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Calorimetric and respirometric characteristics of the decomposition of animal wastewaters in soil ☆

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Abstract

Calorimetric and respirometric studies of the decomposition of animal wastewaters (AWW) in soil at 298.20 K were carried out. A high-volume differential calorimeter (0.5 dm^3) and an electrolytical respirometer were used for separate measurements. The AWW were sampled from a pig-fattening farm. The soil was supplemented with different doses of AWW corresponding to 20, 40, 60 and 80 mg N per 100 g of soil. The heat production rates, total heat effects and the apparent rate constant were determined. The comparative respirometric measurements confirmed that the processes that were investigated calorimetrically are largely aerobic.

Keywords: Animal wastewater; Calorimetry; Energetic coefficient; Respirometry; Soil; Wastewater

1. Introduction

Long-term and heavy application of animal wastewaters (AWW) to soil may cause the pollution of ground waters, eutrophication of surface waters and biological, chemical and physical changes in soil [1]. The AWW from pig farms are characterized by particularily high values of chemical oxygen demand (COD) and biochemical oxygen demand (BOD), and contain large amounts of organic and

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inorganic compounds of N, P and other elements [1,2]. Investigations of the microbial decomposition and mineralization of AWW are of great importance in environmental protection. The majority of research on the calorimetry of soil microbial processes has been concerned with the decomposition of sugars in soil [3,4]. Kono [5] applied calorimetry for characterization of the microbial decomposition of organic wastes and fertilizers in soil.

The main aim of the work reported here was to show the usefulness of a high-volume calorimeter (0.5 dm^3) as an applied method for characterization of the decomposition of AWW in soil. The separate respirometric measurements were performed in order to compare the kinetics of oxygen consumption with the heat evolution. The value of the energetic coefficients (J per cm^3 gas respired) was an indicator of the direction of the metabolic processes during the microbial decomposition of the AWW.

2. Experimental

2.1. Soil

The soil was sampled from the Agricultural Station of the University in Balcyny. The soil was collected from the upper surface layer (0–20 cm), sieved (2 mm^2), stored in polyethylene bags at room temperature (1–2 months) and after that at a temperature of 277 K. The soil samples were preincubated at 295 K for 24 h before use. The air-dry soil had the following characteristics: pH 5.53, N 0.086%, C 0.97%, WHC (water holding capacity) 33.5 g H_2O, texture–sandy loam, sand 49%, silt 29% and clay 22%.

2.2. Animal wastewaters

The fresh AWW were collected from a gutter on the pig-fattening farm. They were passed through a screen (<2 mm^2). The AWW were kept frozen at 263 K between measurements to avoid microbial decomposition and changes in chemical composition. The following parameters characterized the AWW: pH 6.92, 5416 N mg dm^{-3} and 5.63% dry matter.

2.3. Calorimeter

The heat output of soil was measured at 298.20 K in a high-volume (0.5 dm^3) differential calorimeter made by the Institute of Physical Chemistry of the Polish Academy of Science in Warsaw [6]. The equipment contained the calorimeter, a d.c. microvoltage amplifier and a recorder. A temperature difference of 1 K corresponded to a signal of 847 μV. The heat loss coefficient α was equal to 265.7 mJ h^{-1} μV^{-1} and the stability of the baseline was ± 1 μV. The time constant T was determined in the presence of microbiologically inactive soil.

2.4. Procedure

The measuring vessel in the calorimeter contained 25 g of the AWW-amended soils. Doses of AWW corresponded to 20, 40, 60 and 80 mg of N per 100 g of soil. The reference vessel contained 25 g of the twice-sterilized soil. The amount of water in all soil samples covered 60% of the water holding capacity (WHC). The soil and the AWW were prethermostatted before mixing and the subsequent calorimetric measurements.

2.5. Calorimetric calculations

The general differential equation, Eq. (1), describes the dynamic temperature transitions in the internal part of the calorimetric system [7]

$$T\,\mathrm{d}\theta(t)/\mathrm{d}t + \theta(t) = f(t) \tag{1}$$

where $\theta(t)$ is the input function (calorimetric signal), $f(t)$ is the output function characterizing the course of the investigated processes and T is the time constant of the calorimeter.

The function $f(t)$ can express the kinetics of microbial growth during degradation of several sugars in soil [3]. The microbial growth during the exponential phase with limited carbon source is expressed by

$$f(t) = A\exp(kt) + B \tag{2}$$

On the bases of Eq. (2), the value of the growth rate constant k was calculated by the Guggenheim method [8] and estimated by the least-squares method at half-hourly intervals.

The rate of heat evolution (Q_h) of soil samples was calculated at one-hour intervals from Eq. (3)

$$Q_\mathrm{h} = \alpha[\theta(t) + T\,\mathrm{d}\theta(t)/\mathrm{d}t] \tag{3}$$

where α was determined by electrical calibration of the calorimeter for steady-state conditions of heat conduction from the calorimetric vessel to the heat sink. The time constant was assessed on the basis of cooling curves. The total heat effects (Q_total) were obtained by integration of the calorimetric curves.

2.6. Respirometer

The changes in the rate of oxygen consumption (V_h) and its total consumption (V_total) were determined using a modified electrolytical Greenwood and Lees respirometer [9]. The shape volume and material (stainless steel) of the reference and measuring vessels were the same as the calorimetric vessels.

3. Results

The heat production rates of the decomposition of different doses of AWW in soil are shown in Fig. 1. The curves from Fig. 2 present the changes in the total heat

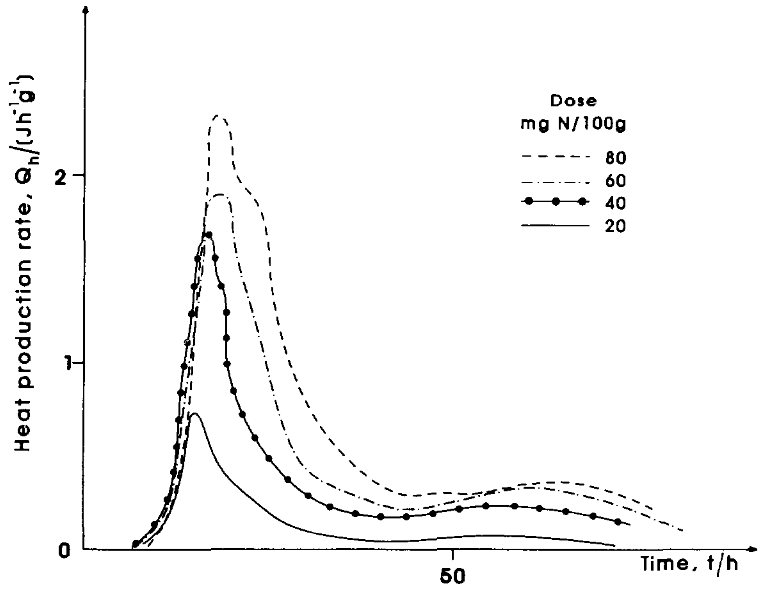

Fig. 1. Heat production rates Q_h for different doses of animal wastewater (AWW).

effect during decomposition of the different doses of AWW. The results of respirometric measurements are shown in Figs. 3 and 4. Peak times (*PT*), maximum values of Q_h and V_h (max · Q_h and max · V_h), and the values of Q_{total} and V_{total} after 50 h

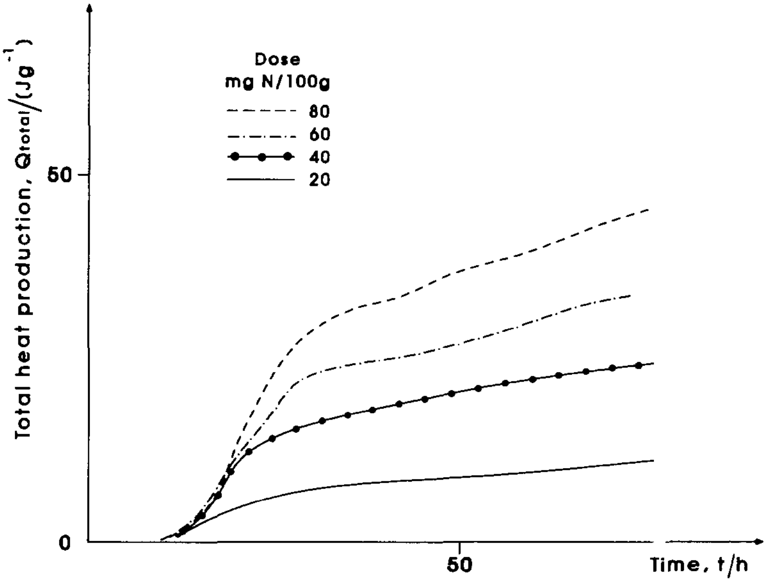

Fig. 2. Time course of the total heat production Q_{total} for different doses of AWW.

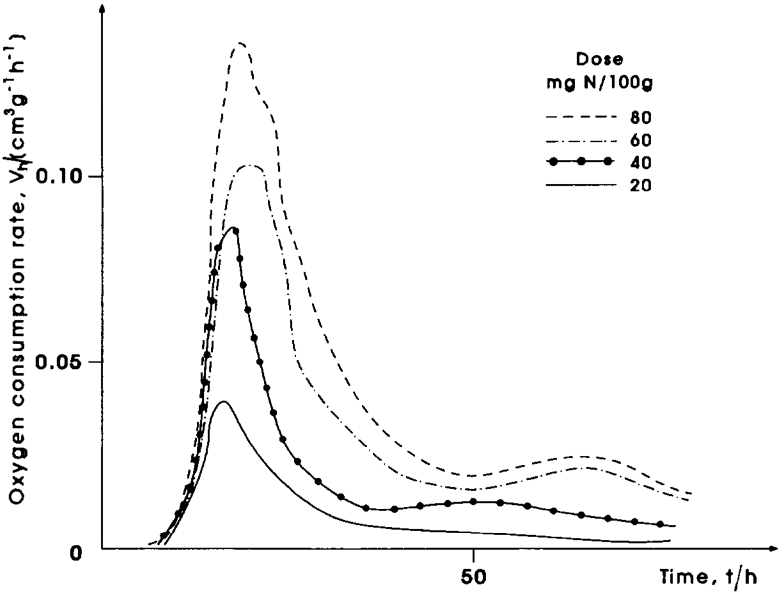

Fig. 3. Oxygen consumption rates V_h for different doses of AWW.

were used for a quantitative comparison of the decomposition of different doses of AWW in soil. These parameters are presented in Table 1.

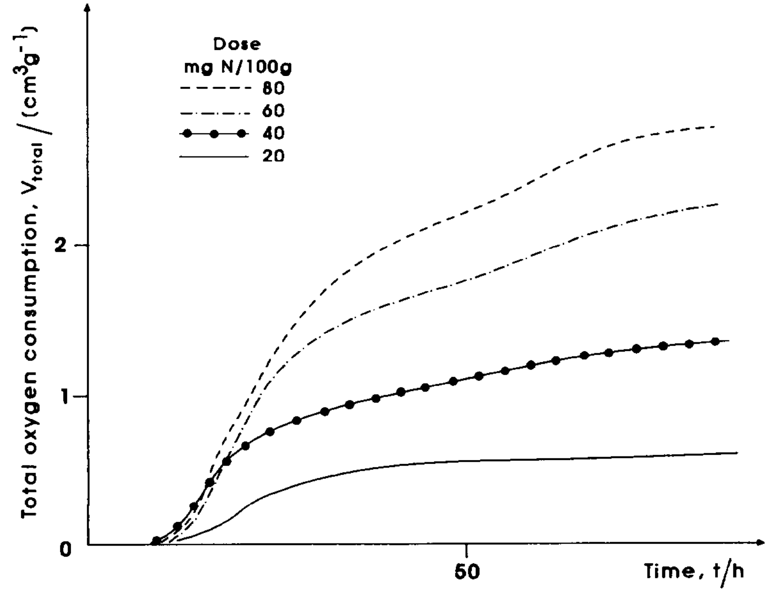

Fig. 4. Time course of the total oxygen consumption V_{total} for different doses of AWW.

Table 1
Chosen parameters of decomposition of the animal wastewater (AWW) in soil

Dose in mg N per 100 g	Calorimetric measurements			Respirometric measurements		
	PT_c in h	Max · Q_h in J h^{-1} g^{-1}	$Q_{total(50)}$ in J g^{-1}	PT_r in h	Max · V_h in cm^3 h^{-1} g^{-1}	$V_{total(50)}$ in cm^3 g^{-1}
20	14	0.72 (200)	8.32	15	0.038	0.53
40	16	1.67 (464)	19.77	17	0.084	1.08
60	18	1.87 (519)	26.66	18	0.101	1.73
80	18	2.31 (642)	35.79	18	0.133	2.19

The symbols max · Q_h and max · V_h express the maximum rates of the heat production and the oxygen consumption in peak time PT_c and PT_r (the time at which the calorimetric and respirometric measurements become maximum). The symbols $Q_{total(50)}$ and $V_{total(50)}$ express the total heat production and the total oxygen consumption after 50 h. Values in parentheses are given in μW g^{-1}.

4. Discussion

The presented calorimetric curves (Fig. 1) are characterized by several stages that are similar to Monod's model of microbial growth [10]. In the first stage, corresponding with the lag phase and phase of exponential growth, increase in Q_h takes place up to the moment of attaining the maximum value at peak time. Then heat production rates decrease to about 40–45 h during the second stage. After the subsequent small increase between 45 and 60 h (3rd stage), the curves progressively decrease until the end of the experiments. The increasing doses of AWW caused an elongation of the peak time, increasing max · Q_h and broadening the calorimetric curves. The 1st and 2nd stages are attributed to the decomposition of easily decomposable organic compounds of AWW in the soil. A knowledge of these stages and of the total heat effects is important because this makes it possible to assess the intensification and degree of biodegradability of organic fertilizers in soil [5]. From changes in the function $f(t)$ in the 1st stage of the calorimetric measurements, the exponential phase of microbial growth was estimated. The average value of the apparent growth rate constant was determined to be 0.371 h^{-1} (SD $\pm$ 0.044) for $n = 4$. It is obvious that the time and method of storage and degree of dilution of the wastewaters affect the chemical composition and biodegradability of the AWW. Application of this altered AWW to soil may have an influence on the kinetics of the AWW decomposition in soil. The separate respirometric measurements (Figs. 3 and 4) confirmed the results of the calorimetric investigations. The shape of the heat production and oxygen consumption curves were almost the same. From the values of Q_{total} and V_{total} after 50 h of the processes, the values of the energetic coefficient (EC) were estimated. The EC corresponded to 15.7–18.3 J cm^{-3}. For comparison, the value of EC for yeast growing aerobically on glucose in 18.08–27.72 J cm^{-3} gas [11] and for glucose-enriched soils it is 22.1 J cm^{-3} gas respired [12].

5. Conclusions

The calorimetric and comparative respirometric experiments described above demonstrated the usefulness of the high-volume (0.5 dm^3) differential calorimeter for studies of AWW decomposition in soil.

The increasing doses of AWW evolved higher heat outputs, with an increase of the peak time and a broadening of the curves of the heat production rate. The average value of the apparent growth rate constant of the decomposition processes of different doses of AWW was equal to 0.372 h^{-1}. The comparative respirometric measurements and values obtained for the energetic coefficient suggest that the metabolic processes during decomposition of AWW are predominantly aerobic.

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