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Virginie Parnaudeau, Bernard Nicolardot, Jérôme Pagès. Relevance of Organic Matter Fractions as Predictors of Wastewater Sludge Mineralization in Soil. *Journal of Environmental Quality*, 2004, 33 (5), <10.2134/jeq2004.1885>. <hal-01862618>

HAL Id: hal-01862618

<https://institut-agro-dijon.hal.science/hal-01862618v1>

Submitted on 4 Sep 2018

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Relevance of Organic Matter Fractions as Predictors of Wastewater Sludge Mineralization in Soil

Virginie Parnaudeau,* Bernard Nicolardot, and Jérôme Pagès

ABSTRACT

Seventeen different wastewater sludges were characterized using both chemical and organic matter fractionation methods (water extraction, Van Soest method, and acid hydrolysis) and 6-mo incubation studies to assess their decomposition in soil. Simple correlation and multiple factor analysis (MFA) were then performed to establish relationships between composition and C and N mineralization of sludges. Carbon and N concentrations covered a wide range of values, but organic carbon (C_o) to organic nitrogen (N_o) ratios were relatively low (from 5 to 19). Carbon and N were mainly distributed in the most soluble fractions of the Van Soest method and in the water-insoluble fraction at 100°C. Carbon mineralization varied from 180 to 661 g C kg⁻¹ organic C added during the 168-d incubation. The addition of sludges led to different inorganic N dynamics: from -3.3 to +120.0 g N kg⁻¹ sludge organic C mineralized after the 168-d incubation. Fractionation studies showed that the most discriminating method was acid hydrolysis. Carbon mineralization was linked with the proportion of sludge N and C present in the lignin-like fraction ($r = -0.68$ and -0.65 , respectively). Significant relationships were established between N mineralization and N_o to C_o ratio ($0.88 < r < 0.95$) and the C_o to N_o ratio of sludges, the C to N ratio of the soluble fraction obtained by the Van Soest method, the water-soluble fraction at 100°C, and the C and N present in the acid-hydrolyzable fraction. Finally, multiple factor analysis also enabled establishing a sludge typology using five clusters based on composition and mineralization characteristics.

RECYCLING NONAGRICULTURAL WASTES in cultivated soils (e.g., input of organic matter, nutrients, lime, etc.) may maintain or increase soil fertility, but it can also lead to harmful environmental effects (i.e., for the quality of soil, water, and atmosphere). Considering all these aspects, the dynamics of waste organic matter in soil play an important role. The decomposition of organic matter controls the dynamics of nutrients (e.g., N) and influences the release of organic and inorganic molecules bound to organic matter (Raber and Kogel-Knabner, 1995). The input of sewage sludge over several years may influence the accumulation and stability of organic matter (Soler Rovira et al., 2002) and improve soil chemical properties (Gigliotti et al., 2001).

The characteristics of these sludges are variable (Sims, 1995). For example, the characteristics of sewage sludges vary with the quality of wastewater, water treatment processes, sludge treatment (Sommers et al., 1976), and

sludge storage. Some authors have shown that the aerobic digestion of sewage sludges results in higher net N mineralization in soil than that obtained with anaerobic treatment (Parker and Sommers, 1983; Serna and Pomares, 1992a). Nevertheless, it seems difficult to establish relationships between all the factors that influence sludge characteristics and the behavior of sludges during their mineralization in soil, especially when factors such as treatments or processes may change with time. Moreover, mineralized N can also be quite variable for sludges treated by the same process (Sommers and Giordano, 1984).

Predicting the sludge fate in soil requires improved knowledge on the influence of sludge organic matter quality on their decomposition and N mineralization, especially by considering chemical and biochemical composition (Heal et al., 1997) and physical characteristics. Apart from abiotic factors that affect soil microbial activity, the quality of organic matter added to the soil is a major factor that determines its decomposition (Swift et al., 1979). Studies performed with crop residues showed that their decomposition and N mineralization are related to their concentration in N (Frankenberger and Abdelmagid, 1985), lignin (Muller et al., 1988), polyphenols (Constantinides and Fownes, 1994), and water-soluble carbon (Oglesby and Fownes, 1992; Trinsoutrot et al., 2000). For sewage sludges, some studies showed the importance of proteins as an available source of carbon and nitrogen for microorganisms (Hattori and Mukai, 1986; Lerch et al., 1992; Rowell et al., 2001). Hattori and Mukai (1986) also brought to the fore the negative correlation between lignin-like and hemicellulose-like concentrations of sewage sludges and their decomposition rates in soil. For many authors, N mineralization is related to the C to N ratio and the N concentration of organic residues, such as crop residues (Quemada and Cabrera, 1995; Trinsoutrot et al., 2000) and sewage sludges (Barbarika et al., 1985; Chaussod et al., 1981; Gilmour and Skinner, 1999).

The general objective of this work was to find composition criteria that could be used to parameterize models and decision support systems for predicting sludge mineralization. To achieve this objective, a large set of wastewater sludges from different origins was studied to explore the relationships between their chemical or biochemical characteristics and their C and N mineralization potentials in soil.

MATERIALS AND METHODS

Wastewater Sludges

Seventeen sludge samples from different French municipal and industrial wastewater treatment plants (Table 1) were

Abbreviations: C_o , organic carbon; MFA, multiple factor analysis; N_o , organic nitrogen.

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Published in J. Environ. Qual. 33:1885–1894 (2004).

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Table 1. Origin, brief description, and analytical data for the different wastewater sludges.

Name	Origin	Sludge treatment	Total C	Inorganic C	Organic C	Total N	NH ₄ ⁺ -N	Organic N	C _o to N _o ratio
B1	dairy	no data available	210.2	41.4	168.8	29.2	1.8	27.4	6.2
B2	wheat distillery	1–10 mo in a lagoon	175.0	1.8	173.2	28.4	4.8	23.6	7.3
B3	sugar beet and molasses distillery	dewatered	380.0	33.4	346.7	56.9	0.5	56.4	6.1
B5	municipal	limed	324.5	17.0	307.5	24.9	0.2	24.6	12.5
B6	municipal	anaerobically digested, limed	228.1	22.8	205.3	24.8	0.1	24.7	8.3
B7	municipal (80%) and industrial (20%)	thickened, anaerobically digested, heated under pressure	215.1	26.0	189.1	12.3	1.7	10.6	17.8
B8	municipal	physicochemical, thickened, dewatered, limed	356.8	14.9	341.9	20.7	2.5	18.2	18.8
B9	municipal	thickened, dewatered	368.9	4.1	364.8	64.0	3.3	60.7	6.0
B10	municipal	thickened, dewatered, limed	176.9	12.9	163.9	26.5	0.1	26.4	6.2
B11	municipal	thickened, dewatered, limed	293.5	37.8	255.8	16.1	0.4	15.7	16.3
B14	municipal	thickened, dewatered	403.4	2.3	401.1	77.3	9.6	67.7	5.9
B15	municipal	thickened, anaerobically digested, centrifuged	290.3	7.7	282.7	30.5	3.0	27.5	10.3
B16	municipal	physicochemical, limed, thickened, dewatered	279.8	30.3	249.5	20.1	0.8	19.2	13.0
B17	municipal (80%) and distillery, winery (20%)	mix of aerobically and anaerobically digested, composted with green waste and wood pieces	334.8	5.6	329.2	34.0	5.5	28.5	11.5
B22	lysine factory	no data available	197.8	50.0	147.8	28.0	0.0	28.0	5.3
B23	malt factory	no data available	531.1	0.4	530.6	100.2	20.1	80.1	6.6
B24	municipal	thickened, dewatered, limed	193.3	27.7	165.7	19.8	0.4	19.4	8.6

used in this research. All the sludges were sampled in the plants during storage and were oven-dried at 40°C and ground to pass a 1-mm sieve.

Fractionation Procedures

Assuming an analogy between chemical reactivity and biological degradability, the sludges were fractionated according to the following three methods:

- (i) The water solubility of dried sludges at different temperatures was determined by using the method described by the Association française de normalisation (1988). One gram of dry sludge was extracted with 100 mL distilled water kept at 20°C for 30 min. The extract was filtered (0.7 µm) and the solid phase extracted again with 100 mL distilled water at 100°C for 30 min. The solid phase was collected by filtration (0.7 µm) and dried at 105°C. Water-soluble compounds from 20 to 100°C were obtained by calculation.
- (ii) Dried sludges were fractionated by using a modification of the method proposed by Van Soest (Van Soest, 1963; Van Soest and Wine, 1967). The soluble fraction was determined by hot water extraction (100°C) for 30 min followed by extraction with neutral detergent (100°C) for 60 min. (Linères and Djakovitch, 1993). Hemicellulose-like, cellulose-like, and lignin-like fractions were obtained as described in the original publication. The glass crucibles used for fractionation had coarse porosity (40–90 µm).
- (iii) Dried sludges were fractionated using an adaptation of the method proposed by Bremner (1965) to characterize soil organic matter. One gram dry matter sludge was shaken with 25 mL 12 M HCl at 20°C for 4 h and left to rest for 20 h. Then, samples were diluted with distilled water to obtain a final HCl molarity of 6 M and heat-extracted under reflux for 16 h. Acid-insoluble solid residue was then separated by filtration (0.7 µm), washed with distilled water, and dried at 40°C. The soluble phase was then collected and distillable N in this phase was obtained by steam distillation (Keeney and Nelson, 1982). Nondistillable soluble N was obtained by calculation.

The C and N concentrations of all the fractions obtained by using the three methods were either measured or calculated. Results were subsequently expressed in g C (N) kg⁻¹ sludge

C (N) (i.e., as the part of sludge C or N present in each fraction for a given method).

Chemical Determinations

Total C and N of dried sludges and solid fractions were determined using an elemental analyzer (NA 1500; Fisons, Milan, Italy). The total soluble N concentration in liquid phases and fractions was measured using a TN3000 analyzer (Euroglass, Delft, the Netherlands) (Alavoine and Nicolardot, 2000), and soluble organic and inorganic C in liquid phases and fractions were determined using a TOC 1010 analyzer (OI Analytical, College Station, TX). Inorganic C in dried sludges was determined using the volumetric calcimeter method (Association française de normalisation, 1986). Inorganic N was measured in dried sludges after extraction with 1 M KCl (sludge dry matter to KCl ratio = 1:100) by continuous flow colorimetry (see below).

Soil Incubations

The soil used for the incubations was a carbonitic Lithic Rendoll, which corresponds to a hypercalcareous rendosol (French soil classification; Baize and Girard, 1995) consisting of a rendzina layer (0–28 cm) overlaying cryoturbated material layer (28–120 cm); the chalk substratum was found below 120 cm. Soil was sampled from the surface layer (0–28 cm), sieved (<6 mm), and stored at 4°C before incubation. Its main characteristics were: clay = 101 g kg⁻¹, silt = 132 g kg⁻¹, sand = 22 g kg⁻¹, CaCO₃ = 734 g kg⁻¹, pH = 8.2, organic C = 17.5 g kg⁻¹, and organic N = 1.94 g kg⁻¹. Dried sludges were homogeneously mixed with soil samples. Sludge input rates were 4 g dry matter kg⁻¹ dry soil; control soil without sludge input was also included. Four replicates were performed for each treatment and sampling date. To prevent sludge decomposition from being limited by inorganic N availability (Re-cous et al., 1995), inorganic N was added to the soil in the form of KNO₃ to obtain an initial concentration of about 60 mg NO₃⁻-N kg⁻¹ dry soil. Soil moisture content was maintained at a matrix potential of 0.05 MPa by weighing and readjusting, if necessary, by the addition of deionized water. The CO₂ produced by the soil was measured by incubating the equivalent of 50-g dry soil samples in hermetically closed

Table 2. List of the two groups of variables used in the multiple factor analysis (MFA).

Group 1†	Group 2‡
Organic C, inorganic C, total C, organic N, NH ₄ ⁺ -N, total N, C _o /N _o , N _o /C _o , pH	C3, C7, C10, C14, C21, C28, C42, C56, C84, C112, C168
CW20, CW20-100, CW100, NW20, NW20-100, NW100, C/NW20, C/NW20-100, C/NW100	N3, N7, N10, N14, N21, N28, N42, N56, N84, N112, N168
CSOL, CHEM, CCEL, CLIG, NSOL, NHEM, NCEL, NLIG, C/NSOL, C/NHEM, C/NCEL, C/NLIG	
CAcS, CAcIns, NDist, NNDist, NAcIns, C/NAcS, C/NAcIns	

† N_o/C_o, organic nitrogen to organic carbon ratio; C_o/N_o, organic carbon to organic nitrogen ratio; C/N, total carbon to total nitrogen ratio; W20, water-soluble fraction at 20°C; W20-100, water-soluble fraction from 20 to 100°C; W100, water-insoluble fraction at 100°C; SOL, soluble compounds; HEM, hemicellulose-like compounds; CEL, cellulose-like compounds; LIG, lignin-like compounds; AcS, acid-soluble fraction; Dist, distillable; NDist, nondistillable; AcIns, acid-insoluble fraction. An abbreviation preceded by C/N, C, or N refers to the C to N ratio or the part of sludge C or N present in that specific organic fraction, respectively.

‡ The number (day) following C or N refers to carbon or nitrogen mineralization at that day.

500-mL plasma vials, with the CO₂ produced being trapped by 10 mL of 0.25 M NaOH. Equivalent 25-g dry soil samples were used to study N mineralization of dried sludges. Each soil sample was placed in a polyethylene pot, which was then put in 2-L jars (the maximum amount reaching 250 g dry soil per jar). In each jar, the CO₂ produced was trapped by 30 mL of 1 M NaOH to obtain atmospheric conditions comparable with that of the plasma vials. The plasma vials and jars were aerated and the CO₂ traps were renewed at 3, 7, 10, 14, 21, 28, 42, 56, 84, 112, 140, and 168 d. Incubation was performed at 28 ± 0.5°C for 168 d.

The CO₂ trapped by 0.25 M NaOH was analyzed by continuous flow colorimetry using an autoanalyzer (TRAACS 2000; Bran+Luebbe, Norderstedt, Germany). The method was described by Alavoine and Nicolardot (2002). Carbon mineralization of sludges was calculated for each sampling date as the difference between the amounts of CO₂ produced by the control soil and soil treatments with sludge inputs. It is assumed that the mineralization from soil was similar with and without addition and whatever the type of sludges (i.e., the priming effect was considered as negligible). Cumulative C mineralization for all sludges was then expressed in g CO₂-C kg⁻¹ sludge organic C.

Soil inorganic N was extracted by 1 M KCl (dry soil to KCl ratio = 1:4). The NH₄⁺-N and NO₃⁻-N were determined by continuous flow colorimetry using an autoanalyzer (TRAACS 2000) using adaptations of the methods proposed by Kamphake et al. (1967) and Krom (1980). The net effect on soil N mineralization of sludge inputs was calculated for each sampling date as the difference between N mineralized in control soil and soil + sludge treatments, and was expressed in g N kg⁻¹ organic C applied to normalize results and thus establish relationships with sludge characteristics.

Statistical Analyses

Linear correlations between the results of mineralization at different dates and sludge chemical characterizations were calculated using Statistica software (StatSoft, 2001). This also enabled fitting the kinetics of C mineralization from the sludges using a two-compartment model (Delphin, 1988; Gilmour et al., 1998; Thuries et al., 2001), by using the nonlinear estimation option:

$$CO_2(t) = A[1 - \exp(-k_1t)] + (1000 - A)[1 - \exp(-k_2t)]$$

where CO₂(t) represents the organic carbon of sludge mineralized by Day t (g C kg⁻¹ C), A and (1000 - A) are the labile and resistant compartments, respectively (g C kg⁻¹ C), and k₁ and k₂ are the decomposition rate constants of the labile and resistant compartments, respectively (d⁻¹).

Relationships between sludge composition and behavior

were also revealed by using a multiple factor analysis (MFA) (Escofier and Pagès, 1998; Pagès and Husson, 2001), which was performed using SPAD software (DECISIA, 1999). This method enabled the global analysis of a complex dataset. The objectives were to (i) determine the characterizations discriminating and explaining the diversity of the sludges objectively, (ii) link the two types of characterizations (composition and mineralization), and (iii) establish a typology of the sludges. This method applies to the set of sludges described by two groups of variables (Table 2): the group of composition variables (Group 1) and the group of mineralization variables (Group 2). It corresponds to a total principal component analysis (PCA) of the complete table in which the influence of each type of characterization is balanced. The main features of MFA can be summed up as follows. It consists in a two-step method: (i) separate PCAs are performed with composition and mineralization variables respectively, and (ii) a global PCA is performed based on the principal components of the previous separate PCA. In this global analysis, the influence of the different groups of variables is balanced by giving weight 1/λ_j¹ to each variable (λ_j¹ being the first eigenvalue of the separate PCA of the variable of group j). As a balanced PCA, the MFA provides a representation of the diversity of sludges (cloud of individuals), by taking into account the composition and mineralization variables in an equilibrated way. The representation of the corresponding scatter of the characterizations (variables) enables interpreting the main factors of this diversity and visualizing the relationships between variables of a group taken alone and of the two groups. Moreover, MFA provides a superimposed representation of the sludges described by each one of the groups of variables onto the subspace generated by the principal components of the global analysis. Thus, in our case, each sludge is represented by three points: two partial points (i.e., described by only one group), and a mean point (in the centroid of the two previous ones). The distance between both partial points of a sludge corresponds to the discrepancy between composition and mineralization.

After this analysis, a hierarchical classification of sludges using Ward's algorithm (Ward, 1963) was performed, based on the principal components from MFA. In this case, the two groups of variables have an equilibrated role in building the classification tree and defining clusters gathering the most similar sludges.

RESULTS

Organic and Inorganic Carbon and Nitrogen Concentrations

Organic C concentrations of wastewater sludges varied from 147 to 531 g C kg⁻¹ dry matter and inorganic

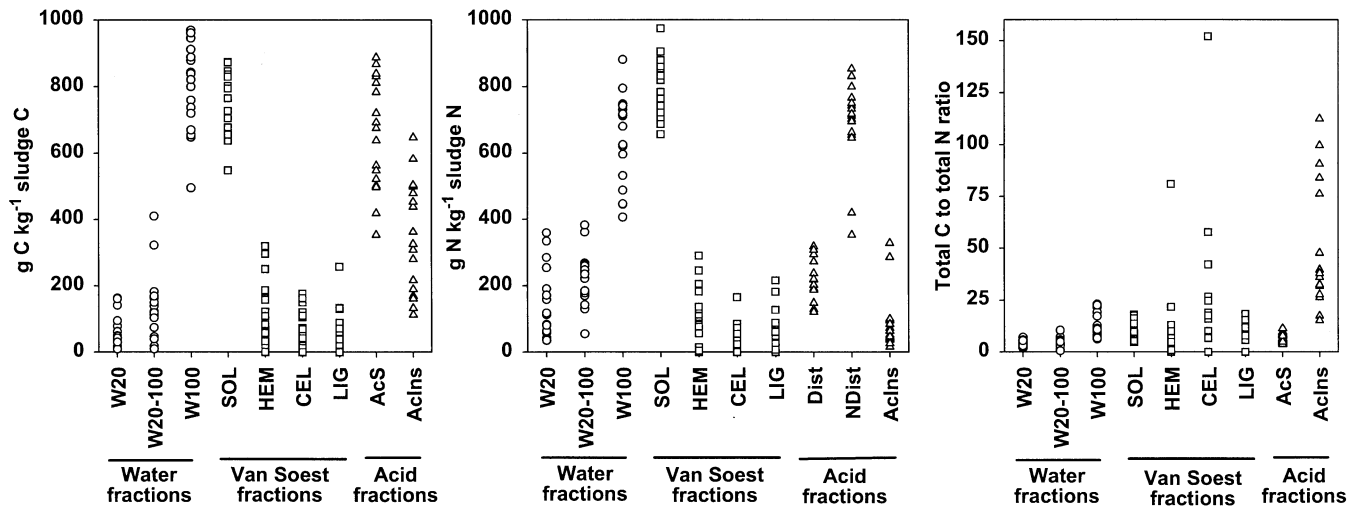


Fig. 1. Carbon and nitrogen distribution (C to N ratio) in the fractions obtained by the fractionation of organic matter of wastewater sludges. W20, water-soluble fraction at 20°C; W20-100, water-soluble fraction from 20 to 100°C; W100, water-insoluble fraction at 100°C; SOL, soluble compounds; HEM, hemicellulose-like compounds; CEL, cellulose-like compounds; LIG, lignin-like compounds; AcS, acid-soluble fraction; AcIns, acid-insoluble fraction; Dist, distillable; NDist, nondistillable.

C concentrations ranged from 0 to 50 g C kg⁻¹ dry matter (Table 1). Organic N concentrations ranged from 10.6 to 80.1 g N kg⁻¹ dry matter. Sludges had relatively low C_o to N_o ratios, ranging from 5 to 19.

Carbon and Nitrogen Distribution in Fractions

Five hundred to 970 g C kg⁻¹ sludge C and 410 to 880 g N kg⁻¹ sludge N were present in the 100°C water-insoluble fraction (Fig. 1). The C to N ratios of the water-soluble fraction at 20°C were lower than those measured for the water-insoluble at 100°C fraction. Most C and N were in the soluble fraction obtained using the Van Soest procedure. Its C to N ratios ranged from 5 to 18. Part of sludge C in soluble and insoluble fractions

obtained by acid hydrolysis varied from 350 to 890 g C kg⁻¹ sludge C and 110 to 650 g C kg⁻¹ sludge C, respectively. By contrast, N was mainly present in the nondistillable acid-soluble fraction. The C to N ratios of the acid-soluble fraction were less than 11, since those of the acid-insoluble fraction were highly variable, ranging from 15 to 112.

Carbon Mineralization Kinetics

Carbon mineralization rates varied from 180 to 661 g mineralized C kg⁻¹ sludge organic C over 168 d (Fig. 2). Two phases of mineralization were observed during all these soil incubations: fast and substantial mineralization during the first days followed by slowing down and

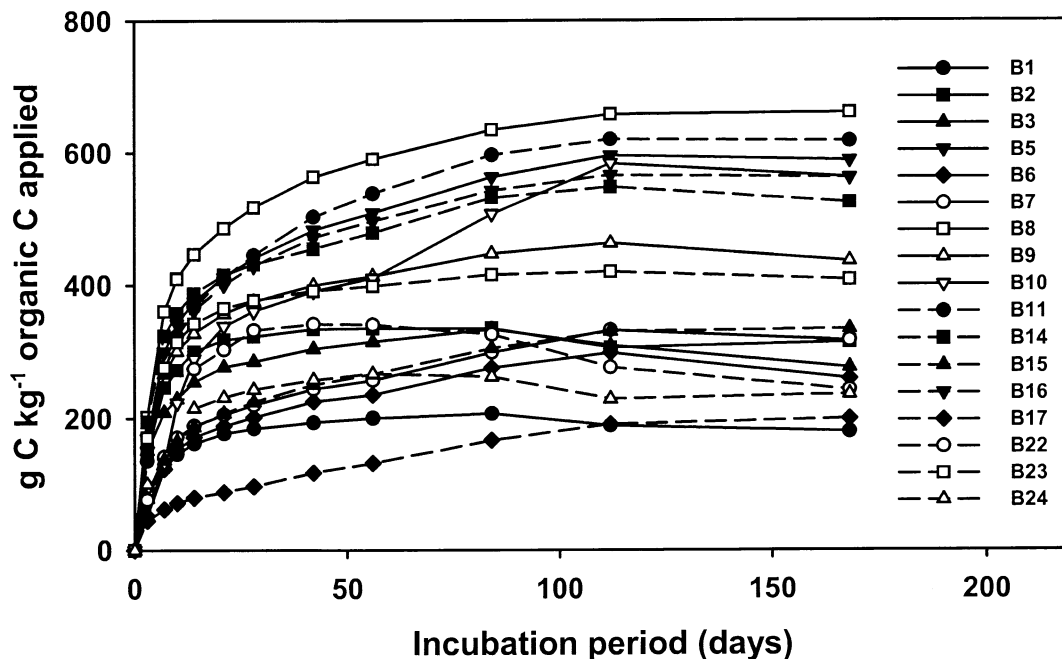


Fig. 2. Cumulative C mineralization of wastewater sludges measured during the 168-d soil incubation.

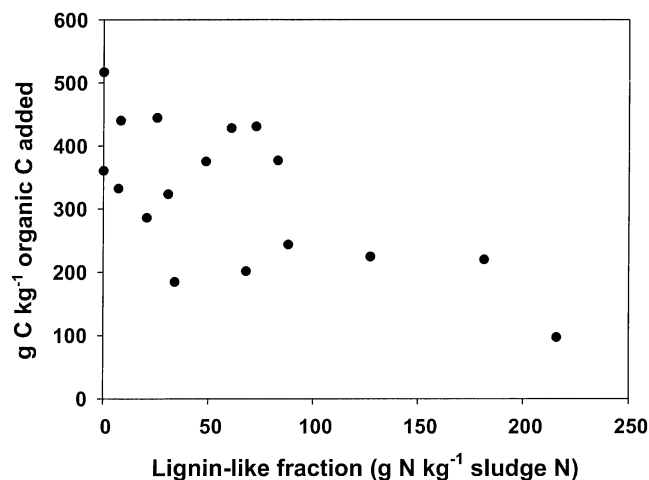


Fig. 3. Relationship between C mineralized during the first 28-d soil incubation and sludge N present in the lignin-like fraction.

low mineralization during the rest of incubation. Carbon mineralization kinetics were then fitted using a two-compartment model. This consisted of labile and resistant compartments that decompose according to first-order kinetics (mean $r^2 = 0.984 \pm 0.014$, individual results not shown). According to the model, the size of the labile compartment (A) ranged from 80 to 494 g C kg⁻¹ sludge organic C, the decomposition rate constants of the labile compartment (k_1) varied from 0.064 to 0.286 d⁻¹, and the decomposition rate constants of the resistant compartment (k_2) from 0 to 0.0030 d⁻¹.

Relationships between C mineralization and composition criteria were weak, even for initial decomposition steps. From Days 14 to 168, the C to N ratio of the acid-insoluble fraction was related to C mineralization ($0.61 < r < 0.68$). Significant relationships were also established between C mineralized at 28 d and N or

C present in the lignin-like fraction (e.g., Fig. 3). The relationships between these sludge quality variables and CO₂-C evolved became weaker as incubation time extended beyond 28 d.

Dynamics of Soil Inorganic Nitrogen

Nitrogen mineralization after sludge incorporation ranged from -3.3 to 120 g N kg⁻¹ sludge organic C at the end of incubation period. No significant relationship was established between C mineralization and N mineralization. Dynamics and amounts of mineralized N were extremely variable (Fig. 4). Four different N dynamics were identified: (i) initial considerable net N mineralization whose intensity decreased after Day 14 (e.g., B9); (ii) constant net N mineralization for the whole incubation period (e.g., B5); (iii) very low N mineralization or immobilization (e.g., B17); and (iv) net N immobilization during the first 10 d followed by net N mineralization until the end of incubation (e.g., B11).

Nitrogen mineralization was nonlinearly linked with C_o to N_o ratio ($-0.89 < r < -0.79$) (Fig. 5), and linearly linked with N_o to C_o ratio ($0.88 < r < 0.95$). Strong relationships were also found between N mineralization and the C to N ratio of the water-insoluble fraction at 100°C ($-0.76 < r < -0.61$) and the C to N ratio of the soluble fraction ($-0.83 < r < -0.72$). Since water-insoluble at 100°C and soluble fractions constituted the main part of sludge C and N, the organic C to organic N ratio of sludge was strongly linked to the C to N ratio of the water-insoluble at 100°C and soluble fractions ($r = 0.91$ and 0.95 , $p = 0.01$). Nitrogen mineralization was also linked with C present in the hemicellulose-like fraction ($0.74 < r < 0.79$), C present in the cellulose-like fraction ($-0.73 < r < -0.67$), and nondistillable N of the acid-soluble fraction, especially at the end of

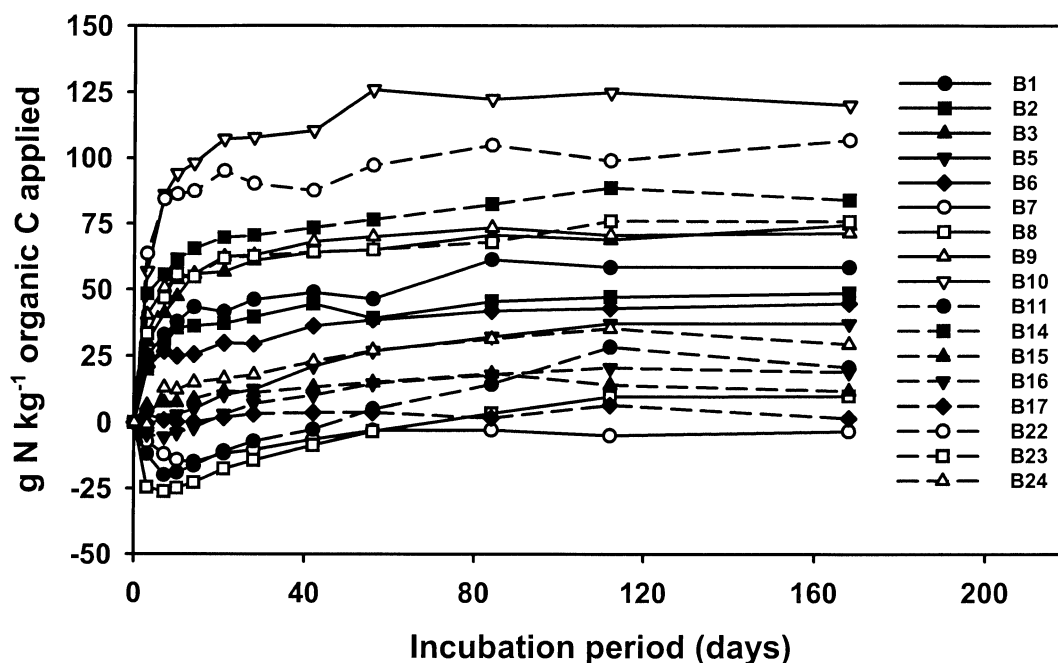


Fig. 4. Soil N dynamics after incorporation of sludges measured during the 168-d soil incubation.

in the lignin-like fraction. Data showed that high C mineralization did not strictly correspond to sludges having a high C to N ratio for the acid-insoluble fraction, while low C mineralization was always associated with a low C to N ratio of the acid-insoluble fraction. Similarly, sludges with a high lignin-like fraction mineralized less carbon; nevertheless, low C mineralization was not always related to a high lignin-like fraction in sludges. Thus, the second principal component discriminated sludges that decomposed easily (e.g., B8, B5) and sludges that were relatively stable (e.g., B1 or B17).

Superimposed Representation of Sludges Described by Only One Group of Variables

Multiple factor analysis completes the representation of the sludges (Fig. 7) by two partial points for each sludge. One partial point corresponds to one sludge described by composition variables alone or mineralization variables alone. A long distance between the two partial points corresponding to the same sludge suggested a discrepancy between the two aspects of the sludge.

Relationships between Composition and Mineralization

Figure 7 shows that there is no major discrepancy considering the first component. It means that two sludges with similarities in their chemical composition have equally comparable decomposition and N mineralization in soil (inter-inertia to total-inertia ratio = 0.95). Only B7 and B10 had the greatest distance between

their partial points; B10 mineralized more N than could be expected by considering its composition (B10-2 at the extremity of the axis), though this was the contrary for B7. Taking into account the second principal component, considerable distances between partial points (Bx-1 and Bx-2) were present in the direction of this axis of inertia. There was more dissension between sludge characterization when using both the composition and mineralization of the different sludges. It was also interesting to notice that B1 and B6 had an average composition (B1-1 and B6-1 in the center of the chart) and led to more extreme behavior than expected, since C mineralization of these two sludges was rather low. Elsewhere, B14 and B8 decomposed more than expected when considering their composition. All of these observations showed the difficulty of identifying sludge composition criteria that effectively determine sludge C mineralization in soil.

Typology of Sludges

The previous description of sludge diversity was synthesized by the clustering method, which suggested five clusters (Fig. 7). Cluster 1 was constituted by relatively stable sludges (B7, B15, and B17) which had low C and N mineralization, C_0 to N_0 ratio more than 10, and large lignin-like (representing more than 12% of total C) and acid-insoluble fractions. Cluster 2 gathered B5, B8, B11, and B16, with a C_0 to N_0 ratio more than 10, high C to N ratios for acid-soluble, acid-insoluble, water-insoluble at 100°C, and soluble fractions, low lignin-like concentrations, and high C mineralization. They led to net N immobilization at the beginning of incubation followed by slow net N mineralization. Sludges B9, B14, and B23 were in Cluster 3; they had the highest C and N concentrations (higher than 360 and 60 g kg⁻¹ dry matter, respectively), a low C_0 to N_0 ratio, high hemicellulose-like fractions, and led to considerable net N mineralization. Cluster 4 included B10 and B22, characterized by a higher N net mineralization than the sludges of Cluster 3, and a low C_0 to N_0 ratio. Finally, Cluster 5 included B1, B2, B3, B6 and B24, which were not discriminated by any of their characteristics, in comparison with the whole sludge panel.

Principal Component 2 - 24.76 %

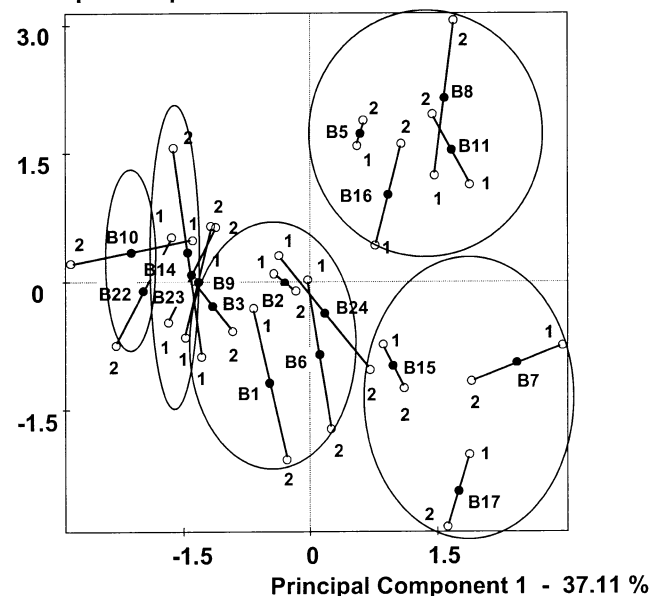


Fig. 7. Projection of the different sludges on the plane defined by the first two principal components; each sludge is represented by three aligned points: the middle point corresponds to the characterization by the two groups of variables ("B" plus one or two digits), with the extremities of the line corresponding respectively to the characterization by the group of composition variables (1) and the group of mineralization variables (2).

DISCUSSION

Wastewater Sludge Organic Matter Quality as Revealed by Fractionation Methods

As assumed when selecting the different wastewater sludges, chemical and biochemical analysis and MFA confirmed a wide range of variation in their characteristics. The variability of C and N concentrations was of the same order of magnitude as for most of the studies (Lerch et al., 1992; Sommers, 1977) and sometimes higher for N concentrations (Sims, 1995). The fractionation of sludge organic matter showed very diverse C and N distributions among fractions, whatever the characterization method used. On the contrary, Hattori and Mukai (1986) found greater similarity in the composi-

tion of various sludges, because they took into account less-contrasted sludges in terms of biochemical composition. However, for each method, a large amount of organic matter was present in only one fraction, that is, the insoluble fraction at 100°C for water solubility, the acid-soluble fraction for HCl hydrolysis, and the soluble fraction for the Van Soest method, as confirmed in a previous paper (Rowell et al., 2001). In our study, acid hydrolysis allowed better evaluation of the diversity of sludge compositions.

Remarkably, the amounts of C and N hydrolyzed in HCl were sometimes lower than the soluble C and N obtained by the Van Soest method. In fact, the latter method probably led to bias due to the porosity of the filters (40–90 μm) used to remove extractants from the fractionated products. Thus, soluble compounds are extracted by neutral detergent in this first step of the Van Soest method (soluble fraction), as are compounds and solid materials less than 90 μm in size (e.g., bacterial bodies present in sludge). These observations raise the question of the pertinence for these organic materials of the Van Soest method, which was initially proposed to determine forage digestibility (Van Soest, 1963). For acid hydrolysis, the small-sized but resistant organic compounds were not eliminated since the acid-soluble phase was obtained by filtration at 0.7 μm . This implies that the role of particle and compound size is frequently underestimated when using this kind of biochemical method.

Carbon and Nitrogen Mineralization of Sludge

No relationship was established between C mineralization and organic N mineralization, which confirmed previous results (Rowell et al., 2001). Carbon mineralization of wastewater sludges in soil was very variable. After incorporation in soil, mineralization occurred during an initial phase with relatively fast change followed by a second phase in which mineralization rates were very low. The kinetics was fitted to a two-compartment model that decomposes using first-order kinetics. Thus the first organic compartment was considered as very labile while the second as very recalcitrant. There was no need to introduce a third compartment that would be resistant and would decompose progressively. Nitrogen mineralization kinetics and amounts of mineralized N were also variable, from high net mineralization rates to relatively low immobilization rates.

However, the four sludges of Cluster 2 were described using a more decomposable second compartment ($0.0021 < k_2 < 0.0030$). In addition, they had the highest final C mineralization rates and the highest net immobilization rates. Their behavior was quite similar to that of plant residues at harvest (Trinsoutrot et al., 2000).

The Advantage of Organic Matter Fractionation Methods for Predicting the Mineralization of Wastewater Sludges

Water solubility fractionation did not identify any relationship between soluble fractions and mineralization. Contrary to previous decomposition studies with

plant residues (Trinsoutrot et al., 2000), amounts of water-soluble C were not related to initial C mineralization.

Considering the Van Soest method, there was a negative relationship between C mineralization and the lignin-like concentration of sludges: C mineralization was high in sludges with very low lignin-like concentrations, whereas C mineralization was low in sludges with the highest lignin-like concentrations. Although the highest lignin-like concentrations represent a relatively small proportion of sludge C and N, those lignin-like concentrations are sufficient to significantly reduce sludge decomposition. In the case of plant residues, lignin has a protective effect on other organic compounds (Chesson, 1997). This can be the case for sludge, where the complex or recalcitrant organic compounds recovered in the lignin-like fraction may play a protective effect. Our findings confirmed the results obtained by Hattori and Mukai (1986), who also noticed significant relationships between mineralization and a hemicellulose-like concentration.

Initially dedicated to characterize soil organic N forms, acid hydrolysis was used in this study to characterize organic C compounds. Separating distillable and nondistillable N in the acid-soluble fraction was unnecessary, since it does not generate additional information for this type of organic material. For sludges, it was assumed that acid-soluble compounds with low C to N ratios were mainly composed of proteinic compounds. This is consistent with the fact that the C to N ratio of this fraction was strongly correlated with sludge N mineralization. Previously, Serna and Pomares (1992b) showed that HCl acid hydrolysis was the best method for estimating N availability in wastewater sludge. However, the C to N ratio of the acid-soluble fraction was not linked to C mineralization. It contrasts with some authors who have concluded that large amounts of proteinic compounds (Lerch et al., 1993) present in the soluble fraction constitute an available source of carbon for soil microorganisms during decomposition processes (Lerch et al., 1992; Sommers, 1977).

Finally, all the fractionation methods used in our work are probably not well adapted to account for the presence of specific recalcitrant compounds in wastewater sludges. For example, this is the case for oil and waxes cited by Strachan et al. (1983) that are not or only slightly decomposable. In addition, sludges contain large amounts of microbial bodies including microbial walls constituted by recalcitrant compounds that are slightly decomposable (Kogel-Knabner, 2002). Therefore, it seems important to verify whether the “soluble” fractions isolated by the fractionation methods used for different sludges have comparable compositions and reactivities in relation to decomposition processes. It has been shown for other organic materials (Melillo et al., 1989; Ryan et al., 1990) that certain organic compounds present in these “soluble” fractions play an important role during the initial decomposition of these organic materials in soil.

Relationships between Organic Matter Quality and Mineralization of Sludges

Soil incubation studies under nonlimiting N conditions showed that the net N mineralization or immobilization induced by sludge addition was strongly related to their C_0 to N_0 ratio (or N_0 to C_0 ratio). In our study, this was the strongest relationship established between composition criteria and mineralization data. This relationship, which has generally been brought to light for crop residues (Quemada and Cabrera, 1995) and animal wastes (Castellanos and Pratt, 1981), has already been established for sludges by several authors (Barbarika et al., 1985; Chaussod et al., 1981; Serna and Pomares, 1992a; Gilmour and Skinner, 1999).

The fractionation methods did not supply any direct or simple criteria to predict C and N mineralization. Nevertheless, the description of the whole dataset using the MFA provided supplementary information. First, it emphasized the main variables responsible for variability. Second, it established a typology in which clusters were composed of sludges that are considered as more homogeneous in terms of composition and behavior in soil. Cluster 1 groups sludges characterized by a high C to N ratio and a relatively high lignin-like fraction; these sludges were considered as rather stable since they caused low C and N mineralization. They are all anaerobically digested sludges and they are projected in the plane next to the other anaerobically digested sludge (B6). On the contrary, Cluster 2 is constituted by sludges characterized by a high C to N ratio and a very low lignin-like concentration. They caused substantial C mineralization and net N immobilization at the beginning of decomposition, this behavior resulting probably from the interaction of both quality criteria. Cluster 3 groups sludges having high organic C and N concentrations and a large hemicellulose-like fraction; they caused high N mineralization and average C mineralization. For the other two clusters, the trends are less evident: Cluster 4 gathered sludges characterized by very high N mineralization, without accentuating the role of specific quality criteria; Cluster 5 is composed of sludges having average composition and mineralization and characterized by weak C decomposition in soil. Finally, the comparison of the results from MFA, analytical determinations, and incubation studies shows that origin or sludge treatment should not be used to predict sludge mineralization, except if extensive stabilization has occurred, which confirmed conclusions of Gilmour et al. (2003). In our study, anaerobic digestion can be considered as a stabilization process, and composting or heating under pressure as extensive stabilization.

CONCLUSIONS

The characterization of sludge organic constituents by means of fractionation procedures coupled with data analysis enabled drawing conclusions on the role of certain criteria. The most discriminating method seems to be acid hydrolysis, which isolates organic fractions related to sludge mineralization. Other interesting points

of this method are its easiness and relative rapidity, which constitute important advantages for routine applications. The other important criteria that may help to predict C and N mineralization of wastewater sludges in soil are the size of the lignin-like fraction and sludge C to N ratio. The next step of our work will be to take these factors into account in existing C and N decomposition models to simulate decomposition kinetics.

Finally, and considering a practical point of view, sludge N mineralization prediction should not be based on a simple description of sludge treatment. In addition, contrary to frequent agronomic advice, it is not realistic to consider one average mineralization rate for all kinds of sludges, since N dynamics and mineralization rates are very variable.

ACKNOWLEDGMENTS

This work was supported by INRA, ADEME (Agence de l'Environnement et de la Maîtrise de l'Énergie), and AESN (Agence de l'Eau Seine-Normandie). We would like to thank Fabrice Marcovecchio, Gonzague Alavoine, Sylvie Millon, and Marie-Jeanne Herre for their technical assistance, Monique Linères, Christian Morel, Armel Guivarch, and Philippe Robert for providing the organic materials and their description, and Sylvie Recous for her interesting comments.

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