Sensitivity of two procedures for estimating the impact of the ionic liquid 1,3-dimethylimidazolium dimethyl phosphate ([C_1C_1Im][DMP]) on soil microbial respiratory activity

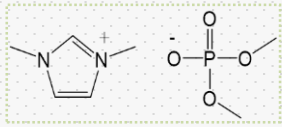
T. Sixto[1], J. Salgado[2], J. J. Parajó[2,3], O. Reyes[4], C. Trasar[1]

[1] Departamento de Bioquímica del Suelo, IIAG-CSIC, Spain
[2] Grupo Nafomat. Departamento de Física Aplicada. Campus Vida. Universidade de Santiago de Compostela, Spain
[3] Departamento de Química e Bioquímica, CIQUP-Centro de Investigaçao em Química da Universidade do Porto, Porto, Portugal
[4] Departamento de Bioloxía Funcional. Campus Vida. Universidade de Santiago de Compostela, Spain

INTRODUCTION

Ionic liquids (ILs) can potentially be used as alternatives to organic solvents in industrial processes due to their tuneable physicochemical properties. Numerous ILs can be synthesized from different combinations of cations and anions or even by changing the alkyl chains of theses ions. Importantly, ILs have negligible vapour pressure, and therefore they do not contaminate the atmosphere and are playing an increasingly relevant role in green chemistry. Nevertheless, before the use of ILs can become generalized, toxicity studies must be performed to determine their potentiality toxicity to terrestrial ecosystems. However, to date studies of the effects on soil and vegetation, which could be affected by accidental spills of ILs, are scare.

The imidazolium-based ionic liquid 1,3 dimethylimidazolium dimethylphosphate, [C_1C_1Im][DMP], has many possible industrial applications, e.g. for increasing the rate of cellulose hydrolysis by cellulase enzyme in the bleaching process in the paper and pulp industry. However, if the use of this IL becomes widespread, there is a high probability that it will reach terrestrial ecosystems. Assessing the toxicity of this compound to these systems is therefore very important.



OBJECTIVES

- To assess the toxicity of [C_1C_1Im][DMP] to soil by analysing the impact on soil microbial activity
- To test the sensitivity of two procedures (microcalorimetry and the classical determination of basal soil respiration) to estimate microbial activity in IL-spiked soils
- To compare and combine the information provided by both procedures to obtain greater insight into the impact of this compound on soil microbial activity.

MATERIAL AND METHODS

Two acid soils with sandy-loam texture and different organic (OM) mater content where selected: a forest soil with high OM and a crop soil with low OM.

Table 1. Main characteristics of the soils used for the study.

	pH(H_2O)	pH(KCl)	%Ct	%Nt	C/N	%Fe_2O_3	%Al_2O_3
Crop	5.44±0.05	4.23±0.06	2.22±0.03	0.20±0.00	11	0.89±0.02	0.46±0.01
Forest	4.45±0.02	3.51±0.03	11.91±0.08	0.58±0.00	21	0.95±0.01	1.08±0.01

The soils where spiked with different amounts of [C_1C_1Im][DMP] (between 0 and 123.48 g IL kg^{-1} air-dried soil) and the soil microbial activity was analysed by two methods.

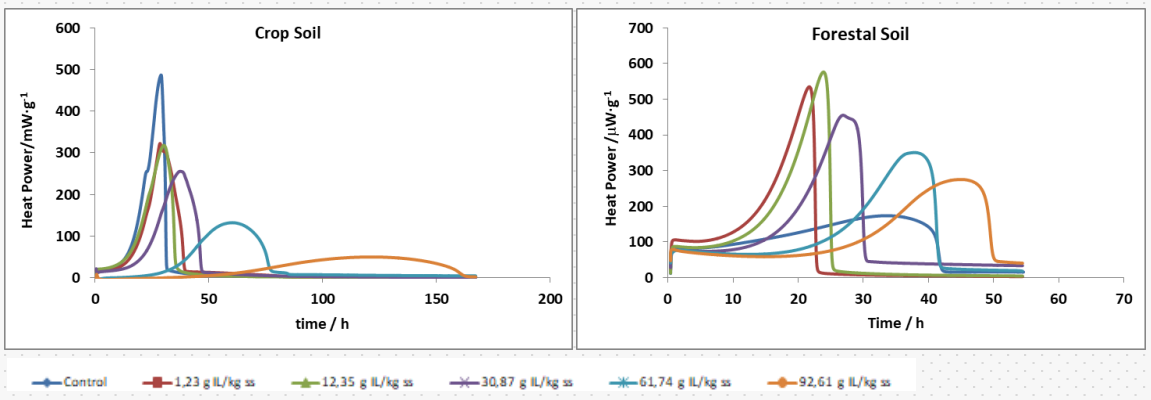
Microcalorimetry: the heat released by soil microbiota, activated with a solution of glucose, was measured against time and dose (only up to 92.61 g de IL kg^{-1} soil) using an isothermal microcalorimeter (TAM III, TA Instrument).

Basal soil respiration: after three days of soil-IL contact time, all soil samples spiked with [C1C1Im][DMP] (0 to 123.48 g IL kg^{-1} soil) were incubated at 25 °C and 80% of water holding capacity. Generally in this assay the incubation time is 10 days; however, in IL-spiked soil this period had to be increased until the CO_2 emitted was stable or had reached the same level than in un-spiked soil (126 days).

The main physico-chemical characteristics of the soils were determined following the methods described in Guitián-Ojea and Carballas-Fernández (1976).

RESULTS AND DISCUSION

Figure 1. Power-time curves of the soils spiked with different doses of [C_1C_1Im][DMP] and expressed in Heat Power/mW g^{-1}.



The power-time curves revealed important differences in the response of the soils to the addition of IL.

Thus, for the lowest doses of IL applied to the forest soil (highest OM content), the amount of heat released increased during the first hours of the experiment, relative to the control, and was followed by death of the microorganisms.

By contrast, the highest doses of IL caused a delay in the growth phase of the activity. In the crop soil (lowest OM content) the delay in the growth phase increased with the dose of IL.

As expected, basal soil respiration was higher in the soil with the highest OM content than in the soil with the lowest OM content.

In both soils, the lowest dose of IL (1.92 g IL kg^{-1}) did not affect soil respiration. All the other doses of IL greatly increased the soil respiration, with a peak in CO_2 emission. This peak increased gradually with the amount of IL up to 61.74 g IL kg^{-1}, and thereafter tended to decrease. In all cases, and similarly to what was observed by microcalorimetry, the timing of the peak was gradually delayed as the dose of IL increased.

The total amount of CO_2 emitted during the 126-day incubation period (accumulated CO_2-C) by the soil with 1.92 g IL kg^{-1} was similar to that of the control in both soils. Although the highest amounts of IL strongly increased the amount of accumulated CO_2-C, the increase was not proportional to the dose. In both the forest and crop soils, accumulated CO_2-C was highest in the soil contaminated with an intermediate amount of IL (61.74 g IL kg^{-1}), while the amount of CO_2 emitted decreased for the two highest doses of [C_1C_1Im][DMP]; the decrease was particularly notable with the highest dose applied to the soil with the lowest OM.

Figure 2. Daily CO_2-C emitted (mg CO_2-C kg^{-1}) by crop and forest soils spiked with different amounts of [C_1C_1Im][DMP].

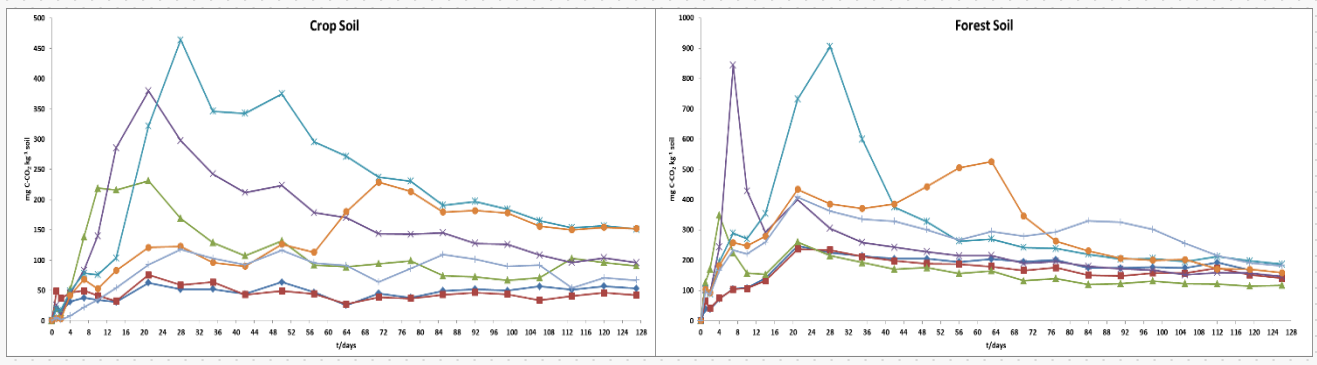
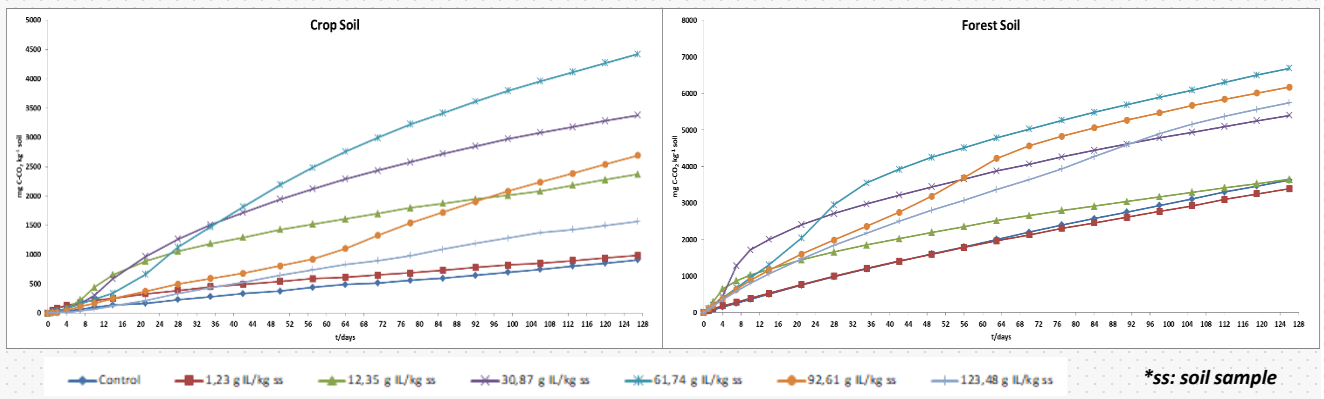


Figure 3. Accumulated CO_2-C emitted (mg CO_2-C kg^{-1}) by crop and forest soils spiked with different amounts of [C_1C_1Im][DMP].



*ss: soil sample

CONCLUSIONS

1. Microcalorimetry and the classical measurement of basal soil respiration proved to be equally sensitive to the presence and the amount of [C_1C_1Im][DMP], in soils with high and low OM contents.
2. Microcalorimetry and soil basal respiration measurement are sensitive to temporal changes in microbial activity in soils amended with different amounts of [C_1C_1Im][DMP].
3. Both methods revealed a similar pattern of CO_2 emissions in the IL-amended soils related to the amount of IL and time.

References: Guitián-Ojea F., Carballas-Fernández T. (1976) Técnicas de análisis de suelos. Pico Sacro Editorial, Santiago de Compostela, Spain.

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