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Quantification of black carbon (BC) and its physical fractionation in urban and peri-urban soils across the metropolitan area of Milan (Italy)

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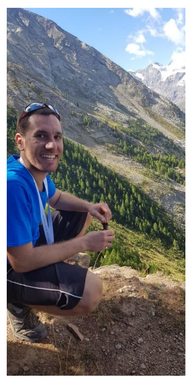


Introduction and Objectives

Black carbon (BC) is a recalcitrant and stable form of organic carbon (SOC) produced by incomplete combustion of biomass and fossil fuels. In cities, major BC sources are vehicular traffic, domestic heating, and industrial emissions. BC accumulates in soils, where it contributes to long-term carbon sequestration and may affect contaminant dynamics. This study is part of the PNRR project (Biodiversity Future Center, Spoke 5: Urban Biodiversity) and aims to:

- ❖ quantify soil organic carbon (SOC) and black carbon (BC) across multiple soil depths in urban and peri-urban sites of the Milan metropolitan area;
- ❖ assess the relative allocation of BC between particulate organic matter (POM) and mineral-associated organic matter (MAOM);
- ❖ compare SOC and BC content between different land uses.

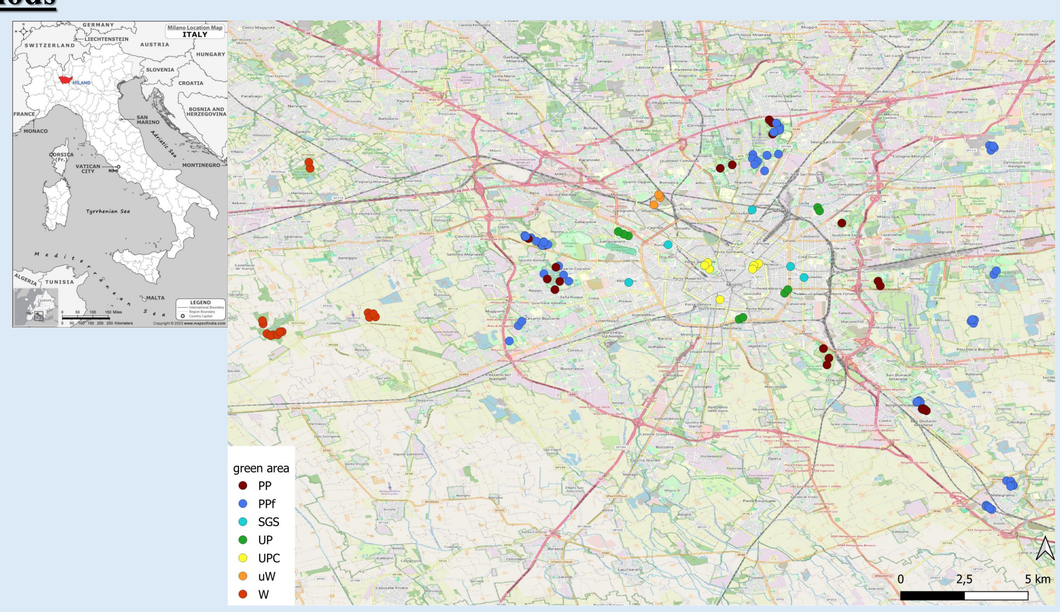
Materials and Methods

Field working

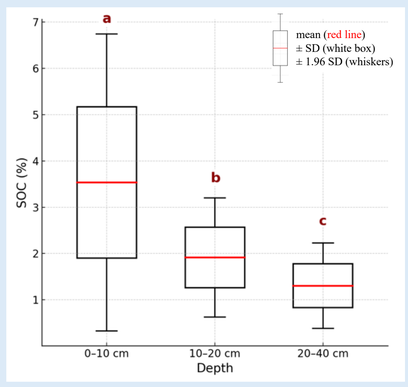
Soil samples were collected in 2024-25 from 134 sites across the metropolitan area of Milan, including urban parks (UPC and UP, both inside and outside the historical city centre), peri-urban parks (PP), peri-urban reforested areas (PPf, divided in 3 classes for age in years: PPf 10-20; PPf 20-40; PPf 40-60), small green spaces (SGS), spontaneous urban woodlands (uW), and mature woodlands (W, with an age more then 80 years). Composite samples were taken at three depths (1: 0-10, 2: 10-20, 3: 20-40 cm) using a gouge auger.

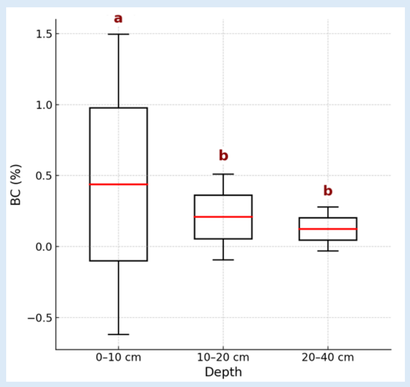
Laboratory Analyses

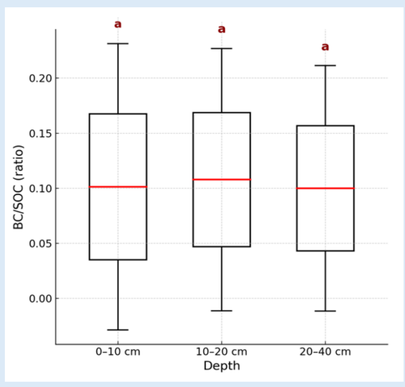
Soil organic carbon (SOC) was determined with an elemental CN analyzer. Black carbon (BC) was quantified by chemothermal oxidation at 360 °C (CTO-360), followed by elemental analysis. Samples from the first two layers (0-10 and 10-20 cm) were physically fractionated into particulate organic matter (POM) and mineral-associated organic matter (MAOM) pools.



Results and Considerations







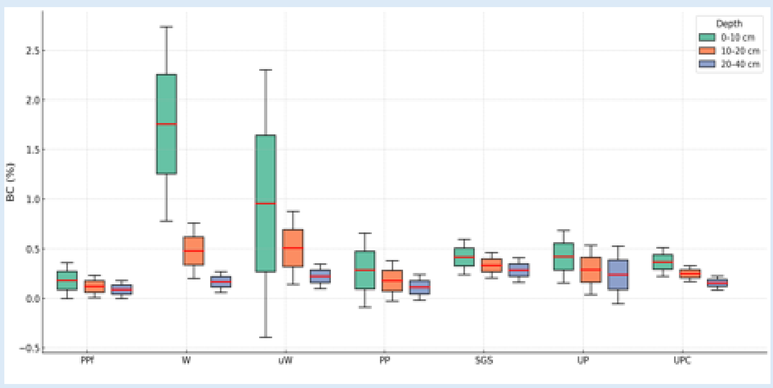
Mean values

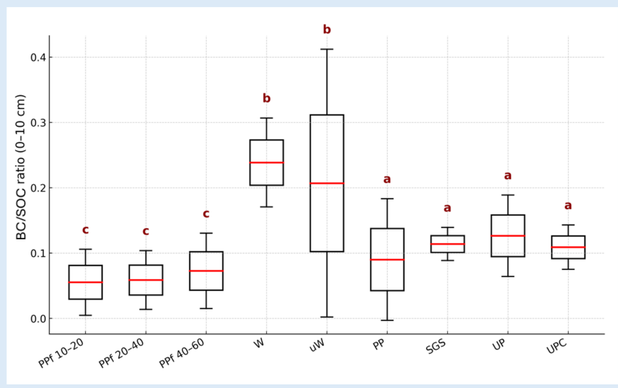
SOC decreased significantly with depth, from 3.5 ± 1.6% at 0-10 cm to 1.9 ± 0.7% at 10-20 cm and 1.3 ± 0.5% at 20-40 cm (ANOVA, $p < 0.001$).

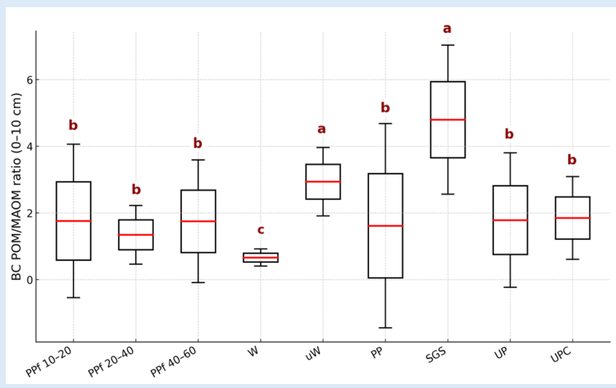
BC followed a similar trend, with 0.44 ± 0.54% in the topsoil, decreasing to 0.21 ± 0.15% at 10-20 cm and 0.12 ± 0.08% at 20-40 cm (ANOVA, $p < 0.001$).

The BC/SOC ratio remained relatively constant across depths, averaging 10-12%, with no significant differences among soil layers.

Comparison between different land uses







Vertical distribution of BC: across all land uses, BC showed a clear vertical gradient, with higher concentrations in the 0-10 cm layer and decreasing values with depth. W had the highest surface contents (1.76 ± 0.6%), reflecting long-term accumulation. uW also showed elevated values (0.96 ± 0.5% at 0-10 cm). In contrast, UPC, UP, PP and SGS contained much lower BC at the surface (0.28-0.42%), with weaker stratification, likely due to disturbance and management. PPf had the lowest values (0.18 ± 0.1% at 0-10 cm), decreasing further with depth, consistent with their relatively recent establishment compared to mature forests.

BC/SOC ratio: at the 0-10 cm, it showed significant differences across green-area types (ANOVA, $p<0.05$), with PPf exhibiting higher values than W, UP and UPC, while SGS) and PP displayed intermediate levels.

BC POM/MAOM ratio: at 0-10 cm, the BC POM/MAOM ratio was significantly higher in SGS (4.8 ± 1.1) compared to other green area categories, which showed lower ratios (ANOVA, $p < 0.01$).

Focus on forested area (PPf and W): the BC POM/MAOM ratio at 0-10 cm differed significantly among groups (ANOVA, $p < 0.05$). All PPf stands showed similarly high ratios (PPf 10-20: 1.76 ± 1.17; PPf 20-40: 1.34 ± 0.45; PPf 40-60: 1.69 ± 0.91), indicating a predominance of BC in the POM fraction. In contrast, W exhibited significantly lower ratios (0.66 ± 0.13), reflecting a greater association of BC with the MAOM fraction.

Conclusions

The strong vertical decrease of SOC and BC highlights the concentration of organic matter inputs at the surface, with a clear reduction between 0-10 cm and 20-40 cm. This is mainly due to soil stability, since the soil in forested areas has not been tilled for a long time. BC/SOC ratio (~10%) remained relatively constant with depth, suggesting consistent incorporation mechanisms.

Most green areas had a POM/MAOM ratio between 1 and 2, whereas SGS stood out with much higher values (~ 5), indicating BC retention in more labile pools.

This pattern likely reflects legacy deposition from local pollution sources combined with limited incorporation into stable MAOM pools. On the contrary, W has a POM/MAOM ratio under 1, indicating BC retention in more stable pools.

A clear contrast emerged between plantations and mature forests: PPf stands retained most BC in POM (~ 56-60%), while W stabilized ~ 60% in MAOM, with older plantations tending toward the mature forest pattern.

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