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Comparison of microbial activity in some Brazilian soils by microcalorimetric and respirometric methods

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Abstract

The microbial activity in a Rhodic eutrudox (R), a Typic eutrudox (V) and a Quartzipsamment (Q) was monitored by respirometric and calorimetric methods. CO_2 evolution was monitored for 98 days by titrimetry and conductimetry for control amended samples (A) with 25% of cattle manure (E), municipal refuse compost (L), earthworm casts (H) or 1.25 kg ha^{-1} of trifluralin (T). Average values of all treatments through respiration at the end of the incubation period were 5.24 ± 0.34, 6.13 ± 0.31 and 6.50 ± 0.33, in mg CO_2 g^{-1} soil, for R, V and Q, respectively, by titrimetry and 8.89 ± 0.44, 10.41 ± 0.54 and 10.41 ± 0.52, in mg CO_2 g^{-1} soil, for R, V and Q, respectively, for conductimetry. Excellent correlation ($r = 1.00$) between titrimetry and conductimetry was observed. The decreasing order for respiration was E, H, L and T. After each incubation time, the conductimetric values were higher than those for titrimetry, for all treatments of these Brazilian soils. Average values of the exothermic thermal effect were: 0.58 ± 0.02, 0.60 ± 0.02 and 0.67 ± 0.01 kJ g^{-1} soil, for R, V and Q, respectively, for 103 days. A significant correlation coefficient of 0.91 and $P < 0.0001$ between calorimetric and respirometric values over 98 days was observed. Based on the obtained calorimetric results, it can be proposed that this technique should be as a useful analytical method for determining the microbial activity in soils.
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Keywords: Brazilian soils; Microcalorimetry; Respirometry; Microbial activity; Organic materials

1. Introduction

Soil microorganisms play an essential role in the environment due to their role in cycling mineral compounds and in the decomposition of organic material [1]. Nutrient cycling occurs as a consequence of microbial activity, and is especially important in the ecosystems where the input of nutrients is low [2].

Addition of organic matter promotes changes in chemical and physical properties of the soil and the biodiversity of the soil microbial community can be influenced by the agricultural management. Therefore, depletion of organic carbon stocks in soils can reduce the microbial activity and thus the fertility of these soils [3].

Soil microorganisms and their controlled processes are essential for the long-term sustainability of agricultural systems [4]. However, many studies of agricultural effects on microbiota in soil are short-term. On the other hand, microorganisms also play an important role in degrading many agrochemicals. This action in the soil can promote a decrease in the toxicity of many organic compounds and influence the health of soil.

The microbial activity measured in soils can indicate its degree of fertility and quality for agricultural management [5]. This procedure leads to the recommendation of desirable soil management, in order to favor agricultural uses [6]. Knowledge of the dominant microbial processes in agricultural soils requires a great number of measurements at different conditions, which also requires a great number of samples and accurate methods [7].

Many investigations have had the objective of defining an index that can establish soil conditions after some treatments, where the soil microbiota reacts to promptly change the physical and chemical characteristics [8,9]. Thus, it would be very interesting to know how microbial activities change, but the use of classical methods, when generally applied, are very time consuming.

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A usual method to quantify microbial activity in soils consists in measuring soil respiration as carbon dioxide evolution or molecular oxygen consumption, which depends on microbial biomass composition in the soil, ambient temperature and moisture content [10]. In these contexts, various authors have evaluated methods to estimate the soil microbial biomass [11,12], but normally in soils from the temperature zones.

Usually, carbon dioxide produced by microorganisms in soil is trapped in a sodium hydroxide solution in order to determine the respective amount through titrimetry or conductimetry. The first technique measures the excess of hydroxide that did not react, allowing its determination, by difference, of the gas evolution from soil. Conductimetry employs the direct conductance measurement of ions in solution, by considering the sum of the total ions present. Thus, application of this technique has correlated with the analyses of mixtures of electrolytes in uniform concentration [13], however, comparisons of these methods are rarely done [14]. These methods employed for monitoring the microbiology of soil, have some advantages and limitations with a common characteristic that consists in measuring a given final product [9].

Another method applied in the investigation of soil microbial activity is the use of a calorimetric technique, which has recently increased due to its facility in data collection. Some calorimetric investigations have been compared with classical methods for soil microbiology, referring to temperate soils [15–18], but such comparisons are scarce for tropical soils. The calorimetric measurements are based on a static ampoule, whose collected data permits the acquisition of knowledge of thermodynamic properties data of some Brazilian soils, as reported recently [19–21].

Calorimetric measurements for a metabolic process have became a method important for studying microorganisms, but the interpretation of the thermal effect observed requires additional biochemical information, including the simultaneous knowledge of molecular oxygen consumption and carbon dioxide evolution [22]. The thermal effect involved can be followed through power–time curves and the great advantage of this procedure is the evaluation of the enthalpy values. Another advantage of the calorimetric method is related to the fact that it is simple and the measurement does not affect the sample. The signal is continuously recorded and enables to follow measurement of the same sample, a procedure which is not possible for other methods [23].

The aim of the present investigation is to obtain information from thermal effects, resulting from microbial activity in Brazilian soils, by using the calorimetric technique. Two respirometric methods are simultaneously employed in order to compare carbon dioxide evolution during a period of 3 months by using titrimetry and conductimetry in different textured soils. For microbial activity stimulation, organic materials of great use in agricultural systems and the effect of the agrochemical trifluralin were applied on selected Brazilian soils.

2. Experimental

2.1. Soil sampling

Soil samples were taken from three different areas in the State of São Paulo, Brazil, such as a Rhodic eutrudox (R), a Typic eutrudox (V) and a Quartzipsamment (Q) [24]. The samples were collected at a depth of 0–10 cm, after removal of the surface litter. They were air dried, homogenized by sieving (2 mm) and stored at 298 ± 3 K. Dry soil samples of 75.0 g were amended with 25.0 g of organic mixtures: cattle manure (E), municipal refuse compost (L), earthworm casts (H) or with 23 μg of agricultural trifluralin (T), moistened and incubated. The quantities applied were similar to those used in most agricultural procedures. Similar soil samples of 100.0 g were used as control, containing only 20% water (A), which corresponded to 60% of the field capacity of soil for water. Soil and organic compound quantities were based on dry weight [25,26].

The main characteristics of the soils and organic materials are listed in Table 1. The percentage of moisture was determined by drying the sample to a constant mass. The organic matter (OM) was obtained by titration of the soil suspension in an acid medium, with the end point indicated by a redox

Table 1
Brazilian soil and organic compound chemical characteristics: organic matter (OM), pH, phosphorus (P), exchangeable cations (K, Ca, Mg), potential acidity (H + Al), base sum (SB) and cation exchange capacity (CEC) for the Rhodic eutrudox (R), Typic eutrudox (V), Quartzipsamment (Q) soils and for modifiers cattle manure (E), municipal refuse compost (L) and earthworm casts (H)

Characteristics/soil	R	V	Q	E	L	H
OM ($g\,dm^{-3}$)	33 ± 2	23 ± 1	3.0 ± 0.2	114 ± 6	99 ± 5	122 ± 6
pH	5.0 ± 0.3	6.2 ± 0.3	4.7 ± 0.2	7.4 ± 0.4	7.5 ± 0.4	6.7 ± 0.3
P ($mmol\,dm^{-3}$)	1.0 ± 0.1	73 ± 4	2.0 ± 0.1	643 ± 32	304 ± 2	712 ± 36
K ($mmol\,dm^{-3}$)	2.5 ± 0.1	1.1 ± 0.1	0.20 ± 0.01	76.8 ± 4	23.8 ± 1	19.3 ± 1
Ca ($mmol\,dm^{-3}$)	23 ± 1	46 ± 2	2.0 ± 0.1	91 ± 5	410 ± 21	113 ± 6
Mg ($mmol\,dm^{-3}$)	12 ± 1	26 ± 1	1.00 ± 0.05	155 ± 8	55 ± 23	62 ± 3
H + Al ($mmol\,dm^{-3}$)	38 ± 2	14 ± 1	11 ± 1	10 ± 1	8 ± 1	13 ± 1
SB (%)	51 ± 3	82 ± 4	23 ± 1	97 ± 5	98 ± 5	94 ± 5
CEC ($mmol\,dm^{-3}$)	76 ± 4	87 ± 4	15 ± 1	333 ± 17	497 ± 25	207 ± 10

reaction. The pH was measured in a strong electrolyte, 1.0 mol dm^{-3} of calcium chloride solution, in a proportion of 1:2.5 for soil/solution. The total acidity ($H^+ + Al^{3+}$) was determined by percolating 5.0 g of air-dried fine soil with 0.10 dm^3 of 2.0 mol dm^{-3} calcium acetate at pH 7.0. The cation exchange capacity (CEC) and the total extractable bases (SB) were obtained by extracting the percolate fraction of 10.0 g of the soil with 0.10 dm^3 of 5.0×10^{-2} mol dm^{-3} nitric acid solution. Na^+ and K^+ were analyzed by flame photometry. The cations Mg^{2+}, Ca^{2+} and Al^{3+} were determined through atomic absorption spectrometry [25,27–29].

Maximum water holding capacity (% WHC) of each soil was measured in tubes with a known relationship between the amount of soil and the volume of water used [25].

2.1.1. Materials

Trifluralin (2,2,2-trifluoro-2,6-dinitro-*N*,*N*-dipropyltrifluoro-2,6-dinitro-*N*,*N*-dipropyl-*p*-toluidine), cattle manure and earthworm casts were obtained commercially and a gift of the municipal refuse compost was kindly supplied.

2.2. Respiration measurements

Soil respiration was measured using 100.0 g samples kept in hermetically sealed glass flasks for up to 98 days at 298 ± 3 K. Erlenmeyers with 25.00 cm^3 of 0.50 or 1.00 mol dm^{-3} NaOH solution was inserted into the glass flasks with soil for capturing the carbon dioxide from respiration. Measurements without soil were performed simultaneously. After each incubation time (1, 2, 4, 7, 8, 10, 11, 14, 17, 18, 21, 23, 28, 32, 35, 39, 42, 46, 49, 53, 58, 63, 67, 74 and 98 days), aliquots for each soil sample had the excess of NaOH solution titrated with standard HCl solution. The end point of the reaction was followed with phenolphthalein as indicator. For other aliquots of the NaOH solution direct measurement of conductance of the ions in solution was carried out (Metrohm Model 712 instrument). Microbial activity was monitored in triplicate for the release of carbon dioxide [25,30,31].

Standard curves for the conductimetric method were obtained. Electrical conductivity values of sample (λ_x), standard NaOH (λ_1) and Na_2CO_3 (λ_2) solutions may be used to estimate the mass (m) of absorbed CO_2 (mg) by expression:

$$m = 22\left[\frac{\lambda_1 - \lambda_x}{\lambda_1 - \lambda_2}\right] VC \quad (1)$$

where V is the volume (cm^3) of the standard NaOH solution and C is its concentration in mol dm^{-3} [14]. To avoid any disturbance in the conductimetric measurements, the solutions were maintained in a water bath at 298 ± 3 K, during data collection.

2.2.1. Microcalorimetry

The thermal effect obtained for masses in the order of mg or g per sample was measured in an isothermal calorimeter, model LKB 2277, to determine changes in the enthalpy of the system. Each thermal effect value was determined from the power–time calorimetric curve. The calorimeter was calibrated by the release of electrical energy in a thermopile of the instrument and each thermal effect of the sample ampoule was adjusted to the electrical calibration. The instrument has a precise control of the isothermal conditions in the thermostat bath for the detection of thermal events in the system [19,32,33].

The thermal effects were measured using 5.0 cm^3 stainless steel ampoules [19]. Teflon sealing discs which controlled evaporation and the transfer of oxygen and carbon dioxide in the hermetically closed ampoules were used. Under such conditions, the risk of carbon dioxide accumulation and an anaerobic process is avoided in the sequence of measurements at 298.15 ± 0.02 K. All determinations were performed in ampoules containing 1.12 g of soil, 0.38 g of organic mixture and 0.25 cm^3 of distilled water. The reference ampoule was charged with 1.50 g soil and 16.7% of water content. In the trifluralin tests, 23 μg of its aqueous solution were transferred to the desired ampoule [19]. After being thermosted, the thermal power effect production associated with degradation was recorded as a function of time. All enthalpy values were obtained from triplicate runs, measured at a period of 103 days.

The power–time scale used in the calorimeter covers 1000 μW. This thermal power effect production (ΔP) represents the difference between the ampoules containing the modified and the control soil samples, which contain soil plus 16.7% of moisture. The results were obtained for a series of samples, during the incubation period, and the measurements were recorded in a stationary state.

Table 2
Two peak times (PT) found in days, pH of soils, the thermal power effect production (ΔP_m) and thermal effect ($-\sum Q_{TOT}$) of calorimetric curves in 1.0 g of Brazilian soil samples[a]

Soil	PT (days)	pH	ΔP_m (μW g^{-1})	$-\sum Q_{TOT}$ (kJ g^{-1})
RA	15/40	5.0 ± 0.3	16.41 ± 0.82	0.15 ± 0.02
RE	12/68	6.4 ± 0.3	144.51 ± 7.23	1.29 ± 0.10
RL	5/68	5.2 ± 0.3	72.36 ± 3.62	0.64 ± 0.06
RH	8/68	7.0 ± 0.4	86.75 ± 4.33	0.77 ± 0.07
RT	8/68	5.0 ± 0.3	7.42 ± 0.37	0.07 ± 0.01
VA	7/40	6.2 ± 0.3	16.41 ± 0.82	0.15 ± 0.02
VE	12/68	6.9 ± 0.3	124.39 ± 6.22	1.11 ± 0.10
VL	5/68	6.3 ± 0.3	68.55 ± 3.43	0.61 ± 0.06
VH	12/68	6.9 ± 0.3	116.98 ± 5.85	1.04 ± 0.10
VT	12/68	6.2 ± 0.3	11.01 ± 0.55	0.10 ± 0.01
QA	15/50	4.7 ± 0.2	25.62 ± 1.28	0.23 ± 0.02
QE	8/75	7.1 ± 0.4	151.92 ± 7.60	1.35 ± 0.10
QL	8/75	5.1 ± 0.3	80.12 ± 4.01	0.71 ± 0.01
QH	23/68	7.0 ± 0.4	115.74 ± 5.79	1.03 ± 0.10
QT	28/75	4.7 ± 0.2	4.49 ± 0.22	0.04 ± 0.01

[a] Rhodic eutrudox (R), Typic eutrudox (V) and Quartzipsamment (Q) for control (A) or with 25% of cattle manure (E), municipal refuse compost (L) or earthworm casts (H) or 23 μg of trifluralin (T), over 103 incubation days at 298.15 ± 0.02 K.

2.3. Statistical analyses

All values obtained are on an oven dried soil basis. The results listed in Tables 1 and 2 are given as the arithmetic mean for each incubation time. The percent standard error was calculated for each amended soil at all times of incubation used. The ANOVA method was used for statistical for determining the significance at the $P \leq 0.05$ level of difference between treatments. The Tukey test was used for comparison of means. The analyses resulted in a statistic parameter of $P < 0.01$.

3. Results and discussion

3.1. Soils and organic material properties

Table 1 summarizes the results obtained, showing the differences between the soils and organic materials. Three different textured soils: R is clay, V a medium sandy soil and Q a sandy soil, were chosen. The soils present different chemical characteristics, such as OM, pH, phosphorous and cations in colloidal soil solution, but all have acidic properties. On the other hand, the organic materials are a good source of carbon, phosphorous and the sum of bases. The soil with organic constituents has OM, P and CEC values higher than those found for the control soils. These amendments are normally used in common agricultural practice in order to increase soil fertilities.

3.2. Effect of organic amendments on microbial respiration

The respirometric results for CO_2 evolution after 98 days of incubation are shown in Fig. 1(a) and (b), as monitored by titrimetry and conductimetry, respectively. The cumulative values obtained by both methods reflect the distinct behavior for the three soils with different textures amended with various organic materials, on a large range of microbial respiration values.

The Tukey test for titrimetric results show a decrease of values: QE ∼ VE > RE > QH > VH > RH > VL ∼ RL ∼ QL > VT ∼ VA ∼ RA ∼ RT ∼ QA ∼ QT. A sequence of well-defined data for E, H and L with different

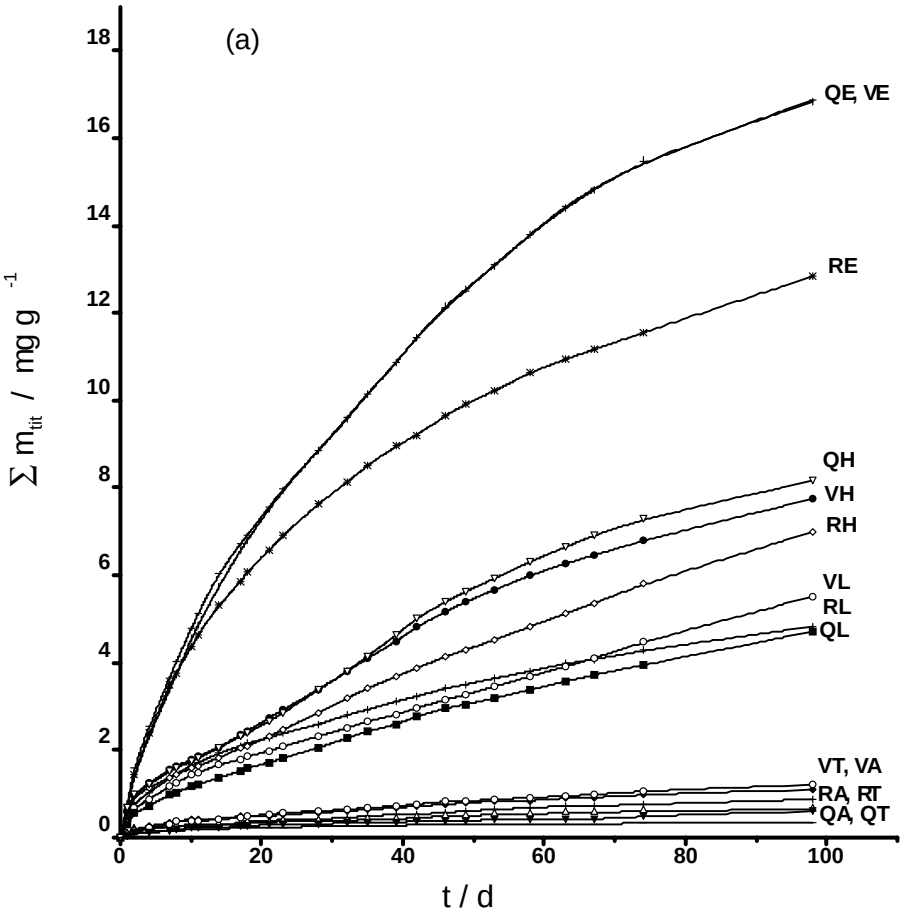

Fig. 1. Sum of mass of carbon dioxide evolved, as measured by titrimetry ($\sum m_{titr}$) (a) and conductimetry ($\sum m_{cond}$) (b) in 100.0 g of Brazilian soil samples for control Quartzipsament (QA), Rhodic eutrudox (RA) and Typic eutrudox (VA); 25% of added cattle manure (RE, VE and QE), municipal refuse compost (RL, VL and QL) or earthworm casts (RH, VH and QH) or 23 μg of trifluralin (RT, VT and QT) over 98 incubation days (t) at 298 ± 3 K.

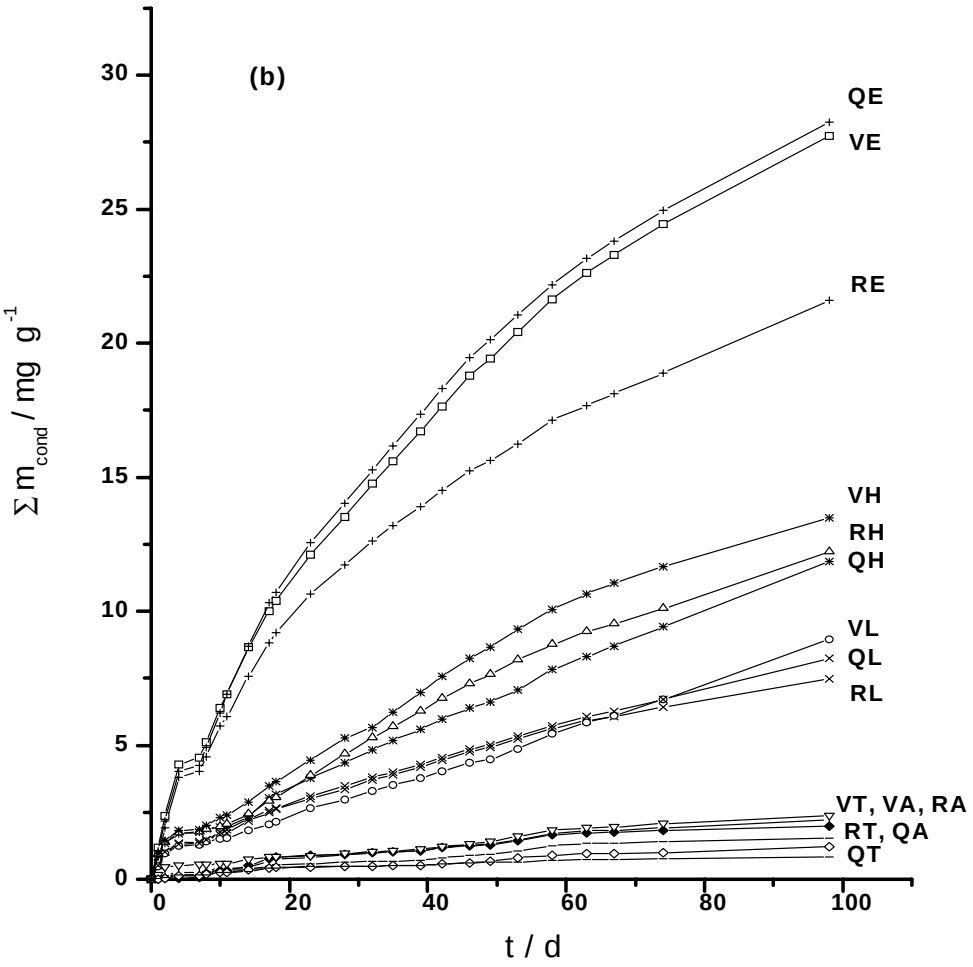

Fig. 1. (*Continued*).

soils, but for the natural soil control (RA, VA and QA), give similar was observed, results due to the fact that this applied technique is not sufficiently sensitive to detect differences, in the present determinations. Based on these collected data, it is suggested that the microbial activity is associated with the type of organic material used and not with the type of soil.

The carbon dioxide values for E presented higher values than those for other materials (H and L). However, the decrease in OM values for the organic materials presented in L, E and H, are listed in Table 1. The difference in CO_2 liberation is attributed to differences in the composition of the organic material present in these mixtures. Thus, it is possible that cattle manure has a larger quantity of labile compounds, than do H or L, which are more promptly attacked by soil microorganisms; consequently, a residual part of microbial activity can be related to the individual characteristics of each particular soil.

The chemical reactions resulting from organic materials introduced into the soil can lead to the neutralization of acidity in Brazilian soils and permit development of major microbial activities for all the soils studied, including the sandy one. This fact can be related to organic material additions, which change all soil pH, as observed in Table 2, causing a possible increase in organic material accessibility for the present microbial community. This behavior can be better understood, by considering the types of groups present in the organic materials, for example, the nitrogen groups ($–NH_3^+$) or weak acidic anions ($–COO^-$) or also the mineral fraction, such as aluminum oxide (Al_2O_3) in the acidic aqueous soil suspension. These and other groups, under determined conditions, are responsible for hydrolysis and proton neutralizations in the colloidal medium. One possible illustration is presented by the following equations:

$$\underset{\text{soil surface}}{\text{MO - NH}_3\,(aq)} + \text{H}_3\text{O}^+(l) \rightleftarrows \underset{\text{soil surface}}{\text{MO - NH}_4^+\,(aq)} + \text{H}_2\text{O}\,(l) \quad (2)$$

$$\underset{\text{soil surface}}{\text{MO - COO}^-\,(aq)} + \text{H}_3\text{O}^+(aq) \rightleftarrows \underset{\text{soil surface}}{\text{MO - COOH}(aq)} + \text{H}_2\text{O}\,(l) \quad (3)$$

$$\underset{\text{soil surface}}{Al_2O_3(s)} + 6\,H^+(aq) \overset{H_2O}{\underset{\rightarrow}{\leftarrow}} 2\,Al[(H_2O)_6]^{3+}(aq) + 3\,H_2O(l) \quad \underset{\text{soil surface}}{} \tag{4}$$

In addition, the high CEC values for organic materials indicate that great amounts of bioavailable nutrients in the colloidal soil solution can be used by the microbial community.

After the incubation time, the respirometric values for RE presented lower values than those for QE and VE. This is not an expected result, because the clay soil (R) has a higher OM value than sandy soil (Q), which suggests the physical and chemical properties of R interfered in the microbial attack. In such a situation, a part of organic materials can be captured by the mineral structure of the clay soil and, consequently, part of OM was unavailable and not degraded in the available period.

The respirometric data for municipal refuse compost L presented values lower than those of other organic cattle manure E and earthworm H. This behavior can be attributed to the composition and consequent material structure. This compost has a high amount of glass, plastic, wood and other components, which are difficult for the soil microbial community to degrade in the period proposed.

The treatment of soil with the agrochemical trifluralin at a dose of 23 μg, corresponding to a dose of 1.25 kg ha^{-1}, presented similar values to those of the control, formed by soil plus water. Therefore, the evaluation of microbial activity by CO_2 evolution does not show an inhibitory effect from the trifluralin.

The accumulated respiration increased with time to attain an asymptotic behavior for all systems, as shown in Fig. 1. This fact is in agreement with the possibility that the soil microbial community reaches equilibrium conditions due the decrease of the OM fraction in the system.

3.3. Respirometric results as function of time

Based on the result acquired from respirometry, another way of representing the carbon dioxide mass data was calculated from the mass per day of incubation, in order to have a better knowledge of the system. This process showed the gradual decomposition of the organic material, probably due to the bioavailable compounds, and the result can give a good indication of the decrease of compounds as a function of time. This fact is related to the rapidity of the degradations of organic materials. Equilibrium was reached after 40, 80 and 50 h for R, V and Q soils, respectively.

The plateau of equilibrium for E, H and L substrates was higher than those of the control, as shown in Fig. 2. In this process, it is also shown that only an organic material fraction is decomposed by microbial activity and a residue remains in the soil. This result indicates an increase in the organic material stock, which is energetically rich in carbon compounds.

3.4. Comparison of respirometric methods

The respirometric methods were both very precise with a significance level of $P = 0.01$ and a variance coefficient of 1.24 and 3.79%, for conductimetry and titrimetry, respectively.

The comparative methods show a linear correlation and in the statistical analyses, a highly significant coefficient of $r = 0.9966$ and significance level $P < 0.01$, indicates compatibility for the measurements investigated. The results are illustrated in Fig. 3.

The conductimetric values were higher than those obtained with the titrimetric method. Conductimetric technique detects the total ions in solution, which is not a specific method for measuring carbon dioxide evolution in such system. These results can be explained by a given degree of restriction of the titrimetric method. In this method, the barium salt used causes mass losses of carbon dioxide that was formed in the carbonate decomposition reaction, when 0.50 and 1.0 mol dm^{-3} of hydrochloric acid solutions are added in the titration, according to the equilibrium shown in Eqs. (5) and (6). The complete liberation of gaseous CO_2 is represented in Eq. (7):

$$CO_3^{2-}(aq) + Ba^{2+}(aq) \rightleftharpoons BaCO_3(aq) \tag{5}$$

$$CO_3^{2-}(aq) + H^+(aq) \rightleftharpoons HCO_3^-(aq) \tag{6}$$

$$HCO_3^-(aq) + H^+(aq) \rightleftharpoons H_2CO_3(aq) \rightleftharpoons H_2O(aq) + CO_2(g) \tag{7}$$

Barium added in the sequence of reactions of decreasing the hydrolysis of carbonate in the course of titration. On the other hand, the capture of carbon dioxide leaves other cations free in solution, which could be a source of errors in measurements. Comparing the preceding technique with the conductimetry, the latter has a series of advantages: (i) it uses instrumentation which is simple to operate, with easy control of temperature in the range of 0.1 K; (ii) it enables measurement of a small amount of carbon dioxide (μg) in the solution; (iii) it is not laborious, permitting a larger number of measurements in a shorten time; (iv) recorded values are obtained with an instrument having errors of less than 2%; (v) it employs sodium hydroxide solution, which easy to handle, for samples in the same experimental sequence.

3.5. Calorimetric method

Fig. 4 shows, as an example, the results obtained for Rhodic eutrudox with cattle manure. Similar behavior was observed for all studied systems. The calorimetric curve represents the average values of the thermal power effect production (ΔP_m) in μW g^{-1} dry soil, which was obtained in

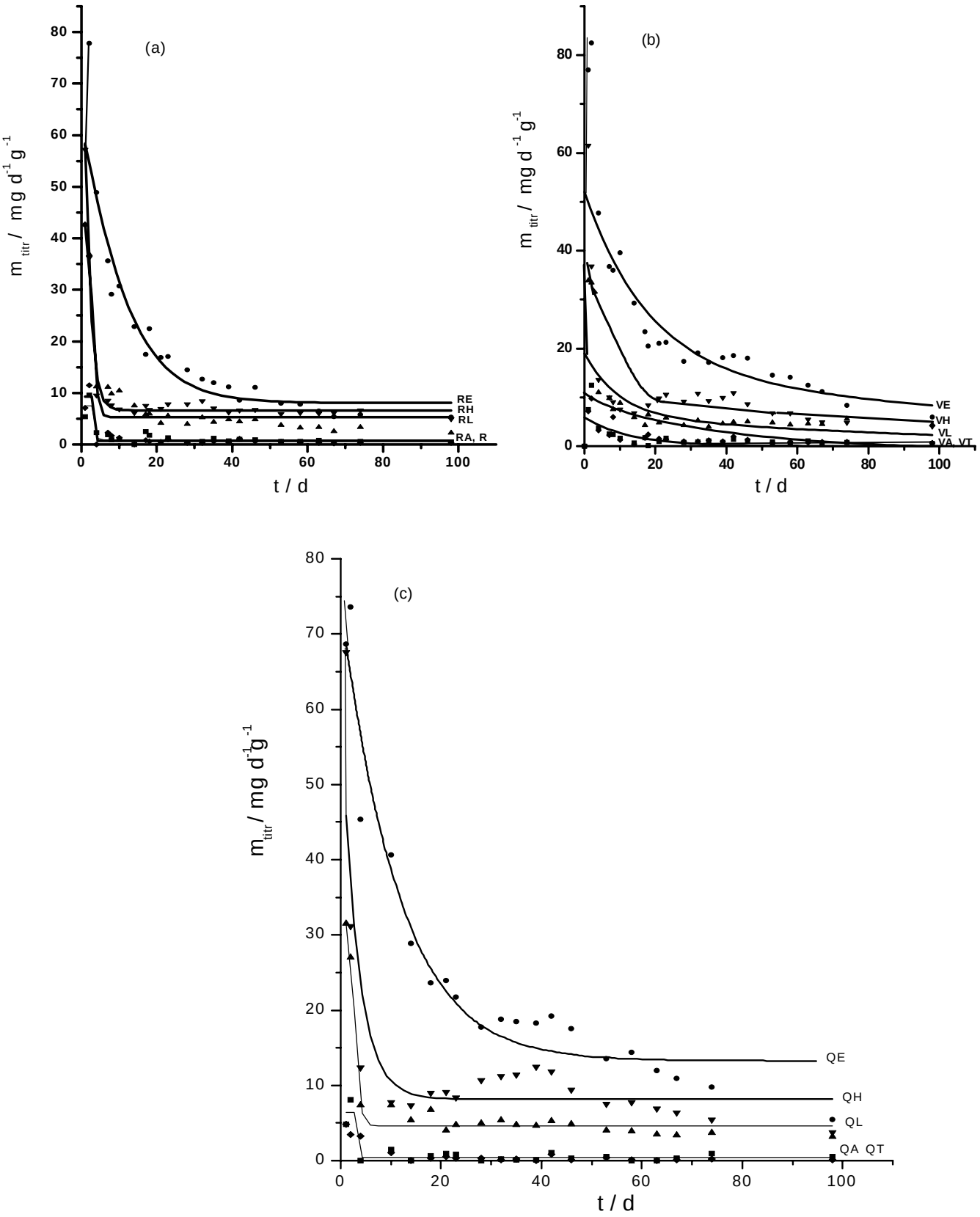

Fig. 2. Mass of CO_2 evolved per day per gram of dry soil measured by titrimetry (m_{titr}) for Rhodic eutrudox (a), Typic eutrudox (b) and Quartzipsament (c), control (A) or with 25% of cattle manure (E), municipal refuse compost (L) or earthworm casts (H) or 23 μg of trifluralin (T), over 98 incubation days at 298 ± 3 K.

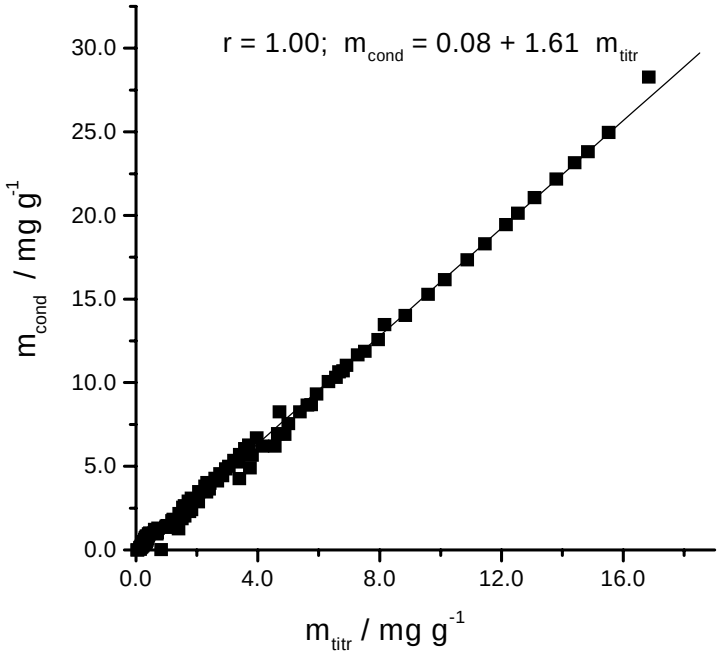

Fig. 3. Linear regression determinations of mass of CO_2 evolved, between titrimetric (m_{titr}) and conductimetric (m_{cond}) methods with $r = 0.9966$ and $P < 0.01$ for all treatments in Brazilian soils.

the calorimeter for 103 incubation days. At the end of this period, the total area of the curve is calculated and the results are expressed as thermal effect ($-\sum Q_{TOT}$), in kJ g^{-1} dry soil, as listed in Table 2.

A typical differential power–time curve is illustrated in Fig. 4 for all studied soils, whose principal characteristic, seen for all systems investigated, is the detection of two distinct peak times (PT) at 10 and 70 days for microbial activities, which is defined as the maximum value of the curve. This behavior may be due to the degradation of the two main carbon sources provided by the organic material. Another interpretation could be related to the development of different microbial communities. For each representation of power as a function of time, the areas of the calorimetric curves were obtained and the sums of exothermic thermal effects ($-\sum Q_{TOT}$) were calculated and are shown in Table 2.

The sequences of both peak times (PT) obtained for each soil are also listed in Table 2 and these values are not similar to those obtained in the respiration studies, where the main activity was due to the addition of organic matter. The peak reflects the time of degradation of part of the organic material, and the R and V values were generally similar for the two peak times for all systems. The Q soil presented higher values for such two peaks, with exception being the first one, where the soil was amended with E. This indicated that, although the Quartzipsament was able to degrade organic material, as viewed by respirometry in Fig. 1, it has different mechanisms of degradation in relation to the other soils. This phenomenon can be associated with various characteristics of this soil, like microbial community, physical and chemical properties, where micro and macro aggregates, porosity, mineral types, pH, CTC and other factors influence the behavior of organic compound degradation.

The results shown in Table 2 present the same sequence in microbial activity as observed for the respirometric method. The thermal effect is the sum of catabolic and anaerobic processes that occur during organic material degradation and reflect the ability of the community present in each soil in acting on these processes. The higher thermal effect than the control one can be associated with the amount of active compounds present in the amended organic material. Part of the thermal effect results from loss of carbon dioxide evolution coming from a chemical reaction in the process. This is confirmed by the same sequence of activity for both methods.

The correlation of thermal effects in organic material degradation with its conversion into biomass was not quantified here. It is expected that part of the thermal effect resulted from the contribution of biomass activity and an increase in the number of microorganisms present [34,35].

The calorimetric results for trifluralin in the three soils presented lower values than those of the control, as observed in Table 2. In all cases, these values indicated an inhibitory effect due the addition of agrochemical to the soil. On the other hand, the respirometric method did not detect differences and presented similar values for the control and the agrochemical trifluralin.

For acid soils, like Brazilian soils here studied, the addition of organic material promotes the increase in soil pH, as shown in Table 2. With the exception of the agrochemical trifluralin, in which the pH remains unaltered, in all other

organic additions, a positive contribution of microbial activity occurred, as measured by the thermal effect increasing to higher values than those of the control. The intensity of these effects is attributed to the composition of the organic material present. In this context, the variation in pH value was a consequence of interactive mechanism between the type of organic material and the physical and chemical properties of the soil environment.

The thermal effect can also reflect in the number and type of organisms in the soil and distinct treatments can cause development of different species. Experiments with Brazilian soils amended with glucose showed thermal effects of 6.75 ± 0.25 J [33] and, for the same soil with cattle manure, a value of 1.35 ± 0.03 J was obtained. This result suggests that the thermal effect was intrinsically related to the fraction and type of OM and also to the microbial species

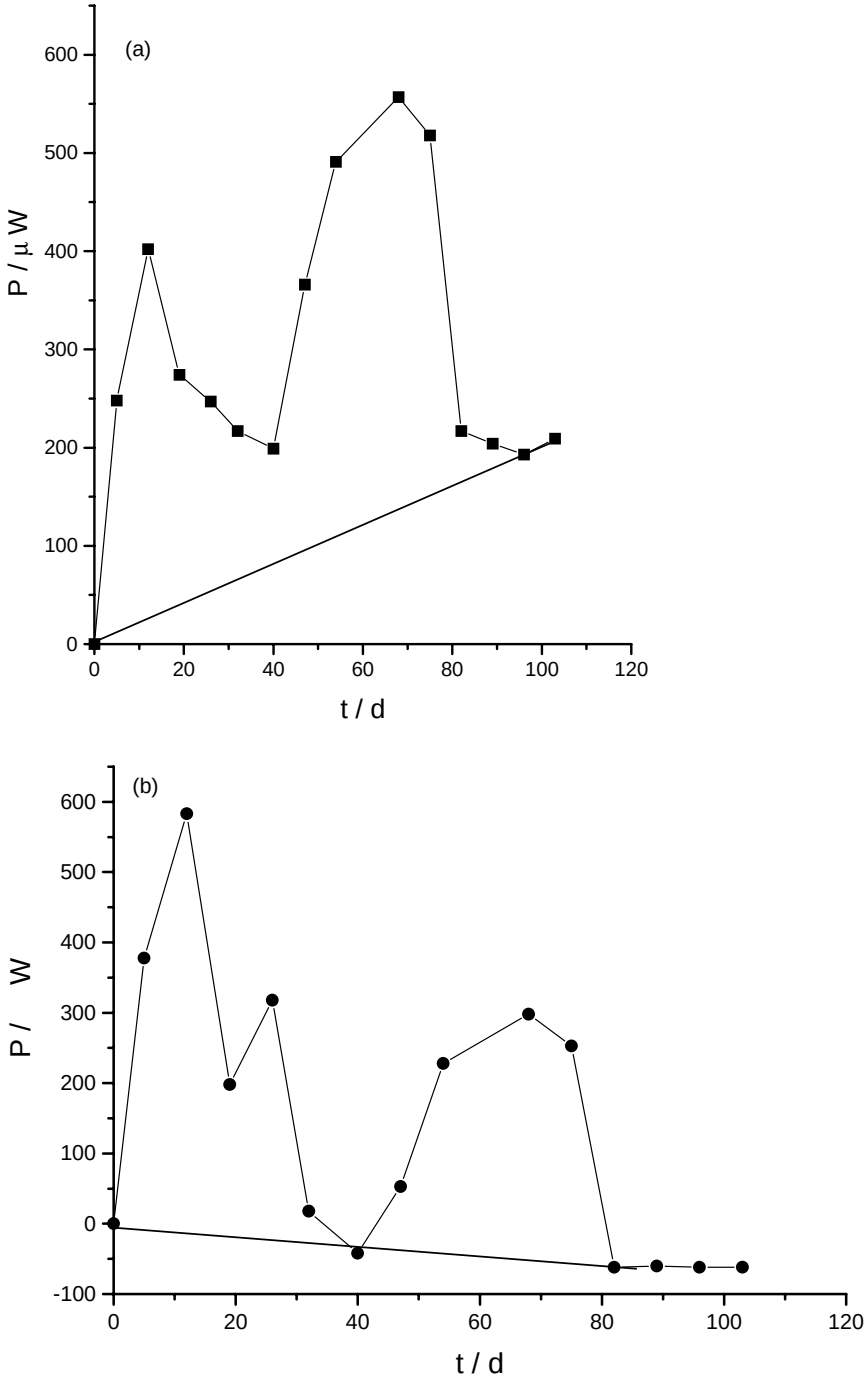

Fig. 4. Power–time curve in μW versus time of the microbial degradation of 25% of cattle manure in Rhodic eutrudox (a), Typic eutrudox (b) and Quartzipsament (c) soil sample, with two peak times over 103 incubation days at 298.15 ± 0.02 K.

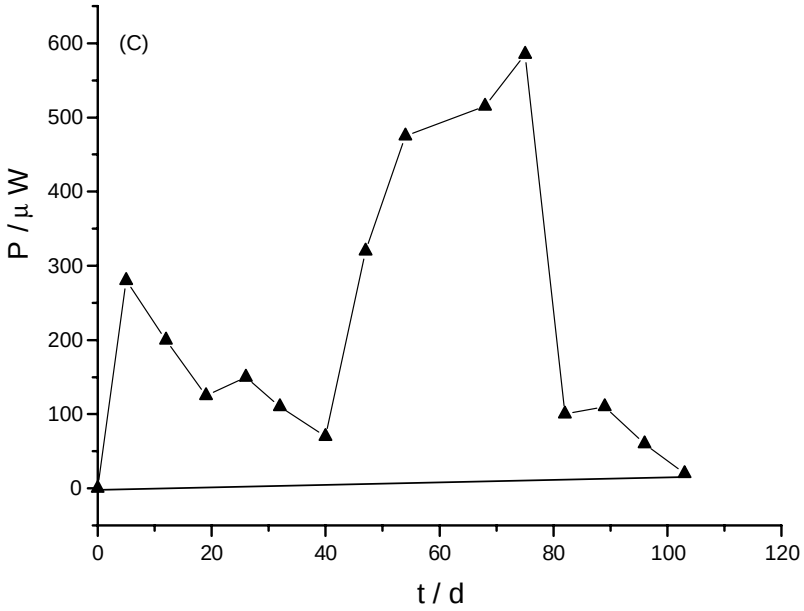

Fig. 4. (*Continued*).

of the soil. For cattle manure, for example, the material will be decomposed by communities that can degrade cellulose, the main component of the organic material, different from glucose that is degraded by the majority of the organisms.

Comparisons of thermal data for tropical soils are scarce, mainly for Brazilian soils, whose results are described herein. Thus, the thermal power effect production varied from 1.71 to 4.56 $\mu W\,g^{-1}$ for dry soil, with exception of horticultural peat with a value of 35.0 $\mu W\,g^{-1}$ in the 24 h time period of the experiments [36]. Their large value was observed for soil with high OM (9.60%) and base saturation (84%) in acid pH (5.2) [15]. In this study, the thermal power effect production (ΔP_m) varied from 4.49 (QT) to 151.92 $\mu W\,g^{-1}$ (RE) for dry soil in 103 experiment days and the largest values were observed for soil amended with cattle manure with 11.4% OM and 97% of base saturation, in an amended soil having a pH value of 6.35, as shown in Table 2.

The comparison of these results is not satisfactory because the thermal power effect production values are not constant as a function of time. As the values varied with the time, then, these facts are significant after 103 days of organic material degradation. Thus, this fact indicates that comparison between our data and data from temperate soils also is not satisfactory. Besides, it is necessary to know that, between temperate and tropical soils, there exist marked differences in structure, chemical and physical properties, and biological communities, due to the origin, formation and weathering processes.

A calorimetric curve of soil microbial activity can be presented with high thermal effect output and decrease rapidly or with profile different with minor initial thermal effect production, but with a slow decrease after the peak time. Thus, the area under the curve (in J) obtained by the thermal power effect production in W as a function of time (in s) can show the intensity and the time necessary for development of activities of a specific soil system. As a consequence, the area and the peak time can be taken as good indicators of microbial activity.

3.6. Correlation between the calorimetric and respirometric methods

The exothermic thermal effect obtained for each soil investigated was plotted as a function of the corresponding carbon dioxide evolution in the system and a linear relationship was observed, as shown in Fig. 5. The correlation values for each period of incubation involving calorimetric and respirometric data gave $r_1 = 0.74$, $P < 0.006$ with the equation of $-\sum Q(m) = 0.02 + 0.04\sum m$, $r_2 = 0.75$, $P < 0.005$ with $-\sum Q(m) = 0.03 + 0.05\sum m$, $r_3 = 0.88$, $P < 0.0002$ with $-\sum Q(m) = 0.12 + 0.05\sum m$ and $r_4 = 0.91$, $P < 0.0001$ with $-\sum Q(m) = 0.20 + 0.07\sum m$, for 20, 40, 60 and 103 days of incubation, respectively, being $\sum Q$ in $kJ\,g^{-1}$ and $\sum m$ in mg of CO_2 mass per gram of soil, respectively. The lowest incubation time presented smaller correlation values than those from longer incubation times and the best correlation data is verified after 103 days of incubation. The lowest correlations may be attributed to bioreactions that can be occurring simultaneously with the respiration process. The close correlation between respirometric and calorimetric values suggests that both methods are appropriate for assessing the relationship between the microbial activity and some properties in Brazilian soils. It is noteworthy that significant correlations between thermal effects and respiration results have already been obtained for temperate soils [15].

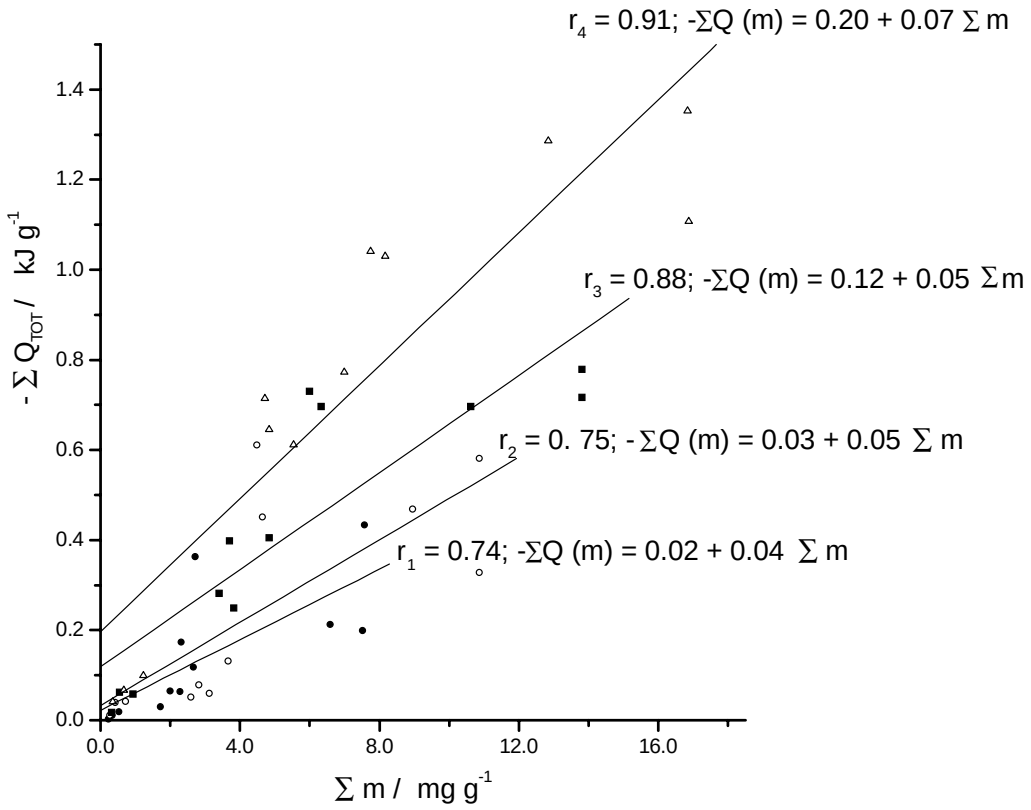

Fig. 5. Linear regression determinations between calorimetric and two respirometric methods, titrimetric and conductimetric, with $r_1 = 0.741$, $P_1 < 0.0058$; $r_2 = 0.748$, $P_2 < 0.0051$, $r_3 = 0.878$, $P_3 < 0.0002$ and $r_4 = 0.910$, $P_4 < 0.0001$ over 20, 40, 60 and 103 incubation days, respectively, for all treatments of the Brazilian soils.

4. Conclusions

The present investigation focused on the acquisition of better knowledge of Brazilian soils, to supplement the scarce calorimetric data involving tropical soils and, for this purpose, soils with different textures and chemical characteristics were explored. Also, different types of organic material of interest in agriculture were evaluated in equivalent doses, as recommended in the cultivated field.

The soil with sandy texture, thus, Quartzipsament with the cattle manure, showed a larger microbial activity than the other soils studied, Rhodic eutrudox and the Typic eutrudox, even though being a soil with low nutrient content. This is attributed to the fact that the amount of organic matter was enough to supply the required carbon and nutrient sources, even when the soil cannot furnish them, as demonstrated for the controls, RA, VA and QA. In this context, the great quantities of organic material added to the soil can modify physical and chemical soil properties, due to the interactions between the soils physical characteristics, for example, texture and macropores, and the organic matter, resulting in a modified soil structure. On the other hand, the organic materials used to soils can mask the original soil properties. A good correlation between titrimetry and conductimetry showed that, although the latter method is not used intensively, it has various advantages in comparison to the titrimetric method. The best correlation is also shown for calorimetric and respirometric methods in the Brazilian soils, as expected, since the thermal effects reflect the catabolic process of microbial degradation [37].

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