



Carbon mineralization kinetics in soils under urban environment



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ABSTRACT

In a short-term laboratory study, carbon mineralization potentials were determined on samples obtained from some representative urban soils located in Pisa (Tuscany, Italy). All the kinetic models tested to describe the mineralization process fitted well to the experimental data. The special model, a modified double exponential model combining first-order mineralization with zero order mineralization, best described the C mineralization of the urban soils. The low variability of rate constants suggests that urban soils of Pisa have similar easily mineralizable organic compounds or the same degree of availability. The parameters calculated according to the special model allowed the detection of a pool of easily biodegradable organic compounds (on average 0.75% of the total organic C of soils) which was exhausted in a very short period. Soil texture was found to influence the rate of the first phase of C mineralization. The mineralization first-order rate constants of the easily mineralizable C (k) were positively correlated with the sand contents, while high clay and silt contents were found to be indicative of low k .

The mineralization parameters C_m (cumulative C mineralized after 25 days of incubation), C_1 (easily mineralizable C) and h (time constant for the slowly mineralizable C) were found to be positively correlated with the organic C contents and negatively related to soil pH.

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1. Introduction

As land is converted to urban uses many factors can influence soil organic matter. These include soil management inputs such as irrigation and fertilization, burial or coverage of soil by fill material and surfaces, soil hydrophobicity (Craul, 1992) and atmospheric deposition of various pollutants (Lovett et al., 2000).

For urban ecosystems, very little data are available to assess whether urbanization leads to an increase or a decrease in soil C pools. Research on urban soils often describes decreased amounts of organic matter contents compared to soils of other systems (Zhu and Carreiro, 1999). In contrast, organic matter quantities in urban soils were found to be substantially higher than in other non-urban soils (Pouyat et al., 2002).

Most research on urban soil organic matter has been quantitative, but qualitative differences have also been measured (Beyer et al., 1996; Scharenbrocha et al., 2005; Lorenz et al., 2006). Certain portions of soil organic matter are more labile than other more recalcitrant fractions.

Atmospheric concentrations of CO₂ in urban environments are higher due to anthropogenic sources such as fossil fuel combustion by vehicles (Pataki et al., 2007). The C loss during litter

decomposition in urban ecosystems shows both slower and faster decomposition rates in urban compared to non-urban soils were reported. In Chicago, the urban soils are usually a net source of CO₂ whereas forested sites exhibit negative fluxes (Grimmond et al., 2002). Soil respiration in urban ecosystems of Fort Collins was five times higher than of native grasslands (Kaye et al., 2005). Urban soils with higher fluxes of CO₂ compared to native soils were also observed by Pataki et al. (2006). In contrast, Beyer et al. (1995) observed that the potential soil CO₂ flux due to microbial activity was comparable between urban and natural superficial soil horizons. However, additional data are needed to clarify whether they may be source or sink of organic C (Grimmond et al., 2002; Pataki et al., 2006).

Correct identification of the “mineralizable” soil C pool is essential as it is an important component in modeling soil C dynamics and ecosystem responses to changing environmental factors (Buchmann, 2000; IPCC, 2007; Schlesinger and Andrews, 2000; Stewart et al., 2008). Various methods have been used to quantify mineralizable soil C (Bremer et al., 1994). Soil incubations are a more direct approach to quantify mineralizable soil C than various procedures using chemical extraction or organic compound class analysis (Ahn et al., 2009).

The description of the dynamics of C mineralization in incubation studies by fitting the experimental values to kinetic models may be of great interest for the prediction of the ability of soils in supplying potentially mineralizable organic carbon and, more generally, for the organic matter balance. These mathematical

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descriptions of C release patterns may also provide useful indices and allow the testing of hypotheses concerning the involved mechanisms. A first-order equation has been frequently employed for the description of the C mineralization process of soil organic carbon. Alternatives to the simple first-order model take into account several organic pools with different stabilities (Lindemann and Cardenas, 1984; Murayama et al., 1990). Other researchers have found that a zero-order equation adequately describes C mineralization (Seyfried and Rao, 1988). Some simulation models described an initial flush of mineralization (Jones, 1984), or a delay in the mineralization (Bonde and Lindberg, 1988). Consequently, it is important to identify models that will simulate the behavior of C mineralization for a wide range of soils.

The rate at which the soil organic matter is degraded to CO₂ depends mainly on the nature of its interactions with the soil matrix. In incubation experiments, the rate of the breakdown of soil organic matter and the amount of mineralizable C were found to be influenced by soil pH and redox conditions (De Laune et al., 1981), clay content (Simard and N'dayegamiye, 1993; Ahn et al., 2009), amount and quality of soil C pool (Riffaldi et al., 1996; Ahn et al., 2009), and exchange capacity and microbial activity (Riffaldi et al., 1996).

The objectives of this study were: (i) to determine the C mineralization potential of some urban soils of Pisa (Tuscany, Italy); (ii) to describe comparatively both the dynamics and kinetics of C mineralization through the fitting of some commonly used decay models; (iii) to evaluate the relationship between the soil properties and the mineralization parameters derived from the best model.

2. Materials and methods

The Pisa urban environment is located in a municipal area of approximately 187 km²; the artificialized surface (impermeable urban area) is approximately 27 km² (about 15% of the total area). The built-up area has been steadily increasing, with the largest increases since the 50s (260% increase from 1954 to 2003).

2.1. Soil sampling

Soil samples were collected at 31 sites around the urban areas of Pisa. The quality of soils in the urban areas was compared to a rural soil, used as control, 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 (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 vegetation. The sub-samples were taken within a 2 m × 2 m square, four from the corners of the square and one from 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 ± 1 °C) and, after manually removing any plant material such as roots and leaves, they were stored at 4 °C until analysis.

2.2. General properties

The main properties of soils (Table 1) were determined according to the official Italian method (Repubblica Italiana, 1999). Texture was obtained by particle-size analysis using Esenwein levigators; bulk density was calculated from the mass and volume of soil samples with a corer equipped with a steel cylinder of 100 cm³; CaCO₃ content (inorganic C) was determined by a gas-volumetric system; pH was measured by potentiometric determination using a Micro-pH 2001 Crison (Crison Instruments, S.A. – Alella,

Barcelona, Spain) pH meter; water holding capacity was determined by using the method described by Naeth et al. (1991).

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

A short-term aerobic incubation procedure was used to determine the potential of the soils to mineralize the organic C; 50 g of soil were incubated at 25 ± 1 °C and moistened to 50% of the maximum water holding capacity (MWHC) in 300 ml glass containers closed with rubber stoppers. Glass vials containing 20 ml of 0.5 N NaOH were placed in the containers to trap the evolved CO₂. The decomposition was monitored daily between the 1st and 25th day of incubation by measuring CO₂ evolution. The excess alkali was back-titrated with 0.5 N HCl after precipitating the carbonate with 1.5 M BaCl₂ solution. Daily opening of the bottles to replenish the NaOH for CO₂ absorption prevented any inhibition of decomposition owing to lack of oxygen.

All data were expressed on a dry weight basis and results are the means of determinations carried out on three replicates.

2.3. Kinetic models and curve fittings

Five different models have been used in this experiment to describe the C mineralization patterns in the soil samples. The equations were tested for each of the 31 urban soils and for control. A non-linear least-square regression analysis provided by GraphPad Prism 5 Software (2007) was used to calculate parameters of the tested models (Table 2) from cumulative data of C mineralization. The mean coefficient of variation, i.e. the standard deviation as a percent of the average of the two values, was always lower than 5%. The comparison of model fits was evaluated by the coefficient of determination, R² (Cameron and Windmeijer, 1997).

3. Results and discussion

The cumulative amounts of C mineralized from the urban soils during the 25-d incubation period (C_m) varied in a range between 22.32 and 107.24 mg of CO₂-C-100 g⁻¹ dry soil, with a mean of 58.96 mg of CO₂-C-100 g⁻¹ soil (Fig. 2). The control site showed a value of 13.26 mg of CO₂-C-100 g⁻¹ soil, much lower than the evolved CO₂-C in all the examined urban soils. Our data are in agreement with several other studies (Imhoff et al., 2000; Koerner and Klopatek, 2002; Grimmond et al., 2002; Kaye et al., 2005; Pataki et al., 2006), suggesting that urbanization leads to enhanced C cycling rates which may in turn alter C budgets. The C_m value, expressed as percent of soil TOC, was different among the urban soils (Fig. 2). During the 25-d incubation period, between 0.81% and 3.24% of the soil total organic C was released as CO₂ with a mean value of 1.97%. The results suggest different C availability for the active microbial biomass during the incubation period.

Cumulative mineralized carbon showed a curvilinear relationship with time over the 25-d incubation period (Fig. 3). All soils showed a similar pattern, with an initial release of CO₂ due to the rapid depletion of the easily mineralizable fraction, followed by a slower linear increase with time throughout the remaining period of incubation. Since the conditions of the incubation were more favorable than those usually existing in the field, the values, extrapolated to longer periods, should not represent the true losses of organic matter. Although the mineralization data may be overestimated, the comparisons between the soils can be considered to be valid.

The time course of organic C mineralization in the soil was analyzed by fitting the experimental values to several kinetic models commonly used to interpolate mineralization data (Table 2). On the

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