





ured under controlled laboratory conditions in thermostated (20°C) closed containers. Slurry samples (10 mL from each of the three independent replicates) were collected from treated slurries and from an untreated control every 8 days through a glass pipette immersed into the middle of the vessel and immediately transferred to separate 120 mL dark glass bottles with Teflon sept caps. Concentrations of methane, hydrogen sulphide, and VFA were measured in the headspace. Ammonia was trapped in 0.2 M sulphuric acid.

Hourly emissions (E) were calculated as:

$$E(\mu\text{moles} \cdot \text{g}^{-1} \cdot \text{h}^{-1}) = \frac{C \cdot V_{\text{gas}}}{w_{\text{sample}} \cdot t} \quad (1)$$

where C is the concentration of gas in the headspace,  $V_{\text{gas}}$  is the void volume of the vial,  $w_{\text{sample}}$  is the dry weight of the sample, and t time in hours. Cumulative emissions were calculated from graphical interpolations.

### Copper addition treatment

The effect of addition of copper ions at different concentrations in the absence of electrolytic treatments was examined in a laboratory experiment.

Different aliquots of a 0.1 M stock solution of  $\text{CuCl}_2$  were added to freshly collected swine slurry at the rate of 0 mg, 200 mg, 400 mg, 800 mg and 1200 mg  $\text{Cu}^{2+} \text{kg}^{-1}$  TS, corresponding respectively to  $1.25 \cdot 10^{-4}$ ,  $2.5 \cdot 10^{-4}$ ,  $5 \cdot 10^{-4}$  and  $7.5 \cdot 10^{-4}$  moles  $\text{L}^{-1}$   $\text{Cu}^{2+}$ . Each treatment, including control, had three separate replicates. The amount of copper added was in the range of  $\text{Cu}^{2+}$  concentrations encountered in electrolytic treatments (Chiumenti and Donantoni, 1991). Slurry samples (one from each of the three separate replicate treatments) were collected through a glass pipette and immediately transferred to dark glass bottles (120 mL) with PTFE/silicon septa for micro-syringe sampling of gases. Bottles (three replicates) filled with 12 mL of slurry (10% volume) were closed, shaken, and incubated for 7 days at 20°C. VFA, methane, and hydrogen sulphide concentrations were measured in the headspace at the end of the incubation.

### Gas chromatographic analysis

A HRGC MEGA 2 FISIONS INSTRUMENTS 8560 GC was used with a FID detector (flame ionisation detector) set at 275°C. The injector operated in splitless mode, ignited through an air and hydrogen mixture at 250°C. A capillary AT-1000 column (Supelco, Bellefonte, PA, USA) was used for analysing acetic acid, propionic acid, butyric acid, isobutyric acid, and valeric acid; the carrier gas was helium with the flow rate of 5 mL  $\text{min}^{-1}$ . Column temperature was initiated at 60°C, with an increasing rate of 4°C per minute up to 112°C for a total time of 13 min; volume injected was 100  $\mu\text{L}$ .

To calculate the concentrations of VFA in the headspace of bottles, pure standards of each VFA (99.9%) were used after a 1:200 dilution with diethyl ether in hermetic vials. The density (Merck index) of each VFA, the dilution and the amount of sample injected in the gas chromatograph (1  $\mu\text{L}$ ) were used to calculate the individual response factors. For the analysis of methane and hydrogen sulphide, samples were handled in the identical way but incubated for 1 h at room temperature. A HRGC MEGA 2 CE/INSTRUMENTS 8540 gas chromatograph equipped with a thermal conductivity detector was used. Temperature was 110°C and 150°C for the filament and bridge, respectively. Column was a packed Poropak Q (ALTECH Srl, Bareggio, MI, USA) and helium at a flux of 20 mL

$\text{min}^{-1}$  as carrier gas, the initial temperature gradient was set at 50°C for 2 min, then at 25°C per minute up to 100°C, followed by a 5 min isotherm; volume injected was 200  $\mu\text{L}$ . To calculate the methane proportion between chromatographic areas and the concentration in the samples, a pure standard (1%) was injected (5 mL) in a 120 mL bottle with PTFE/silicon septa and analysed. Hydrogen sulphide standard was obtained treating a known amount of sodium hydrate sulphide ( $\text{NaS}_2(7-9) \cdot \text{H}_2\text{O}$ ) with sulphuric acid concentrated and in a 120 mL bottle with a PTFE/silicon septa screw cap, which was immediately closed for gas chromatograph analysis. The amount of sulphide (18.6% w/w  $\text{S}^{2-}$ ) in the sodium hydrate; sulphide was determined through iodometric titration.

### Offensivity index

In order to evaluate the effect of treatments on potential odour perception an empiric offensivity index (OI) derived from the odour threshold value (OTV) normalised contributions was devised. The index was calculated as the sum of the concentrations of VFA ( $c_i$ ;  $\mu\text{g m}^{-3}$ ) measured in the headspace of bottles per g of total dry solids, each divided by its relative OTV ( $\mu\text{g m}^{-3}$ ):

$$OI = \sum_i \left[ \frac{c_i}{OTV_i} \right] \quad (2)$$

$OTV_i$  values, are the lowest concentrations perceived by subjects and were taken from Ruth (1986).

### Statistical treatment

Quantitative variables were characterised by the average value and standard deviation of three independent replicates. All measures were based on TS and expressed as mean  $\pm$  standard deviation. The non-parametric Kruskal-Wallis test was performed to examine the significance of difference between treatments ( $P < 0.05$ ). Data were statistically analysed by R software (R Development Core Team, 2010).

## Results and discussion

### Electrolytic treatments

The lower current applied in the electrolytic treatments (25 mA constant current) was chosen as the minimum applied current which enabled to obtain, with copper electrodes, a potential difference between 1.5 and 1.8 V, a range sufficient to induce oxidation and dissolution of  $\text{Cu}^{2+}$  at the anode. With graphite electrodes, at 25 mA, potential differences ranged between 3.0 and 3.5V and were sufficient to precipitate water electrolysis resulting in anodic production of oxygen. The highest current (75 mA constant current) was the highest current that enabled stable continuous operation under the established experimental conditions. In contrast to the control, no stratification and formation of crust was observed in all the electrolytic treatments. In the graphite electrodes treatments, the slurry became greenish and more fluid than the control.

### Chemical parameters

As showed in Table 1, differences in pH, which ranged between pH 7.4-8.2 throughout the experiment, were small and not likely to cause any impact on either production or release of unpleasant smells. The same occurred for specific conductivity

which tended to decrease slightly in all treatments and increased again only at the end of the experiment, ranging between 28.9 and 35.5 mS cm<sup>-1</sup>. Ammonia concentrations in the slurry tended to decrease with time, being insufficiently affected by treatments (0.36-0.49 mol L<sup>-1</sup>) (Table 1). The 75 mA treatment with copper electrodes was the only treatment which caused the redox potential to increase from about -400 mV to -133 mV after 32 days; in the other treatments, redox potentials all remained very negative and typical of fully anaerobic conditions (Table 1).

## Emissions

Hydrogen sulphide emission rates were not significantly

reduced as compared to control in electrolytic treatments; however, cumulative emissions from electrolytically treated slurry were lower (Table 2). Methane emission rates were variable but always lower than control at 75 mA intensity, with either graphite or copper electrodes; at 25 mA intensity no significant differences were found between treatments and control. Cumulative emissions were, however, lower from electrolytically treated slurries (Table 2) even at 25 mA intensity.

Emissions of VFA were larger at the beginning of the experiment and then decreased to increase again at the last sampling for propionic, isobutyric, and valeric acids (Figure 1). Butyric acid emissions were largest at the end of the experiment and emissions

**Table 1. Effects of electrolytic treatments at 25 and 75 mA on pH, conductivity, redox potential and ammonia concentrations of swine slurry during 32 days of incubation. All values are the mean of three independent replicate determinations ± standard deviations.**

	Control	Copper electrodes		Graphite electrodes	
		25 mA	75 mA	25 mA	75 mA
<b>pH</b>					
day 1	7.1±0.2 <sup>a</sup>	7.1±0.2 <sup>a</sup>	7.1±0.2 <sup>a</sup>	7.1±0.2 <sup>a</sup>	7.1±0.2 <sup>a</sup>
day 8	7.4±0.2 <sup>a</sup>	7.4±0.2 <sup>a</sup>	7.4±0.3 <sup>a</sup>	7.5±0.2 <sup>a</sup>	7.7±0.2 <sup>b</sup>
day 16	7.2±0.1 <sup>a</sup>	7.6±0.2 <sup>b</sup>	7.9±0.2 <sup>b</sup>	7.7±0.3 <sup>b</sup>	7.7±0.2 <sup>b</sup>
day 24	7.7±0.2 <sup>a</sup>	7.7±0.3 <sup>a</sup>	8.0±0.4 <sup>ab</sup>	8.0±0.4 <sup>ab</sup>	8.2±0.2 <sup>b</sup>
day 32	7.9±0.2 <sup>a</sup>	8.1±0.3 <sup>a</sup>	7.8±0.2 <sup>a</sup>	8.1±0.3 <sup>a</sup>	8.2±0.2 <sup>a</sup>
<b>Conductivity (mS cm<sup>-1</sup>)</b>					
day 1	29.2±0.4 <sup>a</sup>	29.2±0.4 <sup>a</sup>	29.2±0.4 <sup>a</sup>	29.2±0.4 <sup>a</sup>	29.2±0.4 <sup>a</sup>
day 8	34.8±0.8 <sup>a</sup>	35.5±0.8 <sup>a</sup>	34.2±0.5 <sup>a</sup>	34.9±0.7 <sup>a</sup>	34.2±1.5 <sup>a</sup>
day 16	33.1±1.2 <sup>a</sup>	34.3±1.0 <sup>a</sup>	34.0±1.9 <sup>a</sup>	33.1±0.8 <sup>a</sup>	33.7±0.6 <sup>a</sup>
day 24	29.8±2.3 <sup>a</sup>	30.9±1.9 <sup>a</sup>	29.5±0.8 <sup>a</sup>	30.6±1.8 <sup>a</sup>	28.9±0.8 <sup>a</sup>
day 32	31.4±1.6 <sup>a</sup>	31.7±1.8 <sup>a</sup>	31.7±3.5 <sup>a</sup>	30.3±1.8 <sup>a</sup>	28.9±2.6 <sup>a</sup>
<b>Redox potential (mV)</b>					
day 1	-365±34 <sup>a</sup>	-365±34 <sup>a</sup>	-365±34 <sup>a</sup>	-365±34 <sup>a</sup>	-365±34 <sup>a</sup>
day 8	-392±72 <sup>a</sup>	-393±54 <sup>a</sup>	-388±88 <sup>a</sup>	-392±62 <sup>a</sup>	-391±32 <sup>a</sup>
day 16	-396±76 <sup>a</sup>	-385±34 <sup>a</sup>	-377±44 <sup>a</sup>	-405±35 <sup>a</sup>	-409±51 <sup>a</sup>
day 24	-413±58 <sup>a</sup>	-397±88 <sup>a</sup>	-337±58 <sup>a</sup>	-422±45 <sup>a</sup>	-431±43 <sup>a</sup>
day 32	-419±37 <sup>b</sup>	-395±67 <sup>b</sup>	-133±76 <sup>a</sup>	-428±35 <sup>b</sup>	-442±47 <sup>b</sup>
<b>Ammonia (mol L<sup>-1</sup>)</b>					
day 1	0.59±0.10 <sup>a</sup>	0.59±0.10 <sup>a</sup>	0.59±0.10 <sup>a</sup>	0.59±0.10 <sup>a</sup>	0.59±0.10 <sup>a</sup>
day 8	0.49±0.10 <sup>a</sup>	0.46±0.07 <sup>a</sup>	0.46±0.12 <sup>a</sup>	0.45±0.12 <sup>a</sup>	0.45±0.10 <sup>a</sup>
day 16	0.45±0.12 <sup>a</sup>	0.45±0.10 <sup>a</sup>	0.44±0.12 <sup>a</sup>	0.40±0.10 <sup>a</sup>	0.42±0.10 <sup>a</sup>
day 24	0.41±0.20 <sup>a</sup>	0.45±0.11 <sup>a</sup>	0.43±0.14 <sup>a</sup>	0.40±0.18 <sup>a</sup>	0.41±0.12 <sup>a</sup>
day 32	0.41±0.30 <sup>a</sup>	0.44±0.23 <sup>a</sup>	0.37±0.11 <sup>a</sup>	0.37±0.12 <sup>a</sup>	0.36±0.10 <sup>a</sup>

<sup>a,b</sup>Different letters show significant statistical difference between treatments (Kruskal-Wallis test, P<0.05).

**Table 2. Effect of electrolytic treatment of swine slurry on emission rates and cumulated emissions of hydrogen sulphide and methane. Values are mean of three independent replicates ± standard deviation. Different letters show significant statistical difference between treatments (Kruskal-Wallis test, P<0.05).**

	Control	Copper electrodes		Graphite electrodes	
		25 mA	75 mA	25 mA	75 mA
<b>Hydrogen sulphide (µmol g<sup>-1</sup> h<sup>-1</sup>)</b>					
day 7	43±5 <sup>bc</sup>	37±4 <sup>b</sup>	26±5 <sup>a</sup>	49±5 <sup>c</sup>	50±7 <sup>c</sup>
day 14	64±1 <sup>a</sup>	60±2 <sup>a</sup>	59±1 <sup>a</sup>	60±2 <sup>a</sup>	61±1 <sup>a</sup>
day 19	77±2 <sup>c</sup>	60±9 <sup>b</sup>	37±11 <sup>a</sup>	62±7 <sup>b</sup>	59±11 <sup>b</sup>
day 32	56±5 <sup>b</sup>	44±4 <sup>a</sup>	56±8 <sup>b</sup>	45±8 <sup>a</sup>	55±2 <sup>b</sup>
Hydrogen sulphide cumulative (mmol kg <sup>l</sup> )	1690±10 <sup>d</sup>	1400±10 <sup>a</sup>	1400±13 <sup>a</sup>	1460±13 <sup>b</sup>	1590±10 <sup>c</sup>
<b>Methane (µmol g<sup>-1</sup> h<sup>-1</sup>)</b>					
day 4	00.50±0.00 <sup>b</sup>	00.00±0.00 <sup>a</sup>	00.00±0.00 <sup>a</sup>	00.00±0.00 <sup>a</sup>	00.00±0.00 <sup>a</sup>
day 7	00.22±0.02 <sup>b</sup>	00.29±0.01 <sup>c</sup>	00.09±0.01 <sup>a</sup>	00.30±0.02 <sup>c</sup>	00.08±0.08 <sup>a</sup>
day 14	00.24±0.03 <sup>c</sup>	00.28±0.04 <sup>c</sup>	00.15±0.02 <sup>b</sup>	00.26±0.02 <sup>c</sup>	00.10±0.01 <sup>a</sup>
day 19	00.28±0.04 <sup>d</sup>	00.28±0.01 <sup>d</sup>	00.22±0.01 <sup>c</sup>	00.13±0.01 <sup>b</sup>	00.10±0.01 <sup>a</sup>
day 32	00.31±0.02 <sup>d</sup>	00.21±0.02 <sup>b</sup>	00.26±0.03 <sup>c</sup>	00.27±0.02 <sup>c</sup>	00.17±0.01 <sup>a</sup>
Methane cumulative (mmol kg <sup>-1</sup> )	9.77±0.87 <sup>c</sup>	6.96±0.78 <sup>b</sup>	5.80±0.78 <sup>b</sup>	6.88±0.76 <sup>b</sup>	3.60±0.72 <sup>a</sup>

<sup>a-d</sup>Different letters show significant statistical difference between treatments (Kruskal-Wallis test, P<0.05).

of acetic acid were low at the first sampling, then they increased after 19 days, to decrease again at the last sampling (Figure 1). For each VFA, a cumulative sum of emissions was calculated after the 32 days, results are reported in Figure 2. The number of measures during the 32 days might not have been sufficient to state the

dynamics of acidic emissions; however, the aim of this work was not to monitor emission trends, but to highlight differences among treatments. Timing of measures was chosen on the basis of preliminary experiments. At the intensity of 25 mA, no meaningful difference in cumulative emissions of VFAs was found with respect

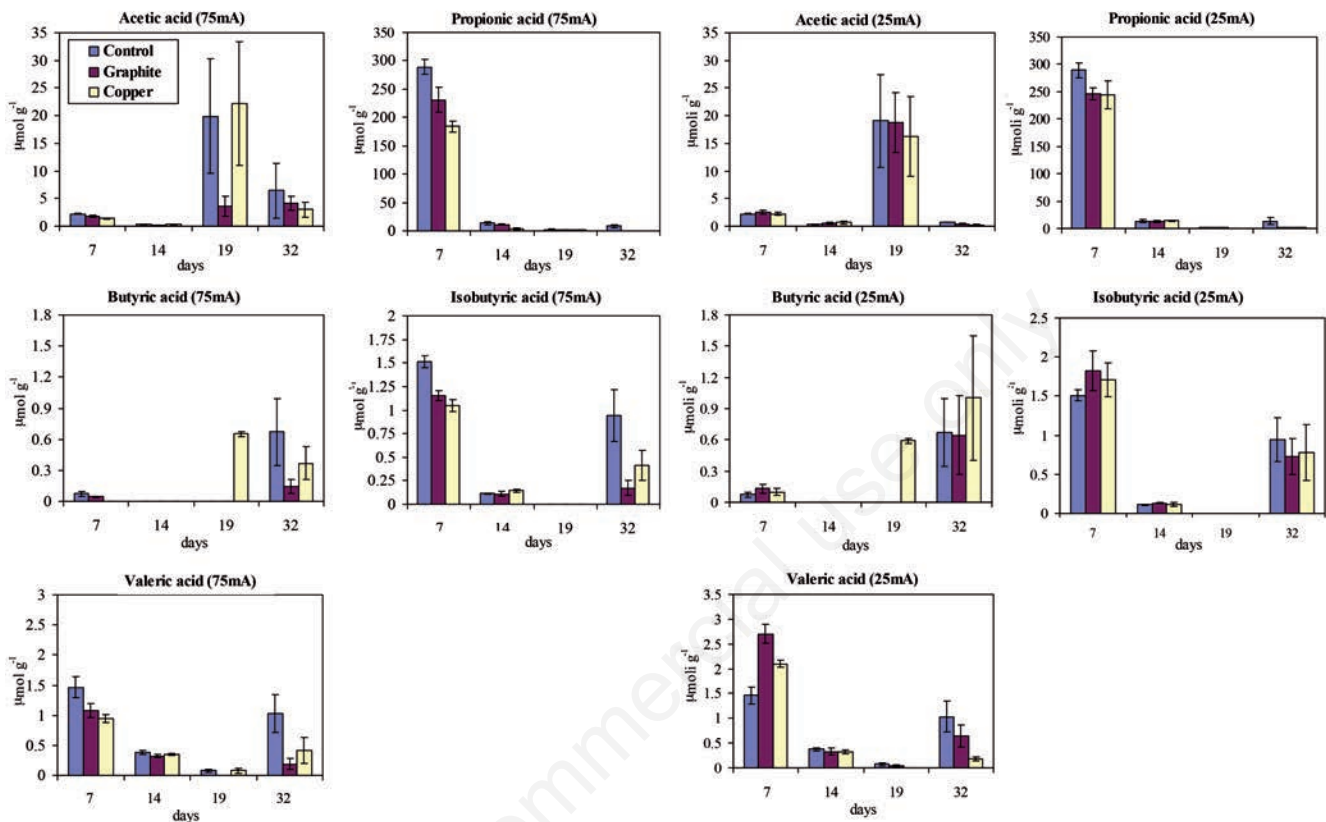


Figure 1. Emissions of volatile fatty acids in  $\mu\text{moles per gram}$  of swine slurry during the experiment. Slurries were electrolytically treated at 25 mA (right) and 75 mA (left). Error bars represent standard deviation.

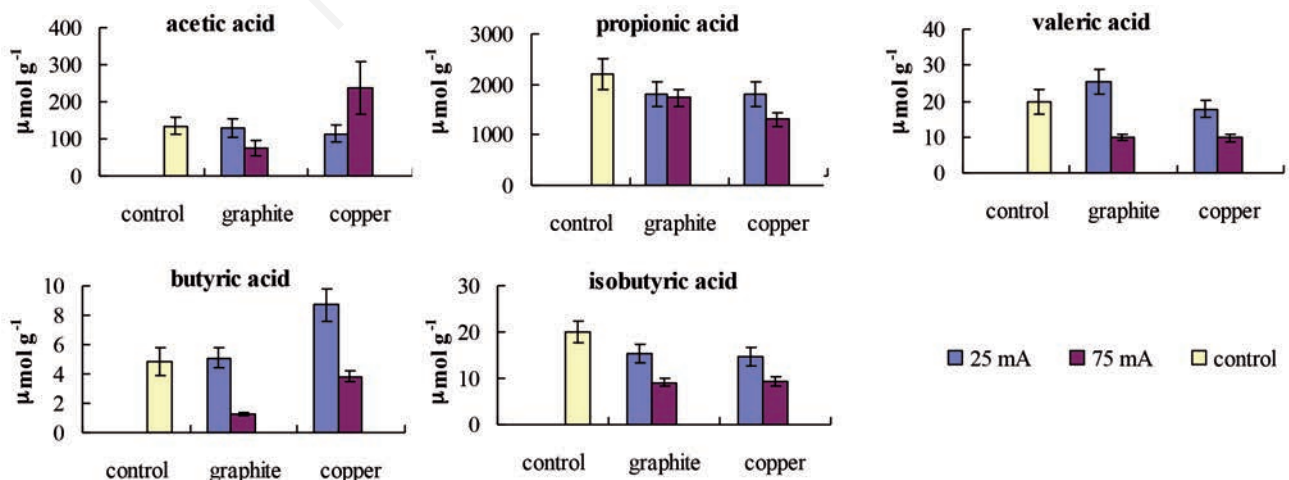


Figure 2. Cumulated emissions of volatile fatty acids from swine slurries treated at 25 mA and 75 mA. Values are expressed in  $\mu\text{moles per gram}$  of slurry. Error bars represent standard deviation.

to the control, most likely due to the high variability of the replicates. Evidently, current intensity was too low to affect the system, with the only exception of propionic acid emissions, which decreased due to the electrolytic treatment. On the contrary, reduction of VFA emissions was significant for the 75 mA intensity treatments and differences between graphite and copper electrodes increased. The only exception of emissions was acetic and butyric acids in the treatment with copper electrodes (Figures 1 and 2).

The 75 mA intensity electrolytic treatment with graphite electrodes reduced the value of OI by about 25% with respect to the control, whereas, that with copper electrodes by about 40%. The 25 mA intensity treatment reduced it of only about 15% with both graphite and copper electrodes (Figure 3).

### Effect of copper addition treatment on emissions

Emissions of VFA were reduced with favourable proportionality to the amount of copper added with the only exception of the slurry treated with 400 mg Cu<sup>2+</sup> kg<sup>-1</sup> TS where emission of acetic acid was larger than the control (Figure 4).

Addition of Cu<sup>2+</sup> ions did not result in inhibition of methane production at the lower addition rates: emissions were even larger than in the control with 400 and 800 mg Cu<sup>2+</sup> kg<sup>-1</sup> TS (Figure 5) but decreased at 1200 mg Cu<sup>2+</sup> kg<sup>-1</sup>. On the contrary, hydrogen sulphide emissions were considerably reduced even at a rate of 200 mg Cu<sup>2+</sup> kg<sup>-1</sup> TS, without differences among copper addition rates (Figure 5).

The OI index revealed that copper additions were effective even at the lowest rate in reducing the potential noxious odour impact of the treated slurries (Figure 6).

## Discussion

Our results confirmed that the release of foul smelling volatile substances from swine slurry could be reduced by applying electrolytic treatments of sufficient intensity. The highest intensity treatment at 75 mA, was within the optimum current intensity interval proposed by Skjelhaugen and Donantoni (1988) and resulted in the strong reduction of the amounts of propionic acid, butyric acid, isobutyric acid, and valeric acid emitted by a

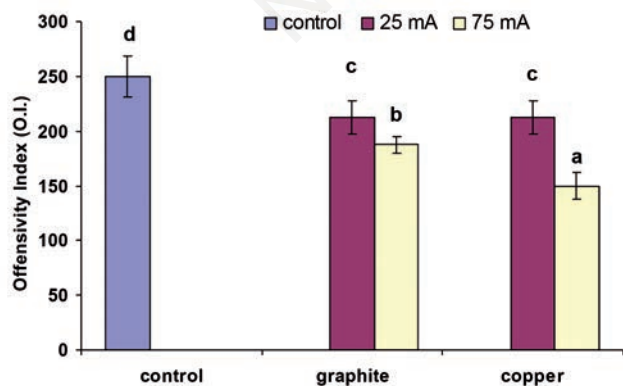


Figure 3. Odour offensivity index values calculated at the end of the experiment for slurries treated at 25 mA and 75 mA. Error bars represent standard error of the mean. Different letters show significant statistical difference between treatments (Kruskal-Wallis test,  $P < 0.05$ ).

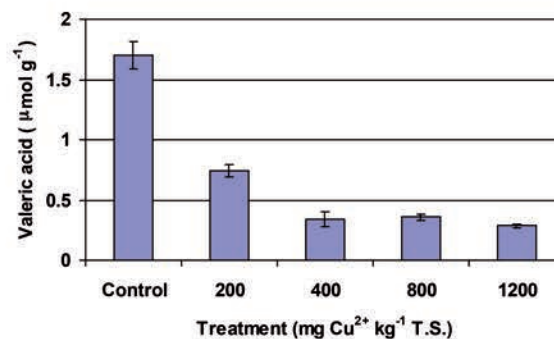
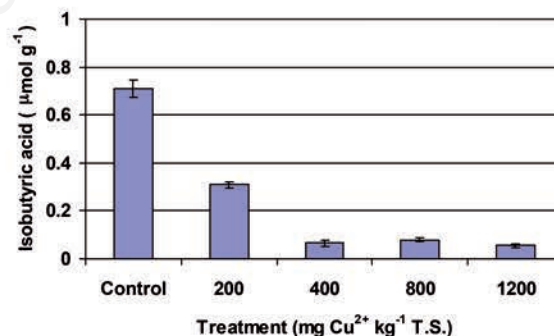
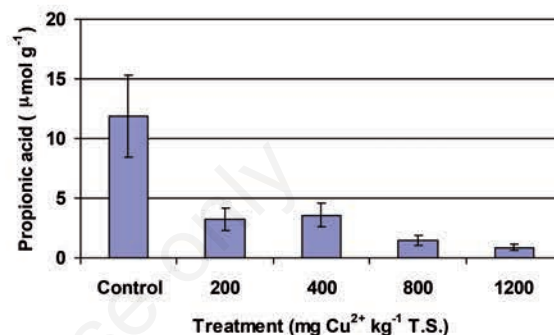
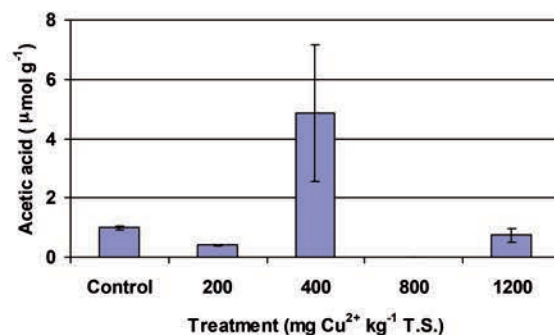


Figure 4. Cumulated emissions (µmol per gram) of volatile fatty acids in swine slurry after 7 days from addition of CuCl<sub>2</sub>. The amount of copper added (mg Cu<sup>2+</sup>) is referred per kg of total solids (T.S.). Error bars represent standard error of the mean.

unit (mass) of slurry (Figure 2). The 25 mA treatment, which was the minimum current intensity outside the suggested range that would result in a potential difference that allowed the dissolution of copper, still demonstrated that VFA production was abated by current application at suboptimal level. Acetic acid emissions were, in all cases, very variable and copper dissolution from electrodes even appeared to promote acetic acid emission, as was in fact confirmed by the experiment with copper addition. The experiment with direct copper addition also proved that hydrogen sulphide emissions could be indeed reduced due to formation of insoluble copper sulphides and microorganism inhibition with no need of any electric current treatment.

The oxidation-reduction potentials measured indicated a relatively lower intensity of fermentation processes with respect to the control, but not so drastic, as to point out a real inhibition of anaerobes, except for the 75 mA intensity treatment with copper electrodes. The change in redox potential observed in this treatment indicated that anaerobic microbial metabolism was impaired by copper ions, because a current of the same intensity had no effect if applied with graphite electrodes. The increase in the redox potential is an adequate indicator of reduced activity of anaerobes, but it is not sufficient to demonstrate foul odour reduction in slurry. However, the lower methane emissions produced by electric current passage in the 75 mA treatments, also confirmed the reduction of fermentation intensity. This is coherent with results obtained for VFA, which are the main substrate for methanogenic bacteria (Montero *et al.*, 2010; Orzi *et al.*, 2010). It is difficult to explain why, for acetic acid, emissions seemed to be increased by electrolytic treatments. The most likely explanation is in the complex microbial community operating

in the slurry; death or stress conditions may not only impair the growth of some types of microorganisms and cause accumulation of intermediate decomposition products, but may also promote the activity of others. Therefore, these data should correspond to the death or growth of a particular strain or family of microorganisms. The dynamics of acetic acid are very interesting due to low emissions at the beginning of the experiment, that increase after 19 days, and then to decrease again, and are apparently stimulated by copper ions.

The superior efficiency in reducing foul emissions of copper electrodes as compared to graphite electrodes is evidently due to copper dissolution as confirmed by the  $\text{Cu}^{2+}$  addition experiment. Figure 6 shows the effect of treatment with copper ions through an odour index calculated from the sum of the cumulated concentration of each volatile fatty acid normalised by its relative OTV. Human odour perception may be based on compounds that are not detected by chromatographic analysis or be affected by synergic effects between different organic molecules (Gralapp *et al.*, 2001). Hence, it is very difficult to predict on the basis of chemical analysis. Normalisation of emissions by OTV, such as in the OI of slurries that has been devised for this work, can provide a realistic evaluation of potential impacts. Similar approaches have been proved useful in the evaluation of the toxicity of mixtures of compounds, such as dioxins (EPA, 2008) and are much more simple, economic, and straightforward in their application than panel-based sensory tests. This simple empiric offensivity index calculated from OTV normalised concentrations was able to differentiate among the different treatments and showed a significant reduction of potential offensiveness with electrolytic treatment at 75 mA intensity. The index also demonstrated an effect of the use of copper electrodes but the difference was not statistically significant. Direct addition of copper ions had a more profound effect (Figure 6). A further standardisation against panel tests is, however, undoubtedly needed to fully validate its application, but our results indicate that it would represent a useful tool for routine monitoring operations or for pre-screening of the effectiveness of measures taken for the abatement of odors.

The amount of copper theoretically dissolved during the 25 mA electrolytic treatment with copper electrodes after 32 days

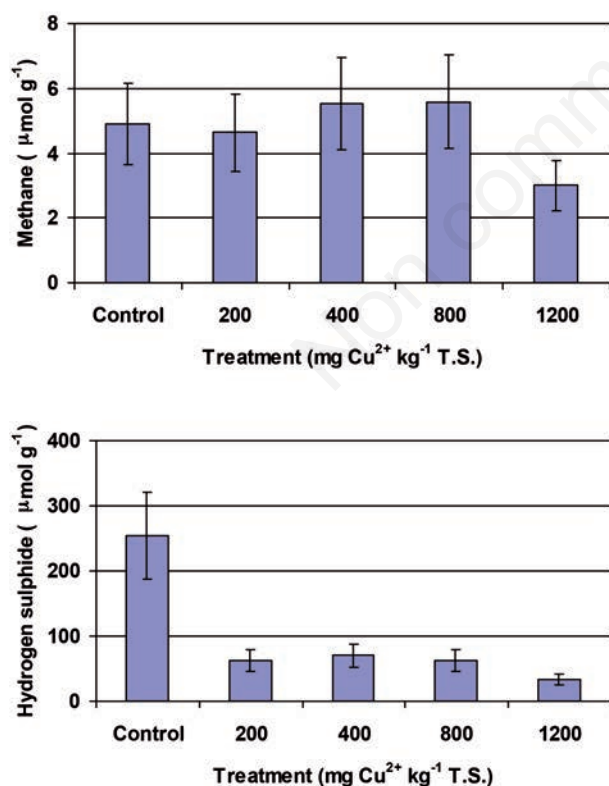


Figure 5. Emissions of methane and hydrogen sulphide in  $\mu\text{mol}$  per gram of slurry, 7 days after addition of  $\text{CuCl}_2$ , the amount of copper is referred to the weight of total solids (T.S.) in the slurry. Error bars represent standard error of the mean.

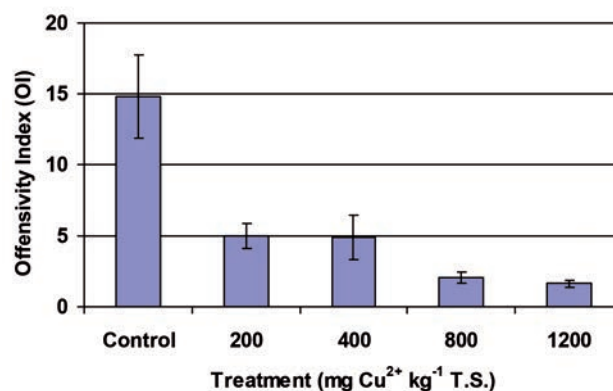


Figure 6. Odour offensivity index values (OI) of  $\text{CuCl}_2$  treated slurries after 7 days from the treatment. OI is calculated as the sum of the emissions of volatile fatty acids, each divided by its odour threshold value, the amount of copper added ( $\text{mg Cu}^{2+}$ ) is referred to the weight of total solids (T.S.). Error bars represent standard error of the mean.

corresponded to about 200 mg Cu<sup>2+</sup> kg<sup>-1</sup> T.S. and that at 75 mA to about 600 mg Cu<sup>2+</sup> kg<sup>-1</sup> T.S. Therefore, direct additions of Cu<sup>2+</sup> ions had a much larger effect than could be predicted from the results of electrolytic treatments with copper electrodes. In fact, in a similar experiment, conducted on a larger scale and at stronger current intensity (600 L and 200 mA), the concentrations of copper measured in the liquid phase and suspended solids of the control, were respectively 1.39±0.03 mg L<sup>-1</sup> and 31.3±0.3 mg kg<sup>-1</sup>, that of the graphite electrodes treatment, were 1.17±0.03 mg/L and 26.83±0.18, whereas, those in the copper electrodes treatment were 1.16±0.02 mg/L and 32.8±0.4 mg/kg. Evidently, much of the copper dissolved at the anode precipitated during the experiment due to the alkaline pH of the slurries (Table 1) and to CuS formation, so that availability of Cu<sup>2+</sup> ions to microorganisms was greatly reduced.

Electrochemical treatments reduced gas emission also at pilot scale (*i.e.*, volume 650 L, copper and graphite electrodes, 0.2-1.0 A current intensity, 1-4 min polarity inversion times) (Da Borso *et al.*, 2002). To correctly scale up the technology, other aspects should be more thoroughly investigated, for example, the difficulty of achieving adequate homogeneity of treatment in large volume tanks and the requirement of higher current intensities than in standard commercial systems (reverse time of 10 min and an intensity of current of 0.5 and 1 A).

## Conclusions

Our results showed that electrolytic treatments do not have a strong influence on the amount of methane, hydrogen sulphide, or ammonia, but they primarily affect VFA emissions. The process can be implemented at full scale only after performing a suitable correction of electrochemical parameters. This work, however, improves our understanding of affecting factors. The OI proposed in this paper, allowed for differentiation among different treatments and showed reduced potential offensivity in the case of higher current application. The effect was only slightly increased by copper dissolution, when the current was applied with copper electrodes, however, copper ions alone, when added as a single addition of CuCl<sub>2</sub> markedly reduced VFA and hydrogen sulphide emissions even at a rate lower than that theoretically released by the 25 mA current treatment. The action of electrolytic treatments, therefore, differed from that of a simple bacteriostatic action exerted by copper ions, as they cannot reach the necessary solution concentrations. The proposed tentative OTV normalised potential offensivity index was found to be very effective in differentiating the effect of the treatments on odorous compounds suppression and, after validation with sensory (olfactometry) tests, could offer an easily determined and sensitive parameter for routine monitoring of outdoor air quality near pig farms and after slurry distribution.

## References

- APHA, AWWA, WPCF, 1992. Standard methods for the examination of water and wastewater. 18th ed. Washington, DC, USA.
- Barth C.L., Hill O.T., Polkowski L.B. 1974. Correlating odour intensity index and odorous components in stored dairy manure. *Trans. Am. Soc. Agric. Eng.* 17:742:7.
- Bejan D., Rabson L., Bunce N. 2007. Electrochemical deodorization and disinfection of hog manure. *Can. J. Chem. Eng.* 85:929-35.
- Bejan D., Sagitova F., Bunce N.J. 2005. Evaluation of electrolysis for oxidative deodorization of hog manure. *J. Appl. Electrochem.* 35:897-902.
- Chiumenti R., Da Borso F., Guercini S. 1993. Guida tecnica per la gestione delle deiezioni zootecniche. Provincia di Padova, Assessorato Tutela Ambiente, Assessorato all'Agricoltura ed., Padova, Italy.
- Chiumenti R., Donantoni L. 1991. Study of the electrolytic treatment applied to livestock manure at pilot scale plant. Proc. CIGR Seminar on Environmental challenges and solutions in agricultural engineering, Aas, Norway.
- Chiumenti R., Donantoni L., Guercini S. 1988. Il controllo degli odori nei liquami zootecnici. *Genio Rurale* 5:33-41.
- Da Borso F., Rodar T., Mezzadri M., Chiumenti A., Chiumenti R. 2002. Control of gaseous emissions from stored pig slurry by means of electrochemical treatment. Proc. 10th Conference Hygiene Safety RAMIRAN, Strbske Pleso, Slovak Republic.
- EPA (U.S. Environmental Protection Agency). 2008. EPA/100/R-08/004. Framework for application of the toxicity equivalence methodology for polychlorinated dioxins, furans, and biphenyls in ecological risk assessment. U.S. Environmental Protection Agency, Washington, DC, USA. Available from: <http://www.epa.gov/sites/production/files/2013-09/documents/tefs-draft-052808-0804.pdf> Accessed: November 2016.
- Gralapp A.K., Powers W.J., Bundy, D.S. 2001. Comparison of olfactometry, gas chromatography, and electronic nose technology for measurement of indoor air from swine facilities. Swine Research Report, 2000.28. Available from: [http://lib.dr.iastate.edu/swinereports\\_2000/28](http://lib.dr.iastate.edu/swinereports_2000/28) Accessed: November 2016.
- Hanajima D., Kuroda K., Morishita K., Fujita J., Maeda K., Morioka R. 2010. Key odor components responsible for the impact on olfactory sense during swine feces composting. *Bioresour. Technol.* 101:2306-23.
- Higgins M.J., Adams G., Chen Y.C., Erdal Z., Forbes Jr. R.H., Glindemann D., Hargreaves J.R., McEwen D., Murthy S.N., Novak J.T., Witherspoon J. 2008. Role of protein, amino acids, and enzyme activity on odor production from anaerobically digested and dewatered biosolids. *Water Environ. Res.* 80:127-35.
- Jones K.B.C. 1977. UK problems and legislation relating to odour control. *Agric. Environ.* 3:245-58.
- Leek A.B.G., Hayes E.T., Curran T.P., Callan J., Beattie V.E., Dodd V.A., O'Doherty J.V. 2007. The influence of manure composition on emissions of odour and ammonia from finishing pigs fed different concentrations of dietary crude protein. *Bioresour. Technol.* 98:3431-9.
- Lovley D.R. 2008. The microbe electric: conversion of organic matter to electricity. *Curr. Opin. Biotechnol.* 19:564:71.
- Montero B., Garcia-Morales J.L., Sales D., Solera R. 2010. Evolution of butyric acid and the methanogenic microbial population in a thermophilic dry anaerobic reactor. *Waste Manage.* 30:1790-7.
- Orzi V., Cadena E., D'Imporzano G., Artola A., Davoli E., Crivelli M., Adani F. 2010. Potential odour emission measurement in organic fraction of municipal solid waste during anaerobic digestion: relationship with process and biological stability parameters. *Bioresour. Technol.* 101:7330-7.
- Persaud K.C., Khaffaf S.M., Hobbs P.J., Sneath R.W. 1996. Assessment of conducting polymer odour sensors for agricultural malodour measurements. *Chem. Senses.* 21:495-505.
- Ranalli G., Chiumenti R., Donantoni L., Sorlini C. 1996.



- Electrolytic treatment of swine liquid manure in a full scale experiment. *J. Environ. Sci. Health*. 31:1705-21.
- R Development Core Team. 2010. R: a language and environment for statistical computing. Wien, Austria. Available from: <http://www.R-project.org> Accessed: August 2010.
- Rappert S., Müller R. 2005. Odor compounds in waste gas emissions from agricultural operations and food industries. *Waste Manage.* 25:887-907.
- Rosenbaum M., Aulenta F., Villano M., Angenent L. 2010. Cathodes as electron donors for microbial metabolism: Which extracellular electron transfer mechanisms are involved? *Bioresour. Technol.* 102:324-33.
- Ruth J.H. 1986. Odor thresholds and irritation levels of several chemical substances: a review. *Am. Ind. Hyg. Assoc. J.* 47:143-51.
- Sheridan B.A., Curran T.P., Dodd V.A. 2003. Biofiltration of n-butyric acid for the control of odour. *Bioresour. Technol.* 199:205-89.
- Shigeta Y. 1976. Odour pollution and deodorization techniques. pp 386-424 in IPC Kogai Boshi Ken Kyukai, Tokyo, Japan.
- Shusterman D. 1992. Critical review: the health significance of environmental odor pollution. *Arch. Environ. Health* 47:76-87.
- Skjelhaugen O.J., Donantoni L. 1988. Combined aerobic and electrolytic treatment of cattle slurry. *J. Agric. Eng. Res.* 70:209-19.
- Spolestra S.F. 1979. Volatile fatty acids in anaerobically stored piggery wastes. *Neth. J. Agric. Sci.* 27:60-6.
- Spolestra S.F. 1980. Origin of objectionable odorous components in piggery wastes and the possibility of applying indicator components for studying odour development. *Agric. Environ.* 265:241-60.
- Varel V.H., Miller D.N. 2001. Effect of carvacrol and thymol on odour emissions from livestock wastes. *Water Sci. Tech.* 44:143:8.
- Yasuhara A., Fuwa K., Jimbu M. 1984. Identification of odorous compounds in fresh and rotten swine manure. *Agric. Biol. Chem.* 48:111.
- Zanardini E., Valle A., Gigliotti C., Pagano G., Ranalli G., Sorlini C. 2002. Laboratory-scale trials of electrolytic treatment on industrial wastewater: microbiological aspects. *J. Environ. Sci. Health* 8:1463-81.
- Zhu J. 2000. A review of microbiology in swine manure odour control. *Agric. Ecosyst. Environ.* 78:93-106.
- Zhu J., Riskowski G.L., Torremorell M. 1999. Volatile fatty acids as odor indicators in swine manure - A critical review. *Trans. ASAE* 42:175-82.