Managing sulphur content of pig diet to control further sulphides production during pig slurry anaerobic storage

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1 INTRODUCTION

In the present configuration of livestock manure management, and particularly for the pig industry, slurry is collected from barns and stored into storage tanks inside and/or outside of livestock buildings before spreading. During this storage period, in anaerobic condition, production and accumulation of sulphur (S) compounds occur. Among the molecules produced, some are of particular concern since they are responsible for odours or are dangerous for health. According to Spoelstra (1980), the major S compounds responsible for odours are hydrogen sulphide (H_2S) and methyl mercaptan. Other authors (Clanton and Schmidt, 2000) extend this list to include dimethyl-sulphide, dimethyl-disulphide, carbon disulfide and carbonyl sulphide. Handling these types of livestock manures can be dangerous when gaseous S forms dissolved in the liquid phase are suddenly transferred and released to the gas phase (Mackie et al., 1998; Oneill and Phillips, 1992). The most dangerous S gas compound is probably H_2S that is toxic and lethal at high concentrations. In most cases, the maximum exposure to H_2S occurs when the effluent is mixed before land spreading (Oesterhelweg and Puschel, 2008). The acute toxicity of H_2S absorbed by inhalation is well documented. Thresholds of toxicity have been identified and regulated to protect exposed populations. For pig slurry, different sources can explain H_2S production. First, in anaerobic conditions, sulphates present in pig excreta (urine and faeces) can be reduced by sulfate-reducing bacteria into sulphite and sulphide, this pathway is well known as dissimilatory sulphate reduction. The microorganisms involved are terminal degraders of organic matter and are widely present in anaerobic ecosystems (Elferink et al., 1994; Stams et al., 2005). Second, H_2S formation may result from the mineralization of organic compounds containing S, such as non digested proteins which contain methionine, cystine and cysteine amino acids that can be reduced to pyruvate and H_2S (Mackie et al., 1998).

In the literature, much documentation is available to correlate odours emitted by pig slurries and gaseous S emissions but little is found to correlate animal feeding strategies, S excretion via faeces and urine and further sulphide production during pig slurry storage. The objectives of this study were to determine the S content of different raw materials usually used to formulate pig's feed, to evaluate the behaviour of the ingested S and to determine the S compounds produced during pig slurry storage.

2 MATERIALS AND METHODS

The S content of 76 raw feedstuffs has been determined by the French Association for Animal Production (AFZ), total S in excreta and manure was determined by elementary analysis using normalised methods. For dietary S retention two independent experiments were realised, one with 6 castrated male pigs with an average initial body weight of 62 kg (±1.5) kg, which were housed individually in metabolic cages. Pig diets tested were principally based on wheat (87%) and on soybean meal (10%) but different wheat distillers dried grains with solubles (DDGS) were incorporated (25%) to partially replace soybean meal (7%) and wheat (65%). The crude protein (CP) content of diets used varied between 20% and 16% for formulation with or without DDGS respectively. For the second experiment, the same protocol was used with fifteen castrated male pigs with an average body weight of 63 kg (±3) kg Four experimental diets based on wheat and soybean meal were compared. They differed by their CP content which amounted to 13 and 16% and by their ingredient composition. For lower CP content, exclusively wheat (90%) and soybean meal (6%) were used. For higher CP content, one pig diet was realised with wheat (69%) and soybean meal (16.5%) and three other diets were formulated by ingredients addition, 20% of DDGS, pulp beet or rapeseed meal, in partially replacement of wheat and soybean meal. These two experiments were conducted during 20 days, pig feed intake was fixed at 2 $kg.d^{-1}$. During the 10 last days, urine and faeces were collected daily, weighed, pooled per pig and at the end of the experimental essay and sampled for analysis. Water was available ad libitum, consumption of water and feed were measured each day. Diet,

faeces and urine were analysed for dry matter. Total S was determined by elementary analysis (LECO SC 144). Sulphates were measured with an automatic flow injected analyser (Lachat QuikChem 8000) directly with diluted urine and after potassium chloride extraction for feed and faeces.

For storage experiment, pig slurry provided by an industrial pig farm was used. In order to restore initial characteristics of this slurry and particularly its volatile fatty acids (VFA) content, additions of acetic, propionic and butyric acids were realised to reach 3, 1.5 and 2 $g.l^{-1}$ respectively. After this operation, this slurry was spiked with sulphate at different concentrations between 0 to 4 $gS\text{-}SO_4^{2-}.l^{-1}$ and incubated in a water bath at 20°C for 45 days. Behaviours of sulphate and VFA were measured every two or three days for 2 weeks at beginning of the experiment and weekly thereafter. Total sulphide content in batch essays was precipitated with zinc acetate and after analysed by GC-PFPD.

3 RESULTS AND DISCUSSION

3.1 Evaluation of total sulphur content of feed ingredients

Based on the tables (INRA-AFZ, 2004), the S content of 76 raw feedstuffs materials commonly used to formulate swine diet varies greatly ranging from less than 0.5 g total S per kg of material to concentrations over 10 g $S.kg^{-1}$ for yeast effluent for example (Figure 1). These different S contents depend on the material composition itself but also on its origin and/or processing. The S content of whole grains (wheat, corn, barley, rice, sorghum, triticale, rye) is relatively low, usually close to 1.3 g $S.kg^{-1}$ and is principally correlated to the S amino acids content. Cereals and their by-products (gluten feeds, distillers dried grains with solubles, etc.) have average grades around 1.8 g $S.kg^{-1}$, these data are comparable with those measured by Kerr et al., (2008). With this same dataset, dried alfalfa and dried grass feedstuffs have similar concentrations close to 2.0 and 2.5 g $S.kg^{-1}$, respectively. For oilseeds, the mean S content is higher ranging between 1.8 g $S.kg^{-1}$ for beans to 3.3 g $S.kg^{-1}$ for rapeseed. However, for oilseed meals, the final S content is generally 1.5 times higher than the one of the oilseed raw materials themselves. This increase of total S is due to oil removal during the industrial process of transformation. Thus, the total S content of rapeseed meal is 5.9 g $S.kg^{-1}$ after oil extraction (oil represents 40 % of the dried weight) while the rapeseed S concentration is 3.3 g $S.kg^{-1}$. In these oilseed by-products, it is clear that total S concentrations should thus correlate to the CP content of the material itself. Molasses and by-products from starch production are the most concentrated in S among all plant-based ingredients. It is surprising since beet and cane molasses are principally composed of sugar like sucrose (60% of their dried weigh) and this high S content cannot be explained only by the S amino acids content. Actually, it is linked to their industrial process. The use of sulphuric acid in the steeping process of molasses increases their S content. For starch by-products, the same explanation is done. Animal-based feedstuffs (dried milk; fish meals, etc.) contain higher concentrations of total S relative to most plant-based ingredients. Because S amino acids are prevalent in various body components, animal based ingredients are high in total S content. This is the case for example for whey and fish meals which are used as protein sources in pig's diets.

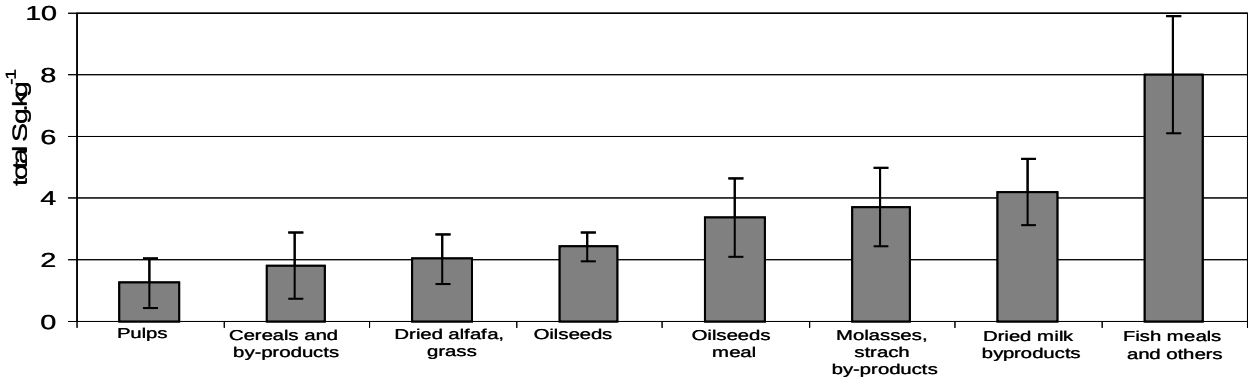

Figure 1: Total S content of different raw materials used for pig feed formulation.

Analysis of all these data suggest that this large variation in the total S content of dietary ingredients (about 20 times difference at most) could influence S feed intake and further S excretion by animals and impact further gaseous S emissions from pig slurry during anaerobic storage. Moreover, since the principal ingredient of pig feed formulation is cereals such as wheat, barley and corn, which have a low total S content, the variation in total S content of meals is strongly correlated to the added ingredients like oilseed meal or industrial by-products, event if these are added in a reduced quantity.

3.2 Sulphur balance in growing pigs

To evaluate S retention by pigs, diets with different total S content were compared in two independent experiments. For these essays, pigs were individually reared in metabolic cages. No feed refusal was observed during the experimental period and feed intake was the same for all treatments. The diets differed in their S concentration between 1.6 and 4.1 g $S.kg^{-1}$. The lower S content was obtained by mixing wheat and soybean meal, with a total CP content of 16%, and the highest S content was obtained by mixing wheat, soybean and wheat distillers dried grains with solubles (DDGS) with an objective of a CP content of 20%. In the first experiment, different wheat DDGS obtained from different process were compared resulting in different S content depending on the industrial process used for ethanol production. Figure 2 presents the S intake by pigs versus S excreted (addition of total S recovered in urines and in faeces) during experiment. S absorption rate (data not shown) measured by difference between S intake and S excreted appeared to be constant for all experiments and for all regimes tested with an average of 80% (±5%). Dietary variation of S level mainly impacted urinary S excretion. Total S in urine increased when dietary S increased, about 55% (±18%) of S intake was recovered in urine for all regimes tested. The same results were obtained for faeces excretion which depended on the ingested S; S recovered in faeces represented 20% (±5%) of S intake. On average from these results it can be calculated that S retained and S excreted represented 25% (±17%) and 75 % (±17%) of the S intake respectively. The high standard deviation observed on measures is due to difficulties in measuring correctly the total S content in urine.

The sulphate content of pig feed, faeces and urine was also determined. With these data it appeared clearly that all the S excreted in urine was sulphate. It was not the case for faeces where less than 50% of S was sulphate, suggesting that S-amino acids have a significant contribution to faecal excretion. Aggregation of all the data acquired from faeces and urine showed that the total S and sulphates contents of fresh pig slurries for these experiments were between 0.3 - 1.9 g $S.kg^{-1}$ and 0.4 - 1.7 g $S\text{-}SO_4^{2-}.kg^{-1}$ respectively. Since sulphate concentrations in drinking water were marginal (average content of sulphate tap waters in Brittany is close to 10 mg $S\text{-}SO_4^{2-}.l^{-1}$) according to the national database on groundwater, we can state that sulphates present in pig slurries come principally from feeding.

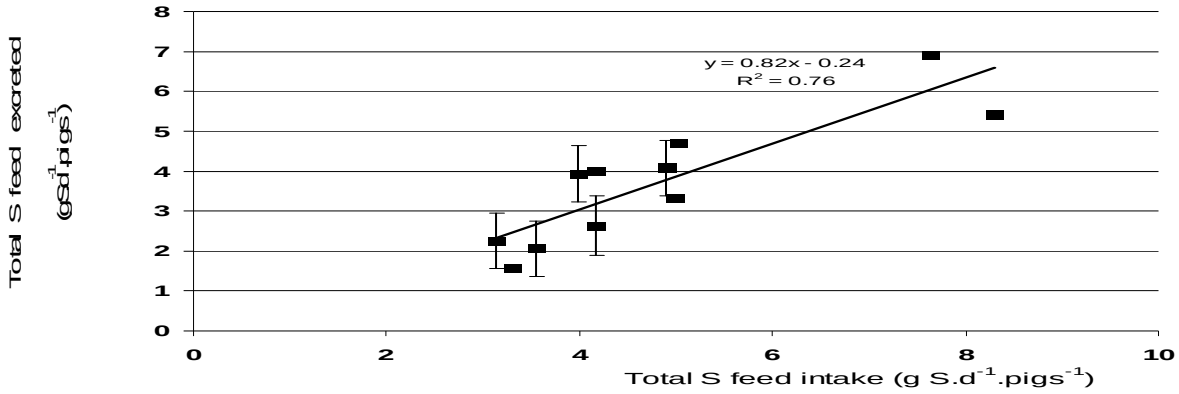

Figure 2: Total S intake versus total S excreted for the 2 dietary experiments realised.

3.3 Behaviour of sulphate during storage of pig slurry

Our experiments demonstrated that S excretion by pigs is mainly as sulphate and that the amount excreted depends on the animal feed used. Currently fresh slurry is collected and stored in anaerobic conditions under the settled floor of the livestock building for few weeks and then stored in large tank outside the barn for several months. To evaluate the behaviour of this sulphate during pig slurry storage, sulphate additions were realised by spiking raw pig slurry. One result of a batch series essays is presented figure 3 with a sulphate spiking of 1 g of S per litter. During this trial, it appears clearly that sulphate concentration was reduced to the detection limit within 20 days while, in the same time, sulphides appeared in slurry and reached a maximum value of 875 mg $S.l^{-1}$ seventeen days after sulphate addition. This depletion of sulphate and accumulation of sulphides could arise by dissimilatory sulphate reduction. At 20°C, this phase started rapidly (but not immediately) after the beginning of the incubation. Few days (4-7) were necessary to produce sulphide. This short lag phase suggested the involvement of sulphate reducing organisms that would be present in large number in pig slurry. Sulphate reduction rate for this essay was estimated to be near 70 µmol $S\text{-}SO_4^{2-}.l^{-1}.h^{-1}$. Since VFA are required by sulphate reducing bacteria to produce sulphide, VFA concentrations were also measured during this experiment. The added propionate and butyrate were consumed more rapidly after sulphate addition than in the control without sulphate addition. Also, acetate concentration increased when sulphate was consumed (data not shown). These

results confirmed that sulphate was consumed in pig slurry by sulphate-reducing bacteria that use propionate and butyrate as electron donors in anaerobic conditions to produce acetate and sulphides.

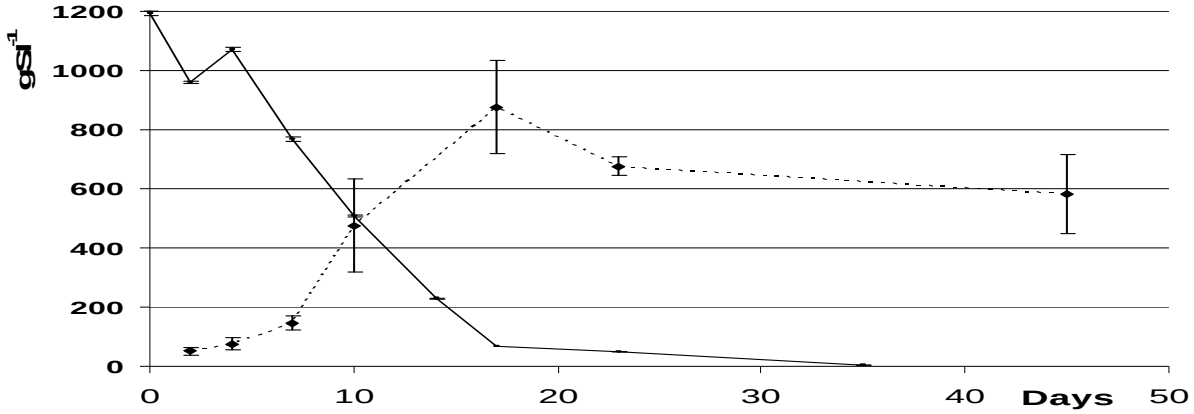

Figure 3: Kinetic of sulphate consumption and sulphide production during lab scale pig slurry storage experiment after sulphate addition at t_0 (continuous line for sulphate and dot line for sulphide).

4 Conclusion

Total S composition of pig diet affects the S content of urine and faeces. The low S control diet generates lower excretion for both urine and faeces. These results show that in all cases the retention of total S content in pig diets is limited; only 25% of S intake is fixed by animals. Most of the S intake is recovered as sulphate in urine. Mixing of urine and faeces in anaerobic conditions conduces to a consumption of sulphates in few days with a large production of sulphide. This reaction is probably realised by dissimilatory sulphate reduction pathway with sulphate reducing bacteria.

ACKNOWLEDGEMENTS

Thanks are due to Pierre Cozannet (PhD Student, Rennes University) for his help for animal experiments. We acknowledge the French Environment and Energy Management Agency (ADEME) for funding this work

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