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Particle size and metal distributions in anaerobically digested pig slurry

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Abstract

Particle size distribution and trace element patterns were studied in a full-scale anaerobic digestion plant treating pig slurry. Mass balance was established for major (N, P, K, Ca, Fe, Mg and S) and minor (Al, Cu, Mn and Zn) elements. Most of the elements were conserved through the process but part of the P, Ca, Mg and Mn was deposited as crystals lining the digester. In the dry matter of the slurry, Cu and Zn occurred at between 170 and 2600 mg kg^{-1} due to pig diet supplements. Analyses of particle size distributions in raw and digested slurries showed a general shift in distribution towards larger sizes due to degradation of small and easily degradable particles as well as formation of large microbial filaments. Graded sieving of digested slurry showed metals to be mainly present on 3–25 μm particles. Less than 2% Cu and Zn was removed by passage through a 250 μm rotary screen.

Keywords: Copper; Zinc; Specific surface area; Macroelements mass balance

1. Introduction

Biogas production from the biological conversion of waste is receiving increasing attention as a source of energy (Rodriguez and Lomas, 2002; Pouech et al., 2005). Furthermore, anaerobic digestion reduces the total amount of dry matter while stabilizing the remaining organic material, leading to a reduction of odour emissions (De la Farge et al., 1983). These are the reasons why such treatment is frequently used to treat animal slurries and wastewater and has been the object of numerous studies (Lake et al., 1985; Elmitwalli et al., 2001; Rodriguez and Lomas, 2002). Some have dealt with the link between particle size distribution and biogas production but without analysing the different constituents of the digested effluent, while others have focused on the transfer of macronutrients such as nitrogen and phosphorus. However, heavy metal transfer and distribution have rarely been considered (Theis and Hayes, 1978).

Nevertheless, Cu and Zn are essential micronutrients for pigs' metabolism and their feed is supplemented with these elements. Due to their poor bioavailability, Cu and Zn are added at levels that largely exceed physiological requirements (Jondreville et al., 2003). As a consequence, most of the dietary supply is excreted so the slurries contain high concentrations of Cu and Zn (French Agricultural and Environment Ministries, 2003). When the slurries are spread on arable land, the Cu and Zn they contain may generate an environmental risk by accumulating in the topsoil (L'Herroux et al., 1997; Gavalda et al., 2005). Lowering the dietary supply of these elements to pigs would be one way to control the environmental impact of Cu and Zn. However, further studies must be performed before the levels can be lowered without adversely affecting growth performance (Jondreville et al., 2003).

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A few studies have dealt with the effect of anaerobic digestion on heavy metal distribution in sewage sludge (Lake et al., 1985) but scarcely any with livestock slurry. Firstly, studies on heavy metals in anaerobic digestion mostly focused on their impact on biomass inhibition (Leighton and Forster, 1997) or biomass accumulation (Ginter and Grobicki, 1995). Secondly, the works dealing with the distribution and availability of metals examined sludge spiked with an inorganic salt (Lake et al., 1985; Bolan et al., 2003). However, according to Bolan et al. (2003), the behaviour of the spiked metals must be different from that of the sludge-born metals. Finally, works performed on unmodified anaerobic digested sludge often compared two biosolids (one digested and one not) coming from different treatment plants (Lavado et al., 2005). In the current work, a single pig slurry was studied before and after anaerobic digestion without spiking.

In all previous works (Theis and Hayes, 1978; Béline et al., 2004), metals were found to be associated with the organic matter in liquid wastewater or manure. We therefore investigated how anaerobic digestion modifies the organic matter firstly by measuring the size distribution of the particles in the raw and digested slurries. In the same way, the level of metals and macronutrients and their fate during the anaerobic treatment was determined by mass balance calculated over the treatment unit.

Moreover, the anaerobic digestion step is not the last stage in the process; the treated slurry still contains organic matter and is usually spread on the fields. To reduce ammonia loss at the time of spreading, the slurry must be spread on the surface of the soil or directly worked into the soil by means of the spreading injectors. Unfortunately, these instruments are liable to clog, so the slurry is pre-treated before spreading to remove the larger particles.

Sedimentation, mechanical screen techniques or centrifugation are then frequently used. This also reduces the levels of dry matter and phosphorus (Møller et al., 2002). Béline et al. (2004) studied the recovery of metals by such separations. Following aerobic treatment, they found that the different separation processes concentrated not only phosphorus but also Cu and Zn while only 10% of the metals were recovered in raw, untreated slurries. Our purpose was therefore to establish the removal percentages of metals and macronutrients in different granulometric fractions of digested slurry, and to find an explanation for this distribution.

2. Methods

2.1. Anaerobic digestion unit and sample collection

The present work was conducted on an anaerobic digestion unit treating slurries from a farrow-to-finish herd at the ADAESO experimental site (Pouech and Castaing, 1999). The anaerobic reactor was run at 37 °C, with a retention time of about 15 days. The slurry was mechanically stirred by three sets of paddles functioning alternately (stirred-tank reactor). The biogas generated was collected in a metal gasometer which maintained it under pressure (25 mbar) and was then directly burned in a boiler (Chappée) to maintain digester temperature. Introduction of approximately 11 m^3 occurred once a day, seven days a week (over a week, daily volumes can vary between 8 and 13 m^3 depending on the pig unit outputs). The volume introduced was calculated by measuring the liquid level of the tank with a laser distance sensor. Simultaneously the same volume was evacuated into an intermediate storage tank. From there, the digested slurry was then pumped through a 250 μm rotary screen (Midi-Limpia, Demoisy Co.). The liquid fraction was stored in tanks of 600 and 1000 m^3 for up to several months before being spread on maize fields. The separated solids were composted on a concrete slab.

Four types of waste were sampled: raw slurry (RS), digested slurry (DS), liquid fraction (LF) and solid fraction (SF) (Fig. 1). The sampling method was designed making the following assumptions. (i) Owing to the management plan of the pig farm, the site always housed the same number of animals at more or less the same physiological stage, whatever the period of the year. The flow of raw slurry from the site towards the digester is continuous. Similarly, the foodstuff was always identical for a given type of animal (piglets, pigs and sows), and their level of assimilation by the animals is perfectly controlled. Noblet and Perez (1993) showed that, for a given foodstuff composition, there is a given digestibility of nutrients, thus determining the composition of the slurries; (ii) for a continuous stirred-tank reactor (CSTR), it is generally accepted that a period of 3–5 hydraulic retention times is necessary to reach a steady state (Houghton et al., 2002). In our experiment, the digester had already been working for several months with regular slurry input. (iii) Hence, as the digester is a CSTR in the steady state, it must be operating at the outlet concentration, this concentration is identical at all points in the reactor and is independent of time at any point.

As a consequence, for each type of waste (Fig. 1), three samples were taken once a day, seven days a week to constitute three weekly samples at each point of the treatment plant. Liquid effluent (RS, DS and LS) was sampled using the following sampling system. During transfers between two points of the process, the effluent was sent past a sampler. The sampler was a three-way tap opened for 8 s per minute during the whole transfer period, and hence it sampled a daily volume strictly proportional to the total volume transferred. For FS, which is a solid, sampling was carried out following the standard AFNOR (2000a) procedure.

Analyses were performed right after sampling. Raw slurry and digested slurry (RS and DS) samples were stored at 4 °C until distribution size analyses were performed; they were not frozen to avoid the formation of larger particles as described by Knocke and Trahern (1989).

Complementary mechanical separations were operated on digested slurry to determine the metal mass balance

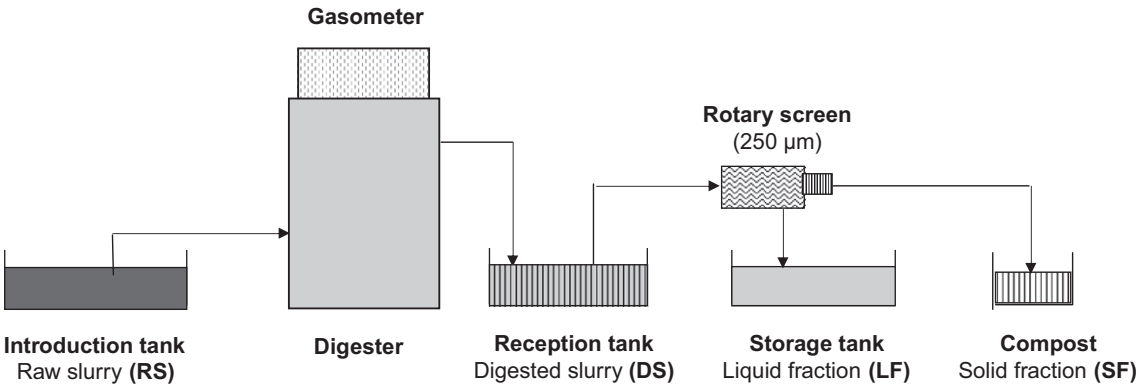

Fig. 1. Flow-sheet of the anaerobic digestion plant and identification of samples.

and identify any link between particle size and metal distribution. Separations were operated at 43 and 25 µm with a SWECO vibrating sieve (pilot unit). Laboratory separation was done by filtration through a Durieux cellulose filter.

2.2. Analysis

2.2.1. Chemical composition

Dry matter (DM) is the weight of each sample after drying at 105 °C for 24 h. Volatile solids (VS) were determined by heating to 200 °C for 2 h and then at 550 °C for 10 h. Total nitrogen (TN) was analysed by means of the Kjeldahl method. The ammonium (NH_4^+) was directly quantified by distillation without any previous mineralization stage.

Extraction of metals in slurry samples was undertaken using a modified strong acid digestion process described by AFNOR (1995), with a Gerhardt Kjeldatherm. An accurately weighed sample of 5 ml was digested with 20 ml 65% HNO_3 and 20 ml 37% HCl. Modifications to the original technique included the use of a 50/50 hydrochloric/nitric acid solution instead of a 75/25 hydrochloric/nitric acid solution, because of the high organic matter content in the samples. Nitric acid was used here for its strong oxidant properties. The samples were kept overnight at 20 °C then heated to 160 °C for 2 h. After cooling to room temperature they were filtered at 3 µm and then adjusted to 100 ml with deionized (UHQ) water. Three extraction replicates were operated for each sample. Al, As, Ba, Ca, Cd, Co, Cu, Fe, K, Mg, Mn, P, Pb, S, Se and Zn were determined by plasma optical emission spectrophotometry (ICP OES Thermo IRIS Intrepid II XDL Duo).

2.2.2. Particle size distribution and separation system

Particle size distribution was studied for two slurries: raw slurry, and digested slurry before any separation treatment by laser diffraction using the Cilas 1180 L n°516 (AFNOR, 2000b). These measurements were performed by the Institute of Filtration and Techniques of Separation (Foulayronnes, 47510 France). The results provided the volume distribution of the particles, as a percentage of the total volume of the solids. Assuming that the particles are spherical and non-porous (Houghton et al., 2002), we can calculate the number of particles and the specific area in each particle size class as a percentage of the cumulative total specific surface area (SSA). The SSA is plotted versus particle size. The distribution of the most abundant metals was studied in a few particle size classes of the digested slurry after separation by 250 µm rotary screen, 43 µm shaking sieve, 25 µm shaking sieve, 3 and 0.45 µm cellulose filter.

2.3. Calculations

Mean values were compared using Student's *t*-test. Difference was considered significant for a probability below 0.05 ($P < 0.05$).

Mass balances of chemical elements were obtained by multiplying the concentrations by the volumes of effluent treated. Separation efficiency is commonly defined as the total mass of solids or nutrients recovered from the solid fraction as a proportion of the total input of solids or nutrients. This removal percentage (Re) was calculated using the procedure described by Møller et al. (2002).

3. Results and discussion

3.1. Nutrients and metals in the different slurries

Dry matter content (Table 1) in the raw slurry (RS) was low in comparison with values from the literature (Nicholson et al., 1999; Levasseur, 2002) due to the conditions at the ADAESO experimental farm, which require frequent cleaning, causing the RS to be quite dilute. Due to the low dry matter contents, N and P levels were also moderate (about 0.28% N total in fresh matter and about five-fold less for P). The quantities of slurry to be spread on the land are generally fixed from the levels of N but also, to a lesser extent, of P. Based on EC regulation (EEC, 1991), organic farming supplies are limited to the maximum load of manure-N, i.e., to 170 kg N ha^{-1} yr^{-1}. The level of nitrogen was nearly constant before and after anaerobic digestion:

Table 1
Composition of slurries and mass balances on the anaerobic digestion plant (mean (standard deviation))

		Raw slurry (RS)	Digested slurry (DS)	Liquid fraction (LF)	Solid fraction (SF)
Percentage fresh matter					
	DM[1]	2.7 (0.1)	1.6 (0.0)	1.5 (0.1)	32.6 (0.8)
	TN[2]	0.28	0.28	0.26	1.77
	NH_4^+–N	0.21	0.23	0.22	0.28
g kg^{-1}DM					
	VS[3]	673 (3)	591 (17)	617 (17)	699 (7)
	P	29.5 (1.3)	31.5 (4.0)	24.9 (1.7)	43.8 (4.2)
	K	37.4 (3.1)	65.6 (2.0)	72.3 (7.1)	4.1 (0.4)
	Ca	51.2 (4.2)	47.2 (4.4)	39.0 (2.0)	96.1 (8.3)
	Fe	2.5 (0.1)	4.0 (0.1)	4.3 (0.0)	4.1 (1.5)
	Mg	14.2 (0.3)	15.9 (0.9)	12.1 (0.3)	6.8 (1.3)
	S	8.1 (0.8)	11.1 (2.2)	10.8 (1.3)	6.8 (0.7)
mg kg^{-1}DM					
	Al	868 (308)	1641 (367)	998 (328)	760 (154)
	Cu	590 (12)	1016 (25)	1001 (13)	170 (16)
	Mn	629 (26)	708 (20)	610 (6)	1042 (70)
	Zn	1507 (18)	2628 (158)	2563 (83)	519 (82)
kg day^{-1}					
	Flow	11297 (2362)	11121 (2325)	10223 (2123)	39 (5)
	DM	301 (9.2)	182 (1.7)	148 (5.9)	13 (0.2)
	Nt	31.6	31.1	26.6	0.7
	NH_4^+–N	23.7	25.6	22.5	0.1
	VS	202 (6.6)	107 (3.2)	92 (3.8)	9 (0.2)
	P	8.9 (0.6)	5.7 (0.5)	3.7 (0.3)	0.6 (0.0)
	K	11.2 (0.9)	11.9 (0.1)	10.7 (0.8)	0.1 (0.0)
	Ca	15.4 (1.0)	8.6 (0.5)	5.8 (0.3)	1.2 (0.1)
	Fe	0.5 (0.4)	0.5 (0.4)	0.4 (0.3)	0.1 (0.0)
	Mg	4.3 (0.1)	2.9 (0.1)	1.8 (0.1)	0.1 (0.0)
	S	2.4 (0.3)	2.0 (0.3)	1.6 (0.2)	0.1 (0.0)
g day^{-1}					
	Al	261 (96)	298 (44)	149 (54)	10 (0.6)
	Cu	177 (7)	185 (1)	149 (8)	2 (0.1)
	Mn	189 (2)	129 (1)	90 (5)	13 (0.7)
	Zn	453 (17)	478 (16)	380 (13)	7 (1.2)

[1] Dry matter.
[2] Total nitrogen.
[3] Volatile solids.

all the liquid slurries contained between 0.26% and 0.28% total nitrogen (TN). The composition of the slurries (RS, DS and LS), will mean spreading 60 m^3 ha^{-1} yr^{-1} leading to annual macronutrient inputs (P, K, Ca, S, Mg and Al) lower than the requirements of most crops (Marschner, 1995). The slurry can thus contribute to the general nutrition of the plants without over-fertilizing with respect to N, P, K, Ca, S and Mg without any accumulation in arable land. The microelements presented a different picture. Cd, Co, As, Ba, Pb and Se were present in such low quantities (about 1 ppm fresh weight, i.e., very close to the detection threshold) that it was not possible to compare their levels in the different slurries. In Table 1, we have only reported the elements that showed a significant abundance.

The levels of P, Ca, Mg, S, Al, Cu, Mn and Zn are very close to those obtained by Levasseur (2002), the only notable differences being that Levasseur only found half the iron but twice the potassium before anaerobic digestion. The levels of Fe and Mn were low, giving rise to soil inputs of the same order as the levels of export in crops. In contrast, Cu and Zn were very abundant and the input from slurry (about 0.9 kg Cu ha^{-1} and 2.5 kg Zn ha^{-1}) was ten-fold typical export values (Marschner, 1995), exceeding the limits laid down by the regulations governing the spreading of sewage sludge (Gavalda et al., 2005). It is for this reason that the present work focused mainly on these two metals.

To consider the effects of anaerobic digestion on the composition of the slurries, the same slurry was compared before and after treatment (RS versus DS). The greatest difference between the two types of slurry is their levels of DM since the hydrolysis reactions coupled to the methanogenesis degraded half the original organic matter. Similar levels of organic matter decomposition during treatment of swine manure had already been found by Hsu and Lo (2001) in aerobic conditions. Moreover, in other works Lake et al. (1985) reported a decrease of between 46% and 55% in the volatile solids during anaerobic digestion of wastewater sludge. The temperature and pH conditions inside the digester were

very close to ours, as were the organic degradation results even though the waste was very different from that of the current work: mixed and primary biological sludge from waste water.

Expressed per unit dry weight, digestion therefore enriches the proportion of mineral in the dry matter. Indeed, Cu and Zn concentrations were increased 1.8-fold by the digestion (Table 1). However, this did not affect the Cu and Zn inputs to the soil since the spreading is calculated with respect to the nitrogen, which remained constant during anaerobic digestion.

3.2. Mass balances of micro and macro nutrients in the anaerobic digestion plant

The anaerobic digestion process consumed 53% of the volatile compounds, which were most likely transformed into biogas in the digester (Table 1). During digestion, most of the mineral elements were conserved without any significant losses for N, K, Fe, S, Al, Cu and Zn. However, significant losses were observed for P, Ca, Mg and Mn with respectively, 36%, 44%, 32.5% and 32% of the respective elements lacking in the output (DS) in comparison to the input (RS). One feasible explanation is the accumulation of these elements in the reactor. Crystals lining the digester were observed when the reactor was opened. Scanning electron microscopy (SEM–EDS) observations clearly showed them to be composed of P, Ca, Mg and Mn. X-ray diffraction analysis produced a spectrum of phosphate different from that of struvite described by numerous authors such as Suzuki et al. (2007). In addition, the overall budget also showed a loss of sulphur which can be attributed to the presence of H_2S in the biogas which was otherwise mainly composed of CH_4 and CO_2.

The solid–liquid separation system used here, i.e., the 250 μm rotary screen, removed very low amounts of dry matter (only 7%). Even if the solid fraction (SF) had high concentrations of macroelements (TN was six-fold above that in the liquid fraction (LF), P and Ca were also more concentrated in SF dry matter than in LF dry matter), the amounts of nutrients thus removed (Table 1) were very low: 3% TN, 14% Ca, 20% Fe and 10% P. In addition, the system did not allow the extraction of Cu or Zn because SF concentrations were five- to six-fold lower than in the whole digester output. This means that the metals did not occur on particles larger than 250 μm in diameter. These results are coherent with those of Westerman and Bicudo (2000) who recommended that solid–liquid separation processes be designed to remove both coarse material and particles smaller than 250 μm in order to significantly reduce the nutrient content of the effluent. In contrast, these performances are low compared to those of Daumer et al. (2005) working on undigested slurry for which the level of separation reached 20% for P and about 10% for Cu and Zn. Unfortunately, these authors did not report the cut-off size for the sieve, but in all likelihood, it was smaller than 250 μm.

3.3. Particle size and elemental distribution

The particle size distribution of the raw and digested slurries is presented in the form of a histogram of the relative frequency per volume class versus the volume class of the particles (Fig. 2). In both types of slurry, 92% of the volume of the solids is made up of particles greater than 3 μm in diameter. In the raw slurry, the median diameter was 67 μm while it was 305 μm in the digested slurry. Both slurries presented a bimodal particle size distribution: a first peak at 28 μm for the raw slurry and 53 μm for the digested slurry then a second peak at 950 μm for the raw and 700 μm for the digested. In the terminology proposed by Levine cited by Shon and Vigneswaran (2006) and adopted by Rodriguez and Lomas (2002), the first peak corresponds to ''supracolloids'' (1–100 μm, including bacterial floc, single cells and organic residues), and the second to settleables (>100 μm, corresponding mainly to organic residues). Fig. 2 therefore shows that it is mainly the smaller particles that are degraded during the anaerobic digestion leading to a relative increase in the proportion of larger particles (>1.4 mm). The same shift in particle size distribution towards larger diameters was noted by Elmitwalli et al. (2001) in anaerobically digested domestic sewage. Production of bacterial floc and filaments during anaerobic digestion leads to a slight increase in the relative volume occupied by the largest particles. Moreover, the degradation of the organic compounds concerns the smallest particles most (i.e., <1 μm) containing carbohydrates, amino acids and fatty acids as well as polysaccharides, proteins and lipids according to Shon and Vigneswaran (2006). Larger particles (i.e., >10 μm) were more resistant to degradation, leading to a general shift in distribution towards larger sizes.

Rather than the size of the particles or the space that they occupy, areas of contact can play a predominant role in the processes of metal adsorption. By enhancing the contact between metals in solution and microbial cells, the specific surface area can increase the adsorption of the metals to the microbial biomass (Ginter and Grobicki, 1995; Leighton and Forster, 1997).

As generally accepted in the literature (Houghton et al., 2002), the smaller particles contributed more in terms of specific surface area than the larger fractions (Fig. 3). Moreover, as anaerobic digestion preferentially attacked the small particles, the total specific surface area was, as expected, slightly lower in the digested slurry (0.395 m^2/g) than in the raw slurry (0.471 m^2/g).

In both RS and DS, particles of over 25 μm in diameter only accounted for 8% of the total specific surface area (SSA). The largest particle size class to make a strong contribution to the SSA was the 3–25 μm class which reached a contribution of 30% and 40% for raw and digested effluent, respectively.

Concentrations and percentage nutrient and metal recovery in the dry matter of digested slurry after the different granulometric separations are reported in Table 2. For

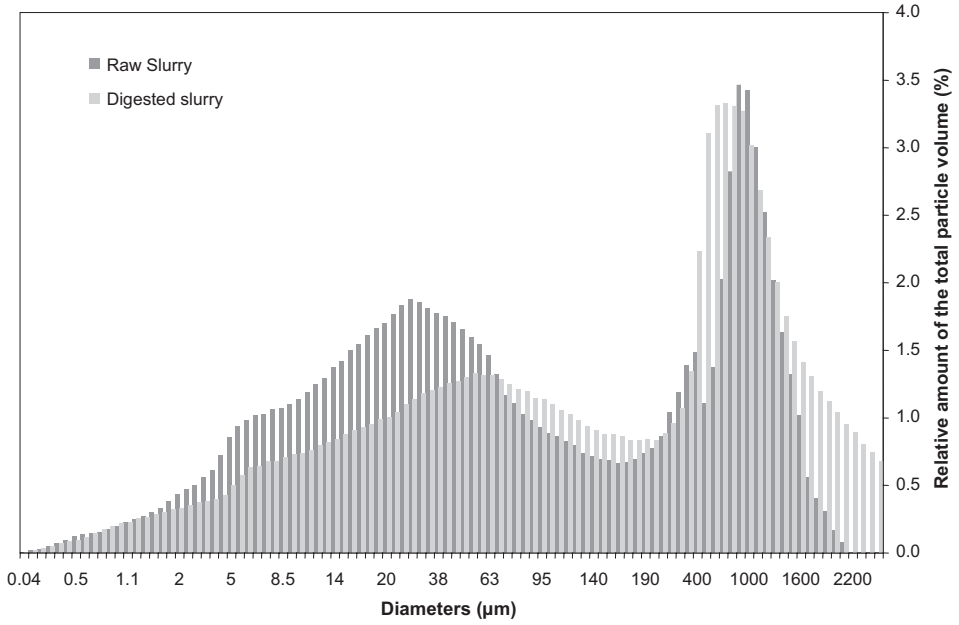

Fig. 2. Distribution of the relative volumes of the various size classes of particles in raw and digested slurry.

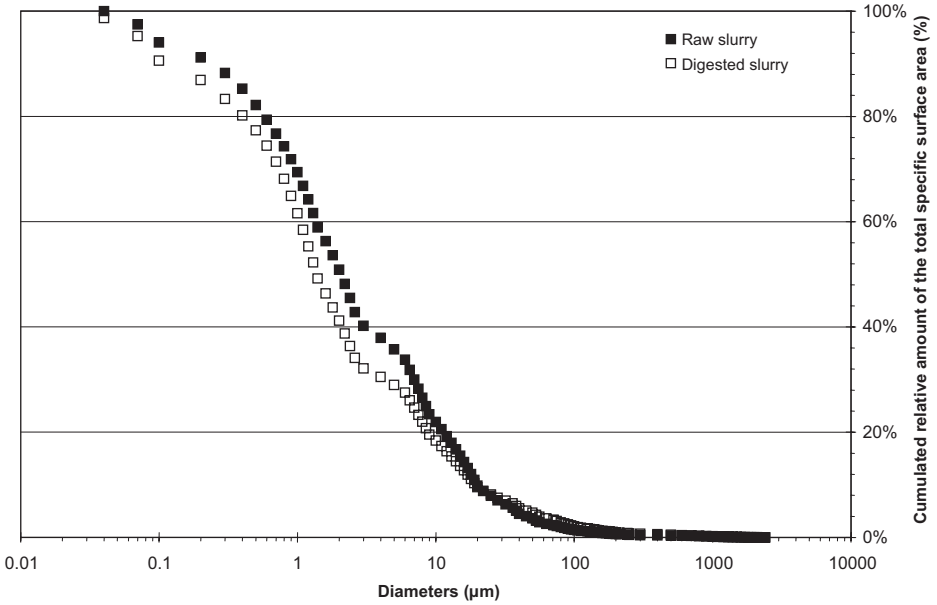

Fig. 3. Cumulative relative distribution of specific surface area in raw and digested slurry.

the concentrations, it can be noted that not all the elements had the same distribution in the various particle size classes. Among the macroelements, Ca and P followed the same pattern: very concentrated in the largest fraction (>250 µm), less concentrated in the intermediate fraction, then a steady increase in concentration once more as the particle size diminished. In contrast, S was present at low levels as long as the particles were larger than 25 µm in diameter. The concentration of S doubled when the separation threshold was lowered to 3 µm. The distribution of K was again different: its level increased going from the 250 µm to the 25 µm fraction and then decreased in the fraction with the finest particles. Owing to the high affinity of potassium for water, its distribution is quite well correlated ($r^2 = 0.8619$) to the moisture remaining in the solid fraction. For the other metals, the distribution was the same: low levels in large particles, but the levels increased as the particle size decreased to reach maximal values for the >3 µm fraction. Lowering the cut-off threshold again to 0.45 µm, the metal concentrations decreased.

If we consider the amount of dry mater recovered after each separation, we have the recovery efficiency (Re) for each element which increased with DM recovery efficiency from 250 to 0.45 µm sieve mesh (Table 2). As mentioned

Table 2
Composition and elemental removal percentage in different particle size fractions of digested slurry (mean (standard deviation))

		Whole digested slurry	>250 μm	>43 μm	Particle size fractions		
					>25 μm	>3 μm	>0.45 μm
Dry matter composition							
$g\,kg^{-1}$	P	31.5 (4.1)	43.8 (4.2)	26.1 (1.3)	37.7 (0.6)	42.5 (4.5)	ND
	K	65.6 (2.0)	4.1 (0.4)	9.6 (0.3)	10.4 (0.4)	7.4 (0.1)	ND
	Ca	47.2 (4.4)	96.1 (8.3)	28.9 (1.9)	36.8 (2.2)	65.3 (1.1)	ND
	Mg	15.9 (0.9)	6.8 (1.3)	15.1 (0.8)	22.7 (0.6)	23.3 (1.6)	ND
	S	11.1 (2.2)	6.8 (0.7)	6.5 (0.5)	6.7 (0.2)	11.4 (0.9)	ND
$m\,kg^{-1}$	Cu	1016 (25)	170 (16)	329 (23)	364 (30)	1402 (8)	1001 (14)
	Mn	708 (20)	1042 (70)	444 (25)	586 (10)	1024 (25)	873 (21)
	Zn	2628 (158)	519 (82)	900 (132)	877 (37)	3563 (172)	2091 (75)
Specific surface area (%)		100	0.77	5.33	8.15	32.12	80.18
Removal percentage (Re)							
Percentage	DM*	100	7.2	16.9	18.8	62.8	ND
	P	100	10.5	17.4	27.8	104.7	ND
	K	100	0.1	2.1	2.5	6.1	ND
	Ca	100	14.0	12.0	16.9	100.6	ND
	Mg	100	3.4	19.0	31.6	108.4	ND
	S	100	5.0	9.7	11.2	63.3	ND
	Cu	100	1.1	5.8	7.1	91.6	99.3
	Mn	100	10.1	12.7	18.5	108.4	ND
	Zn	100	1.5	6.3	6.8	92.8	99.6

* Dry matter.

above, P and Ca were the elements that were the best extracted with the large (250 μm) mesh size. However, with this cut-off, the total quantities of metals extracted were negligible, whereas, they were close to 100% when particles >3 μm were separated. Japenga and Harmsen (1990) showed that while K, Na and NH_4^+ remained in the liquid fraction of the slurry, all the other metals were bound to the solid fraction. These authors used the standard cut-off threshold of 0.45 μm to differentiate between the two fractions. Our results show that 85% of the Cu and the Zn were in particles whose diameters were from 3 to 25 μm while only 8% were recovered with particle sizes of between 0.45 and 3 μm. Separation efficiency of Cu and Zn was similar for all the particle size ranges tested, removal percentages being strictly proportional ($r^2 = 0.9998$) even though Zn was always two- or three-fold more concentrated than Cu: in the RS, the DS and again in the various slurry fractions (Table 2).

A relationship was found between the specific surface area, the Cu and Zn concentrations and the different particle size classes. Fig. 4 shows that the larger the surface area, the greater the concentrations of Cu and Zn. If a second-

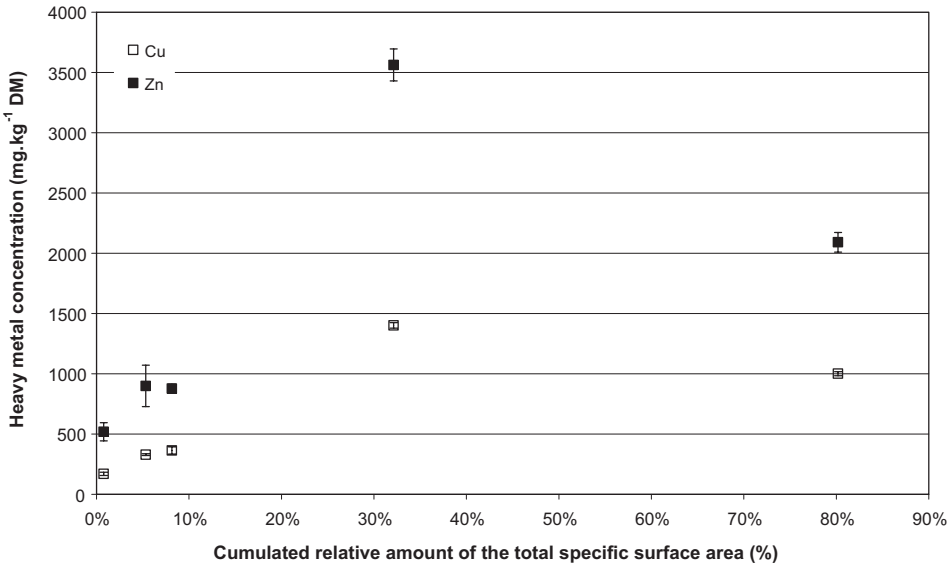

Fig. 4. Cu and Zn dry matter concentration in particles of decreasing size in relation to cumulative specific surface area.

order polynomial model is applied to fit the points of Fig. 4, it reaches a maximum level coinciding with 47% cumulated surface area for Zn and 51% for Cu: values which correspond to particle sizes of between 1.3 and 1.6 μm. Interestingly, this range is the mean size of bacteria, revealing the possible biosorption of Cu and Zn by microorganisms as suggested by Artola et al. (2000). These results are also supported by those of Han and Thompson (1999) referring to the properties of organic matter from anaerobically digested sewage biosolids where the Cu-binding ability decreased as the molecular weight increased.

4. Conclusions

Pig slurry contains nutrient elements (N, P, K, Ca, Fe, Mg and S) at levels corresponding to crop requirements. In contrast, copper and zinc are pig food additives, making their way into the excreta of these animals at high levels and can thus accumulate in slurry-fertilized soils.

By transforming almost half the organic matter in livestock slurry into methane, the process of anaerobic digestion has the effect of doubling the mineral content expressed per unit dry matter without any consequences on soil supplies as long as the amount of effluent spread is calculated on a nitrogen basis because the concentration in fresh effluent is the same. For most elements, there is no loss between the input and the output of the digester even for N, and recovery is not far from 100% except for P, Ca, Mg and Mn, which partially crystallise out in the form of a substituted phosphate which could be put to good use as P fertiliser in its own right.

During the anaerobic digestion of the slurry, it is the small particles that are degraded the most: i.e., those with diameters of between 1 and 60 μm. The major consequence is an increase in the relative abundance in the slurry of larger particles and finally a decrease in the specific surface area of the suspended matter in the slurry.

This modification in the particle size distribution caused by anaerobic treatment is an important factor in that the size of the particles is one of the criteria that determines the distribution of the metals in the digested slurry: most of the Cu and Zn (86%) is trapped within particles between 3 and 25 μm. Above this threshold, the larger the particles, the lower their specific surface area (SSA) and the less they concentrate metals, indicating that suspended organic matter with a high SSA presents more metal binding sites than matter with a low SSA. Finally, less than 2% of the total Cu and Zn are trapped within largest particles, indicating that the 250 μm mesh separation is not sufficient to remove the metals from the digested slurries, Cu and Zn remaining in the part of the slurry to be spread and not retained in the solid fraction. However, further investigations must now be carried out to determine the effect that anaerobic digestion can have on the bioavailability of metals after incorporation of the slurry into the soil.

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