The use of elemental sulphur as organic alternative to control pH during composting

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Abstract

High values of pH may represent a limitation for the agricultural use of the composts, not only when used as soil-less substrate but also as soil amendment in high pH soils. The addition of elemental S during the composting process was evaluated as suitable method to reduce pH of the composts under the organic agriculture regulations. A compost prepared with two phase olive mill waste (OMW) and sheep litter (SL) was used to study the effect of elemental sulphur addition on the pH of the composting mixture. Initially, different bench scale experiments were designed in order to study the influence of moisture, sulphur concentration, and incubation temperature on the sulphur oxidation rate and thus on the pH of the compost. A concentration of 0.5% in sulphur (dry weight basis) and moisture of 40% were proposed as the optimum conditions to decrease the compost pH by 1.1 units without increasing in EC to levels that may suppose a limitation for its agricultural use. Finally, these optimum experimental conditions found at bench scale were tested at full scale in a commercial composting plant treating the same organic materials by windrowing. The pH values of the composting mixture were reduced by one unit after 2 weeks following the addition of elemental S causing no negative effects on the final compost quality.

Keywords: compost, sulphur, pH, olive mill wastes, organic farming.

1. Introduction

For many years, agricultural systems have been ruled only by productive or economic guidelines. However, the increasing consumers demand for organic food products worldwide has led to an expansion of organic farming (Rigby and Caceres, 2001). In the European Union, the implementation of regulation 2092/91 (Council of European Community, 1991) on organic agriculture has meant the creation of a legal framework which sets the requirements for organic production, processing and labelling.

One of the main purposes of organic agriculture is the conservation of soil fertility by the optimal use of natural resources without using synthetic chemical products (IFOAM, 1998). Thus, organic matter must be applied to the soil to provide the necessary nutrients and to impart a suitable structure which will help to prevent erosion. Traditionally, manure, have been used for this purpose, but in recent years an increase in the use of composts made from different wastes has been observed. Benefits of composts amendments to soil have been reported by many authors (Drinkwater et al., 1995; Roig et al., 1987; Stamatiadis et al., 1999). They include higher plant available water holding capacity and cation exchange capacity, lower bulk density, pH stabilization and better aggregation. Bulluck et al. (2002) found that the addition of recycled organic wastes decreased the number of plant pathogenic microorganisms. In this way, two problems can be simultaneously solved: disposal of waste and enrichment of soil with organic matter.

In Mediterranean countries the olive oil industry generates huge quantities of olive mill by-products. The disposal of these wastes has become a great trouble, because of their polluting effects on soil and water. Composting seems to be a feasible method to eliminate their toxicity and to turn them into a valuable product (Cegarra et al., 1996; Filippi et al., 2002; Paredes et al., 1999). Nevertheless, the high increase of pH produced during the composting of olive mill wastes (Cegarra et al., 1999; Paredes et al., 2000) may limit its agricultural use in high pH soils. In Appendix II of EU regulation 2092/91, elemental sulphur appears as an allowed soil fertilizer or conditioner (Council of European Community, 1991).

The oxidation processes of S in soils have been broadly studied and are relatively well known. S is oxidized by heterotrophic bacteria, actinomycetes and filamentous fungi growing on organic substrates (Starkey, 1966), but the most important group of S-oxidizing microorganisms are *Thiobacillus* bacteria. Tisdale et al. (1993) summarized their activity as follows:

$$S^{o} + 1/2\ O_2 + CO_2 + 2\ H_2O \leftrightarrow CH_2O + SO_4^{2-} + 2\ H^{+}$$

The rate of sulphur oxidation in soils has been related to a wide number of factors such as temperature, moisture, particle size of S, aeration, microbial biomass (Attoe and Olson, 1966; Germida and Janzen, 1993; Jaggi et al., 1999). However, there are few studies about the addition of S to improve the quality of a compost by reducing its pH (Mahimairaja et al., 1994 and 1995). In both cases, S is oxidized to H_2SO_4 by sulphur-oxidizing microorganisms, but it is not well known how the S oxidation would be affected by these factors under the composting conditions (higher temperatures, larger microbial population, higher amount of available nutrients, etc).

The aim of this work was twofold. Firstly, to study in a bench scale incubation experiment the effect of different variables (moisture, temperature and sulphur concentration) on the oxidation rate of elemental S, added to an organic compost prepared with two-phase olive mill waste (OMW) and sheep litter (SL). Secondly, to apply these experimental results to a commercial composting plant treating a similar organic mixture by windrowing.

2. Materials and Methods

2.1. Composts

Samples were taken from two composts elaborated at full scale. The composting system was by windrowing. The composts were mixtures of OMW and SL, a mixture of sheep manure with straw and grape husk from the ovine bedding. Composts were prepared in the following fresh proportion (dry weight in brackets):

COMPOST A: 50% OMW + 50% SL (33:66) by weight.

COMPOST B: 74% OMW + 26% SL (60:40) by weight.

A sample of compost A was withdrawn after 40 weeks of composting process and used for the incubation experiment at bench scale. Compost B was withdrawn after 35 weeks of composting and was used for the study of S addition at full scale. Their main characteristics are given in Table 1. Both composts showed the same pH values and similar origin that would enable to reproduce the results found at bench scale to full scale.

2.2. Experimental design of the incubations at bench scale.

Three different experiments were designed to study the effects of sulphur concentration, moisture and temperature of incubation on the sulphur oxidation rate, according to the experimental design exhibited in Figure 1. For each experiment samples of 800 g of fresh compost A (600 g dry weight) were placed into trays and incubated during 20 d.

To study the influence of the sulphur concentration the incubation was carried at 25ºC maintaining the moisture content to 40% adding the required amount of desionized water every day. The sulphur concentration was adjusted to the following levels: 0, 0.1, 0.3, 0.5, 0.75, and 1.0% (dry weight basis), equivalent to 0, 0.48, 1.44, 2.40, 3.60 and 4.80 grams of elemental sulphur per tray.

To study the optimum moisture the samples were adjusted to the following moisture contents: 25%, 40% and 60% water for dry weight on samples containing 0.5% of sulphur. The temperature of incubation was 25ºC.

Finally, to study the optimum incubation temperature the moisture content of the samples was fixed to 40% and the sulphur concentration to 0.5%. The incubation was performed at two different temperatures: 25 and 40ºC.

2.3. Experimental design for the S addition at full scale composting plant.

The effect of S addition at full scale was studied by adding 8 kg of elemental S (REDESUL® 98.5%, *Repsol derivados*) to 2 tons of compost B, adjusted to the moisture content to 40%, to obtain a concentration of 0.5% S (dry weight), that correspond to the optimum experimental conditions found by the incubation experiments performed at bench scale. The amended compost was continuously turned for 30 minutes in a cylindrical drum to ensure the homogeneity of the mixture, and was laid on a concrete pad forming a trapezoidal windrow for 16 weeks. The windrow was turned after 3, 4, 7 and 16 weeks of the experiment with a front-loader tractor to ensure homogeneity and aeration of the pile. The moisture content of the mixture was kept at 40% through regular water additions.

2.4. Analytical Methods.

Samples of composts were analysed for pH in the saturated extract of the fresh sample using a glass electrode (micropH2001 CRISON). Electrical conductivity (EC) was determined in a 1:10 (w:v) water soluble extract using a conductimeter (Conductimeter GLP 31 CRISON). Moisture was assessed by drying at 105ºC for 12 hours and organic matter by determining the loss on ignition at 430ºC for 24 hours (Navarro et al., 1993). Total nitrogen (N_T) and organic carbon (Co) were determined by automatic microanalysis (NA 1500 Carlo Erba Instruments). Extractable carbon (C_{ext}) was measured in a 0.1 M NaOH extraction (20:1 v/w) and the fulvic acid carbon (C_{FA}) after precipitation of the humic acid at pH 2 in the supernatant solution. The humic acid carbon content (C_{HA}) was calculated by subtracting fulvic acid carbon to the extractable carbon. Sulphates were analysed in a 1:10 (w:v) water soluble extract by gravimetry with $BaCl_2$. Phytotoxicity, expressed as germination index was assayed by the *Lepidium sativum* test according to Zucconi et al. (1985).

3. **Results and Discussion**

3.1. Incubation experiments at bench scale

3.1.1. Effect of sulphur concentration.

The evolution of pH during incubation at different sulphur concentrations is shown in Figure 2. The values of pH reflected the formation of H^+ as a result of S oxidation. Hence, the rate of oxidation, reflected as a decrease of the pH values, increased with the amount of sulphur added and reached a steady state for all the treatments after 10 day of incubation. The S oxidation took place mainly during the first 10 days of incubation and achieved a reduction of the pH values nearly 2 units for the largest addition of S (1.0 %).

The pattern of the pH decrease was very similar in all the treatments following an exponential decrease during the incubation. The pH values fitted the following exponential equation:

$$pH = pH_0 + a \exp(-kt)$$

The parameter values for each treatment are shown in Table 2.

According to the results, an increase in the sulphur added led to a greater decrease in pH, but the addition of large amounts of S would have negative effects on the compost. First, high quantities of sulphur in soils may reduce microbial and fungal biomass activities and may have negative effects on different soil enzymes (Gupta et al., 1988). Also, a high concentration in SO_4^{2-}, as a result of the S oxidation, could increase sensibly the EC of the compost limiting its potential use in agriculture. EC was ascertained in all the samples after 20 days of incubation and there was a highly significant correlation ($r = 0.995$; $P <$) between the increases in EC and the decreases in pH (Figure 3). Thus, an addition of 0.5% S (dry weight basis), which decreased pH to 7.66 and increased EC to 5.98 mS cm^{-1}, was considered an acceptable value for compost quality criteria.

Several researchers have measured extractable sulphate to estimate the oxidation rate of sulphur (Jaggi et al., 1999; Zhao and McGrath, 1994). A wide number of extractants have been proposed. In this study water extractable sulphate was measured. In Table 3 the relationship between S added and extractable SO_4^{2-} after 20 days of incubation is shown. Not all the sulphur added is transformed into SO_4^{2-}. Probably a portion of S was incorporated into organic fractions (He et al., 1994) or immobilised by microbial population (Zhao et al., 1996).

3.1.2. Effect of compost moisture

Maximum oxidation rate of S occurred during the incubation of the compost at 40% of moisture content (Figure 4). The rate of oxidation dropped at the two moisture levels assayed above and below this value. During the incubation at 40% moisture, pH reached its lower value after 7 days of incubation, whereas at 60% and 25% moisture needed nearly 17 days. The low availability of water in the driest compost may have limited the oxidation rate because water directly take part on the oxidation reaction and also, because microbial population could have been reduced.

The compost moisture and the compost aeration are closely related. Moisture of 60% may have been too high for this kind of organic matrix (Madejón et al., 2002). Anaerobic processes may have been produced since odours were detected in the compost at 60% moisture and the lack of oxygen would have been a limiting factor for the oxidation reactions. Besides, under anaerobic conditions there is a reduction in the amount of aerobic bacteria which could have inhibited the transformation into sulphate.

3.1.3. Effect of temperature

Many authors have described temperature as an important factor for sulphur oxidation in soils (Attoe and Olson, 1966; Chapman, 1996). Also Jaggi et al. (1999) found a strong influence of temperature (incubations at 12, 24 and 36 ºC) on the rate of S oxidation and suggested that application of sulphur to summer crops would be more beneficial than to winter crops as S oxidation would be favoured at higher temperatures. Nevertheless temperature slightly modified the oxidation rate under the conditions of the present study (Figure 5). The effect of the temperature was more important during the first days of incubation, when the pH decreased faster at 40ºC than at 25ºC. However, the effect of temperature was not appreciable after 20 days of incubation.

3.2 Effect of S addition at full scale

The addition of the elemental S to the full scale composting pile had a similar effect to that found at bench scale. The pH values of the pile dropped very quickly and the reduction was noticeable from the first day of the addition (Figure 6). The pH values of the pile dropped from the initial value of 8.8 to about 7.5 after only 2 weeks of the treatment and the pH remained fairly constant till the end of the experiment. Conversely, the values of EC increased as a consequence of S oxidation to SO_4^{2-}, as shown on the bench scale incubation experiments.

The curve of pH obtained at full scale was fitted to the exponential equation described in section 3.1.1. The parameter values are given in Table 2. Comparing the constant values at bench and full scale, the lower value of *a* and *k* observed at full scale indicated the slower sulphur oxidation rate in the latest compost. This fact can be due to a lesser homogenization of the initial mixture and a lower concentration of oxygen in the pile. This fact illustrates how the specific characteristics of the medium severely influence the development of the process.

The addition of S produced an increase of the temperature of the pile up to 52°C after 1 week of the treatment (Figure 7). The remoistening and the turning of the material caused the reactivation of the microbial population. After this initial rise, the temperature remained over 40°C for 3 weeks and then dropped steadily to that of the ambient. However, the evolution of the main physico-chemical parameters of the composts after the S addition (Table 4) indicated that there were no further degradation of the organic matter after the S addition, and the small changes underwent by the pile corresponded to a typical maturation process (Bernal et al 1998), with a slight OM degradation, by 2% of the initial amount) and partial humification. Both OM degradation and humification indicated that the maturation process was not negatively affected by the S addition. Furthermore, the germination index of the compost was not affected by the S addition, this indicated that the material would not show any phytotoxic effects should it be used for agricultural purposes.

The experimental conditions obtained at bench scale (0.5% S and 40% moisture) achieved a reduction of one unit of pH after 2 weeks of the S addition at full scale, without increasing the EC to levels limiting the agricultural use of the compost. The addition of sulphur could be made either at the beginning of the composting process or at the end because high temperatures did not inhibit its oxidation neither at bench scale (Figure 5) nor at full scale, where temperatures rose up to 50°C (Figure 7).

4. Conclusions

The addition of elemental S was studied as a suitable strategy for pH control during the composting process under the organic farming regulations. An addition of 0.5% in sulphur (dry weight basis) and a moisture content of 40% was considered a recommendable method for decreasing the pH about 1 unit, without increasing the electrical conductivity to levels that could reduce the agricultural value of the compost. Compost treated with elemental S did not show any potential phytotoxic effect as far as germination index was concerned. High temperatures around 40ºC did not inhibit the oxidation, so S may be also added during the bio-oxidative phase of composting. Although temperature was not an important factor for the oxidation rate, the control of moisture was considered to be decisive for the correct development of the process.

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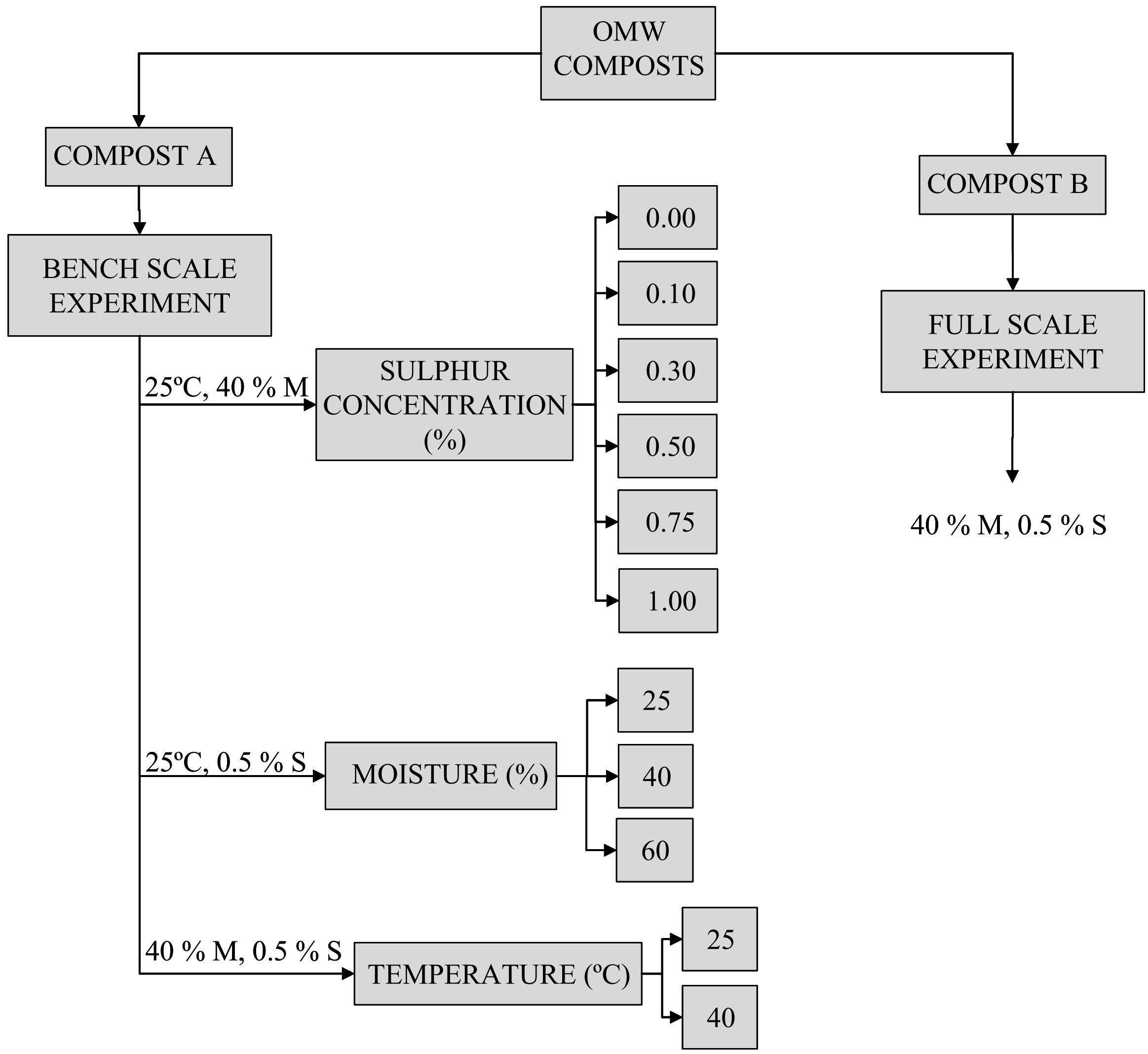


Fig. 1. Diagram of experimental design. OMW: Two phase olive mill waste; M: moisture.

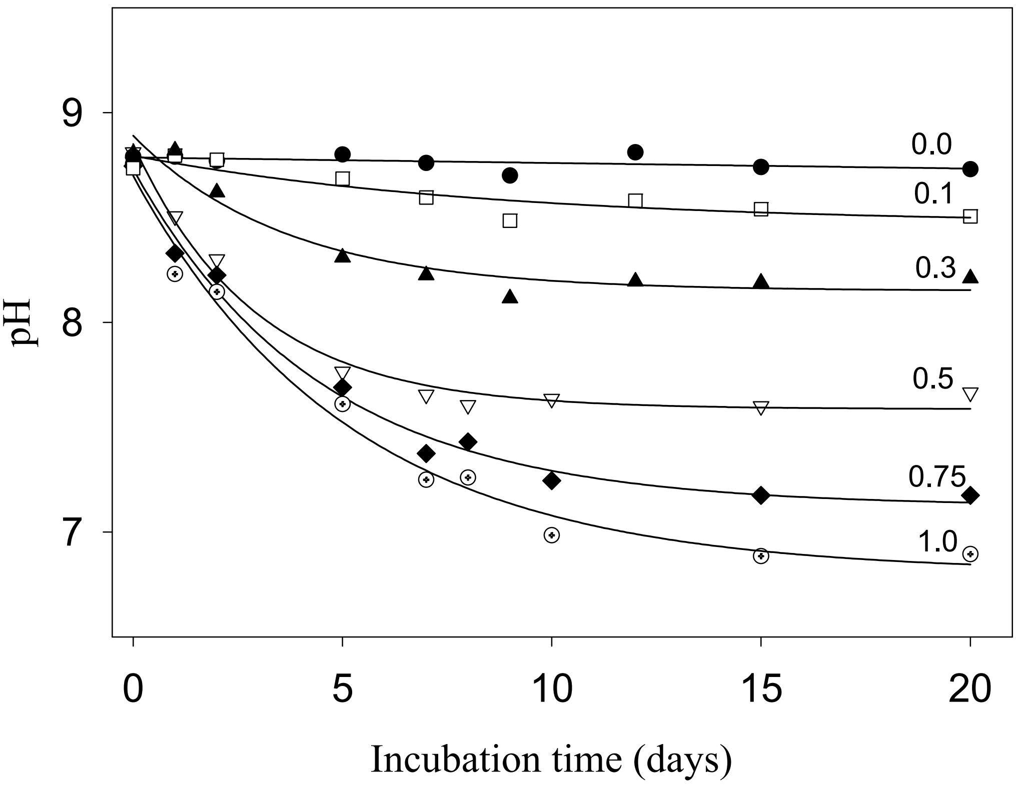
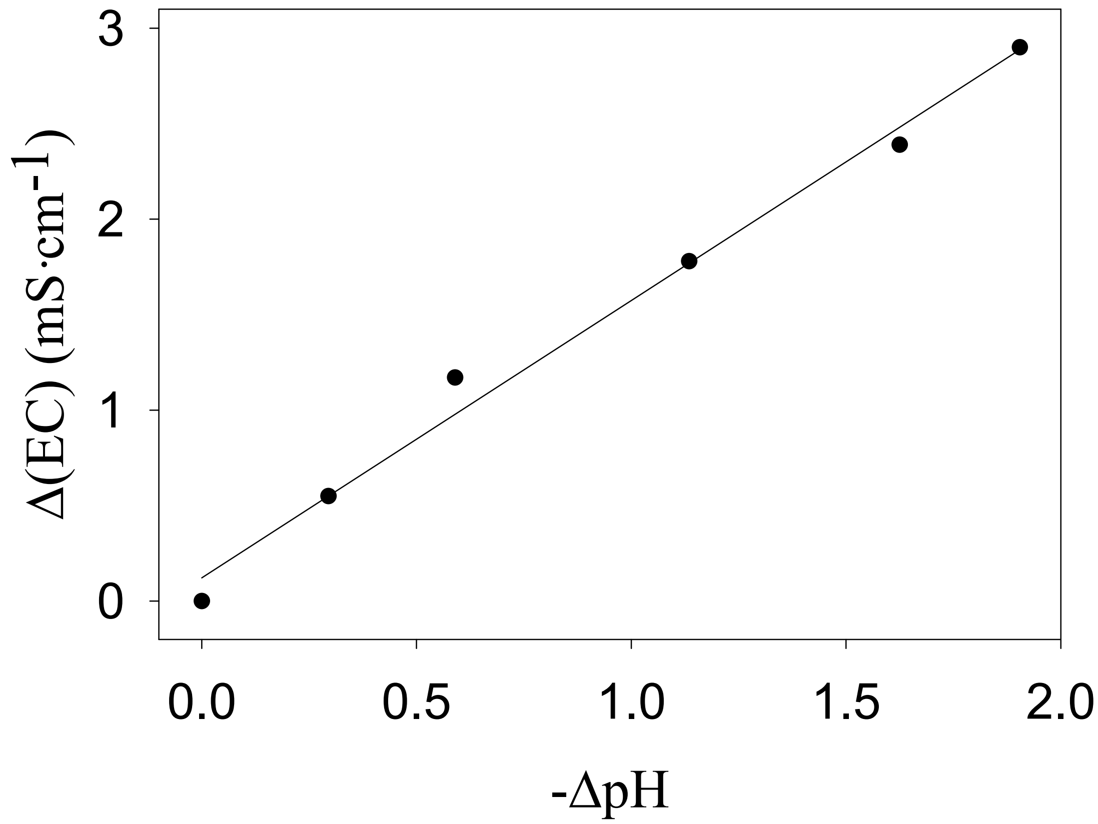


Fig. 2. Evolution of pH during incubation at 25ºC of compost, at 40% of moisture content, with different amounts of sulphur added (0.0, 0.1, 0.3, 0.5, 0.75 and 1.0 % S).



$$\Delta(EC) = 0.12 + 1.45\ (-\Delta pH)$$

Fig. 3. Correlation between increases in EC and decreases in pH

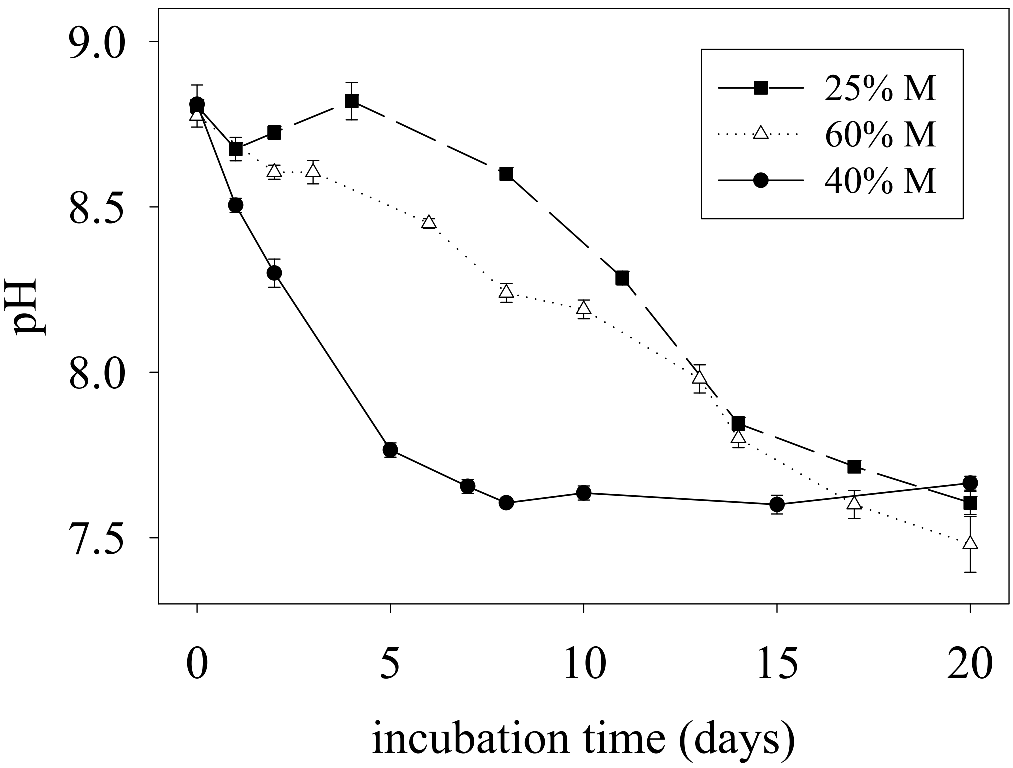


Fig. 4. Influence of compost moisture on the oxidation rate and thus on pH. Incubation at 25ºC with 0.5% S added.

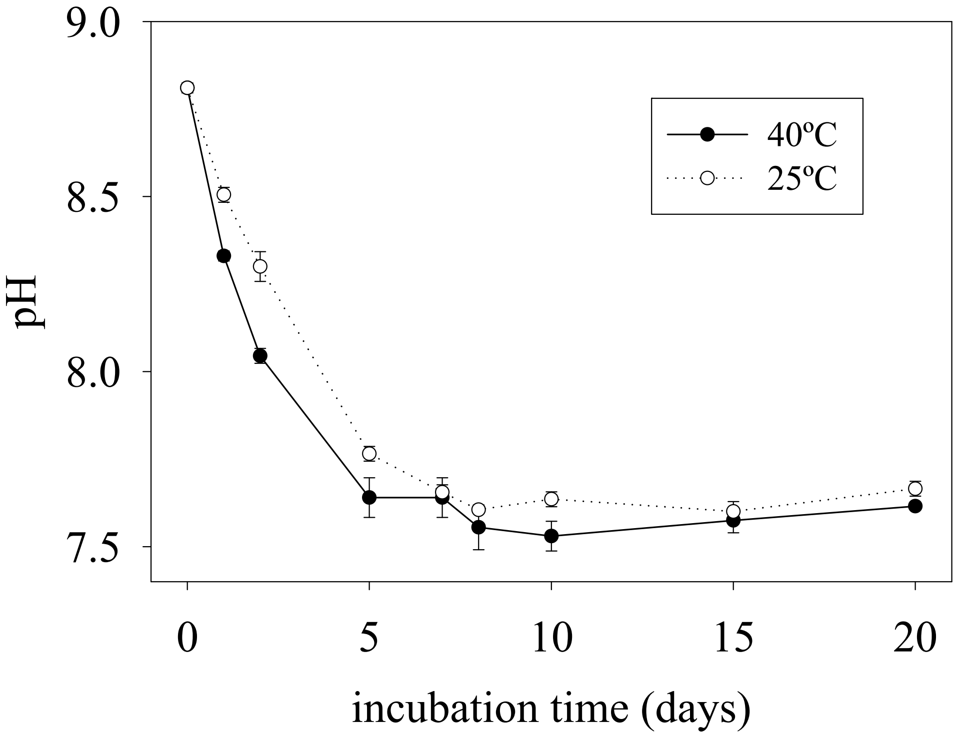


Fig. 5. Comparison between decreases of pH at 25ºC and 40ºC. The experiment was performed with 40% moisture and 0.5% S added.

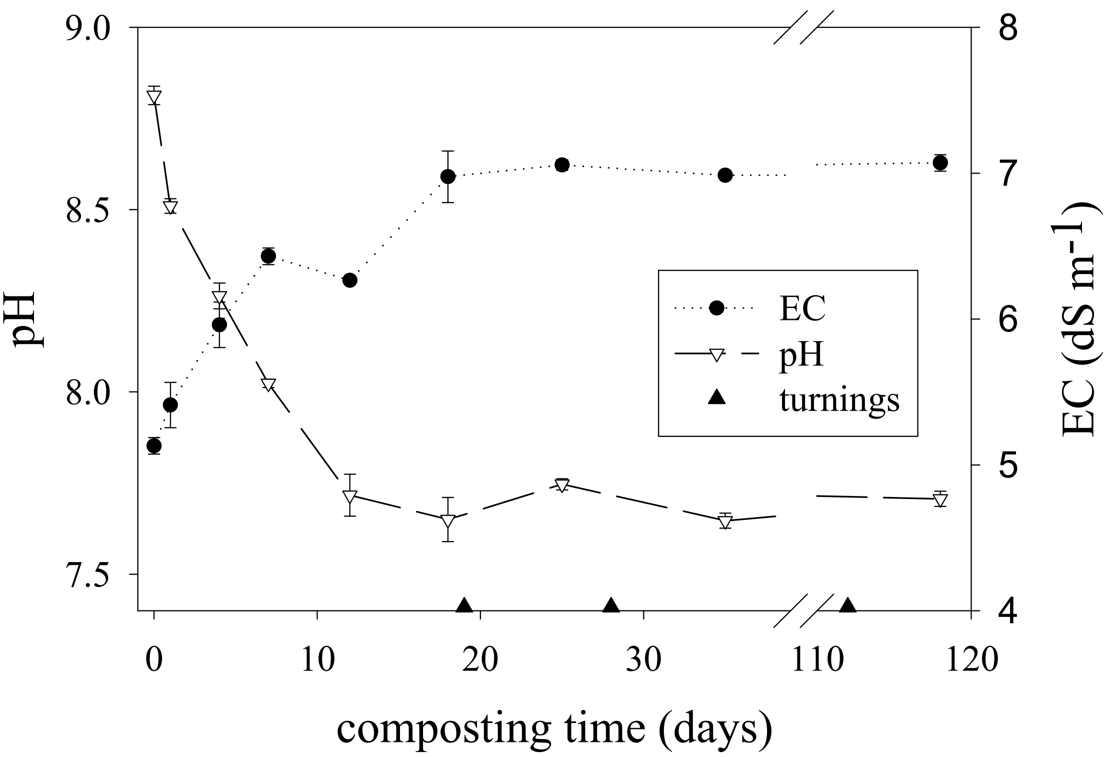


Fig. 6. Evolution of pH and EC after sulphur addition to compost B.

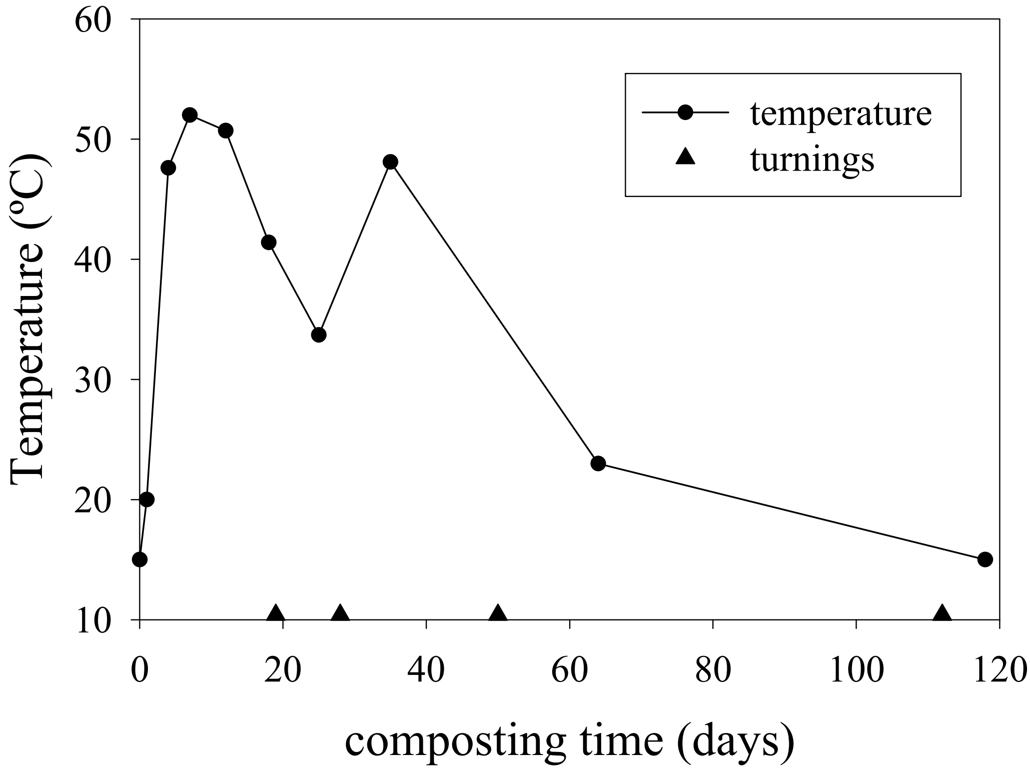


Fig. 7. Temperature evolution after sulphur addition to compost B.

Table 1. Main characteristics of the composts used

	pH	EC ($mS\cdot cm^{-1}$)	Water soluble SO_4^{2-} (S%)	OM (%)	Co/N_T	composting time (weeks)
compost A	8.8	4.2	0.09	46.6	13.8	40
compost B	8.8	5.1	--	63.6	14.1	35

EC: Electrical conductivity; OM: Organic matter, Co: Organic carbon; N_T: total nitrogen

Table 2.
Parameter values of exponential equation $pH = pH_0 + a \exp(-kt)$ for each treatment at bench and full scale.

Experiment	% S° added	pH_0	a	k×10	F
	0.10	8.468	0.327	1.177	14.09**
	0.30	8.150	0.740	2.731	48.98***
Bench scale	0.50	7.587	1.264	3.451	225.24***
	0.75	7.123	1.608	2.249	312.29***
	1.00	6.807	1.892	1.939	223.11***
Full scale	0.50	7.683	1.095	1.873	119.72***

***, **, *: $P < 0.001, 0.01, 0.05$ respectively

Table 3.
Relationship between S added and sulphate extracted after 20 days of incubation.

S^o added (%)	Water extractable SO_4^{2-} (S %)
0.00	0.089
0.10	0.138
0.30	0.316
0.50	0.439
0.75	0.546
1.00	0.560

Table 4.
Changes in compost B during maturation process with sulphur.

Compost	OM (%)	C_{org} (%)	N_T (%)	pH	EC ($dS \cdot m^{-1}$)	C_{org}/N_T	C_{FA} (%)	C_{HA} (%)	GI (%)
Before S addition	63.6	34.1	2.4	8.81	5.13	14.1	2.0	5.9	96.7
After S addition (day 1)	--	--	--	8.51	5.41	--	--	--	94.3
After S addition (day 118)	62.1	33.5	2.6	7.71	7.07	13.0	1.5	6.8	99.1

OM: organic matter, C_{org}: organic carbon, N_T: total nitrogen, EC: electrical conductivity, C_{FA}: fulvic acid-like carbon , C_{HA}: humic acid-like carbon, GI: germination index.