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Calorimetric determination of the effect of ammonium-iron(II) phosphate monohydrate on *Rhodic Eutrudox* Brazilian soil

Nieves Barros [a], Claudio Airoldi [b,*], José A. Simoni [b], Beatriz Ramajo [c], Aránzazu Espina [c], José R. García [c]

[a] *Department of Applied Physics, University of Santiago de Compostela, 15706 Santiago de Compostela, Spain*
[b] *Instituto de Química, Universidade Estadual de Campinas, 13084-971 Campinas, Caixa Postal 6154, Sao Paulo, Brazil*
[c] *Department of Organic and Inorganic Chemistry, University of Oviedo, 33006 Oviedo, Spain*

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Abstract

The fertilizer $NH_4FePO_4 \cdot H_2O$ (AIP) was synthesized under mild hydrothermal conditions to be applied on soils to prevent iron deficiencies. The effect of the addition of AIP on soil microbial activity was studied by calorimetry, determining both basal respiration and carbon mineralization by means of the addition of an external carbon source. Thermal analyses (TG and DSC) were also used to provide additional soil properties. The effect of different amounts of AIP on soil microbial activity was quantitatively analyzed by a mass and energy balance performed via the analysis of the power–time curves. These balances allowed determination of the impact of AIP on soil more rapidly than conventional methodologies. The increase in the amount of added AIP leads to a less efficient metabolism, probably due microbial competition for the nitrogen source provided by the AIP and for the carbon source.

Keywords: Microcalorimetry; Thermal analysis; Thermal yield; Soil basal respiration; Ammonium-iron phosphates

1. Introduction

Control of the utilization of soil for economic purposes is of the utmost importance for sustainable development. The Kyoto protocol states that CO_2 emissions due to soil utilization must be controlled and appropriate methodologies introduced that are rational and allow the monitoring of soil activity. The latter directive faces important limitations due to the complexity of the soil system. Most studies focused soil microbial activity employ the CO_2 dissipated and the biomass as indicators. The methodologies to quantify CO_2 and soil biomass are very laborious, and provide results only after very long experimental phases. These studies have only an empirical focus, since it is very difficult to obtain quantitative indicators of soil microbial activity. The most widely used, the metabolic quotient, was seriously criticized [1,2]. The main consequence of the methodological limitations has been inappropriate soil management, which in many cases has been responsible for important losses in soil fertility [3–5].

Thus, there is need for new methodologies to contribute to a better understanding of the biochemical reactions related to the fertility of soil. Methods for the precise estimation of the microbial biomass and its activity, i.e. the metabolic reactions of the soil biomass involved in the carbon cycle, are needed.

Calorimetry appears to be an important option for determination of both biomass and activity. The latest results show that this method can provide qualitative [6–8] and quantitative [9,10] indicators of soil microbial activity that could be used as early warning signals of soil deterioration. Calorimeters are sensitive enough to detect very low heat rates. They can continuously monitor soil microbial activity in terms of dissipated heat, which is a direct product of the degradation of the soil organic matter. Preparation of the samples is clean and easy, avoiding the use of reagents that may affect the results and that may be pollutants [11,12]. The technique therefore has the twofold advantage of being ecological and of rapidly providing results. It has been applied to carry out a diagnosis of the microbial state of soil [13,14], and interesting results have been reported [15,16]. The aim of the present study is to take a further step towards quantitative application of calorimetric methods for the evaluation of the environmental impact of chemical substances on

* Corresponding author. Tel.: +55 19 37883055; fax: +55 19 3788 3023.
E-mail address: airoldi@iqm.unicamp.br (C. Airoldi).

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soil microbial reactions. A model is suggested for analyzing the power–time curves recorded from soil samples under the effect of different amounts of $NH_4FePO_4{\cdot}H_2O$ (AIP). The synthesis of $NH_4MPO_4{\cdot}H_2O$ [M = Mg, Mn(II), Fe(II), Co(II), or Cu(II)] has been known for more than 100 years [17], and the possibility exist to prepare these compounds by a simple continuous process [18]. Metal ammonium phosphates have been used as pigments for protective paint finishes on metal and as fire retardants in paints and plastics [19,20]. As fertilizers, they can be a source of macro- and micronutrients (P, N, Mg, Fe, Zn, Mn, Cu, and Co) [21]. $NH_4FePO_4{\cdot}H_2O$ has been shown to correct iron deficiency (iron chlorosis) in plants grown in calcareous soils [22]. AIP is hydrothermally synthesized to be applied on soils as a chemical fertilizer and to prevent iron deficiencies in plants. The structure of AIP protects the Fe^{2+} against conversion to Fe^{3+}, which is impossible for plants to assimilate in soils with high pH. It is important to know if the structure of AIP is attacked by soil microorganisms or if it remains intact in the soil and unavailable to plants. Therefore, this study focuses on assessing the effect of AIP on soil microbial reactions and on establishing the role of thermal analysis and calorimetry in the investigation of the soil system. It is believed that this information can be very useful for the agriculture industry and its newly assumed obligations with respect to the Kyoto protocol.

2. Experimental

2.1. Synthesis of AIP

Hydrothermal crystallization of $NH_4FePO_4{\cdot}H_2O$ (AIP) was carried out in a stainless steel (100 cm^3) Teflon-lined vessel under autogenous pressure. $(NH_2)_2CO$ (solid), H_3PO_4 (5.0 mol dm^{-3}), $FeCl_2{\cdot}4H_2O$ (solid) and water were mixed in the molar ratio 2:2:8:67 ($FeCl_2$:H_3PO_4:$(NH_2)_2CO$:H_2O). The autoclave was sealed and heated to 185 °C for 8 days. The obtained solid was filtered off, washed with an excess of distilled water, and dried in air at room temperature. The SEM micrograph (JEOL JSM-6100, 20 kV) shows plates of c.a. 5 μm × 30 μm × 100 μm (see Fig. 1). The phosphorous and iron contents were determined with a Spectra Spectrometer ICP-MS after dissolving a weighed amount of sample in $HF_{(aq)}$. Microanalytical data were obtained with a Perkin-Elmer model 2400B elemental analyzer to give 7.5, 29.6 and 16.7 % for nitrogen, iron and phosphorus, respectively, which correspond to the calculated values 7.49, 29.89 and 16.59%, respectively. Thermogravimetric curves (Mettler TA4000-TG50) was carried out at a rate of 10 °C min^{-1} under a flow of nitrogen. The total weight loss at 600 °C was 22.7% (calculated 23.55%). The weight loss occurs in three steps, with DTG minima at 230, 260, and 500 °C. The final product after thermal decomposition was $Fe_2P_2O_7$.

2.2. AIP solubility in aqueous medium

An excess of AIP was added to buffer solutions (Merck, pH 4.0, 5.0, 6.0, and 8.0 at 20 °C). The P-content in the resulting solutions was analyzed at different intervals of time by UV-spectroscopy [23] with a Perkin-Elmer 200 autosampler.

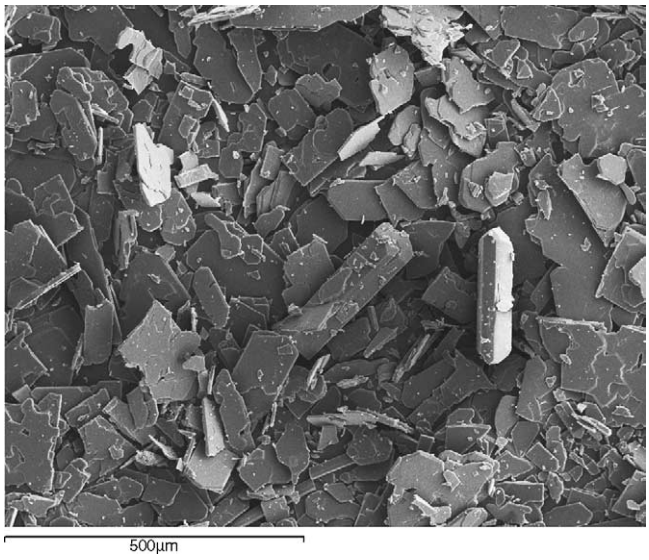

Fig. 1. Scanning electron micrograph of AIP.

The enthalpy of dissolution of AIP was determined by calorimetry with a Setaram Calvet standard 1201. A weighed amount (about 9.5 cm^3) of the buffer solution at pH 4.0, 5.0 or 6.0 was introduced into the calorimetric vessel. Once the heat output was stabilized, 0.10 g of AIP was added and the heat of the endothermic reaction recorded. At the end of the process, the P-concentration in the dissolution was determined by UV-spectroscopy.

2.3. Soil

The soil sample was collected at Campinas University [24,25], in the state of Sao Paulo, Brazil. It corresponds to the *Rhodic Eutrudox* type and was collected at a depth of 5–10 cm after removing the soil surface. The bulk sample was brought to the laboratory, where it was sieved at 2 mm × 2 mm size to remove plants, small insects, small stones and large particles. After this treatment, the sample was kept in polyethylene bags at 4 °C for 3 months before calorimetric experiments.

2.4. Soil organic matter

Microanalytical data (C, H and N, Perkin-Elmer 2400B elemental analyzer) and differential scanning calorimetry (Mettler TA4000-DSC30) were applied to quantify the percentage of soil organic matter (SOM) and the SOM combustion enthalpy, $\Delta_r H_{SOM}$ respectively. DSC experiments were conducted with a heating rate of 10 °C min^{-1} under a flux of air or nitrogen (20 cm^3 s^{-1}).

2.5. Soil biomass

The microbial density of the sample was calculated by the fumigation–extraction method, according to the established method [26]. The sample was kept under refrigeration until the