes have been suggested as biochemical indicators of soil quality, because of their essential role in soil biology, ease in measurements and interpretation, and low cost (Gianfreda & Bollag, 1996), as well as their rapid response to changes in soil

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ecosystem and their intimate relations with surroundings due to their high surface to volume ratio (Kaye et al., 2005; Shi, Lu, Xu, & Fu, 2008; Yang, Campbell, Clark, Cameron, & Paterson, 2006).

Recently, soils were shown to contain plant-derived and newly synthesized antioxidants that were hypothesized to considerably influence soil quality through their biological activity, redox reactions and interactions taking place in the rhizosphere (Rimmer & Smith, 2009). Aeschbacher, Graf, Schwarzenbach, and Sander (2012), who quantified the electron donating capacities of humic substances and natural organic matter, reported that these organic molecules contain phenolic compounds which may act as antioxidants. Rimmer and Abbott (2011) measuring the amount of specific lignin-derived compounds in NaOH extracts of soil, concluded that they contributed to a small percentage to the overall antioxidant capacity. Accordingly, Schlichting et al. (2013) observed that many compound classes identified in the soil extracts were correlated with the antioxidant capacity. Cardelli, Marchini, and Saviozzi (2012), in a study concerning organic matter characteristics, biochemical activity and antioxidant capacity in Mediterranean land use systems, observed a close relationship between the amount of alkali-soluble phenols and the soil antioxidant capacity. The authors asserted that antioxidant capacity appeared to influence the rate of organic matter mineralization more than the relative contents of the easily mineralizable C pools. These results seem to justify the role of phenol compounds as one of the controllers of the rate of organic C mineralization.

Large differences were found between the amounts of individual phenol compounds extracted from different soils, which were dependent on the soil type as well as land use and management. This effect is the result of different plant residues with different phenol compositions being incorporated in the different soils (Rimmer & Abbott, 2011).

Antioxidant processes are considered relevant in soil organic matter stabilization, defined as a mechanism that drives to prolonged turnover times (Kögel-Knabner et al., 2008). The organic matter loss by mineralization in urban ecosystems shows contrasting results as slower and faster decomposition rates in urban compared to non-urban soils were reported by Pouyat, McDonnell, and Pickett (1997) and Pavao-Zuckerman and Coleman (2005).

Existing research is related mostly to cultivated soils and, to date, no research has examined the antioxidant activity and/or the content of phenols in urban soils.

The objectives of this study were to assess the impact of urban environment on soil quality based on a survey on soil properties in the Pisa city, and to illustrate if the soil antioxidant capacity can be used as index for fertility and health of urban soils.

#### 2. Materials and methods

#### 2.1. Study area

The Pisa urban environment was in a municipal area of approximately 187 km<sup>2</sup>; the artificial surface (impermeable urban area) was approximately 27 km<sup>2</sup> (almost 15% of the total area). The builtup area has been steadily increasing, with the largest increases since the 50s (+260% increase from 1954 to 2003): in 2005, the built areas were approximately 2.6% of the total area.

#### 2.2. Soil sampling

Soil samples were collected at 31 sites around the urban areas of Pisa city. The quality of soils in urban areas was compared to a rural soil of similar lithogenic origin, located in "S. Rossore-Migliarino-Massaciuccoli Natural Regional Park" (latitude 43°42′48.84N; longitude 10°21′44.47E), near Pisa city (Fig. 1).

At each site, three samples, each formed by 5 sub-samples, were randomly collected from the topsoil (depth 0-20 cm) after removing the herbaceous cover. The sub-samples were taken within a  $2 \text{ m} \times 2 \text{ m}$  square, four on the corners of the square and one in the middle. The five soil cores of each sub-sample were mixed to avoid local inhomogeneities. For each main sample, a total of 5 kg of soil was taken. In the laboratory, samples were air-dried at room temperature  $(20 \pm 1 \circ C)$  and, after manually removing any plant material, as roots and leaves, they were stored at 4 °C until analysis. Fresh sieved soil samples stored at  $4 \pm 1$  °C were used for enzyme activity assay.

#### 2.3. General properties

The main properties of soils were determined according to the official Italian method (Repubblica Italiana, 1999). Texture was obtained by particle-size analysis using Esenwein apparatus, bulk density was calculated from mass and volume of soil samples collected with a corer equipped with a steel cylinder of 100 cm<sup>3</sup>, CaCO<sub>3</sub> content (inorganic C) was determined by a gas-volumetric system, while pH was measured by potentiometric determination, by using the pH meter Micro-pH 2001 Crison (Crison Instruments, S.A.-Alella, Barcelona, Spain). Water holding capacity was gauged by using the method suggested by Naeth, Bailey, Chanasyk, and Pluth (1991): soil samples were put in plastic cylinders that were saturated for 48 h in a sink and then placed on a tray of damp sand to drain for 48 h; water holding capacity for each sample was determined by subtracting oven dry mass of its cylinder contents from its drained mass, dividing by oven mass and multiplying by 100.

Total carbon was measured by dry combustion with an automatic C analyzer FKV induction furnace 900 CS, Eltra (F.K.V.). The organic carbon content of soil samples was obtained by the difference between total and inorganic carbon.

2.4. Soil antioxidant system (antioxidant capacity and content of *phenol compounds*)

The soil antioxidant capacity was determined on the water and alkali extracts (Rimmer & Smith, 2009) according to the method of Re et al. (1999). The measure of antioxidant capacity (TEAC) is based on the use of ABTS<sup>+</sup> 2,2'-azino-bis-(3-ethylbenzothiazoline-6-sulphonate), a stable coloured radical in aqueous solution. TEAC was expressed as a decrease in absorbance of the solution of ABTS<sup>+</sup> after the addition of an antioxidant. The decrease in absorbance due to the activity of soil extract on antioxidant ABTS<sup>+</sup> radical was expressed as a percentage of initial absorbance.

% Inhibition = 
$$\left[1 - \left(\frac{Abs_{sample}}{Abs_{blank}}\right)\right] \times 100$$

A calibration curve was made using Trolox (6-hvdroxy-2.5.7.8tetramethylchroman-2-carboxylic acid) as reference substance.

On the same water and alkali extracts used for TEAC determination, phenol compounds of the soils were analyzed according to the method of Kuwatsuka and Shindo (1973).

#### 2.5. Community level physiological profile-CLPP

D)

The study of functional diversity of soil microbial communities was performed according to the method of Garland and Mills (1991). The following indices were calculated: The average well color development (AWCD), an index of total microbial activity, was calculated as follows:

$$\mathsf{AWCD} = \sum \frac{(C-R)}{n}$$

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