Technical Report

Project title

Optimising Processes for the Stable Operation of Food Waste Digestion

Defra project Code
WR1208

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Executive Summary

Previous research on the anaerobic digestion of source segregated food waste and operational results from commercial digesters have highlighted potential problems with the stable digestion of this material. When operating on this substrate the digestion process typically has a high ammonia concentration and elevated levels of volatile fatty acids (VFA), which can bring about acidification and failure of the digester if the buffering capacity is overcome. It was postulated that the relationship between ammonia and the elevated VFA concentrations resulted from toxicity to the acetoclastic methanogen population, further complicated by impairment of the function of autotrophic methanogens by trace element deficiency. The research presented explores the possibility of regulating the metabolic pathways leading to methane production under high ammonia concentrations by trace element supplementation and also the possibility of removing ammonia to reduce toxicity to the acetoclastic methanogens.

Trace element analysis of digestate from food waste digesters operating at high ammonia concentration and food waste co-digesters operating at low ammonia concentrations showed very little difference in trace element composition. This confirmed that food waste could meet the trace element requirement for stable digestion provided that there was no ammonia toxicity. At high ammonia concentrations the accumulation of intermediate volatile fatty acids indicated that trace elements necessary to support an ammonia-inhibited methanogenic population were likely to be deficient in the food waste used in previous research. To validate if this was likely to be a widespread problem, representative samples of source segregated food waste were taken two waste collection schemes: one in Luton, South Bedfordshire and the other in Hackney, London. The physicochemical characteristics of these two food waste samples were analysed, including biochemical composition and trace elements. No clear difference in the key parameters was seen between the two waste streams and the Ludlow food waste, which had been used in the earlier projects.

Batch flask experiments were carried out to determine whether high concentrations of VFA in food waste digestate could be reduced by the addition of trace elements. The results showed that although trace elements could increase the rate of VFA destruction in a digester suffering long-term accumulation, they could not initiate this process. It was concluded that a period of non-feeding was a pre-requisite to the initiation of VFA removal, probably to allow time for changes in the microbial population to occur. The result highlighted that any strategy for stable food waste digestion should focus on the prevention of initial VFA accumulation in the digester by trace element supplementation, rather than on recovery of severely VFA-laden digesters. Further batch flask trials showed that in digestate from food waste digesters where VFA had not yet accumulated to very high levels the trace element selenium was essential in promoting VFA removal under high ammonia concentrations, and that cobalt and molybdenum may also be important but not necessarily essential. Experiments showed that at selenium concentrations greater than 0.4 mg l^{-1} the beneficial effects were not improved and at concentrations greater than 1.5 mg l^{-1} toxicity was observed.

In semi-continuous trials the results showed that if a proper trace element supplementation strategy was followed food waste could be digested stably at an organic loading rate (OLR) of 5 kg VS m^{-3} d^{-1} over an experimental period of around 100 days (2.5 retention times) without any VFA accumulation: a much higher loading than achieved in previous laboratory and full-scale trials. The VFA concentration in the pair of digesters supplemented with Se, Mo, Co and W and in the pair of digesters with full trace element supplementation remained

below 200 mg l^{-1} up until the time the project was completed. In these digesters the volumetric biogas production reached 3.8 STP m^3 m^{-3} d^{-1} and the specific biogas production was still stable at 0.76 STP m^3 kg^{-1} VS at the OLR of 5 kg VS m^{-3} d^{-1}.

It can be concluded from the experimental results that selenium and cobalt are the key elements that are essential for long-term stability and are not present in sufficient quantities in food waste. The minimum concentrations recommended for selenium and cobalt in food waste digesters at moderate organic loading rates are around 0.16 and 0.22 mg l^{-1} respectively. A total selenium concentration greater than 1.5 mg l^{-1} is likely to be toxic to the microbial consortium in the digester. Mo, W, and Ni are present in food waste in sufficient quantities for moderate loadings, but may have to be supplemented in digestion at a high organic loading rate. The potential for synergistic effects involving Mo and W has yet to be clarified. Food waste has sufficient Al, B, Cu, Fe, Mn and Zn.

FISH analysis of the methanogenic population found in the food waste digesters operating under high ammonia concentrations showed it to be comprised almost exclusively of members of the order *Methanomicrobiales*. This group of methanogens metabolise by the autotrophic route combining H_2 and CO_2 to form CH_4. Very few methanogens that are known to use the acetoclastic route to CH_4 production were found in the digestate. This result confirmed the initial hypothesis that ammonia caused selective inhibition of the methanogenic population.

For ammonia removal from digestate, gas stripping was chosen as the most suitable method of reducing or eliminating toxicity to acetoclastic methanogens and allowing stable digestion. The process configurations considered were: 1) *in situ* removal, where the ammonia is stripped continuously in the digester using a modified gas mixing system; 2) side-stream removal, where digestate is removed from the main digestion tank to a separate stripping process and returned to the digester; 3) post-hydrolysis removal, where ammonia is first released by a short anaerobic hydrolysis process and then removed prior to adding the waste to the main digester; 4) post-digestion ammonia removal carried out in conjunction with pasteurisation. The experimental work was designed to allow assessment of these four options and to generate data that could be used in a predictive model.

Batch experiments were carried out to investigate the kinetics of ammonia removal with respect to temperature, pH and gas flow rate. Increase in value of any one or a combination of these parameters had a positive effect on the removal rate of ammonia. At 35 and 55 °C ammonia removal timescales were in the order of 600 hours, whereas at 70 °C this could be reduced to around 15-17 hours at an appropriate gas flow rate. With pH adjustment timescales could be further reduced to around 4 hours at 70˚C. High VFA concentrations were shown to have a negative impact on the ammonia removal process as these led to a pH swing that prevented further stripping. This has implications for recovery of anaerobic digestion plants where the process is already operating at increased VFA concentrations, as it may limit the effectiveness of ammonia removal by biogas stripping.

In addition to these batch experiments, two semi-continuous digestion studies were performed to provide data on the integration of ammonia stripping with anaerobic digestion. These were the trial of a side-stream stripping process used in conjunction with mesophilic anaerobic digestion of food waste, and a study to quantify the ammonia release kinetics during a short hydrolysis process.

Under the experimental conditions used the side-stream process was not successful in preventing VFA accumulation, and this in turn limited the effectiveness of the ammonia removal process. A more extensive programme of experimentation is needed to optimise the system, particularly in order to maintain low ammonia concentrations in the initial stages. The stripping process should also be used in conjunction with trace element supplementation to prevent VFA accumulation.

The second experiment showed that the hydrolysis process configuration was not feasible without pH control, as only a small proportion (~15%) of the bio-available ammonia was released during this stage, and there was evidence to indicate that further hydrolysis/fermentation was inhibited.

To further the research, a model was developed using data from the batch stripping experiments to allow simulation of the ammonia concentration in an integrated anaerobic digestion and ammonia stripping process. The outcomes of the modelling suggest that *in situ* mesophilic stripping combined with gas mixing will lead to the lowest in-digester ammonia concentrations. A more thorough analysis of energy requirements is needed, however, and the best practice may be situation specific depending on the availability of waste heat.

1 Introduction

Trace elements are essential for the growth and metabolism of anaerobic microorganisms due to their roles in key enzymes and co-factors in metabolic pathways. Although the requirement for these has been recognised for decades, a proper dosing strategy still presents a challenge in certain circumstances. Food waste appears to be deficient in some trace elements required by the anaerobic digestion process when operating at high ammonia concentrations. This results in the accumulation of volatile fatty acid (VFA) products which may eventually overcome the buffering capacity of the system, with a consequent fall in pH to a point where methanogenic activity stops. The research had two major aims: firstly, to optimise trace element dosing to food waste digesters in an attempt to promote stable operation; secondly, to lower the ammonia concentration in the digester to a point where it was not inhibitory to acetoclastic methanogenesis.

The specific objectives of the work were:

1. To compare the characteristics of source segregated household food wastes obtained from three different sources.
2. To assess the trace element status of digestates with high ammonia and VFA concentrations.
3. To determine whether the high VFA concentrations in digesters could be reduced by selective trace element additions in batch tests.
4. To use selected trace element supplementations in semi-continuous digesters fed on food waste and operating at high ammonia concentrations.
5. To determine whether the methanogenic population changed as a result of high ammonia concentrations and through trace element addition.
6. To investigate the factors controlling ammonia removal from food waste digestates
7. To trial a side-stream removal process in semi-continuous fed digesters.
8. To investigate the feasibility of post-hydrolysis ammonia removal.
9. To develop a predictive model for simulation of ammonia removal.

2 Characterisation of Luton and Hackney food waste streams

A representative sample was taken from each of two source segregated kitchen waste schemes: one collected in Luton/South Bedfordshire and the other collected in Hackney. The physicochemical characteristics of these two food waste samples were analysed, including biochemical composition and essential trace elements for anaerobic digestion and compared with food waste used in the Ludlow digester and used as digester feedstock in projects WR0212[1] and WR1208.

Luton (South Bedfordshire) and Hackney food wastes were collected on the 11th September 2009. 66 food waste bags with a total weight of 98 kg were sampled from the South Bedfordshire collection from fresh material on the tipping floor of the Twin Woods anaerobic digestion plant operated by Biogen-Greenfinch where this material is normally treated. 73 bags were taken from the Hackney collection scheme with a total weight of 74 kg. These bags were taken directly from the designated food waste collection bins of the Shellgrove estate in Hackney, and represent all of the material collected at 4 of the 100 collection points serving the estate over the 3 day period since the previous collection (i.e. a 4% sample).

[1] Defra project code WR0212 (2007-09), Optimising inputs and outputs from anaerobic digestion processes, Banks and Zhang, University of Southampton.

Hackney operates an opt-in scheme and the sample is therefore only representative of waste from those persons who participated in the collection: it may not be typical of the food waste as a whole generated in that area of predominantly inner city multi-occupancy buildings.

After the samples were transported to the laboratory, each food waste bag was weighed. The number of bags by weight category is shown in Figure 1. During preparation of the biodegradable food waste component for physicochemical characterisation analysis, food waste was taken out of the biodegradable plastic bags and any non-biodegradable components and contaminants were removed. These rejected materials were also weighed and their proportions in the total collection weight are shown in Table 1. The biodegradable food waste component was then processed by passing it through a macerating grinder (S52/010 Waste Disposer, Imperial Machine Company (IMC) Limited, Hertfordshire, UK), this produced a very homogeneous consistency material which was further blended in a single vessel using a drill mixer to give a mix of which any part could be deemed representative of the entire batch of collection.

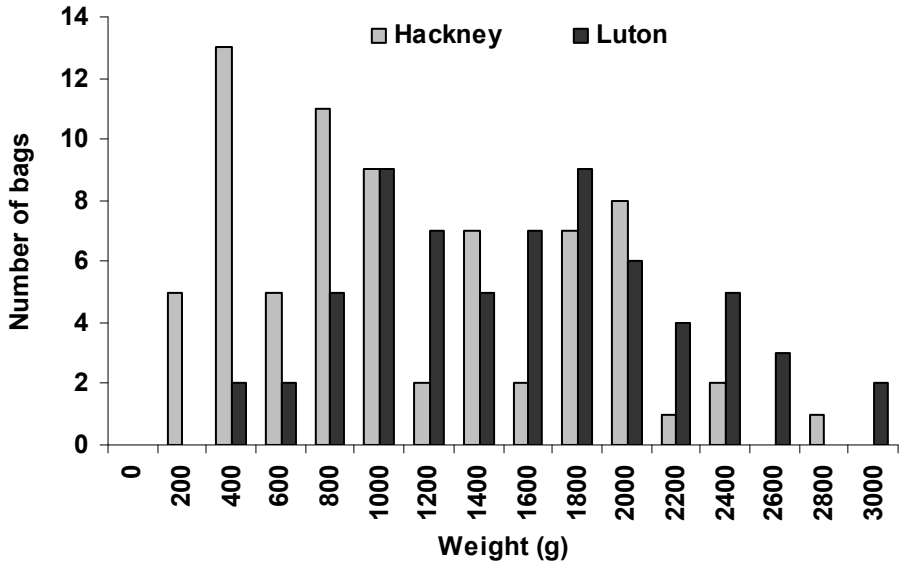


Figure 1 Distribution of food waste bags in different weight fractions from Luton and Hackney food waste streams

Table 1 Percentage of rejected materials from Luton and Hackney food waste streams on the fresh matter basis (%)

Rejected materials	Luton food waste stream	Hackney food waste stream
Bones	1.8	4.0
Fruit stone, corn cobs, etc	3.3	1.3
Paper	0.3	0.9
Garden waste	0.0	0.3
Plastic bags – biodegradable	3.0	2.4
Plastic bags – non-biodegradable	0.0	0.4
Other contaminants	0.4	1.5
Total	8.8	10.8

The physicochemical characterisation analysis was carried out according to the methods described in the technical report for project WR0212, and the results are given in Table Table

2 against a comparison of Ludlow food waste which was used as the feedstock for projects WR0212 and WR1208. No clear difference could be seen in the important parameters between the different food waste streams.

Table 2 Characteristics of Luton, Hackney and Ludlow food waste streams

Source of food waste stream		Luton	Hackney	Ludlow
Fundamental characteristics for anaerobic digestion				
pH		5.12 ± 0.01 (1:2)	5.18 ± 0.01 (1:2)	4.71 ± 0.01 (1:5)
TS (% of fresh matter)		23.70 ± 0.06	25.74 ± 0.18	23.74 ± 0.08
VS (% of fresh matter)		21.84 ± 0.10	23.47 ± 0.31	21.71 ± 0.09
VS (% of TS)		91.28 ± 0.20	91.17 ± 0.91	91.44 ± 0.39
TOC (% of TS)		51.2 ± 1.2	51.3 ± 0.2	48.3 ± 1.0
TKN (% of TS)		3.12 ± 0.01	3.13 ± 0.03	3.42 ± 0.04
CV (kJ g^{-1} TS)		21.43 ± 0.12	21.64 ± 0.11	20.66 ± 0.18
Biochemical composition on a VS basis (g kg^{-1} VS)				
Carbohydrates		418 ± 8	416 ± 2	453 ± 17
Lipids		148 ± 4	157 ± 2	151 ± 1
Crude proteins		213 ± 1	213 ± 2	235 ± 3
Hemi-cellulose		128 ± 5	114 ± 4	38.1 ± 3.7
Cellulose		20.5 ± 5.3	17.2 ± 3.4	50.4 ± 1.6
Lignin		66.6 ± 3.6	68.4 ± 0.3	16.5 ± 0.2
Nutrients on a TS basis (g kg^{-1} TS)				
TKN (N)		31.2 ± 0.01	31.3 ± 0.03	34.2 ± 0.04
TP (P)		4.87 ± 0.08	6.41 ± 0.12	5.41 ± 0.32
TK (K)		12.3 ± 0.1	12.9 ± 0.6	14.3 ± 0.8
Potentially toxic elements on a TS basis (mg kg^{-1} TS)				
Cadmium (Cd)		< 0.05	< 0.05	<1.0
Chromium (Cr)		2.9 ± 0.6	2.9 ± 0.5	29.0 ± 1.2
Copper (Cu)		5.6 ± 0.1	6.5 ± 0.3	7.20 ± 0.81
Mercury (Hg)		< 0.10	< 0.10	< 0.010
Nickel (Ni)		1.71 ± 0.08	1.37 ± 0.31	7.0 ± 2.9
Lead (Pb)		< 1.0	<1.0	< 10
Zinc (Zn)		36.2 ± 2.0	45.0 ± 1.9	33 ± 11
Essential trace elements (mg kg^{-1} TS)				
Cobalt (Co)		0.07 ± 0.01	0.35 ± 0.19	<0.25
Iron (Fe)		148 ± 1	175 ± 58	229
Manganese (Mn)		97.7 ± 1.6	94.5 ± 4.1	85 ± 14
Molybdenum (Mo)		1.1 ± 0.2	1.2 ± 0.2	0.46 ± 0.05
Selenium (Se)		1.2 ± 0.6	0.4 ± 0.3	< 0.30
Tungsten (W)		1.1 ± 0.0	1.0 ± 0.3	< 1.0
Elemental analysis				
% of TS	N	3.12 ± 0.01	3.13 ± 0.03	3.42 ± 0.04
	C	51.2 ± 1.2	51.3 ± 0.2	48.3 ± 1.0
	H	6.56 ± 0.04	6.67 ± 0.13	5.53 ± 0.63
	S	0.21 ± 0.00	0.23 ± 0.03	0.15 ± 0.01
	O	30.7 ± 1.2	29.8 ± 0.4	34.3 ± 2.5
% of VS	N	3.40 ± 0.01	3.43 ± 0.03	3.76 ± 0.04
	C	55.8 ± 1.3	56.3 ± 0.2	52.8 ± 1.1
	O	33.5 ± 1.3	32.7 ± 0.4	36.4 ± 2.8

3 Comparison of trace element concentrations in food waste and other digestates

The concentrations of trace elements from a selection of digesters that were treating food waste as a sole substrate or as a co-digestate as used in Defra project WR0212 'Optimising inputs and outputs from anaerobic digestion processes' were assessed at the beginning of the project. At the time when this analysis was carried out, some of the digesters were in a stable state, and the rest had accumulated VFA which in some cases had led to digester failure. Where digesters had failed these had been maintained in a stirred state with temperature control whilst the VFA degradation profile was monitored after feeding had ceased.

Analysis of these digestates gave a preliminary estimate of the conditions that lead to stable digester operation, in combination with other digestate parameters, especially the concentration of total ammonia nitrogen. Batch and semi-continuous experiments were then conducted to assess whether recovery of volatile fatty acid (VFA)-laden food waste digestate could be enhanced by selective trace element additions.

3.1 Digesters operating in a stable manner

A digester fed with mechanically-recovered biodegradable municipal waste (BMW) and two pairs of laboratory-scale food waste digesters used in co-digestion trials with a food waste/cattle slurry mix and a food waste/card packaging mix as substrates were operating stably at an organic loading rate (OLR) of 4 kg volatile solids (VS) m^{-3} d^{-1} when the project WR0212 was completed. Table 3 shows the concentrations of trace elements, ammonia and VFA present in these digesters. It can be seen that all of the digestates had a total ammonium nitrogen (TAN) less than 2000 mg l^{-1}. The BMW digestate had trace element concentrations around an order of magnitude higher than those found in the food waste co-digestion digestate.

Table 3 Essential elements level in laboratory-scale digesters under steady operational conditions

	Mechanically recovered BMW	Food waste + Cattle slurry	Food waste + Card packaging
Element concentration (mg l^{-1})			
Cobalt (Co)	1.94	<0.10	<0.10
Copper (Cu)	62.8	4.24	5.72
Iron (Fe)	1430	<200	<200
Molybdenum (Mo)	1.31	0.39	0.42
Nickel (Ni)	19.4	1.94	2.02
Selenium (Se)	0.08	<0.03	<0.03
Tungsten (W)	<0.10	<0.10	<0.10
Zinc (Zn)	132	15.7	6.43
Other digestate parameters			
pH	7.4	7.5	7.2
Total ammonium nitrogen (g-N l^{-1})	1.6	1.9	0.9
Total volatile fatty acid (g l^{-1})	<0.10	<0.10	<0.10

3.2 Co-digestion digesters operating with accumulated VFA

Two pairs of laboratory-scale digesters one co-digesting a BMW/pig intestine/flotation fat mix and the other BMW/sheep blood mix had accumulated VFA when project WR0212 was completed. The two digestates had a comparable trace element concentration profile (Table 4) to that of the BMW digestate (Table 3); this was as expected as BMW was the principal

substrate in these co-digestion trials. The 20% addition of co-substrates, however, increased the digestate ammonia level from less than 2000 mg l^{-1} to 5000~8000 mg l^{-1}.

The co-digestion of BMW with the pig intestine and flotation fat mix was at an OLR 4 kg VS m^{-3} d^{-1} when feeding ceased and the VFA concentration had reached between 7600~9700 mg l^{-1} with propionic acid (HPr) as dominate species. Total ammonia nitrogen was around 5000 mg N l^{-1}, and the pH was 7.8, as shown in Table 4. It can be seen from Figures 2 and 3 that this pair of digesters responded to the cessation of feeding with a lowering of the VFA concentration. Total VFA concentration dropped to less than 1000 mg l^{-1} in 80 days after the feeding ceased and the apparent degradation rate of propionate acid was 133 mg HPr l^{-1} d^{-1}.

The pair of digesters fed with BMW and sheep blood had been running at an OLR of 3 kg VS m^{-3} d^{-1} for 235 days when the feeding ceased (Figures 4 and 5). At this point the two digesters were behaving differently. One digester (No. 1) had a relatively low total VFA concentration of 14000 mg l^{-1}, whereas the other digester (No. 2) had a VFA concentration of 47000 mg l^{-1} (Table 4). After 160 days without feeding the acetic acid in digester No. 1 had reduced to less than 1000 mg l^{-1}; however, propionic acid was still around 2000 mg l^{-1} with a maximum apparent propionic acid degradation rate of 30 mg HPr l^{-1} d^{-1}. In digester 2 all VFAs, with the exception of propionic acid, had been sequentially degraded. The concentration of propionic acid, however, remained constant during the 160 days after feeding stopped. The results from this pair of digesters indicate that there are additional factors, other than the concentration of essential elements, that retard the further degradation of propionic acid. This may be caused by the lack of bacteria capable of carrying out propionate oxidation due to the long-term accumulation of VFA or ammonia in the digester. The very high levels of other VFAs which were reached during the digestion and had not yet fully degraded could lead to product inhibition from acetic acid which was still at a concentration of around 5000 mg l^{-1} after 160 days without feeding.

Table 4 Essential elements concentration in stressed laboratory-scale digesters when feeding ceased

	BMW + Pig gut and fat 1	BMW + Pig gut and fat 2	BMW + Sheep blood 1	BMW + Sheep blood 2
Element concentration (mg l^{-1})				
Cobalt (Co)	1.52	2.02	1.30	1.45
Copper (Cu)	70.3	66.2	55.2	52.5
Iron (Fe)	1230	1510	1020	1090
Molybdenum (Mo)	1.07	1.80	0.88	1.17
Nickel (Ni)	13.9	25.0	11.8	15.6
Selenium (Se)	0.10	0.11	0.07	0.06
Tungsten (W)	<0.10	<0.10	<0.10	<0.10
Zinc (Zn)	119	138	92.3	135
Other digestate parameters				
pH	7.9	7.8	8.0	7.2
TAN* (g-N l^{-1})	5.3	4.8	7.5	8.4
Total volatile fatty acid (g l^{-1})	7.6	9.7	13.9	47.1
Acetic acid (g l^{-1})	1.4	0.5	6.9	22.1
Propionic acid (g l^{-1})	5.3	7.8	4.6	7.0

* TAN: total ammonium nitrogen

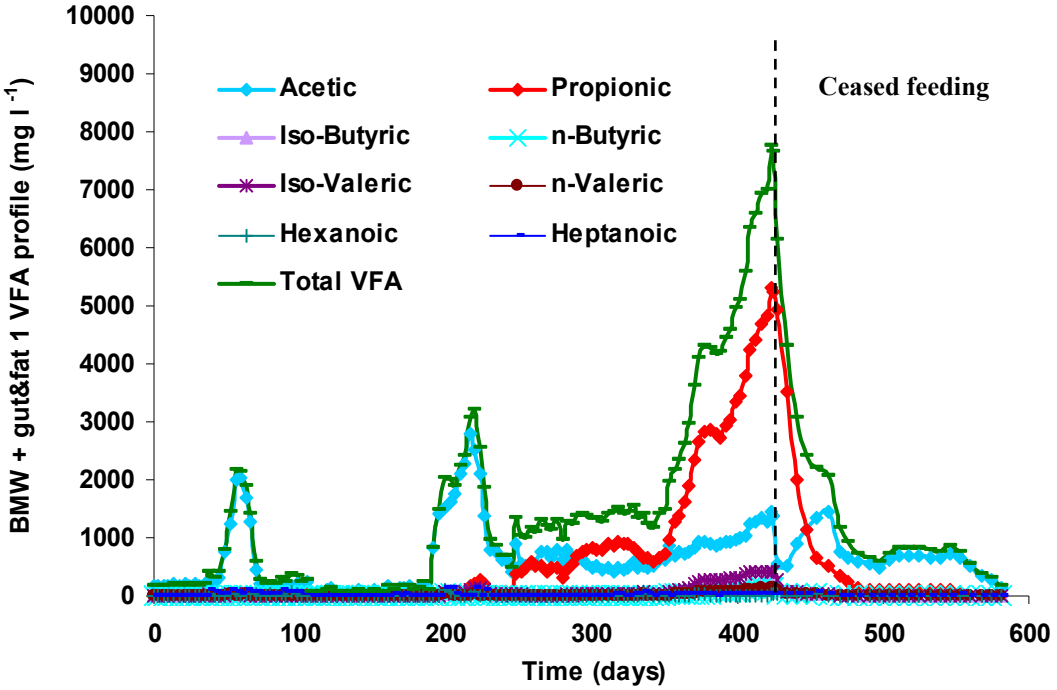


Figure 2 VFA concentration profile in the co-digestion trial using BMW mixed with a pig gut and flotation fat mixture (digester No. 1)

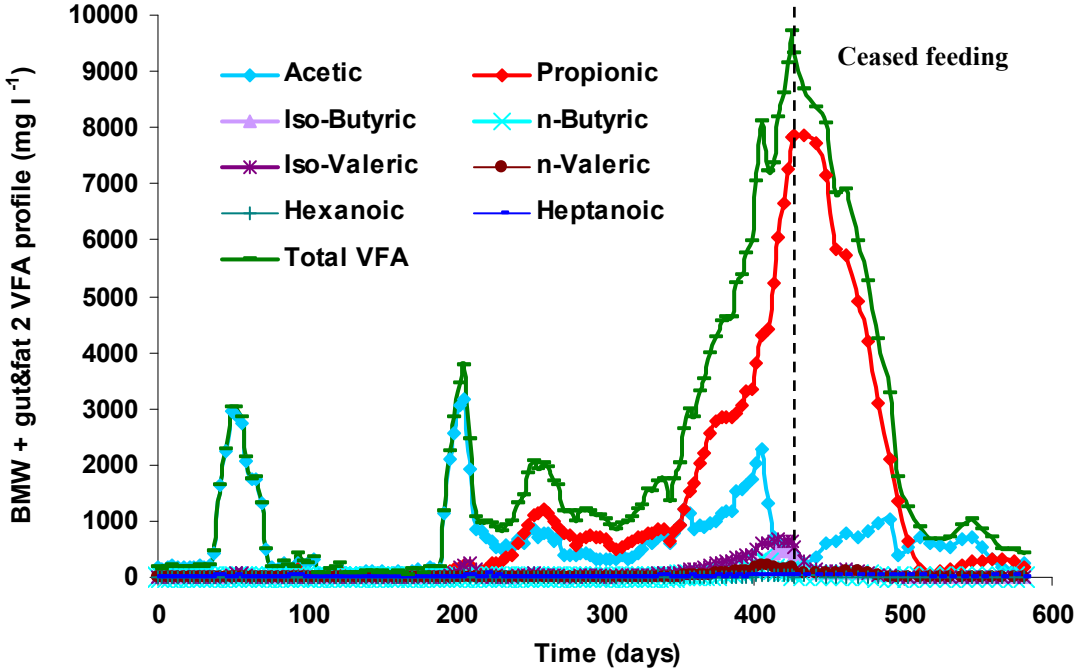


Figure 3 VFA concentration profile in the co-digestion trial using BMW mixed with a pig gut and flotation fat mixture (digester No. 2)

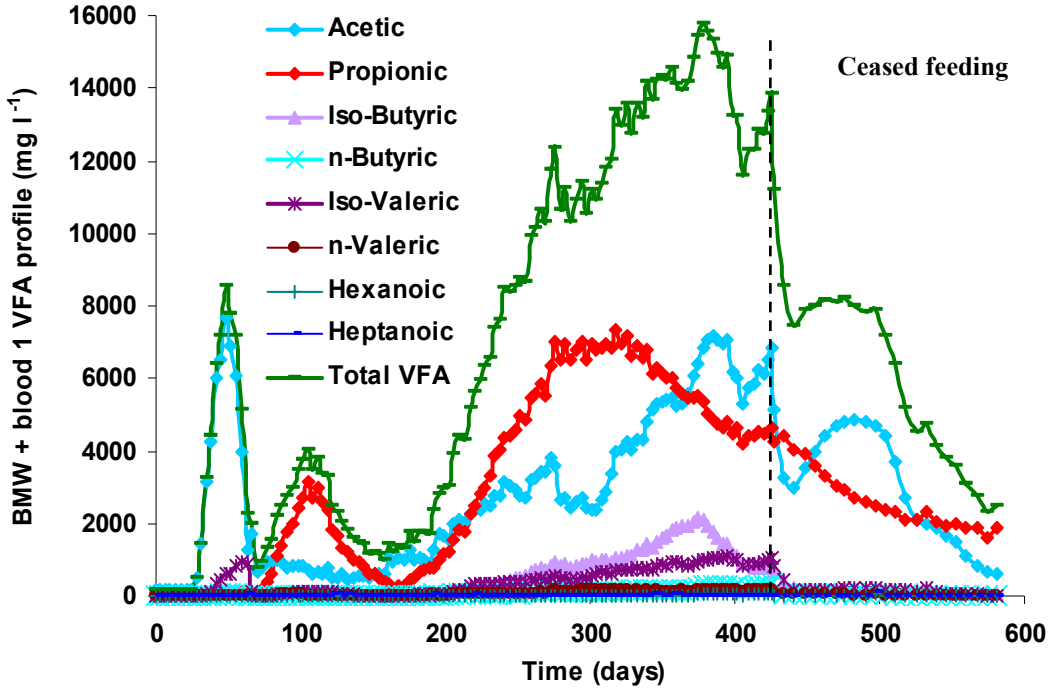


Figure 4 VFA concentration profile in the co-digestion trial using BMW mixed with sheep blood (digester No. 1)

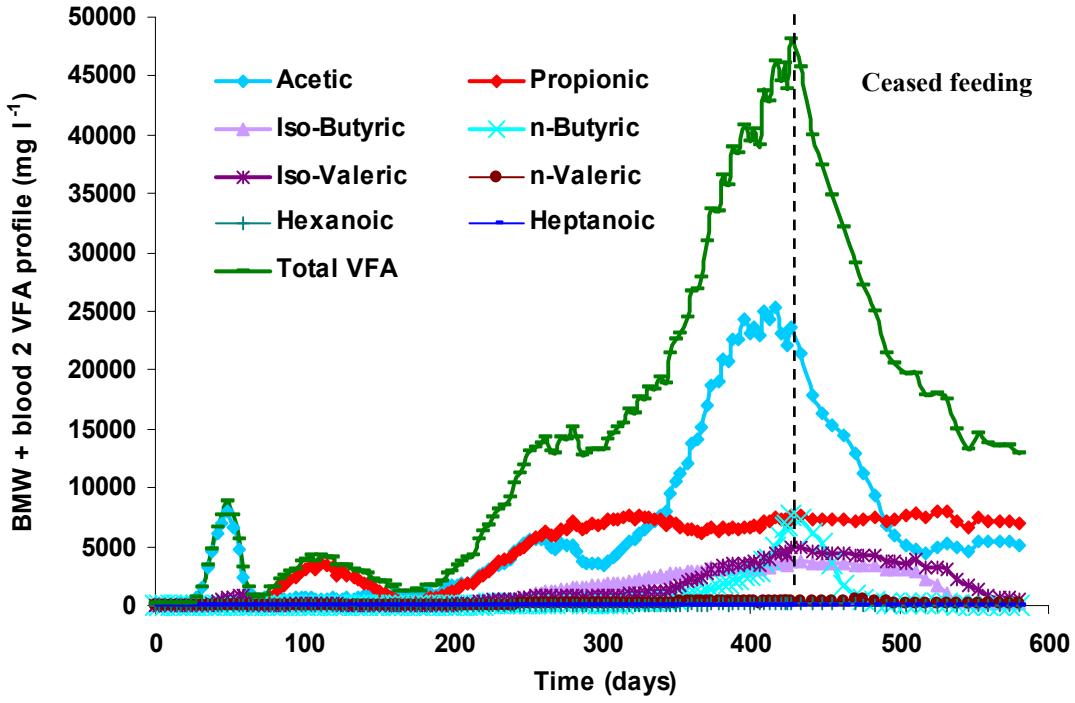


Figure 5 VFA concentration profile in the co-digestion trial using BMW mixed with sheep blood (digester No. 2)

3.3 Digesters in a failed state

The pair of laboratory-scale digesters co-digesting a food waste/potato waste mix and the pair digesting food waste only, both failed as indicated by the pH dropping to below 5.8. In both these cases the digestate had a comparable essential element concentration profile (Table 5) to two of the digestion trials where food waste was co-digested with cattle slurry and also with card packaging, see (Table 3). The total ammonium nitrogen in the failed digesters was also no higher than 3000 mg l^{-1}.

Table 5 Trace element, VFA and ammonia concentrations in laboratory-scale digesters food waste digestion and co-digestion trials

	Food waste + Waste potato 1	Food waste + Waste potato 2	Food waste
Element concentration (mg l^{-1})			
Cobalt (Co)	0.09	0.03	0.07
Copper (Cu)	4.55	1.59	7.58
Iron (Fe)	175	47.4	82.4
Manganese (Mn)	28.9	11.0	13.8
Molybdenum (Mo)	0.35	0.14	0.43
Nickel (Ni)	3.57	1.98	7.15
Selenium (Se)	0.03	0.01	0.02
Tungsten (W)	0.16	0.12	0.33
Zinc (Zn)	12.0	4.43	6.55
Other digestate parameters			
pH	6.3 (5.6)*	5.7	5.6
Total ammonium nitrogen (g-N l^{-1})	2.8	2.9	3.0
Total volatile fatty acid (g l^{-1})	20.5	22.0	22.4
Acetic acid (g l^{-1})	7.3	7.0	9.9
Propionic acid (g l^{-1})	6.9	8.9	7.6

* pH was 5.6 before spiking of cattle slurry for 14 days, and pH was 6.3 when digester was stopped feeding eventually.

The pair of digesters co-digesting potato waste showed a rise in VFA to over 20000 mg l^{-1} and a drop in pH to 5.7. In one of this pair of digesters feeding was stopped (No. 2) directly and the other (No. 1) was fed with 120 ml cattle slurry every day for two weeks to increase the buffering capacity and possibly add 'unidentified essential supplements'. There was no obvious immediate recovery within this two week period and feeding was also ceased. After a further 42 days digester No. 1 showed a rapid consumption of HAc (Figure 6) resulting in a concentration of less than 1000 mg l^{-1} with a pH increase to 7.8. There followed a second VFA degradation peak 21 days later in which there was a rapid drop in the concentration of propionic acid (HPr) at an apparent rate of 247 mg HPr l^{-1} d^{-1}. In digester 2 rapid consumption of HAc appeared after 150 days without feeding with the pH increasing to 7.1. After an initial decrease in acetic acid (HAc) this increased again to 5500 mg l^{-1} as a result of the degradation of n-butyric acid and then rapidly dropped again to less than 1000 mg l^{-1} (Figure 7). During the next 80 days the concentration of HPr dropped gradually with an apparent rate of 127 mg HPr l^{-1} d^{-1}.

The relatively rapid recovery of digester 1 compared to digester 2 could be attributed to the pH rising as a result of the spike of cattle slurry, in addition it could also possibly be attributed to the trace elements and microbial population it added to the digester.

The laboratory-scale digester fed with food waste as sole substrate failed when the pH dropped to 5.6 and the biogas contained less than 10% of methane. The VFAs which had accumulated in this digester started to be degraded 200 days after feeding stopped. The loss of VFA (Figure 8) followed the same consumption sequence as that in the pair of digester co-digesting potato waste. There was a drop first in acetic acid, followed by a lowering of n-butyric acid, and then iso-butyric and iso-valeric acids. Propionic acid was the last major VFA species to be consumed with an apparent degradation rate was 194 mg HPr l^{-1} d^{-1}.

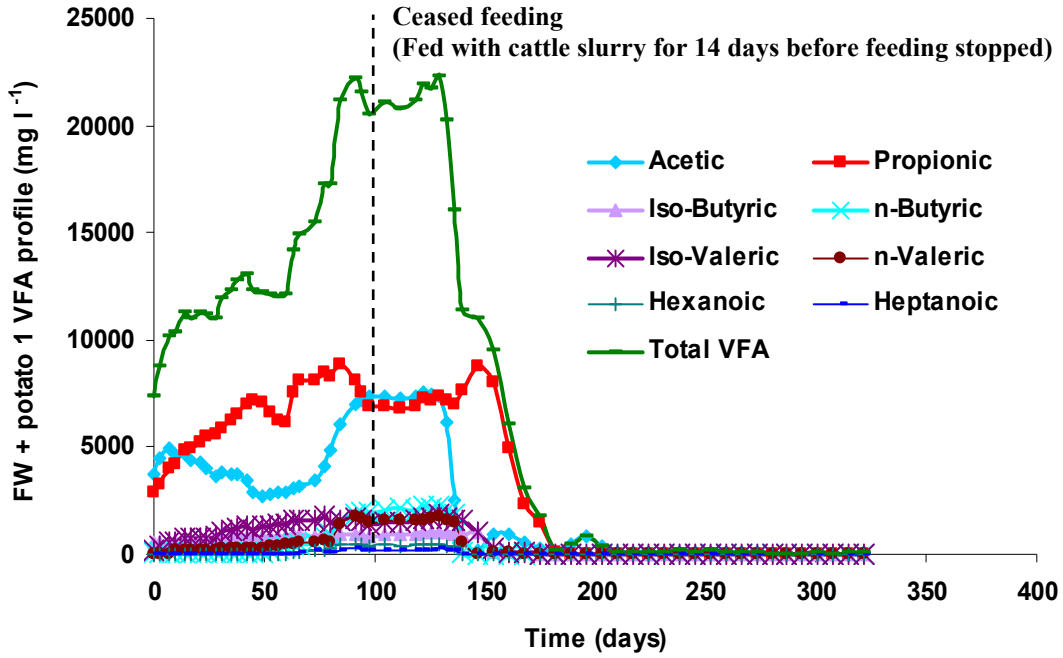


Figure 6 VFA concentration profile in the laboratory-scale co-digestion trial using food waste mixed with waste potato (digestion No. 1)

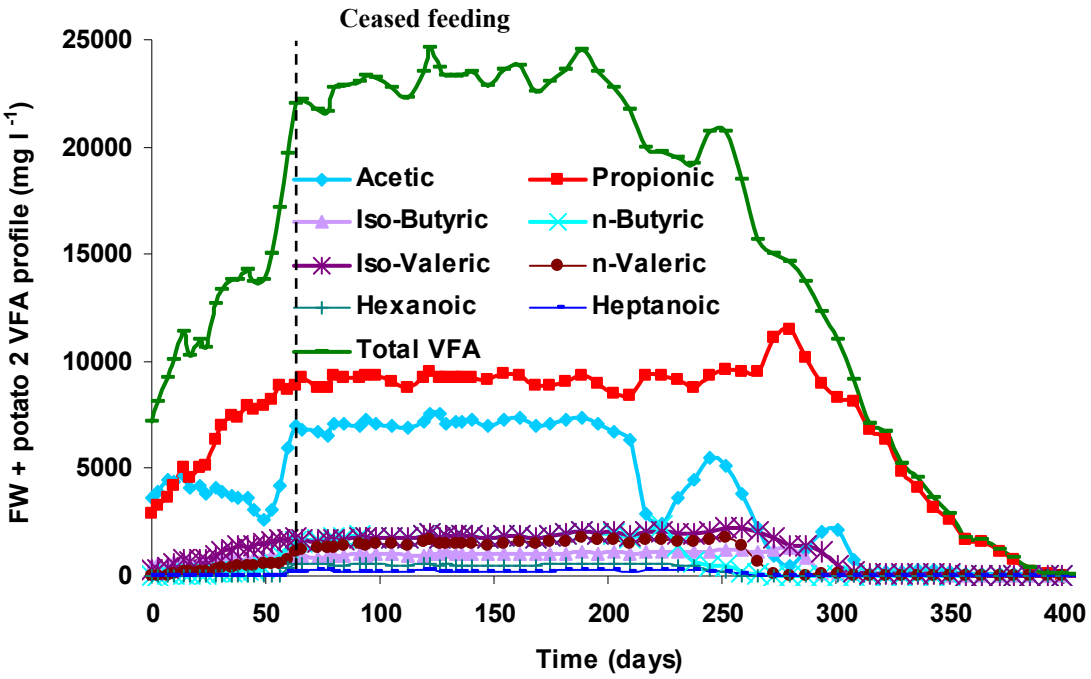


Figure 7 VFA concentration profile in the laboratory-scale co-digestion trial using food waste mixed with waste potato (digester No. 2)

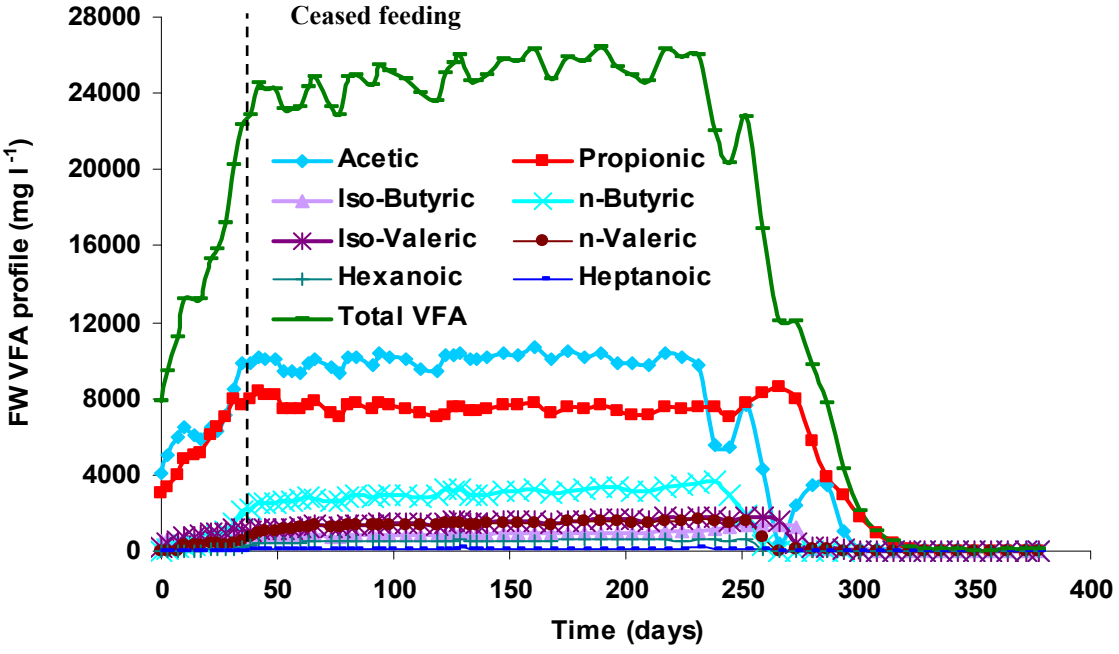


Figure 8 VFA concentration profile in the laboratory-scale food waste digestion control

From the results presented it was not possible to single out trace element concentration in the digestate as the only factor influencing VFA-laden digestate recovery. This can only be explained by consideration of a variety of digester parameters including: trace element level, total ammonium nitrogen concentration, pH, and the period of digester operation after VFA accumulation which could allow for a growth mediated population shift.

4 Batch screening tests on selection of essential trace elements for VFA degradation

Specific methanogenic activity tests using VFA spikes were carried out to identify whether specific trace element addition could have a positive effect in digestate that had not suffered long term VFA accumulation. These tests were carried out in batch flask trials and allowed screening of which trace element(s) in the trace element supplementation matrix had the greatest effect on VFA consumption. The optimal concentration of selenium supplementation was also investigated using batch tests. One food waste digestate with long term accumulation of VFA and one with a lower VFA concentration were used as inoculum in these trials.

4.1 VFA-laden food waste digestate recovery trials

These experiments were conducted using digestate taken from a commercial food waste digestate with high VFA concentration. The effect of trace element supplementation was investigated using digestate in two states. In the first the digestate had been rested from feeding for a period of 80 days and was at a point when it was beginning to recover (Section 4.1.1). In the second the digestate was taken from the main digester tank which had been receiving daily feed additions until the point the sample was taken (Section 4.1.2). The trace element concentration and some other digestate parameters associated with both these digestate samples are shown in Table 6.

Table 6 Trace element, ammonia and VFA concentrations in commercial food waste digestate used in trace element supplementation experiments

	Trial 1: digestate without feeding for 80 days	Trial 2: Fresh digestate
Element concentration (mg l^{-1})		
Aluminium (Al)	-	49.6
Boron (B)	-	3.45
Cobalt (Co)	0.07	0.05
Copper (Cu)	4.05	1.85
Iron (Fe)	114	92.4
Manganese (Mn)	16.7	5.69
Molybdenum (Mo)	0.53	0.05
Nickel (Ni)	3.69	0.70
Selenium (Se)	0.03	0.02
Tungsten (W)	0.10	-
Zinc (Zn)	11.7	7.09
Other digestate parameters		
pH	8.3	8.2
Total ammonium nitrogen (g-N l^{-1})	5.6	7.1
Total volatile fatty acid (g l^{-1})	13.1	35.0
Acetic acid (g l^{-1})	1.9	4.7
Propionic acid (g l^{-1})	10.5	21.1

4.1.1 Trial 1 - using digestate without feeding for 80 days

Food waste digestate collected from a commercial food waste digester was maintained in a fed condition at an OLR of 2 kg VS m^{-3} d^{-1} for 30 days after collection in a 35 litre laboratory-scale digester. After this time the pH had dropped to around 7.4 and the VFA concentration increased to around 25,000 mg l^{-1}. Feeding was then halted but the digester

mixing and temperature control were maintained. The VFA degradation profile was also monitored, as shown in Figure 9. Six litres of digestate were drained out from the digester on day 110 in the middle of the digester recovery process, and this sample of digestate liquor was used in the batch trace element supplementation trial.

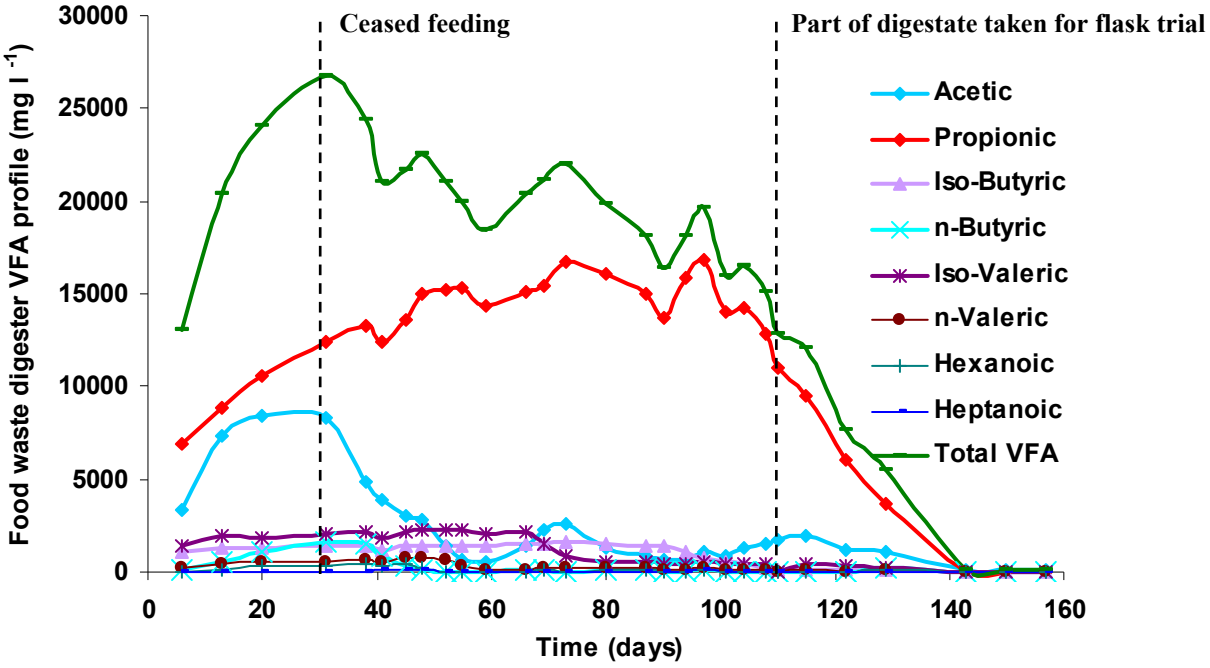


Figure 9 VFA concentration profile in food digestate taken from a commercial food waste digester with accumulated VFA-laden and fed for 30 days before feeding stopped

Four trace element supplementation strategies were tested in this batch trial (Table 7). Strategy 1 used a widely cited trace element supplementation recipe used in anaerobic digestion research by Gonzalez-Gil et al (1999). Strategies 2 to 4 were developed based on literature indicating that selenium, molybdenum and tungsten may play an important role in propionic acid degradation. The design was based on the theory that: oxidation of propionate to acetate, carbon dioxide, H_2 and formate, can only proceed if the products H_2, formate and to a lesser extent acetate are removed by methanogens or other H_2 and formate utilising bacteria. Selenium, as well as molybdenum and tungsten, are essential trace elements for certain enzyme catalysing reactions, such as formate dehydrogenase (FDH), and therefore the availability of selenium, molybdenum and tungsten is expected to be crucial for propionate oxidation.

The tests were carried out in an orbital shaking incubator at a mesophilic (36±1 ºC) temperature and arranged as follows: 24 × 250-ml Erlenmeyer flasks were used and each filled with 200 ml of digestate liquor as described above. Each trace element supplementation strategy was tested in 4 replicates, and 4 flasks were run as controls without trace element addition. The headspace of flasks were purged with a gas mixture of N_2 and CO_2 (80:20) and then flasks were sealed using butyl rubber stoppers connected to biogas sampling Tedlar® bags. Digestate in each flask was sampled and analysed at certain intervals until all VFAs were consumed. It can be seen from Figure 10 that trace element supplementation promoted the VFA degradation rate with an increase in the average apparent propionic acid degradation rate of 530 mg HPr l^{-1} d^{-1}, compared with 300 mg HPr l^{-1} d^{-1} in the controls. No clear difference, however, could be distinguished from the four trace element dosing strategies; this

indicated that selenium was probably a key essential element in this case, although the additional supplementation of other elements might also contribute to the VFA degradation.

Table 7 Trace element supplementation strategy in the batch VFA consumption trials using food waste digestate recovering from VFA accumulation

Essential elements	Compounds used	Supplementation concentration (mg l^{-1})			
		1*	2	3	4
Aluminium (Al)	$AlCl_3 \cdot 6H_2O$	0.010	-	-	-
Boron (B)	H_3BO_3	0.009	-	-	-
Cobalt (Co)	$CoCl_2 \cdot 6H_2O$	0.495	-	-	-
Copper (Cu)	$CuCl_2 \cdot 2H_2O$	0.014	-	-	-
Iron (Fe)	$FeCl_2 \cdot 4H_2O$	0.562	-	-	-
Manganese (Mn)	$MnCl_2 \cdot 4H_2O$	0.139	-	-	-
Molybdenum (Mo)	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	0.027	-	-	0.027
Nickel (Ni)	$NiCl_2 \cdot 6H_2O$	0.012	-	-	-
Selenium (Se)	Na_2SeO_3	0.058	0.058	0.116	0.058
Tungsten (W)	$Na_2WO_4 \cdot 2H_2O$	-	-	-	0.129
Zinc (Zn)	$ZnCl_2$	0.024	-	-	-

* Trace element recipe was based on Gonzalez-Gil et al. (1999).

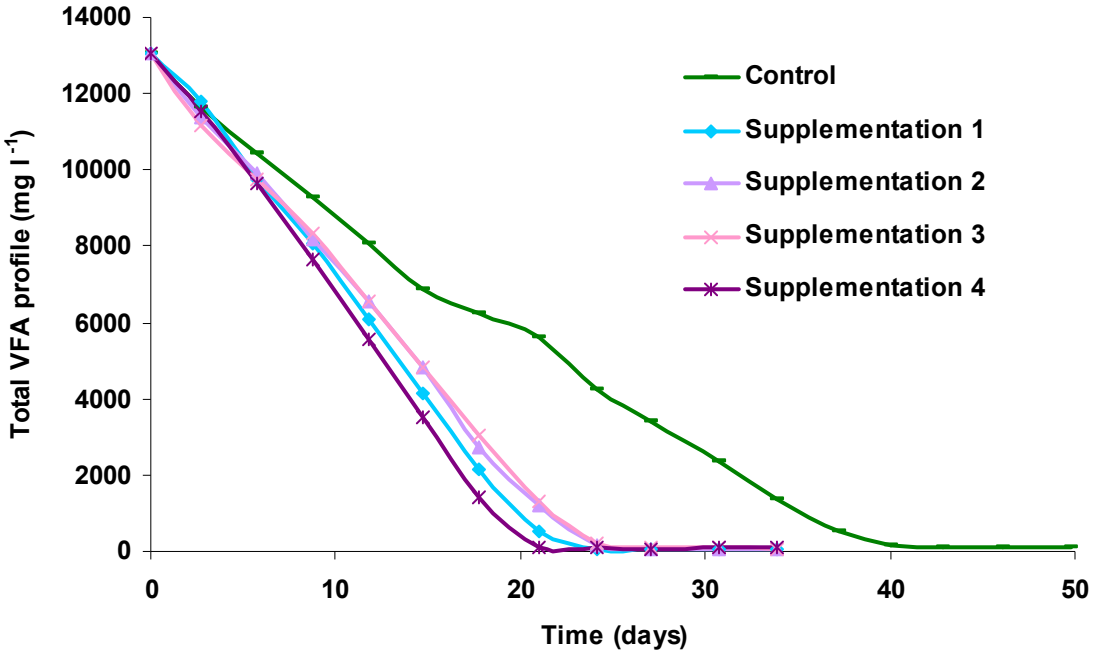


Figure 10 Total VFA degradation profiles in the batch VFA consumption trials using recovering food waste digestate with essential elements supplementation

4.1.2 Trial 2 - using fresh food waste digestate

Food waste digestate was collected from the same commercial food waste digester as above but at a later date. At the time of sampling the digester had accumulated VFA to a concentration of more than 20,000 mg l^{-1} and had an ammonia concentration of around 7000 mg l^{-1}. Two experiments were carried out, the first trial was a preliminary assessment and the second study was a screening test to determine which element(s), in the trace element supplementation matrix, had the greatest effect on VFA degradation.

4.1.2.1 Preliminary trial using fresh food waste digestate with accumulated VFA

The trial was conducted in an orbital shaking incubator at a mesophilic (36±1 ºC) temperature and arranged as follows: 4 × 250-ml Erlenmeyer flasks were used and each filled with 200 ml of collected food waste digestate liquor. Two of the flasks were added with trace element solution as described in supplementation strategy 1 in Table 7, and the other two were run as controls without trace element addition. The flasks were then sealed using butyl rubber stoppers connected to biogas sampling Tedlar® bags. Digestate in each flask was sampled and analysed at certain time intervals until all VFAs were consumed. Figure 11 and 12 show the total VFA degradation profiles and that of the individual VFA species. It can be seen that trace element supplementation showed, to a limited extent, a positive effect on VFA degradation.

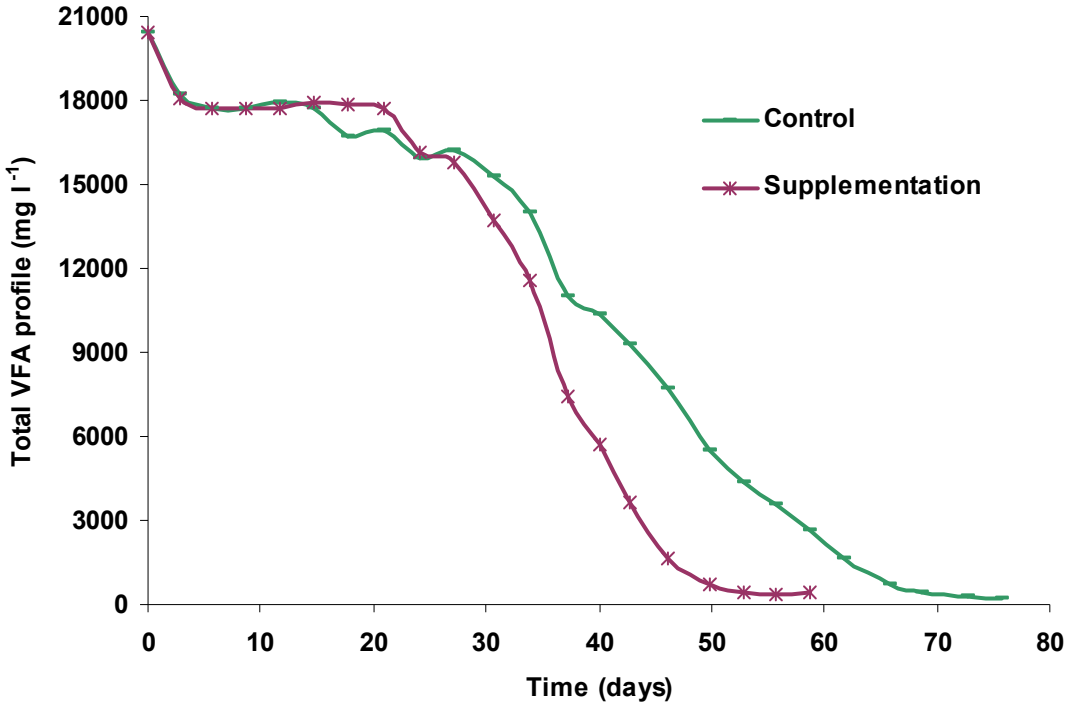


Figure 11 Total VFA degradation profiles in the preliminary VFA consumption trial using fresh commercial food waste digestate with and without trace element supplementation

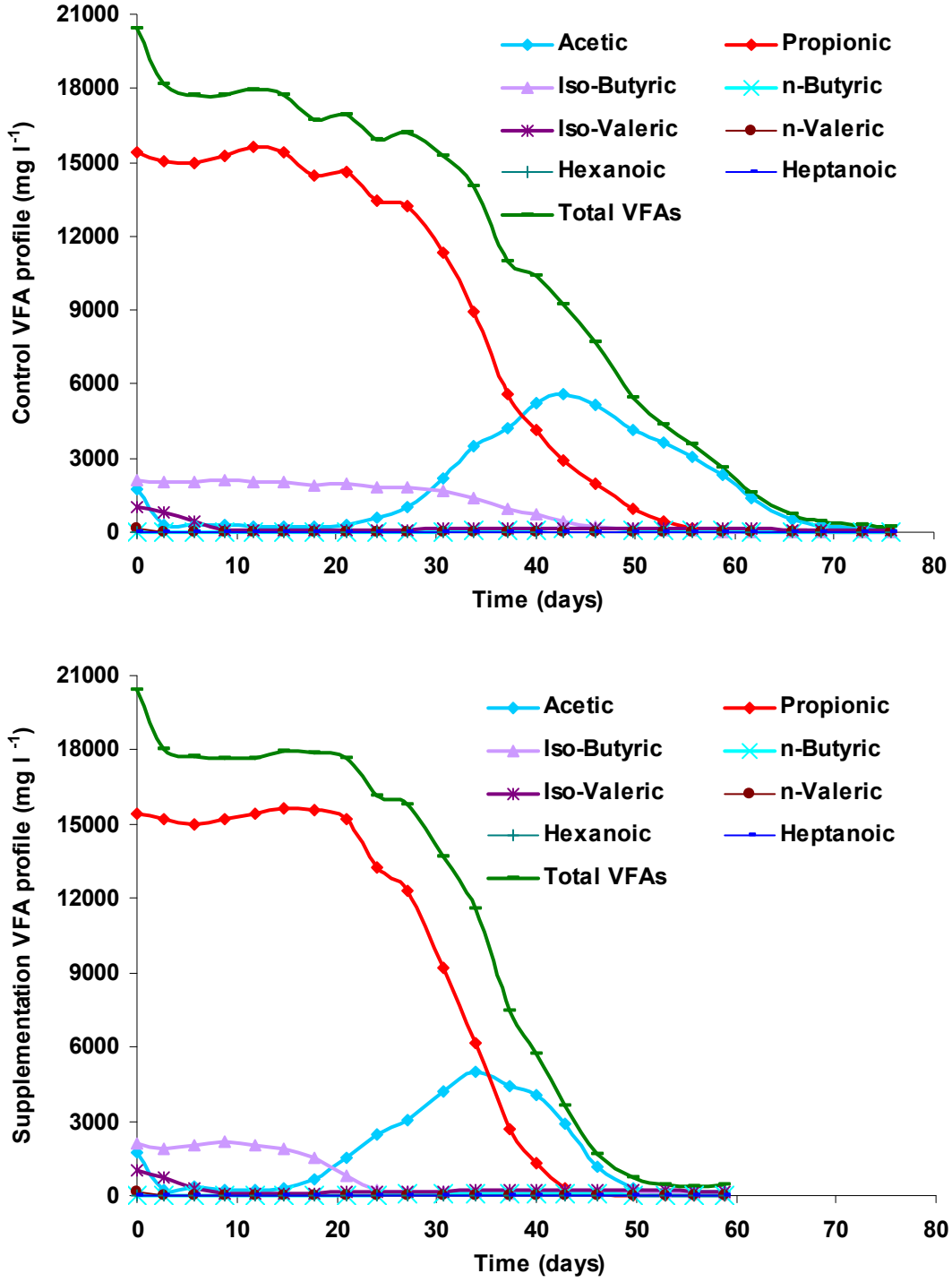


Figure 12 VFA concentration profile in the preliminary VFA consumption trial using fresh commercial food waste digestate with (supplementation) and without (control) trace element element addition.

4.1.2.2 Fractional factorial design to screen different trace element combinations for recovery of fresh food waste digestate with accumulated VFA

This set of experiments was conducted using stressed digestate from a commercial food waste digester with high VFA concentration. The digestate was collected from the main digester tank which had been receiving daily feed additions until the point the sample was

taken. The digestate liquor was used in the experiment, which was obtained by collecting the portion of digestate passing through a 1mm mesh sieve. The trace element concentration and some other digestate parameters associated with the digestate liquor are shown in Table 8.

A fractional factorial design with a resolution of IV and 15 of 2-factor interactions was used in setting up the batch of tests as shown in Table 9. The trace element supplementation levels (Table 10) were chosen based on the results from previous trials and their baseline concentration in the test digestate. The principle was to add elements to a concentration where the addition would show a clear effect if there was one, whilst at the same time avoiding the element concentration reaching a toxic level.

The tests were carried out in an orbital shaking incubator at 36±1 ºC as follows: 36 × 250-ml Erlenmeyer flasks were used with 4 trace element supplementation runs in duplicates. Each flask was filled with 200 ml of digestate liquor, and then the required dose of a stock solution of the element (Table 10) was added to the flasks according to the design (Table 9) and mixed thoroughly with the digestate liquor. The headspace of flasks were purged with a gas mixture of N_2 and CO_2 (80:20) and the flasks were then sealed using butyl rubber stoppers connected to biogas sampling Tedlar bags. Digestate in each flask was sampled and analysed at set intervals.

The VFA profiles of the control, full trace element supplementation, and a partial trace element supplementation are shown in Figure 13. No clear difference in VFA profile can be seen between any trace element supplementation strategy and the control at the beginning of the test; this probably indicates the absence of certain microbial groups in the population and/or a severe inhibition of some metabolic pathways in the digestate suffering long term VFA accumulation. After 180 days the VFA concentration started to reduce in some flasks with trace element dosing in a rather random pattern: the VFA concentration dropped rapidly to 4000 mg l^{-1} with the supplementation of Co, Se, Ni, Zn, and Fe around day 290, although the VFA concentration with full trace element supplementation still stayed at around 17000 mg l^{-1} when the test terminated. The VFA concentration in the control remained around 25000 mg l^{-1} for 260 days without significant VFA degradation. The test was terminated after the trial had been running for 340 days. This is because trace element supplementation could not promote rapid VFA degradation in this food waste digestate and no meaningful results could be generated by continuation of this trial.

Table 8 Concentrations of trace elements in commercial food waste digestate at the start of the experiment

Trace element	Concentration in digestate (mg l^{-1})
Aluminium (Al)	49.6
Boron (B)	3.45
Cobalt (Co)	0.05
Copper (Cu)	1.85
Iron (Fe)	92.4
Manganese (Mn)	5.69
Molybdenum (Mo)	0.05
Nickel (Ni)	0.70
Selenium (Se)	0.02
Zinc (Zn)	7.09
Other digestate parameters	
pH	8.2
Total ammonium nitrogen (g-N l^{-1})	7.1
Total volatile fatty acid (g l^{-1})	35.0
Acetic acid (g l^{-1})	4.7

Propionic acid (g l^{-1})	21.1

Table 9 Fractional factorial design in the VFA degradation trial using VFA-laden commercial food waste digestate with trace element supplementation

Run	Pattern	Co	Se	W	Mo	Ni	Zn	Fe	Mn	Al	B	Cu
1	−−−−−−−−−−−	-	-	-	-	-	-	-	-	-	-	-
2	−−−−+++++++	-	-	-	-	Ni	Zn	Fe	Mn	Al	B	Cu
3	−−−+−++++−−	-	-	-	Mo	-	Zn	Fe	Mn	Al	-	-
4	−−−++−−−−++	-	-	-	Mo	Ni	-	-	-	-	B	Cu
5	−−+−−++−−++	-	-	W	-	-	Zn	Fe	-	-	B	Cu
6	−−+−+−−++−−	-	-	W	-	Ni	-	-	Mn	Al	-	-
7	−−++−−−+++	-	-	W	Mo	-	-	-	Mn	Al	B	Cu
8	−−+++++−−−−	-	-	W	Mo	Ni	Zn	Fe	-	-	-	-
9	−+−−−+−+−+−	-	Se	-	-	-	Zn	-	Mn	-	B	-
10	−+−−+−+−+−+	-	Se	-	-	Ni	-	Fe	-	Al	-	Cu
11	−+−+−−+−++−	-	Se	-	Mo	-	-	Fe	-	Al	B	-
12	−+−+++−+−−+	-	Se	-	Mo	Ni	Zn	-	Mn	-	-	Cu
13	−++−−−++−−+	-	Se	W	-	-	-	Fe	Mn	-	-	Cu
14	−++−++−−++−	-	Se	W	-	Ni	Zn	-	-	Al	B	-
15	−+++−+−−+−+	-	Se	W	Mo	-	Zn	-	-	Al	-	Cu
16	−++++−++−+−	-	Se	W	Mo	Ni	-	Fe	Mn	-	B	-
17	+−−−−+−−+−+	Co	-	-	-	-	Zn	-	-	Al	-	Cu
18	+−−−+−++−+−	Co	-	-	-	Ni	-	Fe	Mn	-	B	-
19	+−−+−−++−−+	Co	-	-	Mo	-	-	Fe	Mn	-	-	Cu
20	+−−+++−−++−	Co	-	-	Mo	Ni	Zn	-	-	Al	B	-
21	+−+−−−+−++−	Co	-	W	-	-	-	Fe	-	Al	B	-
22	+−+−++−+−−+	Co	-	W	-	Ni	Zn	-	Mn	-	-	Cu
23	+−++−+−+−+−	Co	-	W	Mo	-	Zn	-	Mn	-	B	-
24	+−+++−+−+−+	Co	-	W	Mo	Ni	-	Fe	-	Al	-	Cu
25	++−−−−−++++	Co	Se	-	-	-	-	-	Mn	Al	B	Cu
26	++−−+++−−−−	Co	Se	-	-	Ni	Zn	Fe	-	-	-	-
27	++−+−++−−++	Co	Se	-	Mo	-	Zn	Fe	-	-	B	Cu
28	++−++−−++−−	Co	Se	-	Mo	Ni	-	-	Mn	Al	-	-
29	+++−−++++−−	Co	Se	W	-	-	Zn	Fe	Mn	Al	-	-
30	+++−+−−−−++	Co	Se	W	-	Ni	-	-	-	-	B	Cu
31	++++−−−−−−−	Co	Se	W	Mo	-	-	-	-	-	-	-
32	++++++++++	Co	Se	W	Mo	Ni	Zn	Fe	Mn	Al	B	Cu

Table 10 Concentration of element addition in the VFA degradation trial using VFA-laden commercial food waste digestate

Essential element	Compound used	Element concentration (mg l^{-1})	
		Level 0	Level 1
Aluminium (Al)	$AlCl_3 \cdot 6H_2O$	0	10
Boron (B)	H_3BO_3	0	1.0
Cobalt (Co)	$CoCl_2 \cdot 6H_2O$	0	2.0
Copper (Cu)	$CuCl_2 \cdot 2H_2O$	0	1.0
Iron (Fe)	$FeCl_2 \cdot 4H_2O$	0	20
Manganese (Mn)	$MnCl_2 \cdot 4H_2O$	0	10
Molybdenum (Mo)	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	0	0.4
Nickel (Ni)	$NiCl_2 \cdot 6H_2O$	0	1.0
Selenium (Se)	Na_2SeO_3	0	0.4
Tungsten (W)	$Na_2WO_4 \cdot 2H_2O$	0	0.2
Zinc (Zn)	$ZnCl_2$	0	10

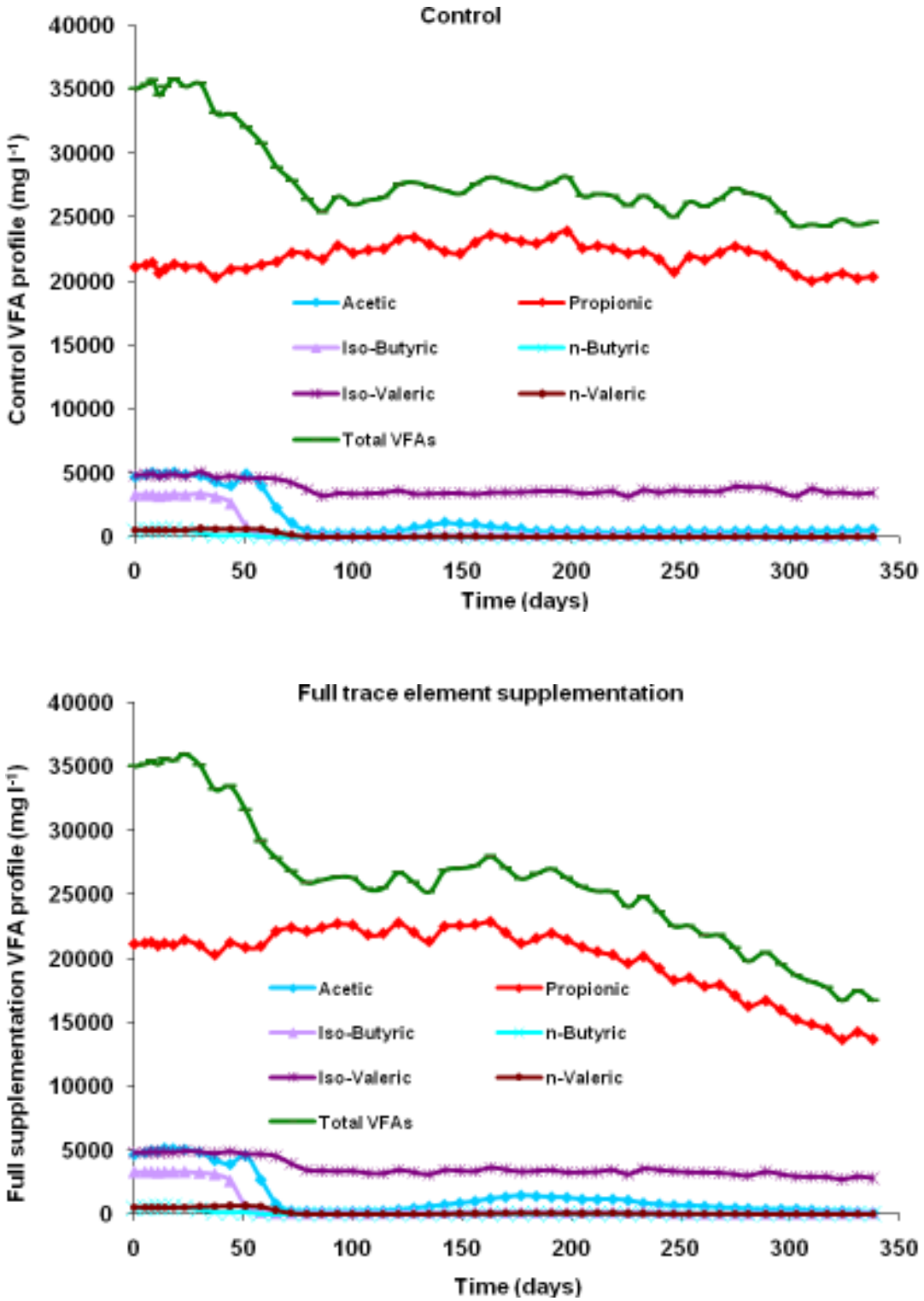


Figure 13 VFA concentration profiles of the control and trace element supplemented batch digestion tests using a commercial food waste digestate with accumulated VFA

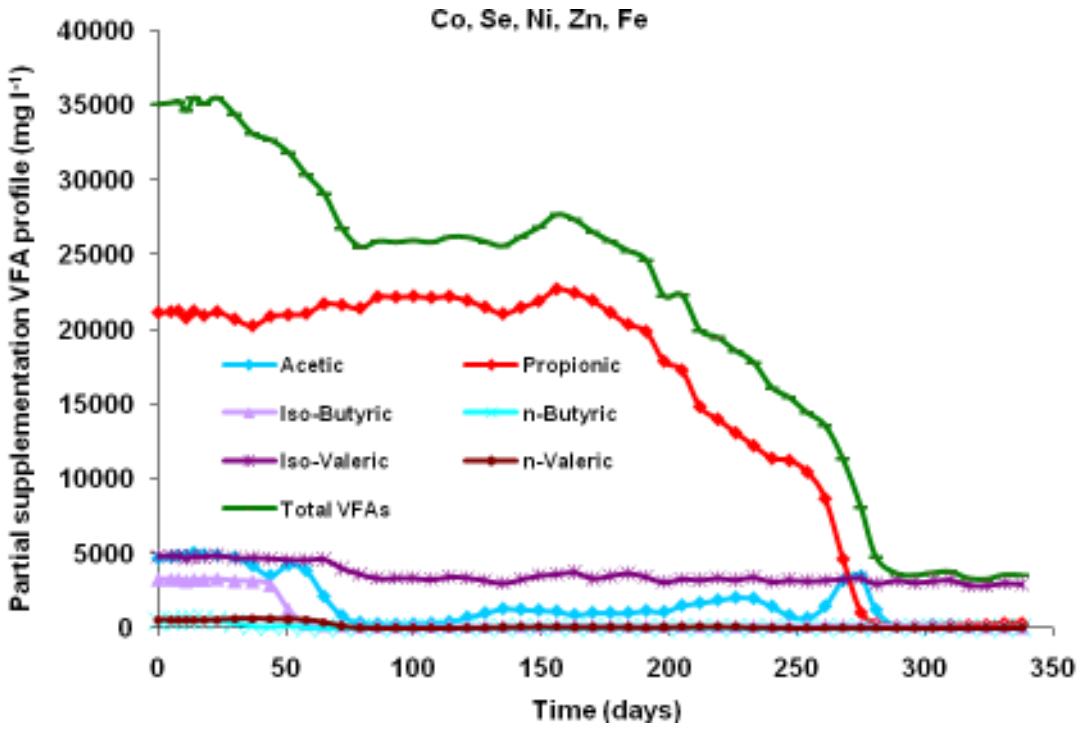


Figure 13 continued VFA concentration profiles of the control and trace element supplemented batch digestion tests using a commercial food waste digestate with accumulated VFA

The results indicated that trace element addition, to a large extent, can only facilitate an increase in VFA degradation rate rather than initiate the VFA consumption process in digesters with very high VFA concentrations. It appears that after a digester has been subjected to accumulation of VFA for a period of time, the onset of VFA degradation depends on other factors in addition to those of trace element concentrations. Once the VFA degradation process has started the supplementation of a specific trace element or multi-component trace element matrix can, however, accelerate the VFA consumption rate. As such, a strategy for stable food waste digestion should focus on the prevention of initial VFA accumulation in the digester by trace element supplementation, rather than the recovery of a severely VFA-laden digester.

4.2 Recovery of laboratory food waste digestate with short term low level VFA accumulation

The aim of the study in this section was to investigate the effect of a range of trace element supplementation on VFA degradation in a food waste digestate which was begining top show signs of VFA accumulation. These experiments used a spike of VFA addition as well as the VFA which was naturally present to follow the VFA degradation. The experiments used digestate liquor from a laboratory 75-litre (working volume) food waste digester; the history of this digester is described in detail in the technical report for WR0212. This digestate was described as 'slightly stressed' at the time of testing as both the VFA and ammonia concentrations were less than 5000 mg l^{-1} as shown in Table 11 and 12.

A preliminary full range trace element supplementation trial was first carried out with a propionic acid spike. That trial demonstrated that trace element supplementation stimulated the VFA degradation to some extent, although this digestate maintained high specific

methanogenic activity itself under the conditions at the time it was sampled. Therefore, a substrate spike with higher strength was used in the second set of experiments in an attempt to extend the experiment duration and magnify the effect of the trace element supplementation.

4.2.1 Initial trial using a propionic acid spike

This initial trial was conducted to test the feasibility of the approach described above and to determine if the microbial population in digestate under test could respond rapidly to propionic acid both with and without trace element supplementation. The amount of trace element dosed was also tested and including the trace element supplementation strategy 1 shown in Table 7 as a baseline trace element dosing concentration as well as 4 times and 8 times this concentration. As tungsten is not a part of the Gonzalez-Gil et al (1999) supplement recipe the individual effect of this was also tested at concentration levels 0.2 and 0.5 mg W l^{-1}. The combined effect of the baseline trace element supplementation strategy 1 in Table 7 and 0.2 mg l^{-1} tungsten was also tested to cover all combinations.

Table 11 Characteristics of the laboratory large-scale food waste digestate used in the initial trial

	Large-scale food waste digestate
Element concentration (mg l^{-1})	
Cobalt (Co)	<0.10
Copper (Cu)	7.57
Iron (Fe)	343
Molybdenum (Mo)	0.31
Nickel (Ni)	2.93
Selenium (Se)	0.04
Tungsten (W)	<0.10
Zinc (Zn)	11.1
Other digestate parameters	
pH	8.0
Total ammonium nitrogen (g-N l^{-1})	4.7
Total volatile fatty acid (g l^{-1})	4.2
Acetic acid (g l^{-1})	3.8
Propionic acid (g l^{-1})	0.3

The trial was conducted in duplicate in an orbital shaking incubator at a mesophilic (36±1 ºC) temperature, and the total VFA degradation results are shown in Figure 14. The VFA profiles demonstrated that trace element supplementation stimulated the VFA degradation to some extent, although this digestate maintained high specific methanogenic activity itself even under the slightly stressed condition. The overall specific methanogenic activity was 900 mg VFA d^{-1} without trace element supplementation, and 1200 mg d^{-1} with a full range of trace element supplementation. In addition, the VFA dropped to less than 100 mg l^{-1} on day 11 without trace element supplementation and day 8.5 with trace element supplementation, respectively. It also can be concluded from this trial that the different concentration of trace element supplementation tested had no additional effect on VFA degradation, and tungsten itself had no clear effect to facilitate the VFA degradation rate.

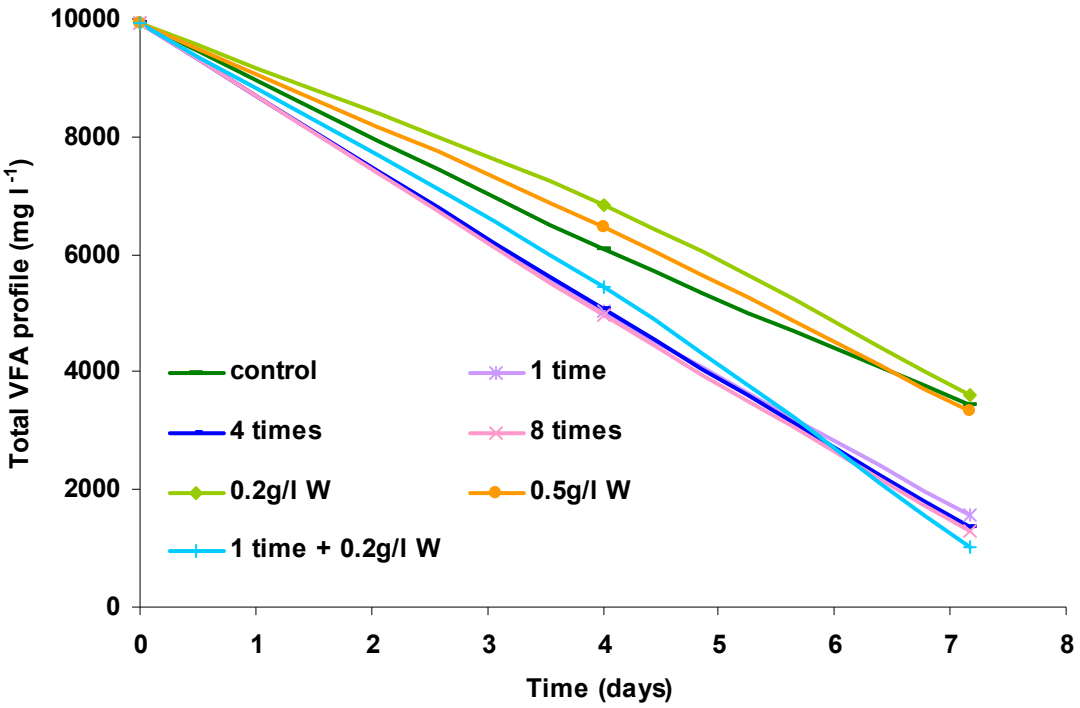


Figure 14 Total VFA degradation profiles in the preliminary batch trial using food waste digestate with short term low level VFA accumulation with a propionic acid spike and trace element supplementation

4.2.2 Trial using fractional factorial design

This set of trace element supplementation experiments was started at the same time, and was run as two batches under two unfavourable environmental conditions using ammonium and salt spikes, respectively. In one batch the digestate was spiked with 2000 mg N l^{-1} total ammonium nitrogen (TAN) using ammonium chloride to reach a TAN concentration of 6700 mg l^{-1} in the tested digestate, similar to that found in commercial food waste digestion plant. In the other batch the digestate was spiked using sodium chloride with the same molar concentration as the ammonia spike. The salt spike was tested as it is also a potential inhibitory factor for anaerobic digestion, and could be present in food wastes in relatively large amounts.

The mix of substrate spike included sodium acetate, sodium propionate, glucose and starch, as shown in Table 13. The use of sodium salts of acetic and propionic acids in this set of experiments, rather than acetic and propionic acids themselves, was because the direct addition of the un-ionised acids would shift the digestate pH to an acidic level. Glucose and starch, the precursors of VFA during anaerobic digestion, were also included in the substrate spike as the food storage for digestion process, also as an attempt to investigate the effect of trace elements on hydrolysis and acidogenesis process. This purpose, however, was not achieved because of the high specific methanogenic activity of the digestate and the significantly positive effect of trace element supplementation on the methanogenic activity, which overshadowed the minor effect of trace elements on hydrolysis and acidogenesis if there was any.

6 trace elements (Co, Fe, Mo, Ni, Se, and W) were used in a fractional factorial screening test which had a resolution IV and 7 of 2-factor interactions, as shown in Table 14 (runs 1 to 16).

These six elements are widely accepted as being essential for acetogenetic and methanogenic activity. Five other trace elements commonly included in the supplementation recipes were also tested (runs 17 to 19). The level of trace element supplementation (Table 15) was chosen based on previous results and the baseline trace element concentrations in the digestate. The principle was to add elements to a concentration where the addition would show a clear effect if there was one, whilst at the same time avoiding their concentrations reaching a toxic level.

Each batch was carried out in duplicates using 38 of 200ml flasks, with the supplementation of different trace element mixes according to the design, also the controls without any trace element supplementation. The tests were conducted using orbital shaking incubators at 36±1 ºC and a shaking speed of 60 rpm. The headspace of flasks were purged with a gas mixture of N_2 and CO_2 (80:20) after the digestate and spike addition and trace element supplementation, and the flasks sealed using butyl rubber stoppers connected to biogas sampling Tedlar bags. Digestate in each flask was sampled and analysed at intervals. The volume of biogas produced and its methane concentration were also measured during the phase of intensive biogas production. It was calculated that the theoretical methane potential based on the digestate VFA concentration and the concentration of spiked substrates was 2.31 litres per flask at standard temperature and pressure.

Table 12 Characteristics of the 75-litre laboratory food waste digestate used in the trials with fractional factorial design

Trace elements (mg l^{-1})	
Aluminium (Al)	63.3
Boron (B)	2.5
Cobalt (Co)	0.083
Copper (Cu)	5.75
Iron (Fe)	173.7
Manganese (Mn)	18.5
Molybdenum (Mo)	0.29
Nickel (Ni)	2.9
Selenium (Se)	0.050
Tungsten (W)	<0.035
Zinc (Zn)	8.11
Potentially toxic element (mg l^{-1})	
Cadmium (Cd)	0.038
Chromium (Cr)	5.25
Lead (Pb)	0.63
Mercury (Hg)	<0.010
Micro nutrients (g l^{-1})	
Calcium (Ca)	2.16
Magnesium (Mg)	0.168
Potassium (K)	2.63
Sodium (Na)	1.13
Phosphorus (P)	0.700
Total Kjeldahl nitrogen (N)	8.47
Other digestate parameters (g l^{-1})	
pH	8.0
Total ammonium nitrogen (NH_3-N)	4.7
Total volatile fatty acid	4.4
Acetic acid	4.1
Propionic acid	0.1

Table 13 Concentration of components of the mixed substrate used as a spike addition to the digestate

Substrate	Concentration (mg l^{-1})
Sodium acetate	4500 as acetic acid
Sodium propionate	8000 as propionic acid
Glucose	4000
Starch	4000

Table 14 Fractional factorial design in the VFA degradation trial using slightly stressed laboratory-scale food waste digestate with essential element supplementation

Run	Pattern	Co	Ni	Mo	Se	Fe	W	Zn	Cu	Mn	Al	B
1	−−−−−−−−−−−	-	-	-	-	-	-	-	-	-	-	-
2	−−−+++−−−−−	-	-	-	Se	Fe	W	-	-	-	-	-
3	−−+−++−−−−−	-	-	Mo	-	Fe	W	-	-	-	-	-
4	−−++−−−−−−−	-	-	Mo	Se	-	-	-	-	-	-	-
5	−+−−+−−−−−−	-	Ni	-	-	Fe	-	-	-	-	-	-
6	−+−+−+−−−−−	-	Ni	-	Se	-	W	-	-	-	-	-
7	−++−−+−−−−−	-	Ni	Mo	-	-	W	-	-	-	-	-
8	−++++−−−−−−	-	Ni	Mo	Se	Fe	-	-	-	-	-	-
9	+−−−−+−−−−−	Co	-	-	-	-	W	-	-	-	-	-
10	+−−++−−−−−−	Co	-	-	Se	Fe	-	-	-	-	-	-
11	+−+−+−−−−−−	Co	-	Mo	-	Fe	-	-	-	-	-	-
12	+−++−+−−−−−	Co	-	Mo	Se	-	W	-	-	-	-	-
13	++−−++−−−−−	Co	Ni	-	-	Fe	W	-	-	-	-	-
14	++−+−−−−−−−	Co	Ni	-	Se	-	-	-	-	-	-	-
15	+++−−−−−−−−	Co	Ni	Mo	-	-	-	-	-	-	-	-
16	++++++−−−−−	Co	Ni	Mo	Se	Fe	W	-	-	-	-	-
17	+++++++−−−−	Co	Ni	Mo	Se	Fe	W	Zn	-	-	-	-
18	+++++++++−−	Co	Ni	Mo	Se	Fe	W	Zn	Cu	Mn	-	-
19	++++++++++	Co	Ni	Mo	Se	Fe	W	Zn	Cu	Mn	Al	B

Table 15 Concentration of trace element supplementation in the VFA degradation trial using slightly stressed laboratory-scale food waste digestate

Essential element	Compound used	Element concentration (mg l^{-1})	
		Level 0	Level 1
Aluminium (Al)	$AlCl_3 \cdot 6H_2O$	0	0.1
Boron (B)	H_3BO_3	0	0.1
Cobalt (Co)	$CoCl_2 \cdot 6H_2O$	0	1.0
Copper (Cu)	$CuCl_2 \cdot 2H_2O$	0	0.1
Iron (Fe)	$FeCl_2 \cdot 4H_2O$	0	5.0
Manganese (Mn)	$MnCl_2 \cdot 4H_2O$	0	1.0
Molybdenum (Mo)	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	0	0.2
Nickel (Ni)	$NiCl_2 \cdot 6H_2O$	0	1.0
Selenium (Se)	Na_2SeO_3	0	0.2
Tungsten (W)	$Na_2WO_4 \cdot 2H_2O$	0	0.2
Zinc (Zn)	$ZnCl_2$	0	0.2

4.2.2.1 Recovery with artificially increased ammonia concentration

In this trial the mixed substrate spiked digestate was also supplemented with 2000 mg-N l^{-1} total ammonium nitrogen (TAN) (as ammonium chloride) at the beginning of the test to give

a final TAN concentration of 6700 mg l^{-1}; this is a similar concentration to that found in the commercial food waste digestate described in section 4.1.

It was observed that the acetic acid concentration reduced to around 1000 mg l^{-1} after about 10 days in all the flasks supplemented with selenium. Table 16 shows that the other flasks needed 20 days of operation to reach this low level. Also given in Table 16 is the maximum acetic acid degradation rate for each run. Statistical analysis was carried out using the SAS software package, and the average of the duplicate values was inputted for calculation of the significance of the different trace elements on acetic acid degradation. It can be seem from Figure 15 that only selenium (Se) significantly improved the acetic acid degradation, compared with Co, Fe, Ni, Mo, W, and their 2-factor interactions. Although the effect of Al, B, Cu, Mn and Zn could not be tested statistically, they did not show any clear further positive effect in comparison with the trace element supplementation mix of Co, Fe, Ni, Mo, Se and W.

Table 16 Effect of trace element supplementation on acetic acid degradation at an elevated ammonium level

Run	Trace elements added	Time when acetic acid dropped to 1000 mg l^{-1} (day)		Maximum acetic acid degradation rate (mg l^{-1} d^{-1})	
		Duplicate 1	Duplicate 2	Duplicate 1	Duplicate 2
1	Control	21.9	22.1	571	568
2	Se, Fe, W	9.1	9.2	1463	1379
3	Mo, Fe, W	22.3	21.6	551	593
4	Mo, Se	9.0	9.0	1514	1444
5	Ni, Fe	21.7	22.2	616	574
6	Ni, Se, W	10.0	9.7	1288	1371
7	Ni, Mo, W	21.5	22.1	632	579
8	Ni, Mo, Se, Fe	10.0	9.9	1340	1344
9	Co, W	21.1	21.1	587	566
10	Co, Se, Fe	11.1	11.2	1074	1087
11	Co, Mo, Fe	21.0	21.5	605	596
12	Co, Mo, Se, W	9.1	9.1	1469	1414
13	Co, Ni, Fe, W	20.9	21.7	629	620
14	Co, Ni, Se	11.7	11.8	1176	1154
15	Co, Ni, Mo	21.7	21.7	620	624
16	Co, Ni, Mo, Se, Fe, W	9.6	9.6	1413	1418
17	Co, Ni, Mo, Se, Fe, W, Zn	9.9	9.7	1347	1393
18	Co, Ni, Mo, Se, Fe, W, Zn, Cu, Mn	9.7	9.8	1395	1355
19	Co, Ni, Mo, Se, Fe, W, Zn, Cu, Mn, Al, B	10.0	10.0	1328	1351

NH4Cl - HAc- Fit Least Squares

Least Squares Fit

Response Rate

Sorted Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Se	369.125	13.05667	28.27	0.0012*
Mo	44.75	13.05667	3.43	0.0756
Co*W	40.375	13.05667	3.09	0.0906
Co*Se	-34.625	13.05667	-2.65	0.1176
Co*Mo	34.25	13.05667	2.62	0.1198
W	33.375	13.05667	2.56	0.1250
Co	-24.25	13.05667	-1.86	0.2044
Ni*Se	-18.625	13.05667	-1.43	0.2898
Co*Ni	18.5	13.05667	1.42	0.2922
Ni*Mo	-11	13.05667	-0.84	0.4882
Fe	-8.625	13.05667	-0.66	0.5768
Ni	-2.5	13.05667	-0.19	0.8658
Co*Fe	-1.875	13.05667	-0.14	0.8990

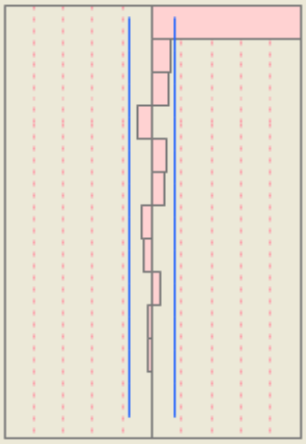


Figure 15 Statistical analysis on essential trace elements for acetic acid degradation at an elevated ammonium level

It was noted that the propionic acid consumption accelerated only after the acetic acid concentration reduced to around 1000 mg l^{-1}, this is because the acetic acid acted as product-induced feedback inhibitor for propionic acid degradation. The maximum degradation rate of propionic acid in each flask is listed in Table 17 and the average was taken for statistic analysis. It can be seen from Figure 16 that Se, Mo, and the mix of Co and W had a significant effect on propionic acid degradation at the 0.05 level, and Co can also be included as essential at the 0.10 level. Again, the addition of Al, B, Cu, Mn and Zn did not show any clear further positive effect on propionic acid consumption compared with the trace element supplementation mix of Co, Fe, Ni, Mo, Se and W.

From the above analysis, it can be concluded that Se, Mo, Co and W had a significant positive effect on the propionic acid degradation in this batch of food waste digestate at an ammonia level of 6.7 g l^{-1}. This confirmed the statement in the literature that selenium, molybdenum and tungsten may play an important role in propionic acid degradation. This is because the oxidation of propionate to acetate, carbon dioxide, H_2 and formate, can only proceed if the products H_2, formate and to a lesser extent acetate are removed by methanogens or other H_2 and formate utilising bacteria. Selenium, as well as molybdenum and tungsten, are essential trace elements for certain enzyme catalysing reactions, such as hydrogenase and formate dehydrogenase (FDH) as shown in Table 18, and therefore the availability of selenium, molybdenum and tungsten is expected to be crucial for propionate oxidation. The significant effect of selenium on acetic acid degradation indicated the syntrophic acetate oxidating route might be the dominant methanogenic pathway from acetate in the food waste digestate used. Cobalt works mainly in carbon monoxide dehydrogenase and corrinoid cofactors of methyltransferase that are involved in methyl transfer reactions.

Table 17 Effect of trace element supplementation on propionic acid degradation at an elevated ammonium level

Run	Trace elements added	Maximum propionic acid degradation rate (mg l^{-1} d^{-1})	
		Duplicate 1	Duplicate 2
1	Control	161	193
2	Se, Fe, W	424	423
3	Mo, Fe, W	159	197
4	Mo, Se	816	783
5	Ni, Fe	131	173
6	Ni, Se, W	360	352
7	Ni, Mo, W	176	168
8	Ni, Mo, Se, Fe	660	618
9	Co, W	314	296
10	Co, Se, Fe	450	477
11	Co, Mo, Fe	330	338
12	Co, Mo, Se, W	737	760
13	Co, Ni, Fe, W	281	262
14	Co, Ni, Se	368	399
15	Co, Ni, Mo	284	317
16	Co, Ni, Mo, Se, Fe, W	828	817
17	Co, Ni, Mo, Se, Fe, W, Zn	810	786
18	Co, Ni, Mo, Se, Fe, W, Zn, Cu, Mn	839	811
19	Co, Ni, Mo, Se, Fe, W, Zn, Cu, Mn, Al, B	810	862

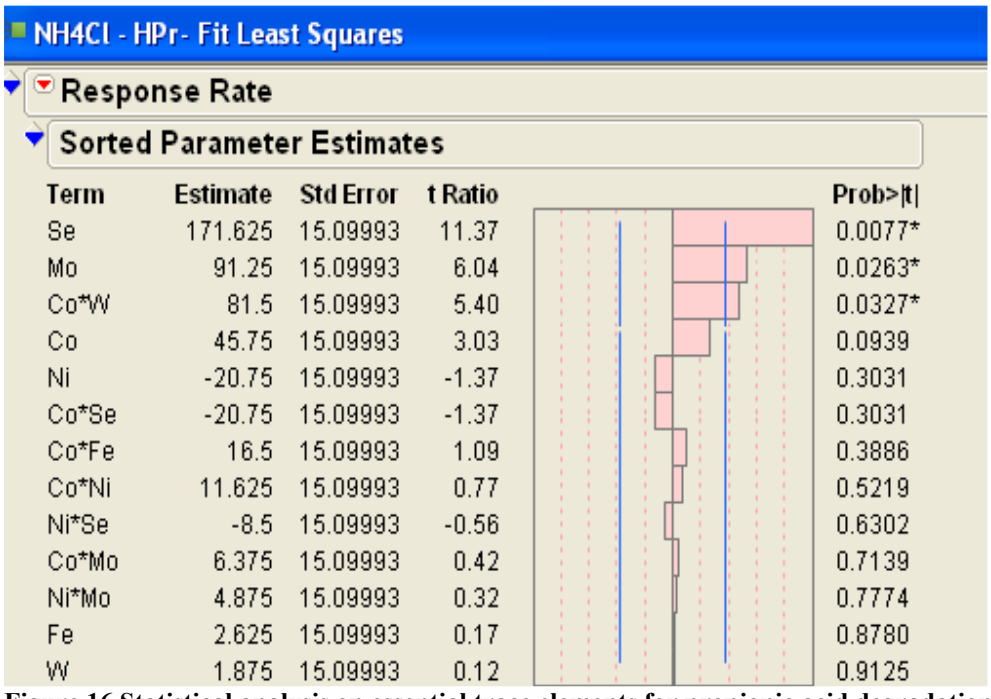


Figure 16 Statistical analysis on essential trace elements for propionic acid degradation at an elevated ammonium level

Table 18 Role of essential trace elements in various enzymes involved in anaerobic reactions

Element	Functions
Co	B12-enzymes, CO-dehydrogenase, Methyltransferase
Mo	Formate dehydrogenase, Formylmethanofuran-dehydrogenase
Se	Hydrogenase, Formate dehydrogenase
W	Formate dehydrogenase, Formylmethanofuran-dehydrogenase

Figure 17 shows the VFA degradation profiles from seven of the supplemented flask tests. These show the average VFA degradation in the control, with supplementation of Se and Mo, with supplementation of Se, Mo, Co and W, with supplementation of Se, Mo, Co, W, Fe and Ni, and also with supplementation of all the 11 elements tested. The effect of supplementation of Fe+Ni and Co+W on VFA degradation was also included as the examples of the ineffective and partially effective trace element supplementation to the food waste digestate. Figure 18 shows the methane production profiles of the same set of flasks as shown in Figure 17, and the peaks of methane production observed at the time when the maximum acetic or propionic acid degradation rate was achieved.

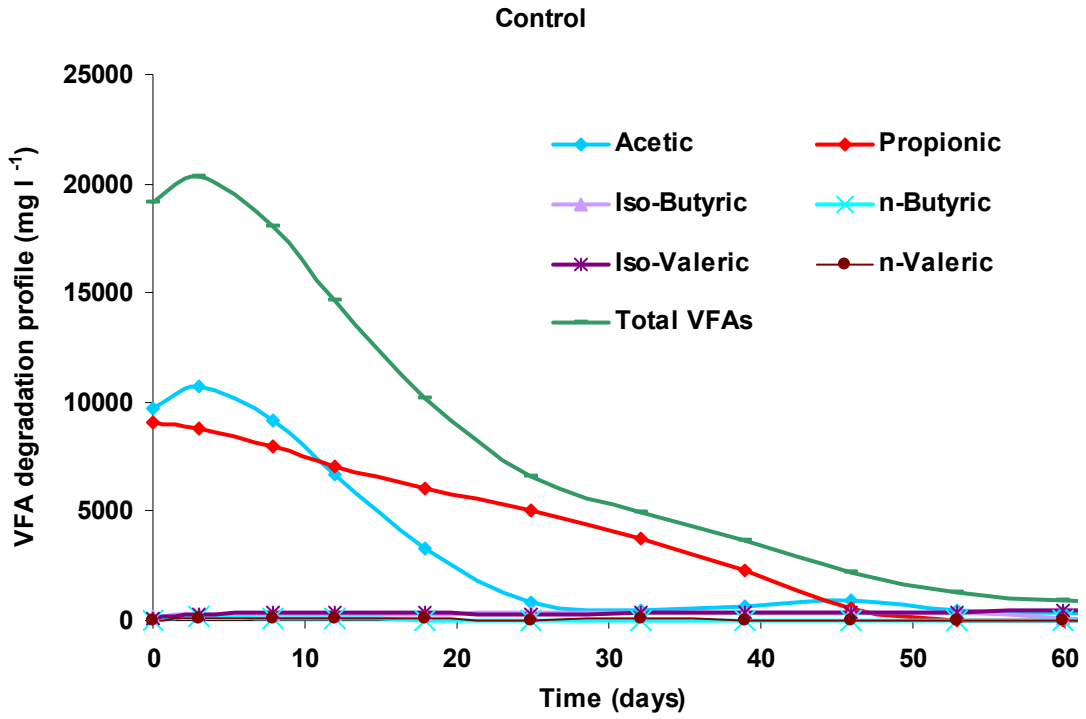


Figure 17 VFA degradation profiles in food waste digestate with different trace element supplementation strategies at an elevated ammonium level

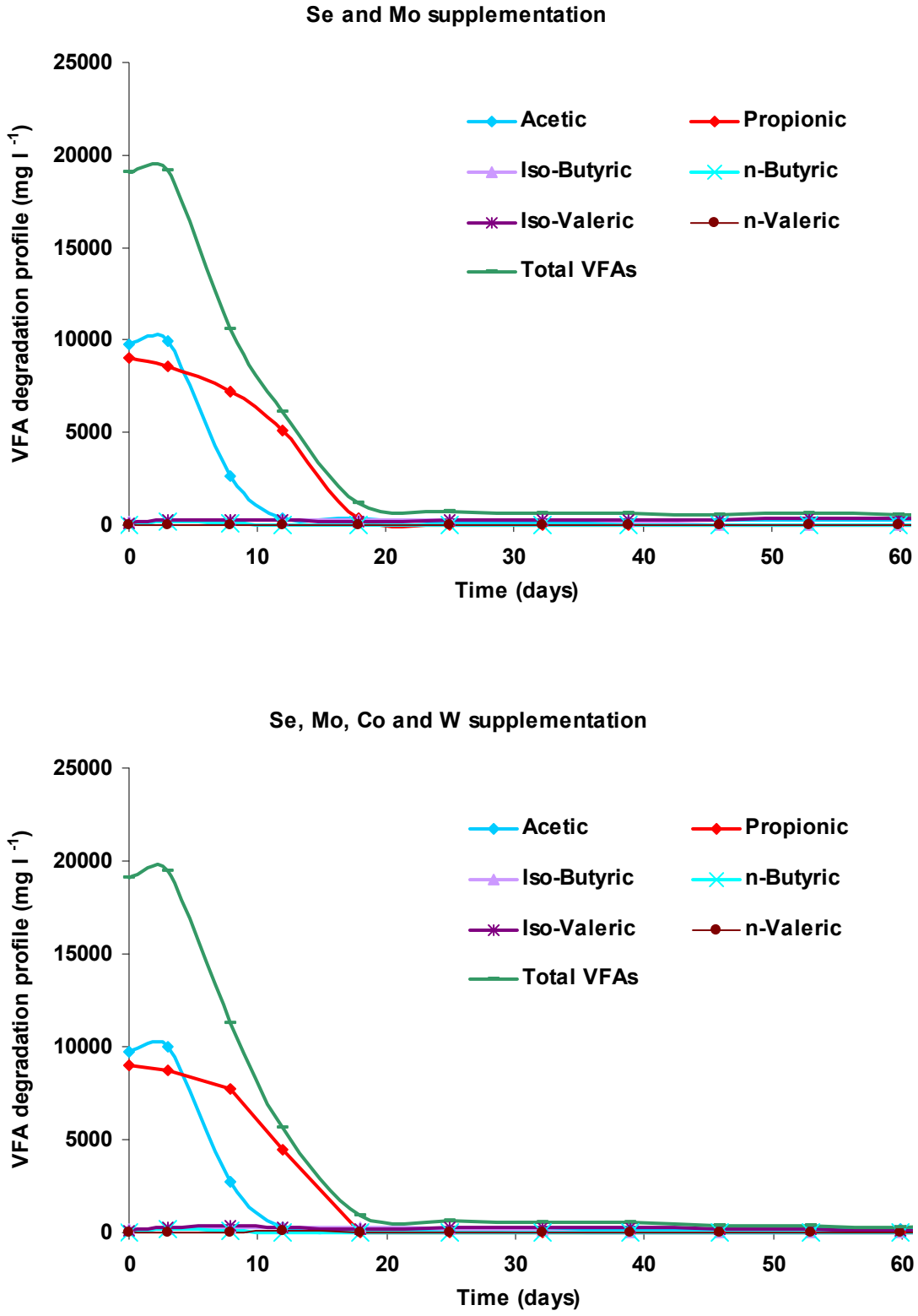


Figure 17 continued VFA degradation profiles in food waste digestate with different trace element supplementation strategies at an elevated ammonium level

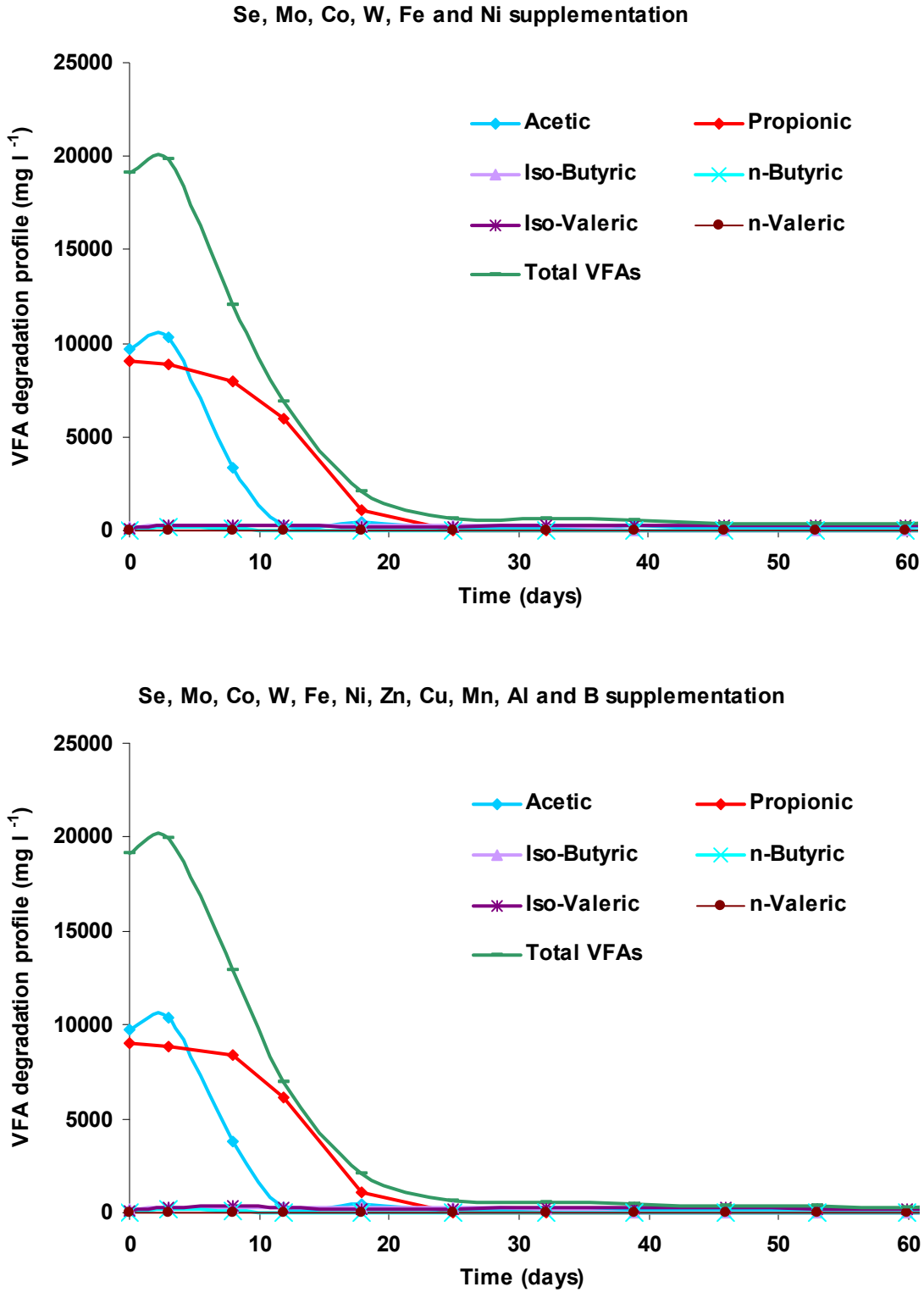
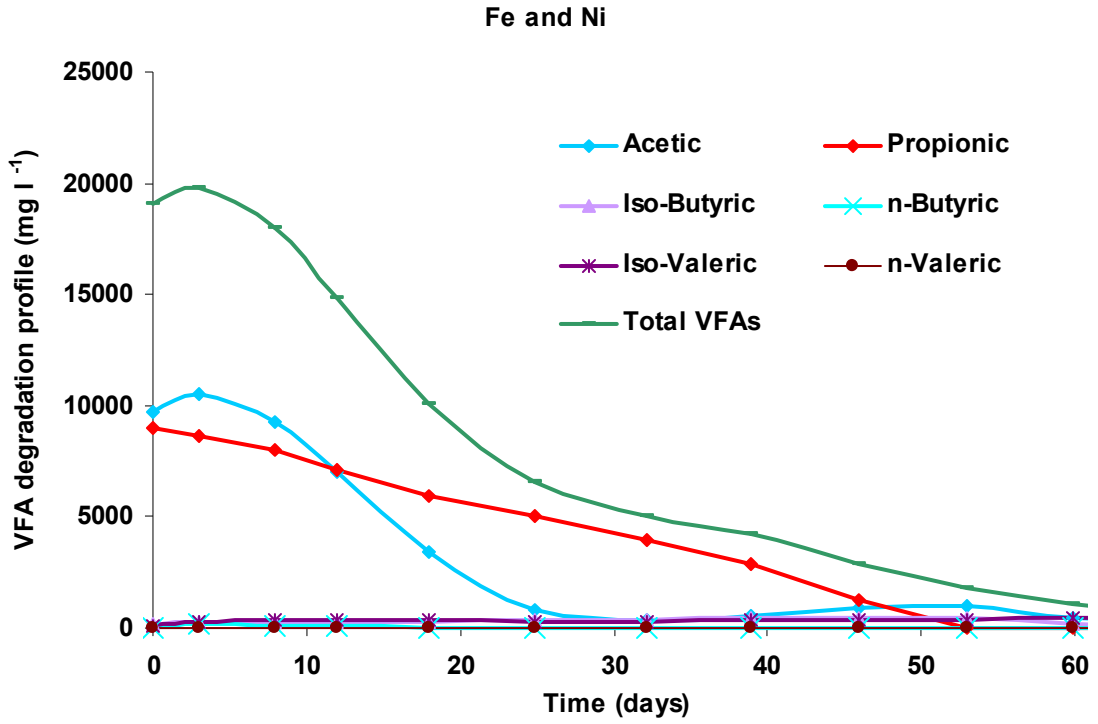


Figure 17 continued VFA degradation profiles in food waste digestate with different trace element supplementation strategies at an elevated ammonium level



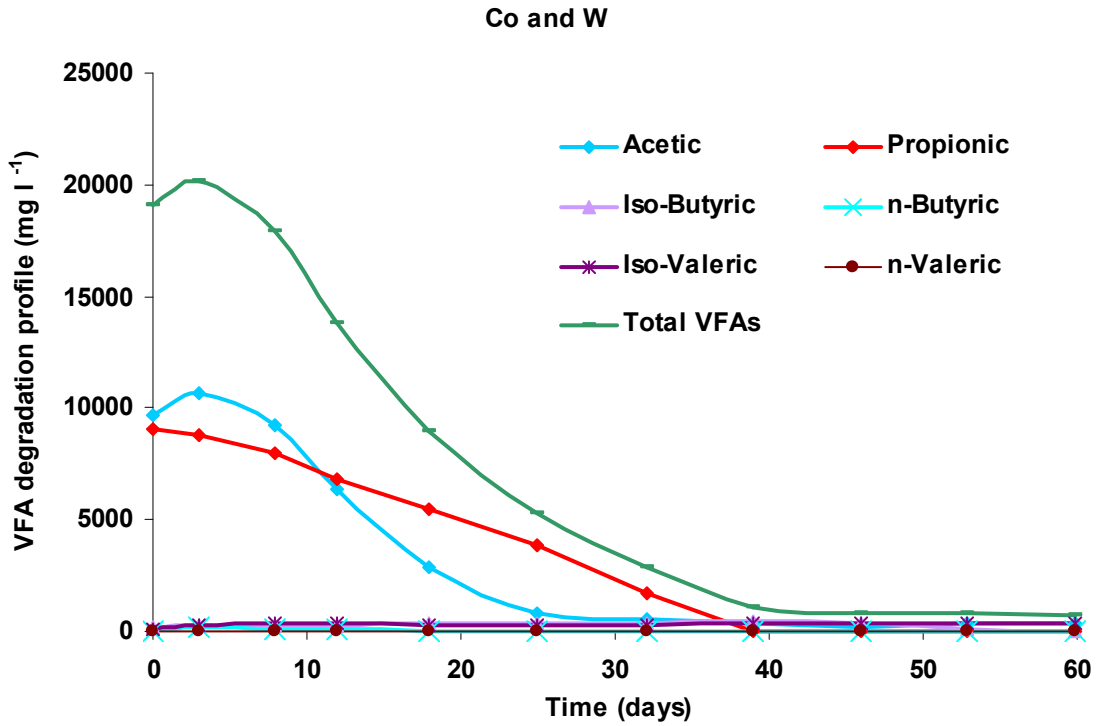


Figure 17 continued VFA degradation profiles in food waste digestate with different trace element supplementation strategies at an elevated ammonium level

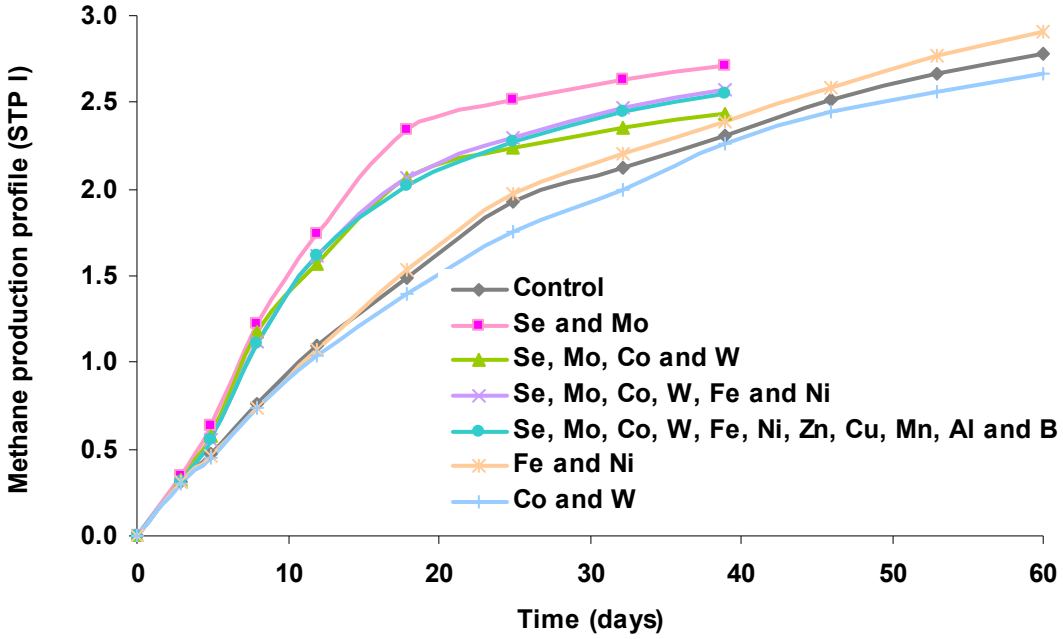


Figure 18 Methane production profiles in food waste digestate with different trace element supplementation strategies at an elevated ammonium level

4.2.2.2 Recovery where the salt concentration had been artificially increased

In this experiment the mixed substrate spiked digestate received a 3200 mg l^{-1} dose of Na (as sodium chloride) at the beginning of the test. This was added at the same molar concentration as the NH4Cl in section 3.2.2.1. Salt was tested as it is also an inhibitory factor in anaerobic digestion, and the concentration in food waste may be elevated relative to other waste types.

The acetic and propionic acid degradation data are shown in Table 19 and 20, respectively. The addition of salt had a negative effect on VFA degradation with longer degradation time and lower degradation rate compared to the rates observed when ammonia was added. The effect of trace element addition on VFA consumption, however, followed the same pattern. The statistical analysis again showed selenium had a positive influence on acetic acid degradation (Figure 19). The analysis also showed that none of the elements added had a significant effect on propionic acid degradation at the 0.05 level, although molybdenum, selenium, and the interaction of cobalt and tungsten clearly promoted propionic acid degradation at the 0.10 level (Figure 20).

Table 19 Effect of trace element supplementation on acetic acid degradation at an elevated salt level

Run	Trace elements added	Time when acetic acid dropped to 1000 mg l^{-1} (day)		Maximum acetic acid degradation rate (mg l^{-1} d^{-1})	
		Duplicate 1	Duplicate 2	Duplicate 1	Duplicate 2
1	Control	20.9	21.2	621	582
2	Se, Fe, W	11.4	11.4	1263	1287
3	Mo, Fe, W	20.9	21.4	666	612
4	Mo, Se	11.5	11.4	1228	1178
5	Ni, Fe	21.4	21.6	629	633
6	Ni, Se, W	11.6	11.5	1328	1340
7	Ni, Mo, W	22.1	22.0	599	636
8	Ni, Mo, Se, Fe	11.7	11.6	1429	1388
9	Co, W	20.4	22.8	644	648
10	Co, Se, Fe	12.0	11.9	1170	1234
11	Co, Mo, Fe	20.6	20.1	692	686
12	Co, Mo, Se, W	11.5	11.5	1268	1235
13	Co, Ni, Fe, W	20.6	20.9	684	651
14	Co, Ni, Se	12.5	12.6	1230	1227
15	Co, Ni, Mo	21.0	21.5	685	655
16	Co, Ni, Mo, Se, Fe, W	11.7	11.7	1389	1352
17	Co, Ni, Mo, Se, Fe, W, Zn	11.6	11.7	1383	1463
18	Co, Ni, Mo, Se, Fe, W, Zn, Cu, Mn	11.8	11.7	1433	1410
19	Co, Ni, Mo, Se, Fe, W, Zn, Cu, Mn, Al, B	11.9	11.8	1453	1488

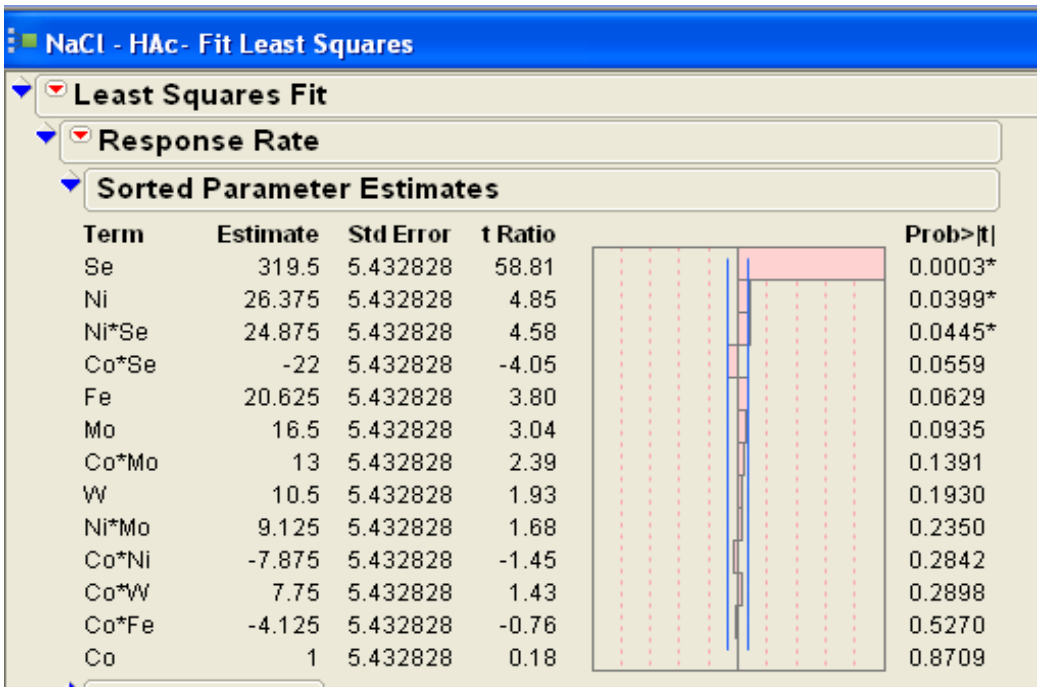


Figure 19 Statistical analysis on essential trace elements for acetic acid degradation at an elevated salt level

Table 20 Effect of trace element supplementation on propionic acid degradation at an elevated salt level

Run	Trace elements added	Maximum propionic acid degradation rate (mg l^{-1} d^{-1})	
		Duplicate 1	Duplicate 2
1	Control	164	175
2	Se, Fe, W	301	331
3	Mo, Fe, W	230	215
4	Mo, Se	530	527
5	Ni, Fe	134	163
6	Ni, Se, W	247	265
7	Ni, Mo, W	200	187
8	Ni, Mo, Se, Fe	695	672
9	Co, W	353	356
10	Co, Se, Fe	374	350
11	Co, Mo, Fe	441	453
12	Co, Mo, Se, W	802	793
13	Co, Ni, Fe, W	395	373
14	Co, Ni, Se	268	285
15	Co, Ni, Mo	369	335
16	Co, Ni, Mo, Se, Fe, W	621	641
17	Co, Ni, Mo, Se, Fe, W, Zn	600	545
18	Co, Ni, Mo, Se, Fe, W, Zn, Cu, Mn	623	633
19	Co, Ni, Mo, Se, Fe, W, Zn, Cu, Mn, Al, B	535	554

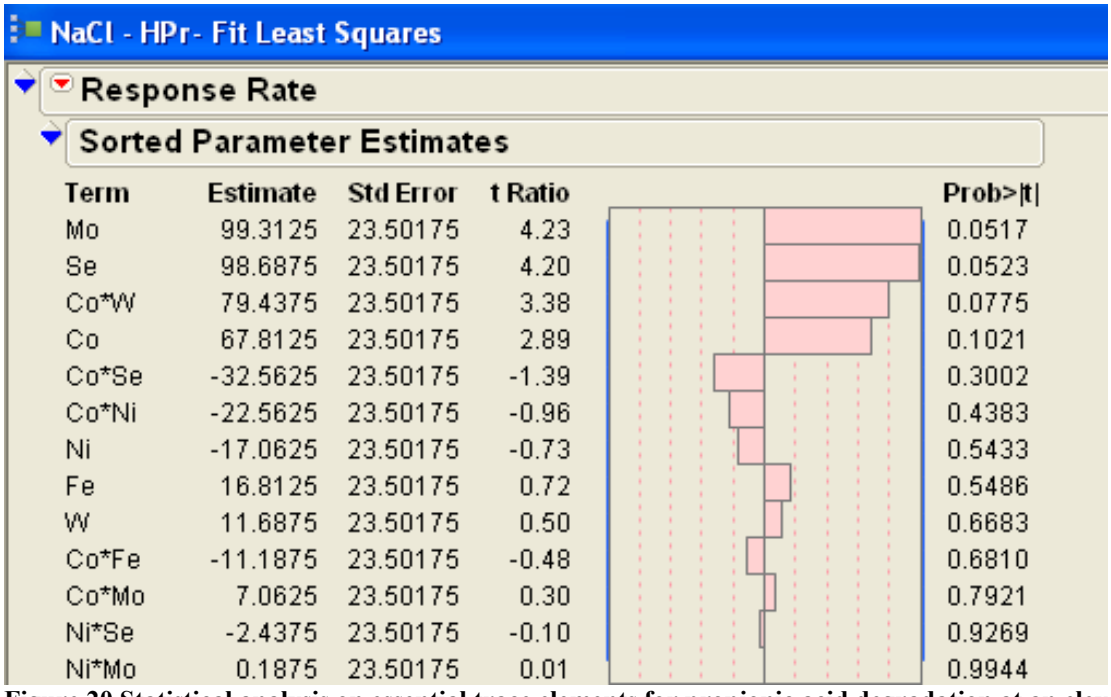


Figure 20 Statistical analysis on essential trace elements for propionic acid degradation at an elevated salt level

Figure 21 shows seven sets of VFA degradation profiles. These show the VFA degradation of: the control, with supplementation of Se and Mo, with supplementation of Se, Mo, Co and W, with supplementation of Se, Mo, Co, W, Fe and Ni, and also with supplementation of all the

11 elements tested. The effect of supplementation of Fe+Ni and Co+W was also included as examples of an ineffective and partially effective trace element supplementation to the food waste digestate. Figure 22 shows the methane production profiles of the same set of flasks as shown in Figure 21, and the peaks of methane production observed at the time when the maximum acetic or propionic acid degradation rate was achieved.

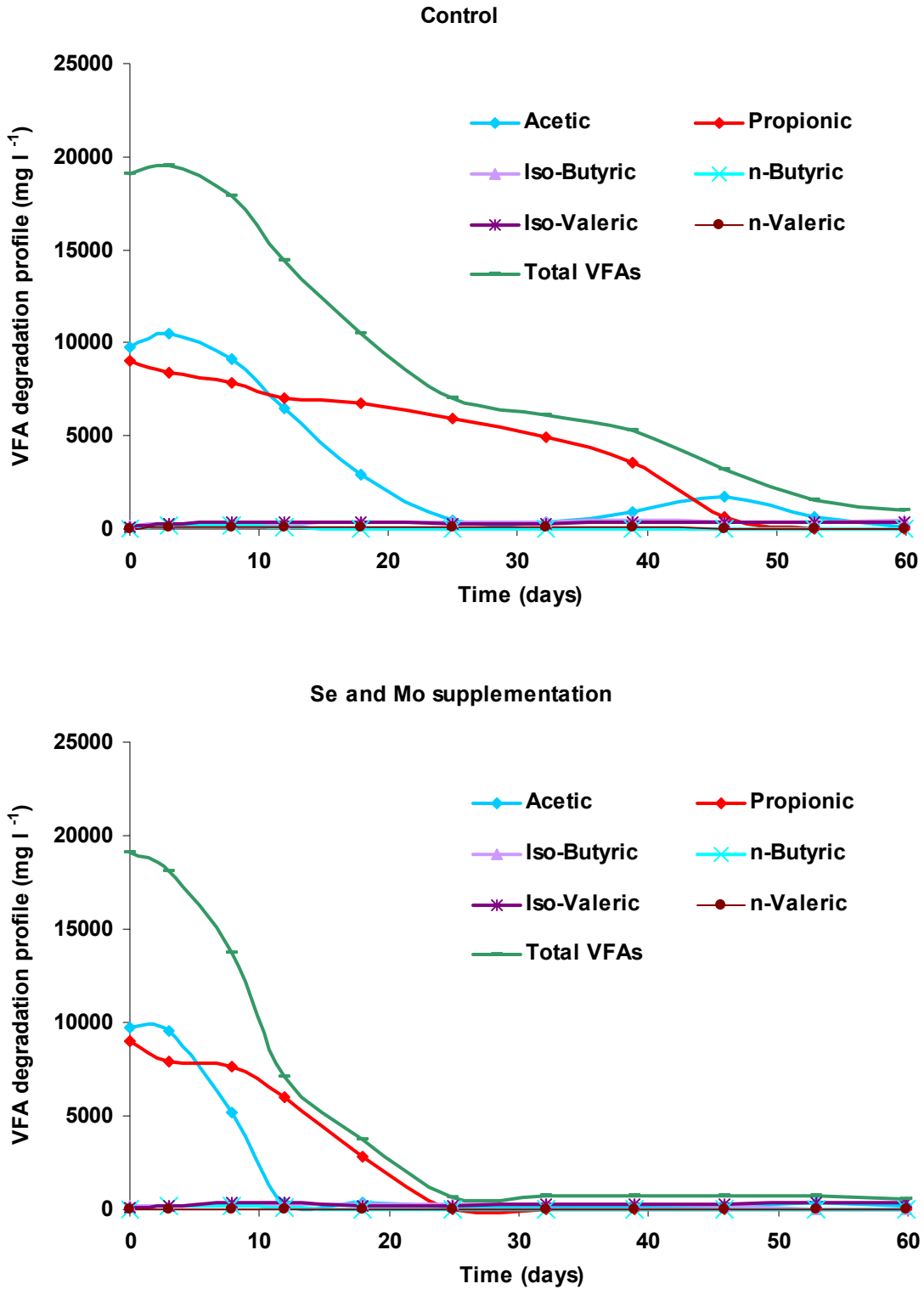
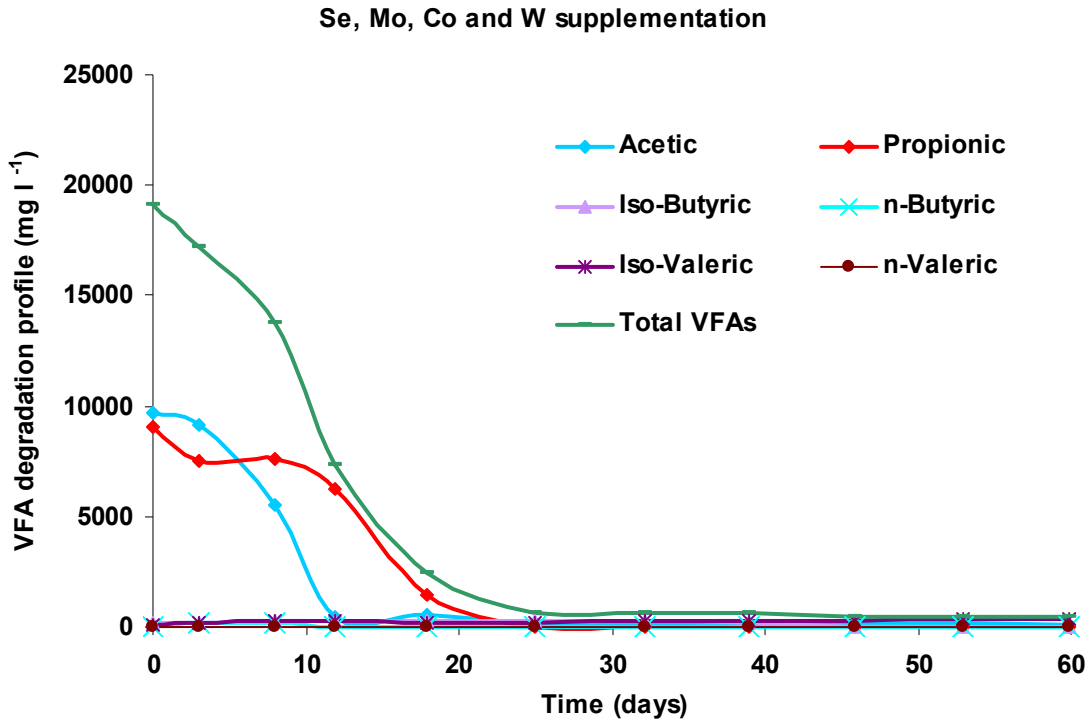


Figure 21 VFA degradation profiles in food waste digestate under different trace element supplementation strategies at an elevated salt level



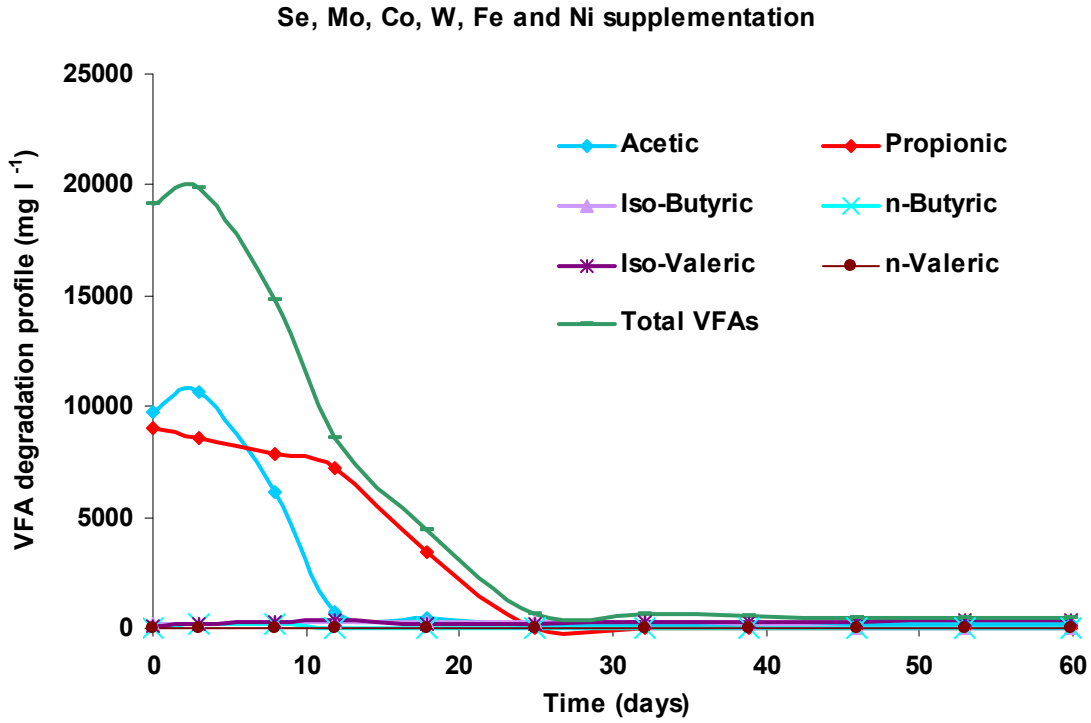


Figure 21 continued VFA degradation profiles in food waste digestate under different trace element supplementation strategies at an elevated salt level

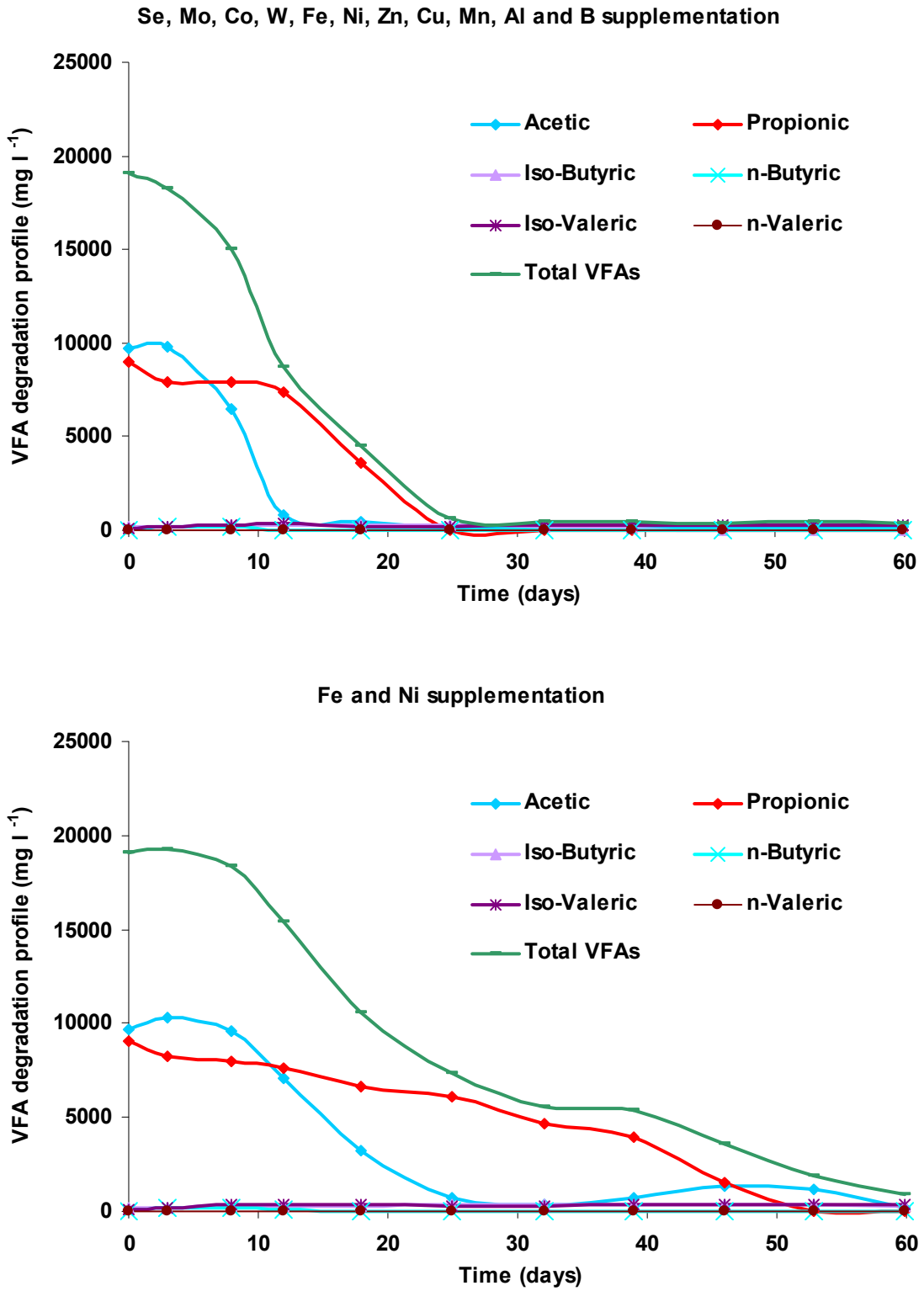


Figure 21 continued VFA degradation profiles in food waste digestate under different trace element supplementation strategies at an elevated salt level

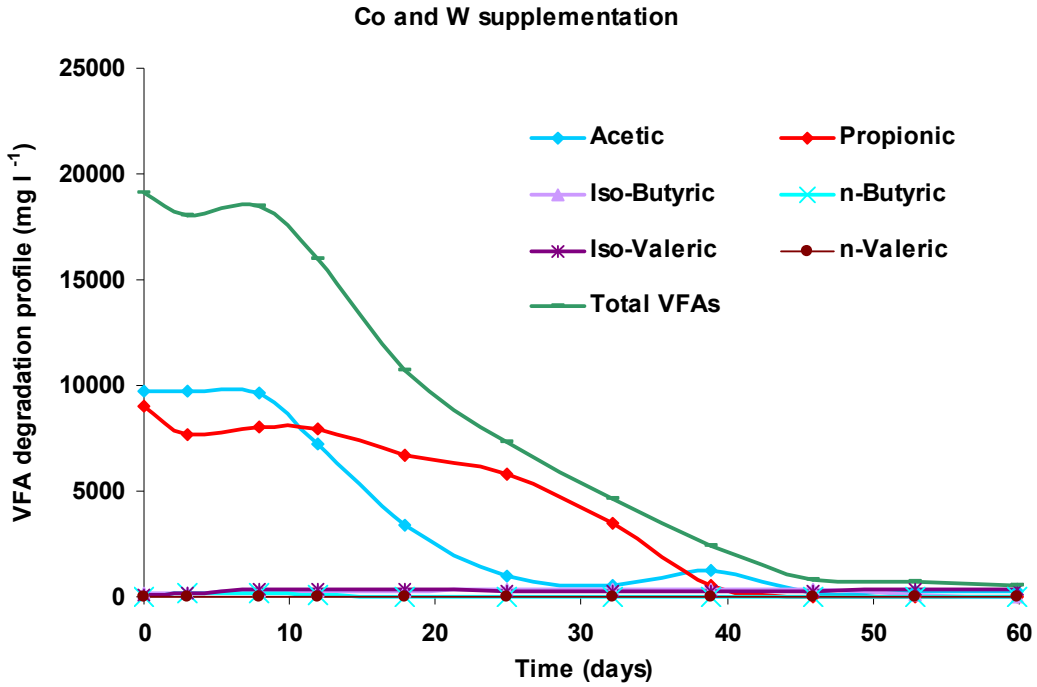


Figure 21 continued VFA degradation profiles in food waste digestate under different trace element supplementation strategies at an elevated salt level

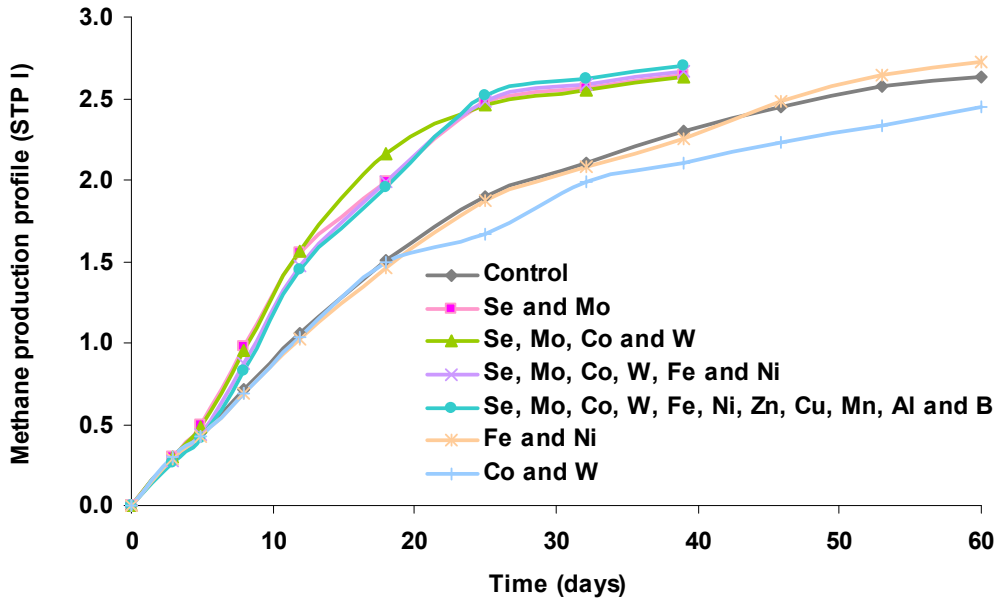


Figure 22 Methane production profiles in food waste digestate under different trace element supplementation strategies at an elevated salt level

4.3 Effect of Se concentration on VFA degradation

Although trace elements are essential for the growth and metabolism of anaerobic microorganisms due to their role in key enzymes and electron carrier molecules in metabolic

pathways, they could become toxic if present at a higher concentration. The concentration of trace elements can be categorised as: limiting, optimal, excessive, and toxic. It is therefore important to find the optimal concentration for the essential trace elements. The experiments were conducted to investigate the concentration effect of Se supplementation on VFA degradation in both slightly and severely stressed digestate. Selenium was chosen for two reasons, firstly, it has been shown to be a most important essential trace element for VFA degradation in food waste digestion and secondly, it is also known to be toxic to a wide range of organisms.

Two batch trials were carried out using duplicate 200 ml flasks and Se supplementation at different concentrations and a control without Se supplementation. The tests were carried out in an orbital shaking incubator at 36±1 ºC at a shaking speed of 60 rpm. The headspace of flasks were purged with a gas mixture of N_2 and CO_2 (80:20) after the digestate addition and Se supplementation, and the flasks sealed using butyl rubber stoppers connected to biogas sampling Tedlar bags. Digestate in each flask was sampled and analysed at intervals.

4.3.1 Experiment using digestate with initial VFA of 6000 mg l^{-1} as inoculum

This set of experiments used digestate liquor taken on day 112 from the control food waste semi-continuous digester trial at OLR 2 kg VS m^{-3} d^{-1} (as described in section 5.1.1 in this report). This digestate had accumulated VFA to a concentration of around 6,000 mg l^{-1} as shown in Table 21. The digestate was further spiked with 10,000 mg l^{-1} of acetic acid, as sodium acetate at the beginning of the test.

The Se concentration in the digestate itself was 0.04 mg l^{-1}, and concentrations of sodium selenite (Na_2SeO_3) were added to give an additional dose of 0.025, 0.05, 0.1, 0.2, 0.4, 0.8, 1.5, 3, 6, 10, 30, 60, 100, 300, 600 mg l^{-1} as Se. At concentrations greater than 30 mg l^{-1} Se had an acute toxic effect with no VFA degradation and even slightly elevated levels of VFA during the 20-day test period. Figure 23 shows the acetic acid degradation profile in the control flasks and flasks supplemented with Se up to 30 mg l^{-1}. Figure 24 shows the acetic acid degradation rate at Se supplementations between 0.025 and 3 mg l^{-1}. It can be seen from these two figures that a Se dosing between 0.05 to 0.4 mg l^{-1} should be optimal for the digestate tested, and there is evidence of toxicity when its concentration was greater than 1.5 mg l^{-1}.

Table 21 Digestate parameters at the beginning of the experiment before spiking with sodium acetate

pH	7.9
Total ammonium nitrogen (mg NH_3-N l^{-1})	5000
Total volatile fatty acid (mg l^{-1})	5800
Acetic acid (mg l^{-1})	3500
Propionic acid (mg l^{-1})	1400

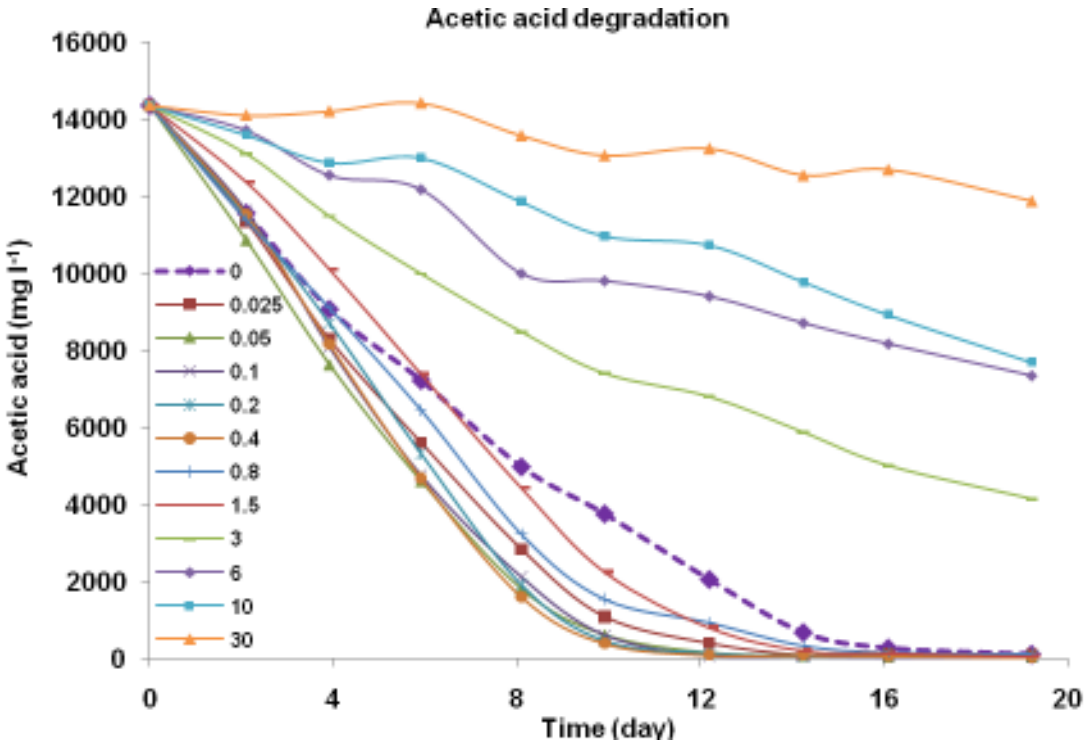


Figure 23 Acetic acid degradation profiles in food waste digestate with different levels of Se supplementation

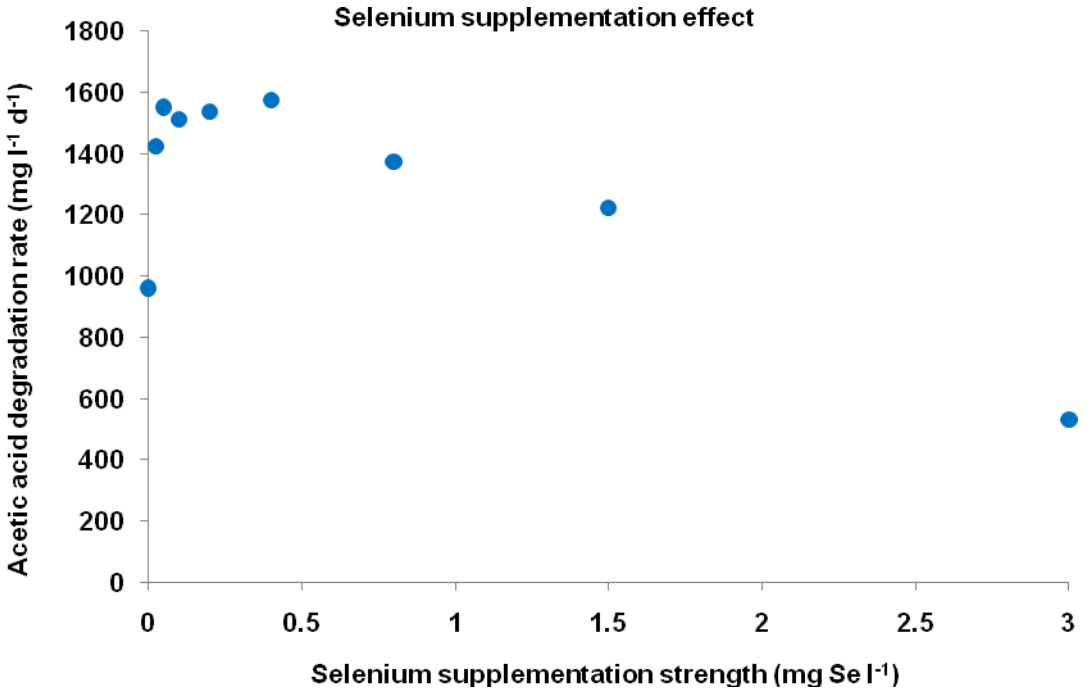


Figure 24 Effect of Se supplementation strength on acetic acid degradation

4.3.2 Experiment using digestate with initial VFA of 32000 mg l^{-1} as inoculum

This set of experiments used digestate liquor from the control food waste digester operated at OLR 3 kg VS m^{-3} d^{-1} (as described in section 5.1.1 in this report). This digestate accumulated VFA concentration as high as 32000 mg l^{-1} (Table 22).

Table 22 Digestate parameters

pH	7.4
Total ammonium nitrogen (mg NH_3-N l^{-1})	5900
Total volatile fatty acid (mg l^{-1})	32000
Acetic acid (mg l^{-1})	9000
Propionic acid (mg l^{-1})	14000

Sodium selenite (Na2SeO3) was supplemented to give additional concentrations of 0.025, 0.05, 0.1, 0.2, 0.4, 0.8, 1.5, and 3. In addition, a commercial cattle feed supplementation Alkosel was also tested as a potential organic source of Se, as it contains an elevated level of Seleno-methionine with a concentration of 2 mg Se g^{-1}. Two dosing strengths of 0.2 and 1.5 mg l^{-1} were tested. The results (Figure 25) showed no difference in VFA degradation between the control and flasks supplemented with between 0.2 mg l^{-1} and 1.5 mg l^{-1} Se when using sodium selenite. It was also shown that the dosing strength of 1.5 mg l^{-1} showed signs of toxicity. As shown in Figure 26 the VFA degradation profiles followed the same trend the digestate was supplemented using Alkosel. The test was terminated after the trial had been running for 54 days. This is because Se supplementation could not promote rapid VFA degradation in the heavily stressed food waste digestate and no meaningful results could be generated in the trial.

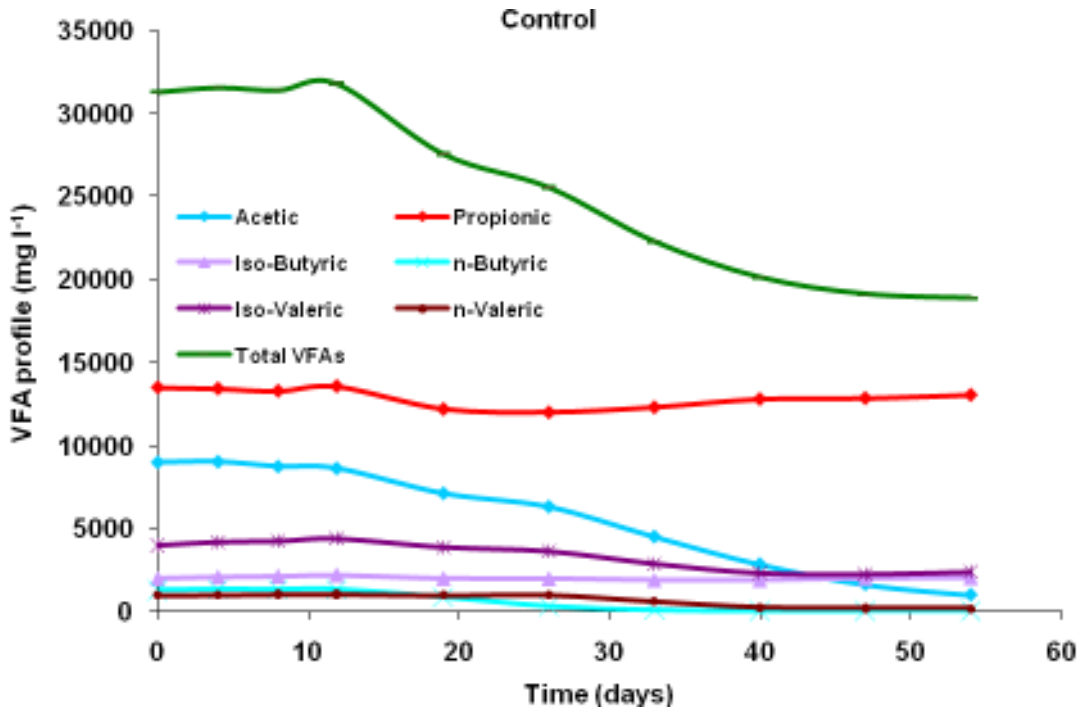


Figure 25 VFA degradation profiles of control and after Se supplementation at 0.2 and 1.5 mg l^{-1} using sodium selenite

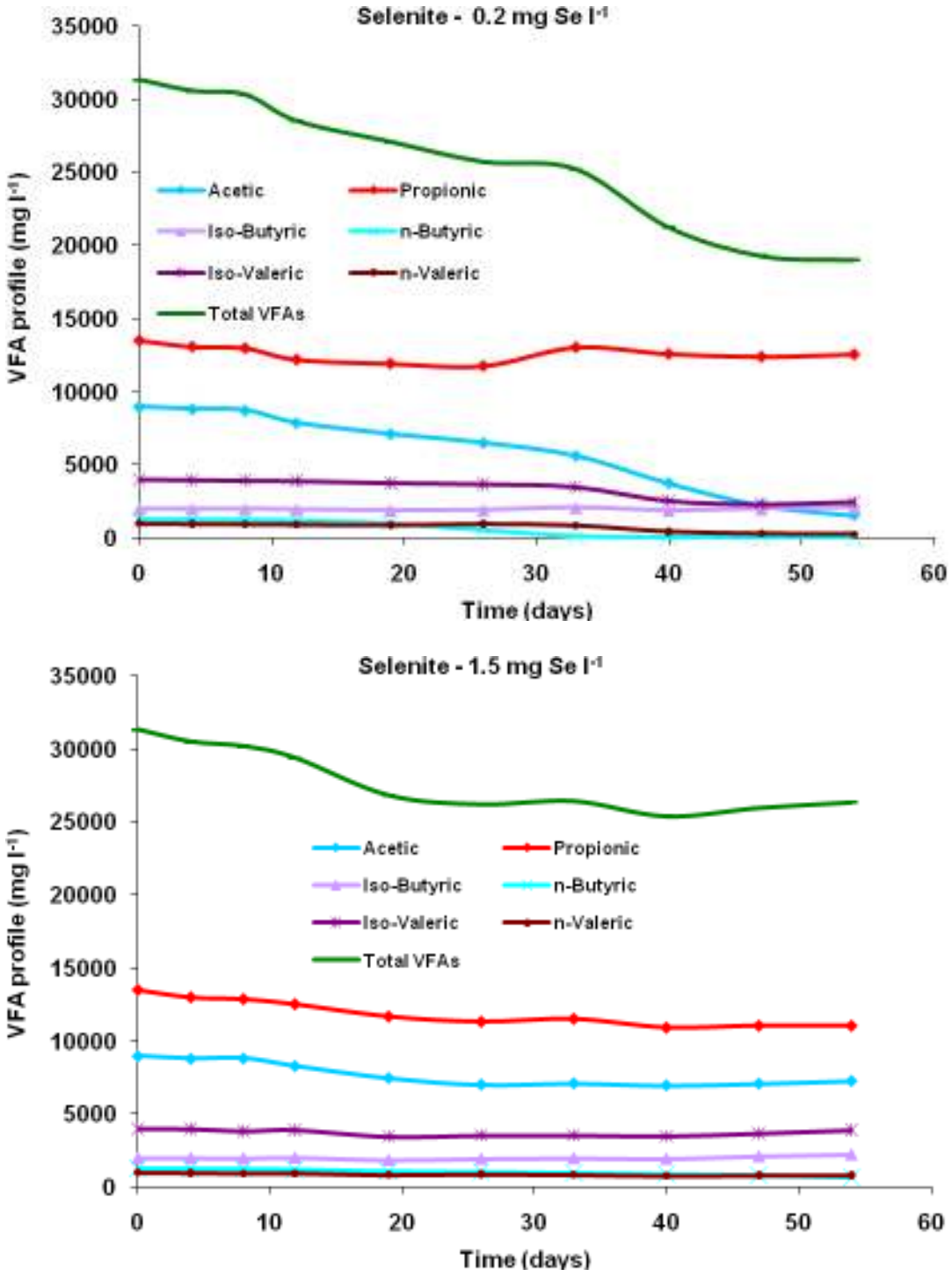


Figure 25 continued VFA degradation profiles of control and after Se supplementation at 0.2 and 1.5 mg l^{-1} using sodium selenite

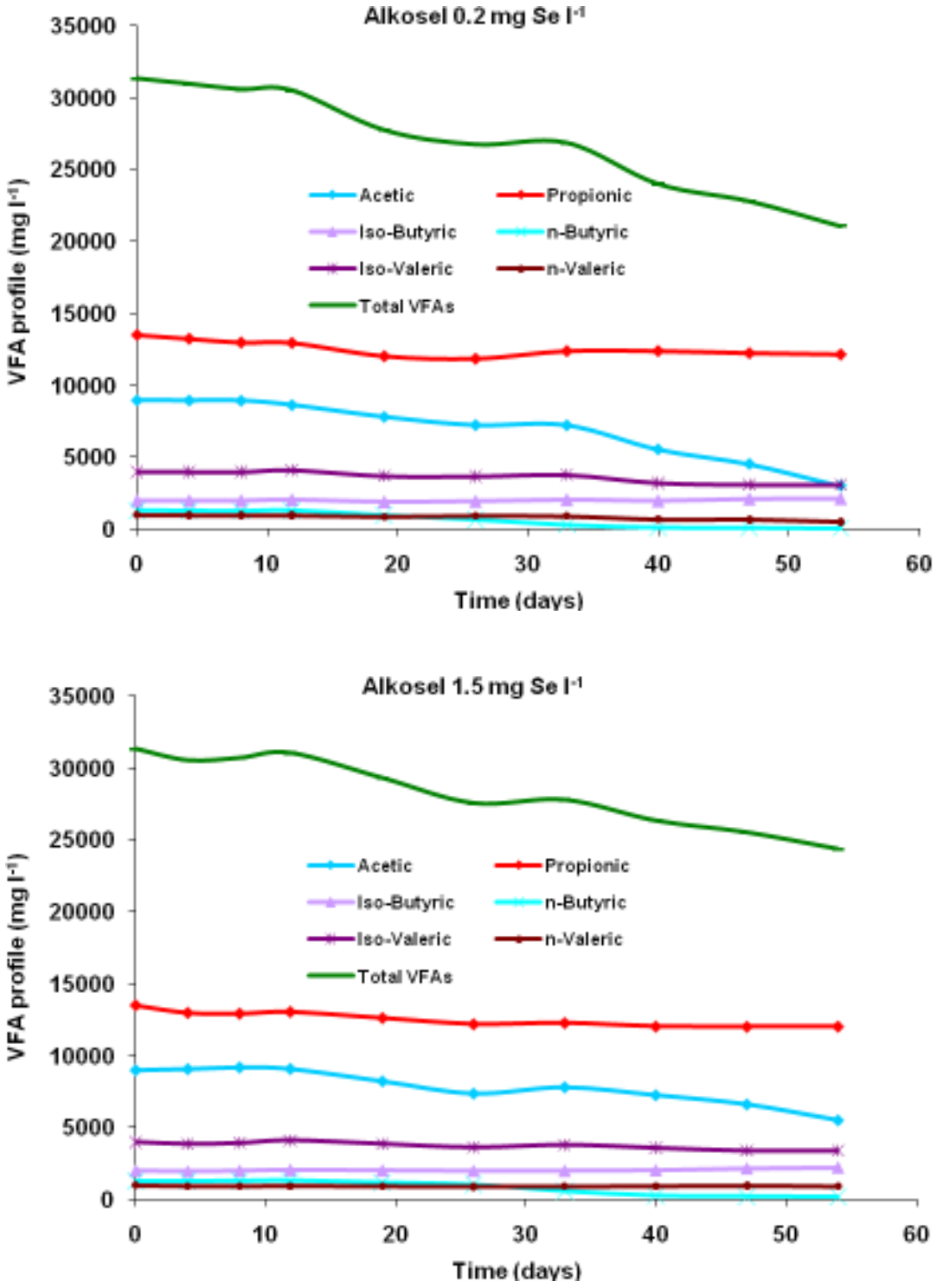


Figure 26 VFA degradation profiles after Se supplementation at 0.2 and 1.5 mg l^{-1} using Alkosel

5 Semi-continuous food waste digestion trials with trace element supplementation at high ammonia concentration

A number of semi-continuous food waste digestion trials were conducted to investigate trace element supplementation requirements. The results indicated that among the eleven trace elements tested, selenium, cobalt, and molybdenum were the key essential elements that are needed to promote stable food waste digestion and were present in insufficient quantities in the food waste itself.

5.1 Supplementation with trace element combinations

Semi-continuous food waste digestion trials were carried out to investigate what trace element combinations, in the trace element supplementation matrix, had the greatest effect on VFA degradation and stable food waste digestion. Both severely and only slightly stressed food waste digestate were used as the inoculum in the experiments.

5.1.1 Experiment using a food waste digestate acclimated but slightly stressed as inoculum

Six pairs of digesters operating at 36±1 ºC were used in the experiment, these were supplemented with: 1) Se and Mo , 2) Se, Mo, Co and W , 3) Se, Mo, So, W, Fe and Ni, 4) Se, Mo, Co, W, Fe, Ni, Zn, Cu, Mn, Al, B. 5) No trace element addition, and 6) No trace element addition. Two pairs of controls were run to test independently the impact of increasing the food waste load on the digesters irrespective of trace element additions.

At the start of the experiment the digesters were inoculated with 3.5 litres of digestate liquor as described in section 4.2.2. Food waste collected from the Biocycle anaerobic digestion plant in Ludlow, Shropshire was the sole substrate for the digesters. The digesters were run at an organic loading rate (OLR) of 1.6 kg VS m^{-3} d^{-1} without any wastage of digestate until a 4 litres of working volume had been reached. The trace element addition was made on Monday the 12th October 2009 to those digesters receiving supplementation by the amount as given in Table 23; the element concentrations in the digestate before the element supplementation are also shown in Table 23.

Table 23 Existing and additional concentration of trace elements in digesters on the 12th October 2009 when the semi-continuous trials started

Essential element	Compound used	Element concentration (mg l^{-1})	
		Additional trace element addition made on the 12th October 2009	Existing trace element concentration in the inoculum digestate
Aluminium (Al)	$AlCl_3 \cdot 6H_2O$	0.1	63.3
Boron (B)	H_3BO_3	0.1	2.5
Cobalt (Co)	$CoCl_2 \cdot 6H_2O$	1.0	0.083
Copper (Cu)	$CuCl_2 \cdot 2H_2O$	0.1	5.75
Iron (Fe)	$FeCl_2 \cdot 4H_2O$	5.0	173.7
Manganese (Mn)	$MnCl_2 \cdot 4H_2O$	1.0	18.5
Molybdenum (Mo)	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	0.2	0.29
Nickel (Ni)	$NiCl_2 \cdot 6H_2O$	1.0	2.9
Selenium (Se)	Na_2SeO_3	0.2	0.050
Tungsten (W)	$Na_2WO_4 \cdot 2H_2O$	0.2	<0.035
Zinc (Zn)	$ZnCl_2$	0.2	8.11

The organic loading rate in all digesters at the time of the initial trace element addition was raised to 2.0 kg VS m^{-3} d^{-1}. This was gradually increased further, as shown in Figure 27, except in one of the pair of control digesters where it remained at 2.0 kg VS m^{-3} d^{-1}. Food waste was added each day to maintain the desired loading rate and digestate was removed once per week to maintain a constant volume of 4.0 litres. There was no recirculation of liquor or fibre. The retention time was therefore determined by the volatile solids content of food waste and the hydraulic retention time of the digester, and was around 95, 63, 48, and 38 days at organic loading rates of 2, 3, 4, and 5 kg VS m^{-3} d^{-1} respectively. Trace element additions were made weekly. The amount added was equal to the amount calculated as removed each week in the digestate wasted from each digester; this calculation did not take into account any additional trace element input arising from the food waste itself.

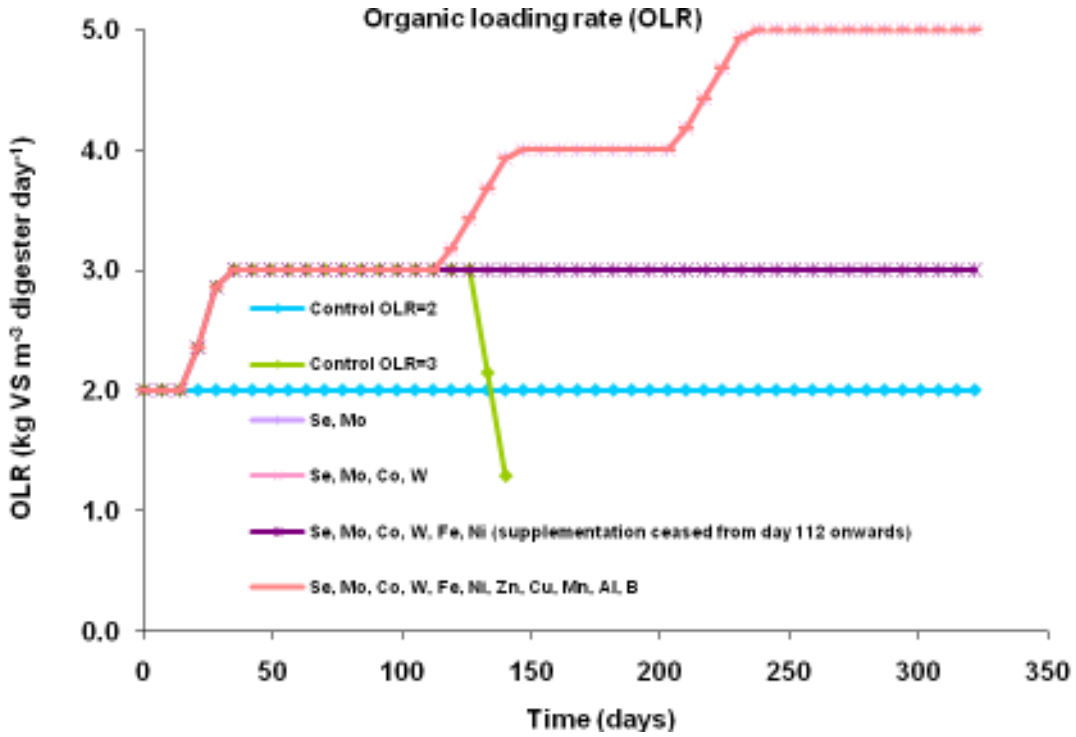


Figure 27 The organic loading rate applied to the trace element supplemented digesters and the controls.

Biogas production was measured daily and biogas composition and VFA determined twice weekly. Other digestate parameters such as pH, solids, total ammonia nitrogen (TAN) and alkalinity were analysed once per week. The process efficiency was estimated by calculating the specific biogas production (SBP) and volumetric biogas production (VBP). The stability of digester operation was evaluated by reference to other parameters such as pH, VFA, ammonia and alkalinity. The experimental results, using average values from each digester pair, are shown graphically from Figure 28 to 35; there was generally less than 5% difference between the duplicates for all parameters. Day 0 is the first day when trace elements were fed to the digesters and day 322 was 30th August 2010, when the final samples were taken and analysed.

It can be seen from Figure 28 that trace elements had an immediate effect, with VFA concentrations showing a rapid reduction to less than 1000 mg l^{-1} by day 10 in all the

digesters receiving a supplement. Although a small rise in VFA concentration to 1200 mg l^{-1} was observed when the OLR rose from 2 to 3 kg VS m^{-3} d^{-1}, a value of less than 200 mg l^{-1} was restored within two weeks of the loading increase taking place. After maintaining the OLR at 3 kg VS m^{-3} d^{-1} for 1.4 retention times the loading in the digesters supplemented with trace elements was gradually increased to 4 kg VS m^{-3} d^{-1} from day 112 over a 4-week period. This was the case except in the pair of digesters which had received a supplement of Se, Mo, Co, W, Fe and Ni. This pair was maintained at an OLR 3 kg VS m^{-3} d^{-1} throughout the rest of the experiment and trace element addition stopped from day 112 onwards: in this way the effect of trace elements being diluted out of the digesters could be monitored. At the end of the experimental period, this pair of digesters had run at an OLR 3 kg VS m^{-3} d^{-1} without trace element supplementation for 210 days (around 3 retention times), and an elevated VFA concentration were observed from the end of the 2nd retention time and this gradually increased to 3500 mg l^{-1} at the end of 3rd retention time. Acetic acid was the dominant VFA in this pair of digesters, and the proportion of other VFA species present (propionic acid, iso-butyric acid, and iso-valeric acid) was less than 10% of total VFA concentration.

The three pairs of digesters where supplementation with different trace element combinations was maintained and the OLR increased to 4 kg VS m^{-3} d^{-1} continued to perform well without any VFA accumulation. All other monitored parameters also remained more or less constant with TAN around 5400 mg l^{-1} (Figure 31), pH 8.0 (Figure 32), and methane percentage around 59% (Figure 33). The average specific biogas production was 0.74 STP m^3 kg^{-1} VS (Figure 34) and volumetric biogas production 3.0 STP m^3 m^{-3} d^{-1} (Figure 35). The organic loading rate was gradually increased to 5 kg VS m^{-3} d^{-1} on day 228, and at the end of the experimental period these three pairs of digesters had been running at this loading for 95 days (around 2.5 retention times). It can be seen from Figure 28 that the VFA concentration gradually increased to 2000 mg l^{-1} in the pair of digesters supplemented with Se and Mo after the loading increase. The sequence of appearance of the VFA species and their proportion in the total VFA at the end of the experimental period was: acetic acid (30%), iso-butyric acid (35%), iso-valeric acid (25%), and propionic acid (10%). The VFA concentration was still below 200 mg l^{-1} in the pair of digesters supplemented with Se, Mo, Co and W and in the pair of digesters with full trace element supplementation, as shown in Figure 28. The volumetric biogas production had increased to 3.8 STP m^3 m^{-3} d^{-1} (Figure 35) and the specific biogas production was still stable at 0.76 STP m^3 kg^{-1} VS (Figure 34) at the OLR of 5 kg VS m^{-3} d^{-1}.

In contrast to the digesters supplemented with trace elements, both pairs of control digesters showed an increase in VFA concentration. In the pair where the loading remained constant at 2.0 kg VS m^{-3} d^{-1} this increased to around 6000 mg l^{-1} after two weeks of operation and stabilised around this value up until day 120 when a further increase in concentration was observed. This corresponded to an increase in the concentration of propionic acid which soon became the dominant species, as shown in Figure 29, with the total VFA concentration increasing to around 14000 mg l^{-1} by day 150. The total VFA concentration stayed at this plateau for around 100 days while acetic acid replaced propionic acid as the VFA species with the highest concentration. A third increase in total VFA concentration was observed from day 250 when propionic acid again became dominant, and at the end of the experimental period the total VFA was around 17000 mg l^{-1}.

The second pair of control digesters had their OLR increased to 3.0 kg VS m^{-3} d^{-1} at the same time as the trace element supplemented digesters. The VFA concentration rapidly rose to around 10000 mg l^{-1} and remained at this level for around 50 days. Propionic acid then became the dominate VFA species and there was a general increase in concentration of all the

VFA species reaching 29000 mg l^{-1} (Figure 30). On day 126 an attempt to recover this pair of control digesters was made by lowering the organic loading rate as shown in Figure 27. This was not effective, however, and the pH continued to drop reaching 6.9 (Figure 32) by day 140 with only 44% of methane in the biogas (Figure 33). At this point feeding was stopped for around 20 days and then a second attempt at recovery was made by adding a single trace element supplementation as described in section 5.2.2 in this report.

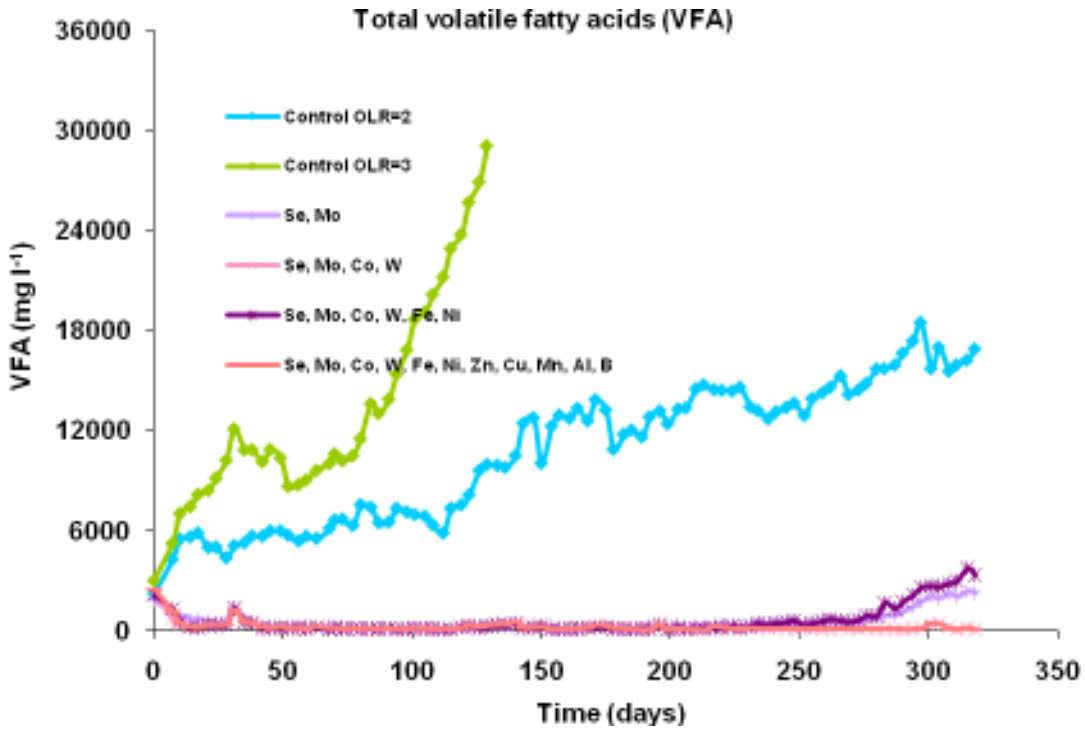


Figure 28 Total VFA concentration in control and trace element supplemented digesters.

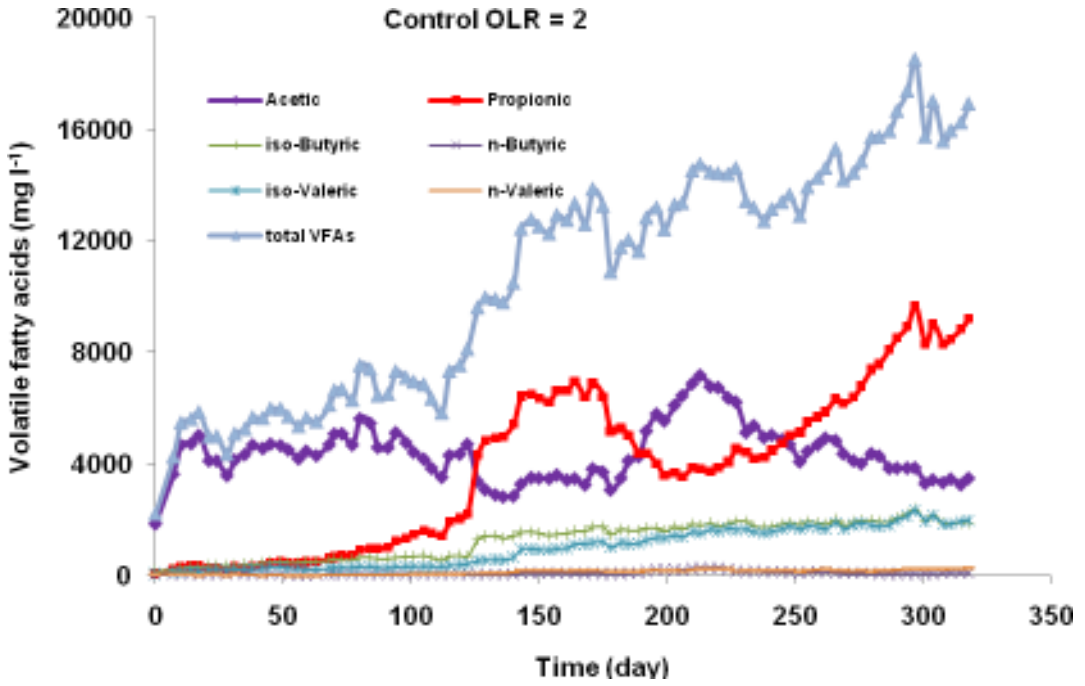


Figure 29 VFA concentration profile in control digesters at an OLR of 2 kg VS m^{-3} d^{-1}

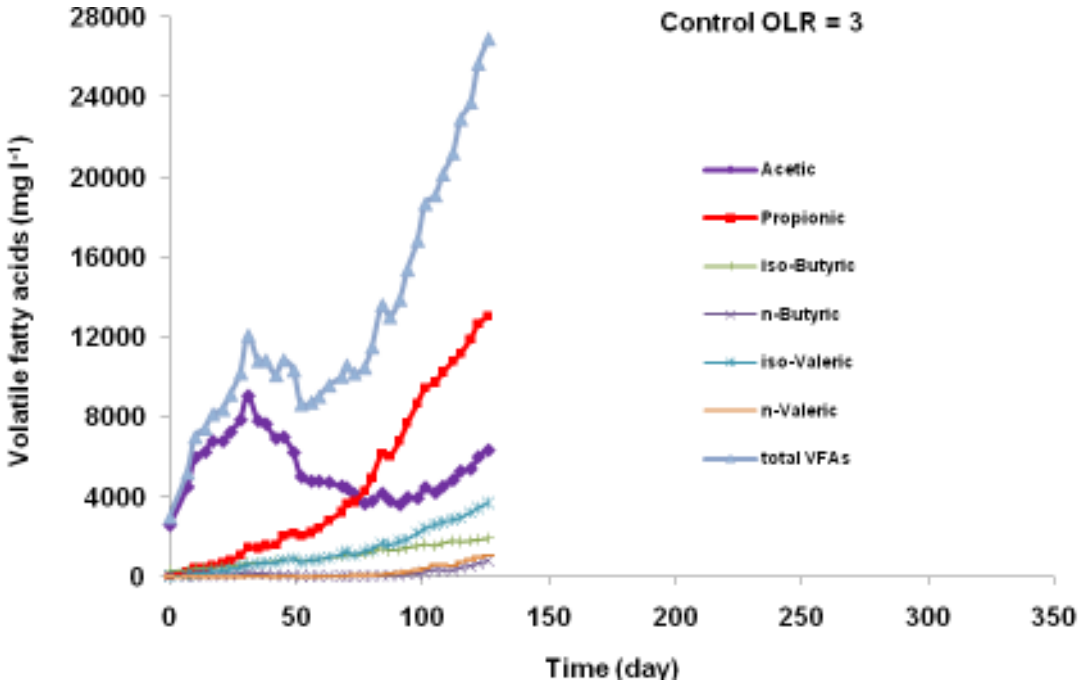


Figure 30 VFA concentration profile in control digesters at an OLR of 3 kg VS m^{-3} d^{-1}

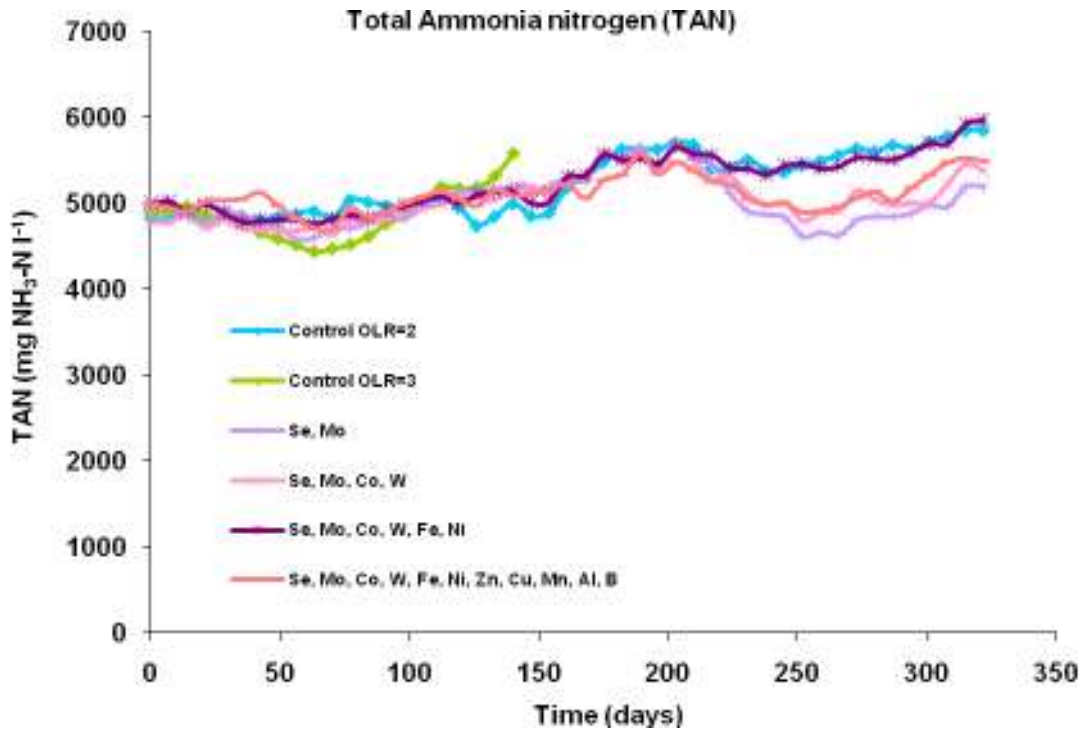


Figure 31 Total ammonia nitrogen in control and trace element supplemented digesters.

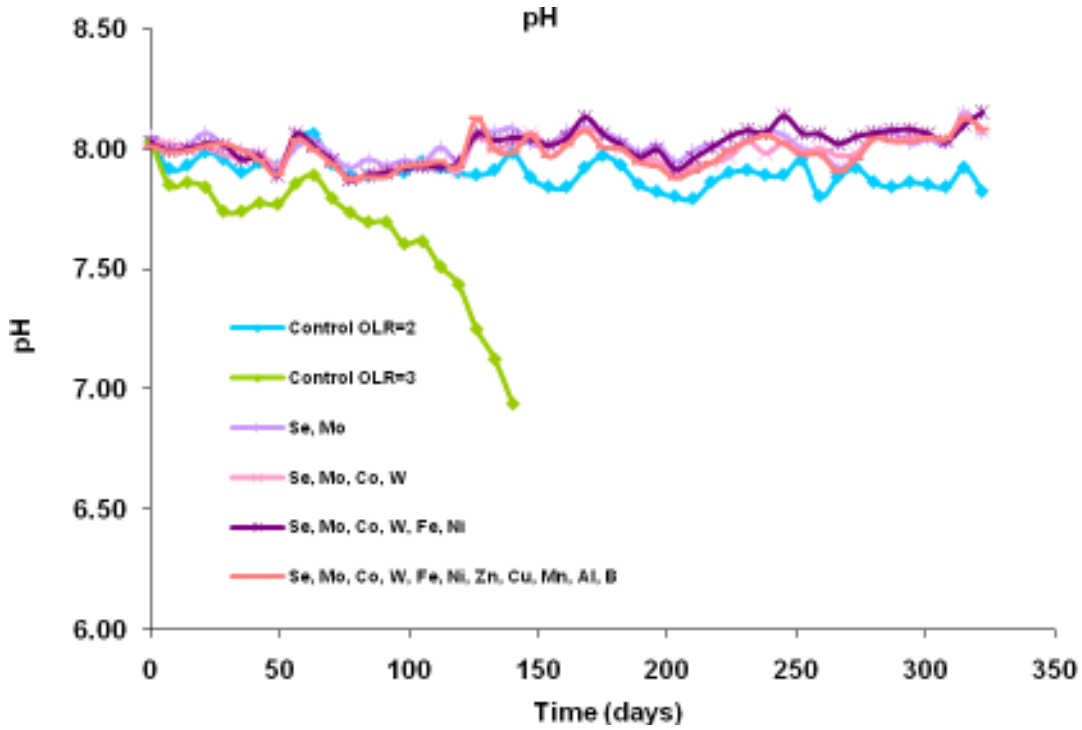


Figure 32 pH values in control and trace element supplemented digesters.

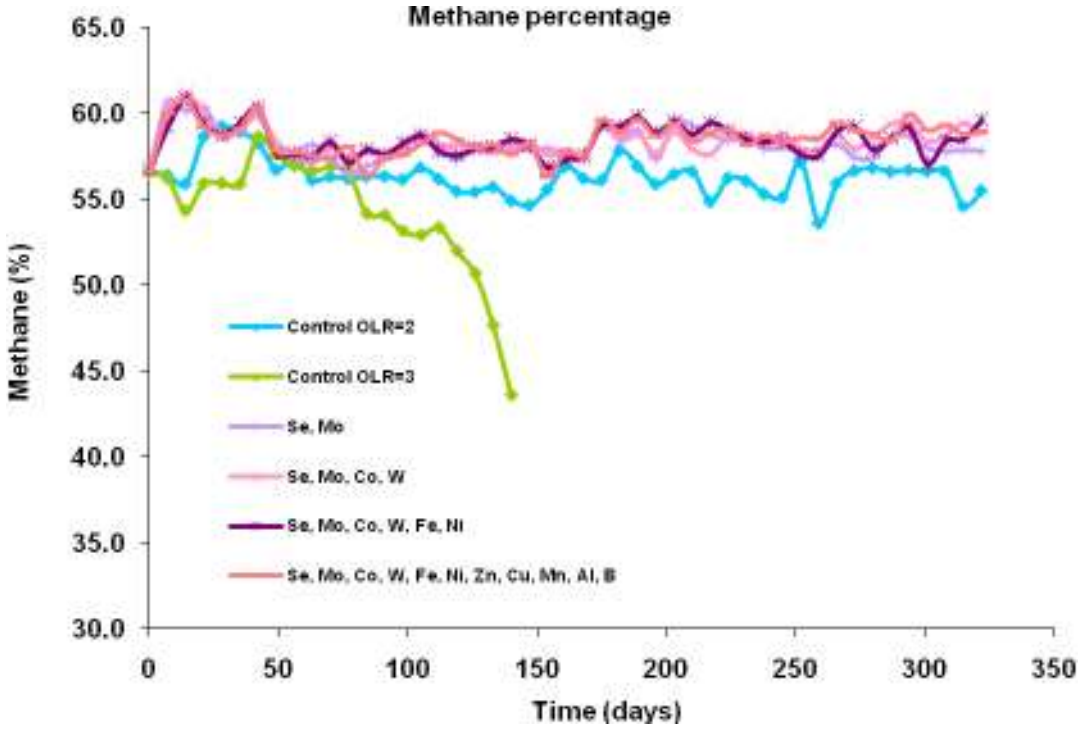


Figure 33 Weekly average methane content in control and trace element supplemented digesters.

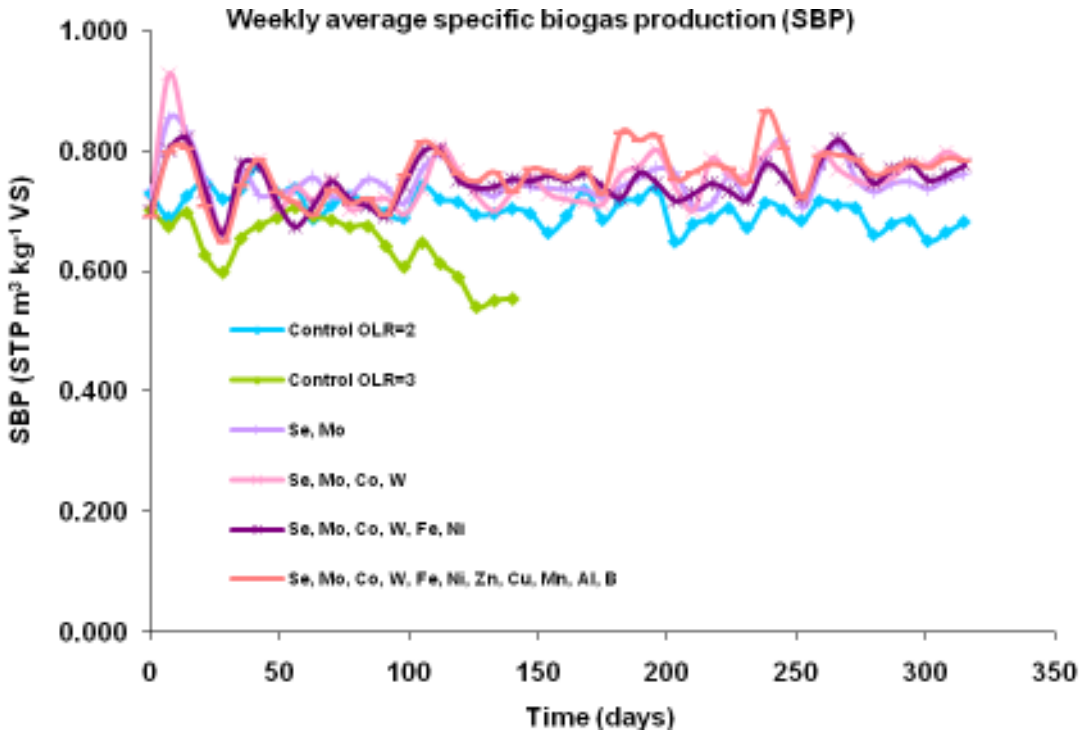


Figure 34 Weekly average specific biogas production in control and trace element supplemented digesters.

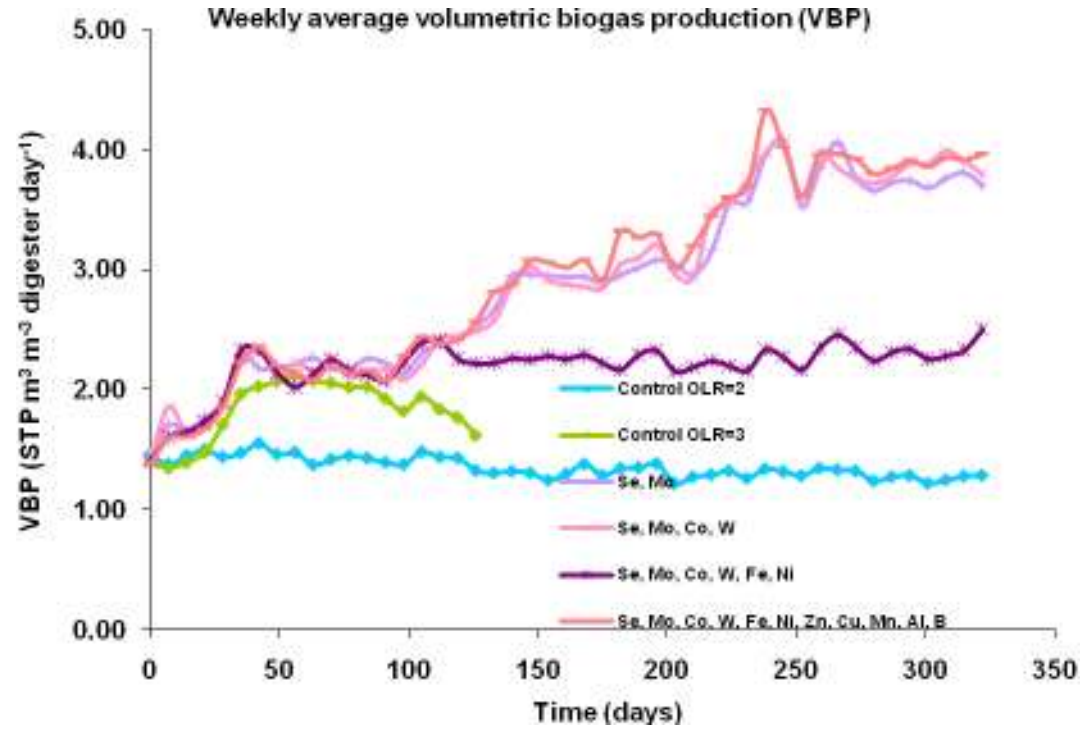


Figure 35 Weekly average volumetric biogas production in control and trace element supplemented digesters.

The concentration of trace elements in the digesters was analysed on day 112 (1st February 2010). This was at the time when trace element addition to the pair of digesters which had received a supplement of Se, Mo, Co, W, Fe and Ni ceased, and when the organic loading rate to the other digesters receiving trace element supplementation increased from 3 to 4 kg VS m^{-1} d^{-1}. Samples were again taken for trace element analysis on day 301 (9th August 2010) when the digesters with trace element supplementation had been running at an organic loading rate of 5 kg VS m^{-1} d^{-1} for 74 days (around 2 retention times). The trace element concentration in the pair of digesters where supplementation of Se, Mo, Co, W, Fe and Ni ceased was monitored at shorter time intervals, and the duplicate digesters were sampled separately to investigate the repeatability of the experiment. It can be seen from Table 24 that selenium and cobalt had a very low concentration in the control digesters (0.04~0.08 mg l^{-1}) and the supplementation significantly increased the quantity in the digestate. Molybdenum had a slightly higher concentration in the control digesters (0.08~0.17 mg l^{-1}), and the additional dosing doubled its concentration in the digestate. No clear difference can be seen in Al, B, Cu, Fe, Mn, Ni, and Zn concentration in all digesters, mainly because food waste has a relatively high total concentration of these elements compared with the level of supplementation.

Table 24 Trace element concentration in digesters in both the supplemented and control digesters (mg l^{-1})

Digesters		Al	B	Co	Cu	Fe	Mn	Mo	Ni	Zn	Se
Control OLR=2	Day 112	26.4	2.01	0.038	2.23	79.7	10.4	0.168	1.10	3.62	0.044
	Day 301	31.8	2.13	0.035	1.79	39.3	14.5	0.210	1.27	5.12	0.073
Control OLR=3	Day 112	23.2	1.98	0.057	1.82	50.3	10.2	0.083	0.438	3.72	0.044
	Day 301	see Table 29, section 5.2.2									
Se, Mo	Day 112	32.3	2.81	0.048	2.58	56.1	13.9	0.339	1.08	5.26	0.297
	Day 301	26.6	1.80	0.027	1.29	25.9	14.6	0.297	1.35	4.67	0.328
Se, Mo, Co, W	Day 112	32.1	2.48	0.644	2.26	48.9	12.8	0.276	0.616	4.62	0.263
	Day 301	27.3	2.08	0.765	1.36	23.8	16.0	0.279	0.536	4.92	0.341
Full supplementation	Day 112	29.3	2.21	0.605	2.26	59.3	12.5	0.324	1.62	4.34	0.297
	Day 301	30.8	2.15	0.835	1.82	58.5	17.4	0.780	1.49	5.13	0.467
Digesters in which supplementation of Se, Mo, Co, W, Fe, and Ni ceased on day 112	Day 112	27.5	2.48	0.620	2.05	56.3	12.3	0.319	1.44	4.56	0.271
		29.4	2.33	0.614	2.02	50.6	11.4	0.299	1.39	4.16	0.269
	Day 154	30.5	1.93	0.522	1.77	39.8	12.4	0.305	1.46	4.92	0.251
		27.4	1.88	0.532	1.87	40.0	11.7	0.334	1.46	4.68	0.283
	Day 196	27.3	2.26	0.346	1.68	34.3	13.1	0.258	1.20	5.02	0.207
		29.4	1.98	0.374	1.71	35.1	13.0	0.289	1.21	4.97	0.191
	Day 245	30.3	2.05	0.212	1.53	30.7	13.6	0.222	0.873	4.94	0.150
		30.3	2.09	0.220	1.57	30.4	13.5	0.212	0.778	4.84	0.165
	Day 301	33.1	2.40	0.158	1.59	35.2	16.6	0.296	1.72	5.36	0.139
		31.3	2.24	0.161	1.58	33.2	15.8	0.278	1.46	5.08	0.165

Simulated dilute-out concentration profiles for cobalt and selenium are shown in Figure 36. These were calculated from the concentrations of cobalt and selenium in the digesters on day 112, when supplementation ceased, and from the concentration of these two elements in the food waste used as substrate. The simulated concentration profiles matched fairly well with the measured concentrations of these two elements, these are also plotted in Figure 36. When

considered in relation to the VFA profile shown in Figure 28, it can be concluded that the concentrations of total cobalt and total selenium in the food waste digester should be kept above 0.22 and 0.16 mg l^{-1} respectively when feeding at an organic loading of 3 kg VS m^{-3} d^{-1}. Considering the low concentration of these elements in the food waste streams (Section 2), their supplementation is essential for VFA degradation and stable food waste digestion.

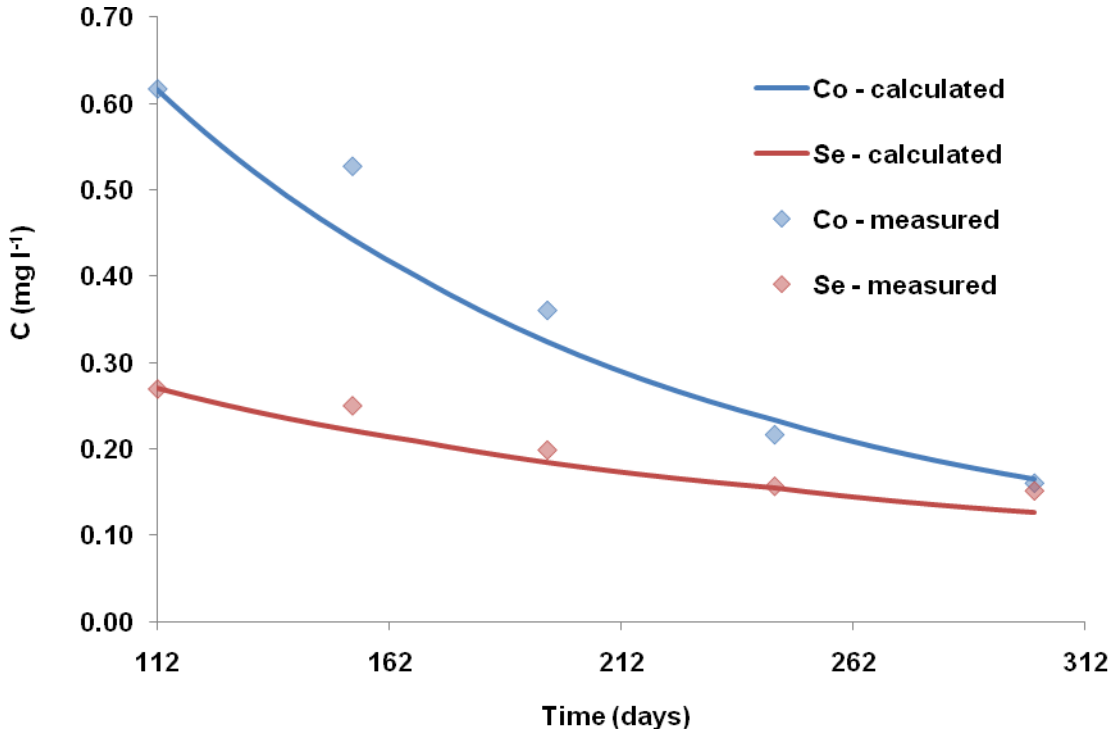


Figure 36 Simulated cobalt and selenium dilute out curves and the measured concentrations of these in the pair of digesters where Se, Mo, Co, W, Fe, and Ni supplementation ceased on day 112. By day 245 the VFA concentration in the digesters had risen above 500 mg l^{-1}.

5.1.2 Microbial community structure

All the digesters were sampled on day 316 (24th August 2010) for microbial community structure analysis using the Fluorescence In-Situ Hybridisation (FISH) technique. Density gradient centrifugation with Nycodenz was used to separate the microbial biomass from the food waste residues before performing the analysis. The separated microbial biomass was then fixed with 4% of paraformaldehyde (PFA) solution. The positive probes (Thermo Electron Biopolymers, Ulm, Germany) used and their target orders or families are listed in Table 25. Hybridised samples were visualised using a Leica TCS SP2 confocal laser scanning microscopy, and 20 different microscrope fields were randomly selected for each hybridisation treatment. The laser wavelength to excite the fluorochrome dyes 6-Fam, Cy3, and Cy5 was 488nm, 561nm, and 633nm, respectively.

The FISH observation showed that the predominant methanogenic group in both control digesters and the test digesters with trace element supplementation were members of the order of Methanoimicrobiales (Figure 37), which indicated the dominant metabolic pathway of food waste digestion was the syntrophic acetate oxidising acetogenesis and hydrogenotropic methanogenesis pathway. This backed up the proposed hypothesis that syntrophic acetate oxidation is the main mechanism for acetate degradation in the presence of

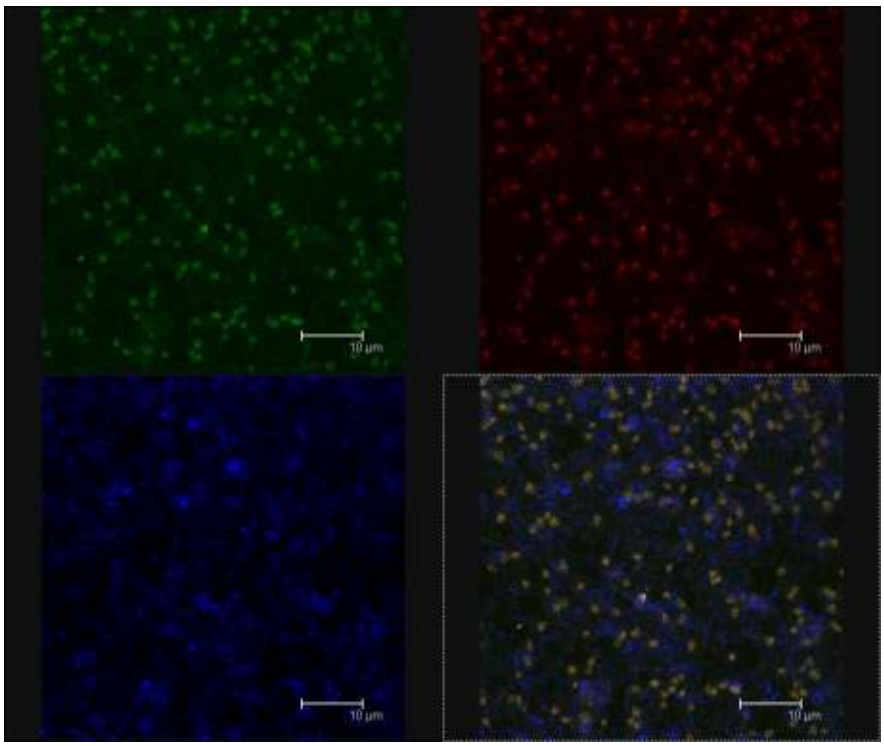
inhibitors, such as ammonia, because the acetate utilising methanogens are more sensitive to ammonia than hydrogenotrophic methanogens.

Sewage sludge digestate and a vegetable waste digestate with an ammonia concentration less than 2000 mg l^{-1} were also analysed and the dominant methanogenic bacteria belonged to the family of Methanosaetaceae and the family of Methanosarcinaceae respectively (Figure 38), which are acknowledged as the only two families of methanogens which can undertake acetoclastic methanogenesis.

Table 25 Oligonucleotide probes used with target groups and optimised formamide concentrations

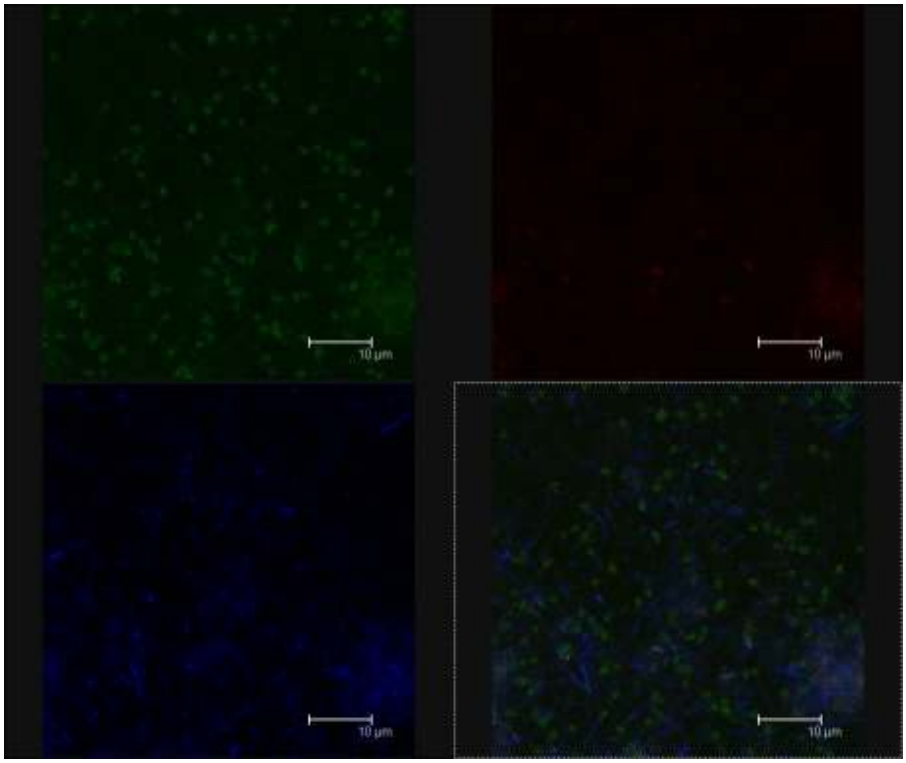
Probe name	Target group	Probe sequence (5'-3')	Fluoro-chrome	Fluorescence colour	Formamide (%)
EUB338	*Bacteria (most)*	GCTGCCTCCCGTAGGAGT	Cy5	blue	20~50
EUB338+	*Bacteria (remaining)*	GCWGCCACCCGTAGGTGT	Cy5	blue	20~50
ARC915	*Archaea*	GTGCTCCCCCGCCAATTCCT	6-Fam	green	20~50
MX825	*Methanosaetaceae*	TCGCACCGTGGCCGACACCTAGC	Cy3	red	50
MS1414	*Methanosarcinaceae*	CTCACCCATACCTCACTCGGG	Cy3	red	50
hMS1395	MS1414-helper	GGTTTGACGGGCGGTGTG	-	-	50
hMS1480	MS1414-helper	CGACTTAACCCCCCTTGC	-	-	50
MSMX860	*Methanosarcinales*	GGCTCGCTTCACGGCTTCCCT	Cy5	blue	45
MG1200	*Methanomicrobiales*	CGGATAATTCGGGGCATGCTG	Cy3	red	20
MB1174	*Methanobacteriales*	TACCGTCGTCCACTCCTTCCTC	Cy3	red	45
MC1109	*Methanococcales*	GCAACATAGGGCACGGGTCT	Cy3	red	45

Note: W, A+T mixed base.

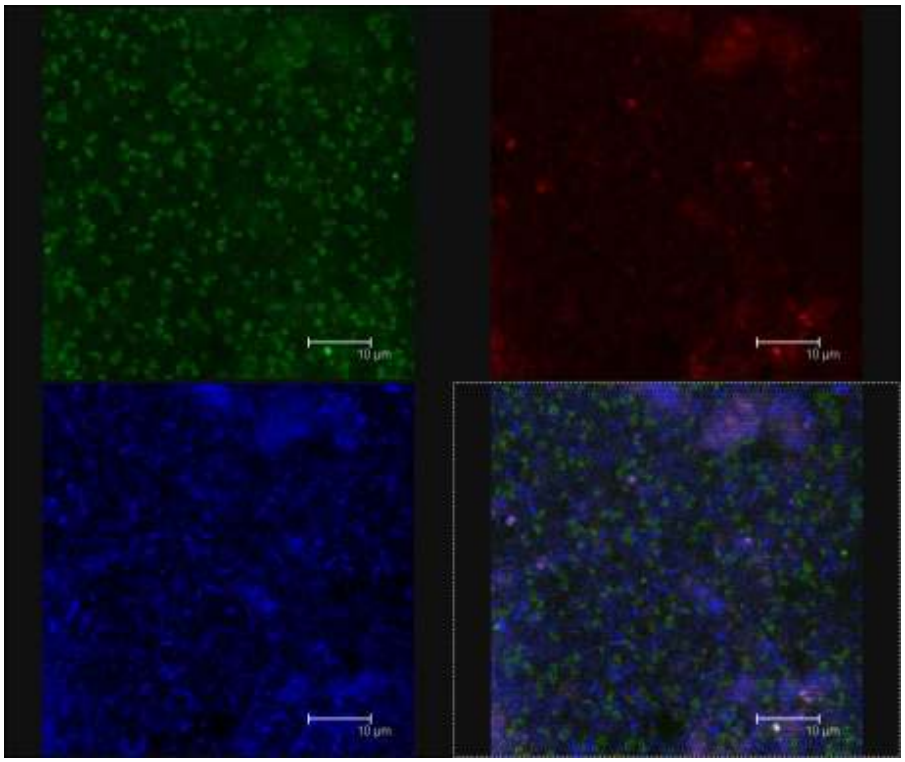


a) *Archaea* (green), *Methanomicrobiales* (red), and *Bacteria* (blue)

Figure 37 FISH images of food waste digestate

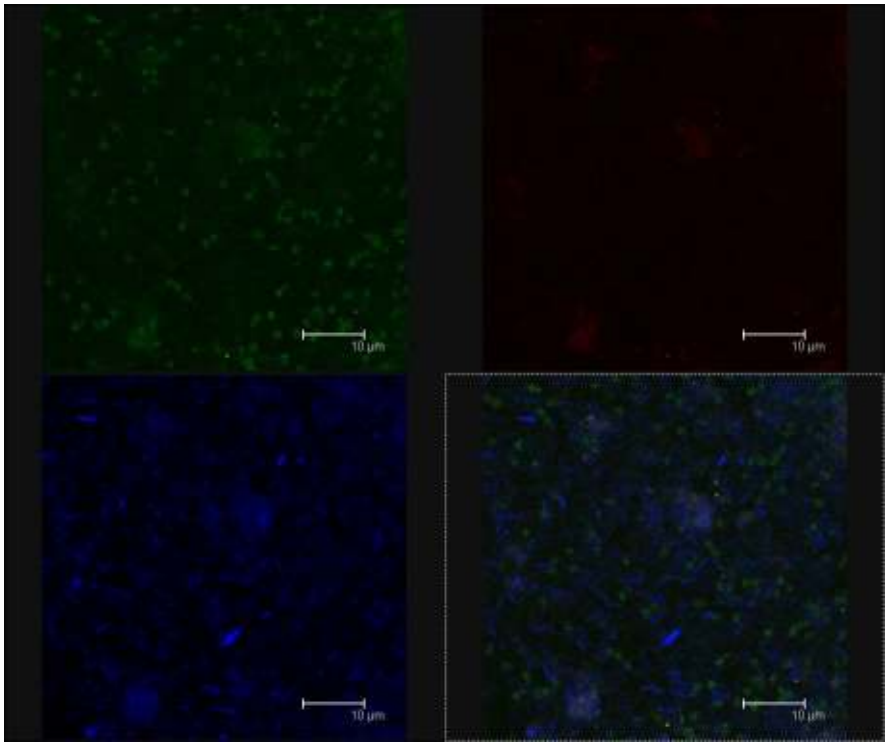


b) *Archaea* (green), *Methanobacteriales* (red), and *Bacteria* (blue)

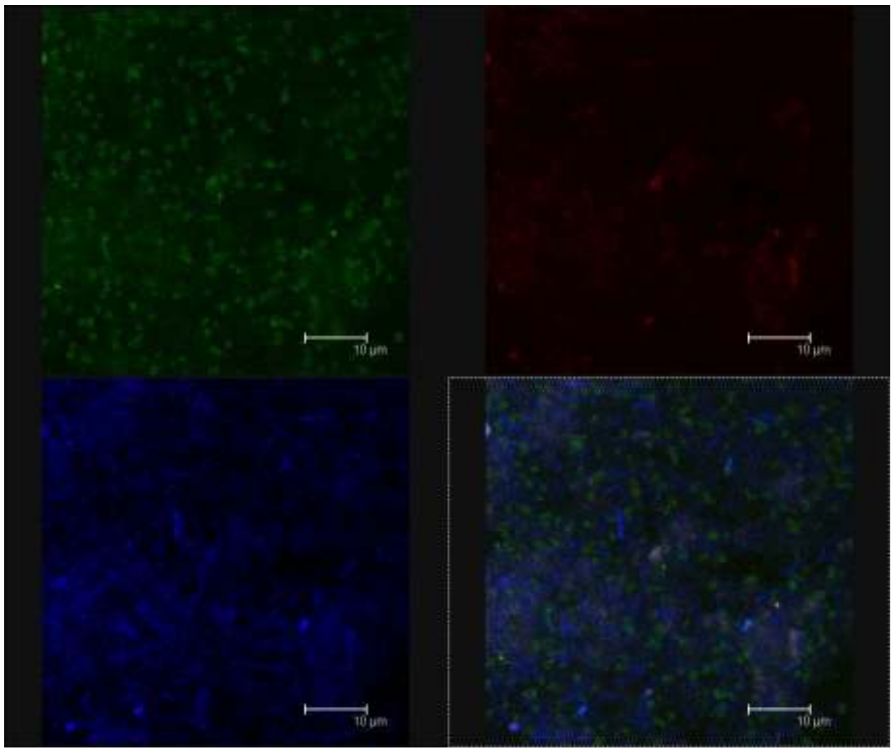


c) *Archaea* (green), *Methanococcales* (red), and *Bacteria* (blue)

Figure 37 continued FISH images of food waste digestate

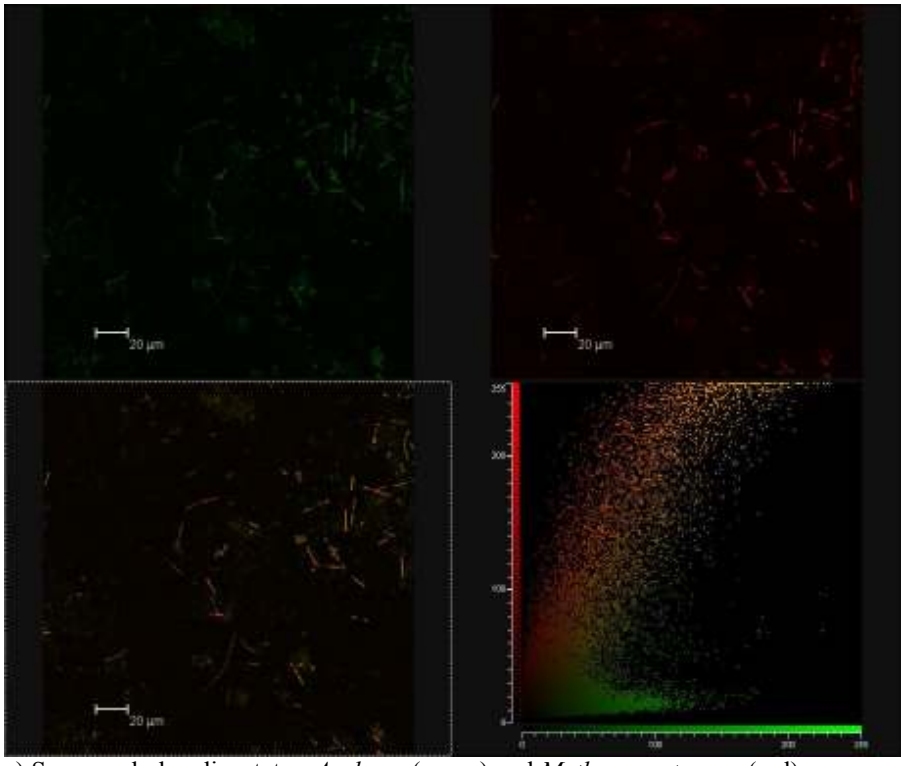


d) *Archaea* (green), *Methanosarcinaceae* (red), and *Bacteria* (blue)

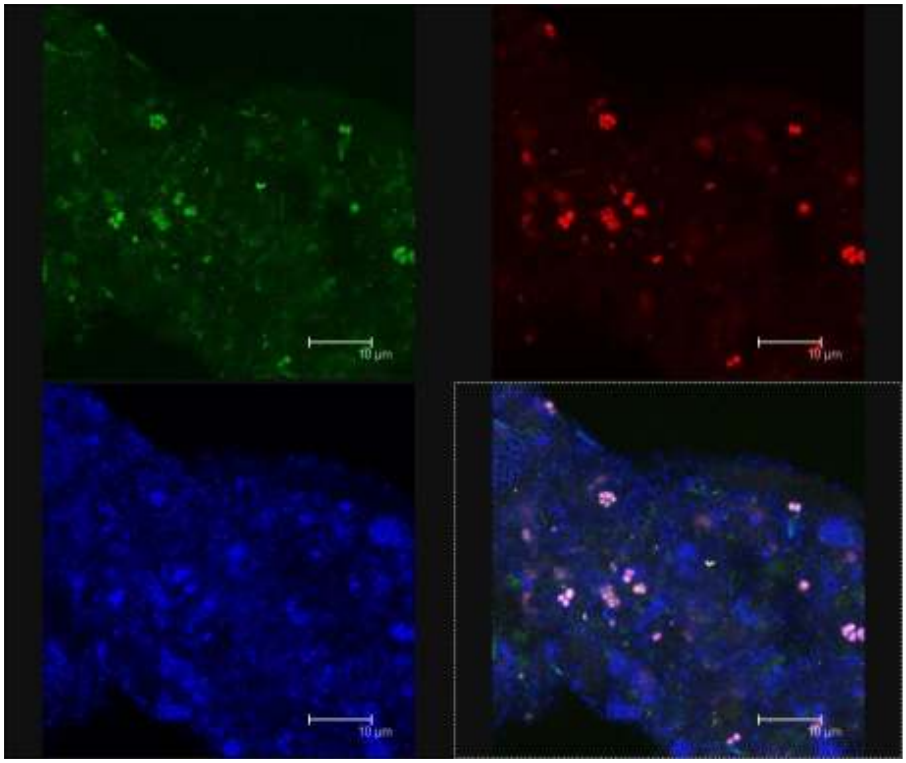


e) *Archaea* (green), *Methanosaetaceae* (red) and *Bacteria* (blue)

Figure 37 continued FISH images of food waste digestate



a) Sewage sludge digestate - *Archaea* (green) and *Methanosaetaceae* (red)



b) Vegetable waste digestate - *Archaea* (green), *Methanosarcinaceae* (red), *Methanosarcinales* (blue), and *Bacteria* (blue)

Figure 38 FISH image of two digestate samples with total ammonia nitrogen less than 2000 mg l^{-1}

5.1.3 Semi-continuous fed digesters using the food waste digestate with a long term VFA accumulation as an inoculum

The semi-continuous trace element supplementation trial was also carried out using a commercial food waste digester as inoculum (Table 8) in a pair of digesters. The trace element addition was made on 17th June 2009 by the amount shown in Table 26; trace element concentrations in the digestate before supplementation are also shown in Table 26. Feeding was ceased after running at organic loading of 2 kg VS m^{-1} d^{-1} for 4 days due to the rapid VFA increase, as shown in Figure 39. Food waste addition was restored at a weekly average OLR of 0.25 kg VS m^{-1} d^{-1} from day 16 to day 120. The loading was then increased to 0.5 kg VS m^{-1} d^{-1} when the pH of digestate was around 7.7 and total ammonia nitrogen was around 7000 mg l^{-1}. There were no control digesters without trace element addition as these have been shown to have operational difficulties, including severe foaming.

Table 26 Existing and additional concentration of trace elements in digesters on the 17th June 2009

Essential element	Compound used	Element concentration (mg l^{-1})	
		Additional trace element addition made on the 17th June	Existing trace element concentration in the inoculum digestate
Aluminium (Al)	$AlCl_3 \cdot 6H_2O$	10	49.6
Boron (B)	H_3BO_3	1.0	3.45
Cobalt (Co)	$CoCl_2 \cdot 6H_2O$	2.0	0.05
Copper (Cu)	$CuCl_2 \cdot 2H_2O$	1.0	1.85
Iron (Fe)	$FeCl_2 \cdot 4H_2O$	20	92.4
Manganese (Mn)	$MnCl_2 \cdot 4H_2O$	10	5.69
Molybdenum (Mo)	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	0.4	0.05
Nickel (Ni)	$NiCl_2 \cdot 6H_2O$	1.0	0.70
Selenium (Se)	Na_2SeO_3	0.4	0.02
Tungsten (W)	$Na_2WO_4 \cdot 2H_2O$	0.2	-
Zinc (Zn)	$ZnCl_2$	10	7.09

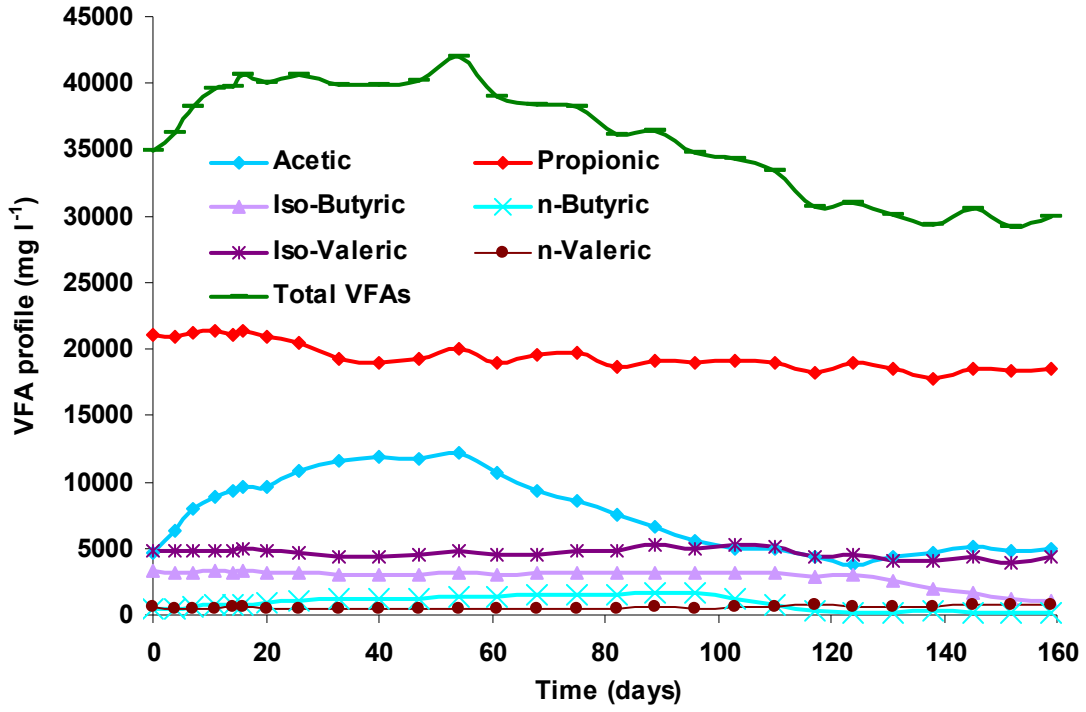


Figure 39 VFA concentration profile in semi-continuous digestion using commercial food waste digestate as an inoculum.

5.2 Single trace element supplementation in semi-continuous fed digesters

These experiments were carried out to distinguish the function of Se, Mo, and Co, as individual supplements rather than as a trace element combination.

5.2.1 Recovery of digesters showing a moderate accumulation of VFA by supplementation with Se, Mo, and Co respectively

The experiment used a set of 4 mesophilic digesters in which the VFA concentration had reached 14000 mg l^{-1}. Trace element additions were made on the 25th January 2010 (day 0) with one digester receiving Se (0.2 mg l^{-1}), one Mo (0.2 mg l^{-1}), and one Co (1.0 mg l^{-1}). The fourth digester was run as a control without any trace element input.

The organic loading rate to all the digesters was 2.0 kg VS m^{-3} d^{-1} and was provided by daily additions of food waste with weekly removal of digestate to maintain a constant volume. Trace element additions were made weekly, with the amount added equal to that calculated as removed in the digestate wasted from each digester each week; this calculation did not take into account any additional trace element input arising from the food waste itself. Biogas production was measured daily and biogas composition and volatile fatty acids determined twice weekly. Other digestate parameters such as pH, solids, total ammonia nitrogen (TAN) and alkalinity were analysed once per week. The process efficiency was estimated by calculating the specific biogas production (SBP) and volumetric biogas production (VBP). The stability of digester operation was evaluated by reference to other parameters such as pH, VFA, ammonia and alkalinity. The VFA profiles of these four digesters are shown graphically in Figure 40, and the other digester parameters are given in Table 27 using average values from the last 60 days.

Although the initial VFA concentration was around 14000 mg l^{-1}, this dropped rapidly at the beginning of the experiment (Figure 40) indicating that the digestate still maintained a high VFA degradation potential. The maximum rate of VFA degradation was observed in the digester supplemented with Co which was around 990 mg l^{-1} d^{-1}. The digester supplemented with Se also showed a rapid rate of response at 770 mg l^{-1} d^{-1}. The control digester and the one supplemented with Mo showed slower rates of VFA breakdown at 330 and 590 mg l^{-1} d^{-1}, respectively. After the digesters reached steady state from day 40 to 150 the lowest VFA concentrations were in the Se and Co supplemented digesters (<1000 mg l^{-1}), whilst the digester receiving Mo and the control digester had VFA concentrations of around 5000 mg l^{-1}.

An increase in VFA concentration was observed in the control digester and the digester supplemented with Mo from day 150 onwards. This corresponded to an increase in the concentration of propionic acid which soon became the dominant VFA species, with the total VFA concentration reaching around 14000 mg l^{-1} when the project was completed. It is interesting to note that the profiles of VFA species in the digester supplemented with Se and the one with Co were different, although the total VFA concentration was similar in these two digesters. The second dominant VFA species in the digester dosed with Se was iso-butyric acid which followed the same pattern as the pair of digesters supplemented with Se and Mo as described in section 5.1.1. In the digester supplemented with Co the second dominant VFA species was propionic acid. This may suggest that selenium and cobalt have different roles in the metabolic pathways and they are unlikely to be mutually interchangeable.

Other performance indicators shown in Table 27 also confirmed that the digesters supplemented with Se or Co had much better digestion efficiency than the digester

supplemented with Mo and the control digester. Although molybdenum is reported as being an essential trace element for anaerobic digestion, supplementation of it alone did not improve the food waste digester operation even at a low organic loading rate. In the set of digesters with multiple trace element additions the combined supplementation of selenium and molybdenum showed a better performance than in the digester that was supplemented with selenium only. This can be seen by comparing the VFA profile of digesters with Se and Mo addition (Figure 28) with the Se only supplementation (Figure 40). The digesters supplemented with Se and Mo could operate at an organic loading of 4 kg VS m^{-3} d^{-1} with a VFA concentration less than 200 mg l^{-1}, while the digester supplemented with Se alone only ran at an OLR of 2 kg VS m^{-3} d^{-1} with the VFA concentration fluctuating between 300 to 1600 mg l^{-1}. This result should be regarded with caution, however, since these two sets of digesters had slightly different histories, and further testing is needed to clarify whether molybdenum can act in a synergistic way with other trace elements even though supplementation with molybdenum alone is not sufficient to prevent a rise in VFA concentration.

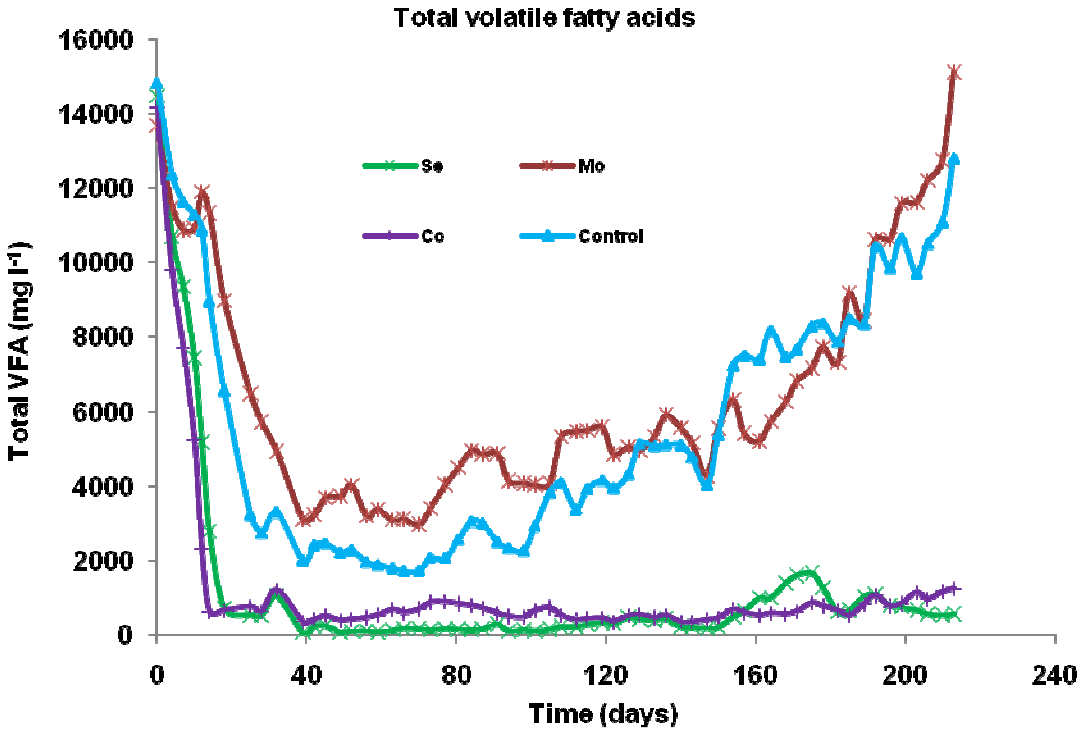


Figure 40 Total VFA concentration in the single trace element supplemented and control digester.

Table 27 Digester performance indicators for the digesters supplemented with a single trace element and the control digester

Digester	Se	Mo	Co	Control
pH	8.1 ± 0.0	7.9 ± 0.1	8.1 ± 0.0	8.0 ± 0.0
Partial alkalinity (mg $CaCO_3$ l^{-1})	17800 ± 600	14600 ± 1500	18200 ± 500	15000 ± 900
Intermediate alkalinity (mg $CaCO_3$ l^{-1})	8400 ± 400	10000 ± 900	8700 ± 300	10000 ± 400
Total alkalinity (mg $CaCO_3$ l^{-1})	26300 ± 500	24600 ± 600	26900 ± 300	25100 ± 600
Intermediate alkalinity: Partial alkalinity	0.47 ± 0.03	0.70 ± 0.14	0.48 ± 0.03	0.67 ± 0.07
Total ammonia nitrogen (mg NH_3-N l^{-1})	5300 ± 200	5400 ± 200	5400 ± 100	5500 ± 100
Methane percentage (%)	59.0 ± 0.4	55.2 ± 1.8	57.9 ± 0.6	56.5 ± 1.7
Specific biogas production (N m^3 kg^{-1} VS)	0.790±0.035	0.689±0.018	0.758±0.020	0.708±0.024
Volumetric biogas production (N m^3 m^{-3} d^{-1})	1.58 ± 0.07	1.38 ± 0.04	1.52 ± 0.04	1.42 ± 0.05

Table 28 Trace element concentration in digesters supplemented with a single trace element and the control digester on day 196 (9th August 2010)

Digester	Se	Mo	Co	Control
Aluminium (Al, mg l^{-1})	34.9	35.1	34.5	35.2
Boron (B, mg l^{-1})	2.48	2.38	2.65	2.11
Cobalt (Co, mg l^{-1})	0.033	0.032	0.692	0.047
Copper (Cu, mg l^{-1})	2.00	2.18	2.07	2.02
Iron (Fe, mg l^{-1})	39.9	38.0	46.7	42.6
Manganese (Mn, mg l^{-1})	16.4	16.0	15.6	16.1
Molybdenum (Mo, mg l^{-1})	0.199	0.424	0.307	0.274
Nickel (Ni, mg l^{-1})	0.829	1.03	1.36	1.79
Zinc (Zn, mg l^{-1})	5.67	6.66	5.51	5.66
Selenium (Se, mg l^{-1})	0.352	0.105	0.087	0.090

5.2.2 Recovery of failed control digester from the semi-continuous trial using Se supplementation

This experiment used the pair of digesters that had been run at an OLR of 3 kg VS m^{-3} d^{-1} and reached a VFA concentration of 30,000 mg l^{-1}, as described in section 5.1.1. Before the Se supplementation (which took place on 12th April 2010) the digesters were run at a reduced OLR of 0.6 kg VS m^{-3} d^{-1}, to confirm that the digesters would not be further stressed by the reduced loading alone. One of the digesters received 0.2 mg l^{-1} of Se; and the other continued running without any trace element addition as a control.

The organic loading rate to both digesters was maintained at 0.6 kg VS m^{-3} d^{-1} until day 105, and then the loading was increased to 0.9 kg VS m^{-3} d^{-1} until the project completed. Food waste was added each day to maintain the desired loading rate and digestate was removed once per week to maintain a constant volume of 4.0 litres. There was no recirculation of liquor or fibre. Se additions were made weekly, with the amount added was equal to that calculated as removed in the digestate wasted from each digester each week; this calculation did not take into account any additional Se input arising from the food waste itself. Biogas production was measured daily and biogas composition and volatile fatty acids determined twice weekly. Other digestate performance indicators such as pH, total ammonia nitrogen (TAN) and alkalinity were analysed once per week. The experimental results are shown graphically from Figure 41 to 45 with digester recovery evaluated mainly by reference to pH, VFA, methane percentage and biogas production. Day 0 is the first day when Se was supplemented and day 140 was the 30th August 2010, when the latest samples were taken and analysed.

Unlike to the prompt response to the trace element supplementation in the trials started at lower VFA concentrations as shown in section 5.1.1 and section 5.2.1, the effect of Se only became clear 10 days after its addition. From that time, as can be seen in Figure 41, the acetic acid in the digester with Se addition degraded gradually with a concurrent slight increase in propionic acid. After the concentration of acetic acid dropped to less than 1000 mg l^{-1}, propionic acid started to be consumed and its concentration fell below 2000 mg l^{-1} at day 105. This is consistent with previous observations on the sequence of VFA degradation, where propionic acid and other VFAs with a carbon number more than 2 are only consumed after acetic acid is degraded. It is worth mentioning that the dominant VFA species was iso-butyric acid (around 2500 mg l^{-1}) when the project was completed: this was the same as in the digester supplemented with Se as described in section 5.2.1.

In response to the acetic acid and propionic acid degradation in the digester with Se supplementation, the pH (Figure 42) and the methane content in the biogas (Figure 43) both increased from day 14 to 49 and from day 70 to 98. The highest calculated specific biogas production in this digester also reached around 1.3 STP m^3 kg^{-1} VS at day 90 when the propionic acid degradation achieved its maximum rate (Figure 44): this was higher than the 0.79 STP m^3 kg^{-1} VS specific biogas production seen at steady state as shown in section 5.1.1 of this report and again reflected the consumption of the accumulated VFA in the digester. The specific biogas production in the control digester was only 0.60 STP m^3 kg^{-1} VS, however, indicating incomplete stabilisation. There was no clear difference in total ammonia nitrogen concentration between the digester with Se supplementation and the control digester (Figure 45); at 6300 mg l^{-1} this was also higher than that in the trials described in section 4.1.1 and section 4.2.1 of this report. The reason for this was that a high total VFA concentration trapped ammonia in the digesters at the beginning of the experiment, which could not be washed out from the digester supplemented with Se even after the VFA dropped to less than 4000 mg l^{-1} due to the very low loading rate.

The trace element concentrations in these two digesters are shown in Table 29, and were comparable to the concentrations in other digesters as described in section 5.1.1 and 5.2.1. Selenium was the only element which showed a clear difference between digesters with supplementation and the control digester, and is likely to be the reason for the rapid VFA degradation in the digester with Se supplementation. The low concentrations of cobalt and molybdenum in this digester may explain the persistent iso-butyric acid level even though the organic loading rate was less than 1 kg VS m^{-3} d^{-1}.

Table 29 Trace element concentrations in the digester supplemented with Se and the control digester on day 119 (9 August 2010). Unit: mg l^{-1}

	Al	B	Co	Cu	Fe	Mn	Mo	Ni	Zn	Se
Se	33.5	2.06	0.033	2.02	41.2	15.5	0.200	0.855	5.39	0.064
Control	53.1	2.29	0.033	1.89	40.5	13.5	0.184	1.11	4.99	0.298

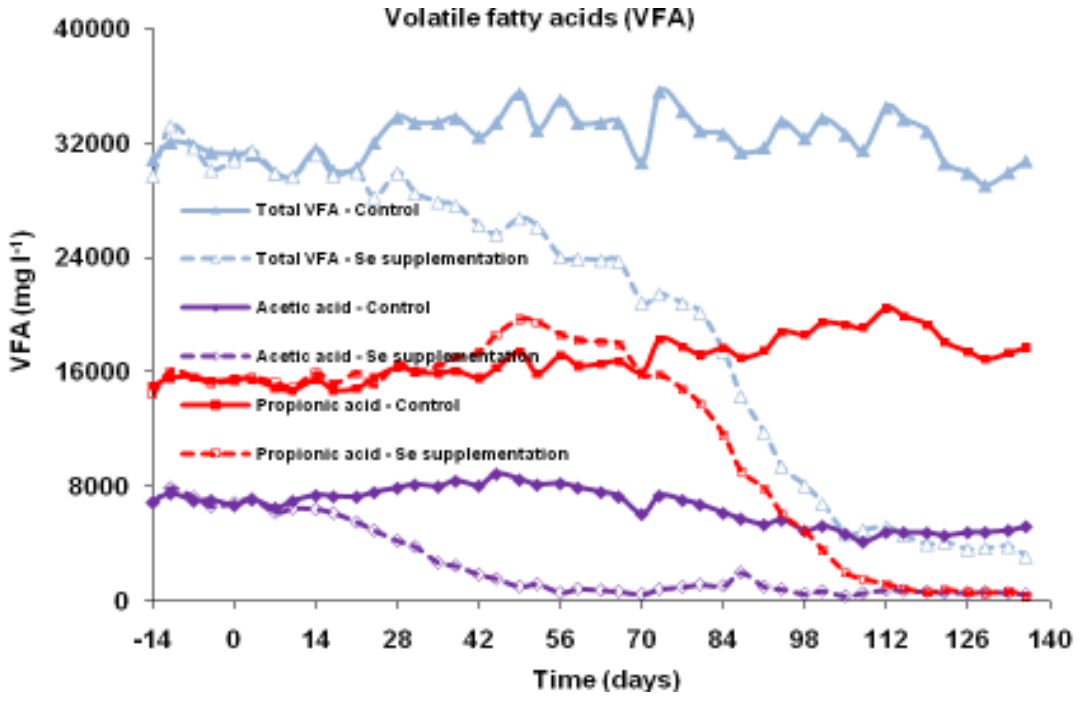


Figure 41 VFA concentration profile in digester supplemented with Se and its control.

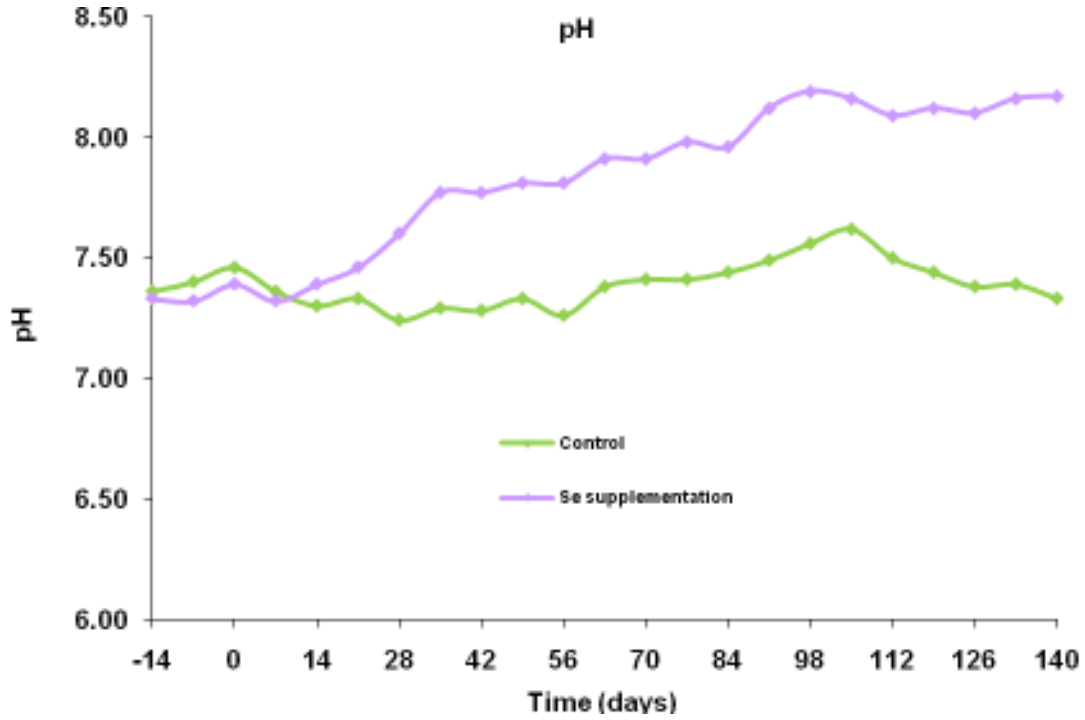


Figure 42 pH profile in digester supplemented with Se and its control.

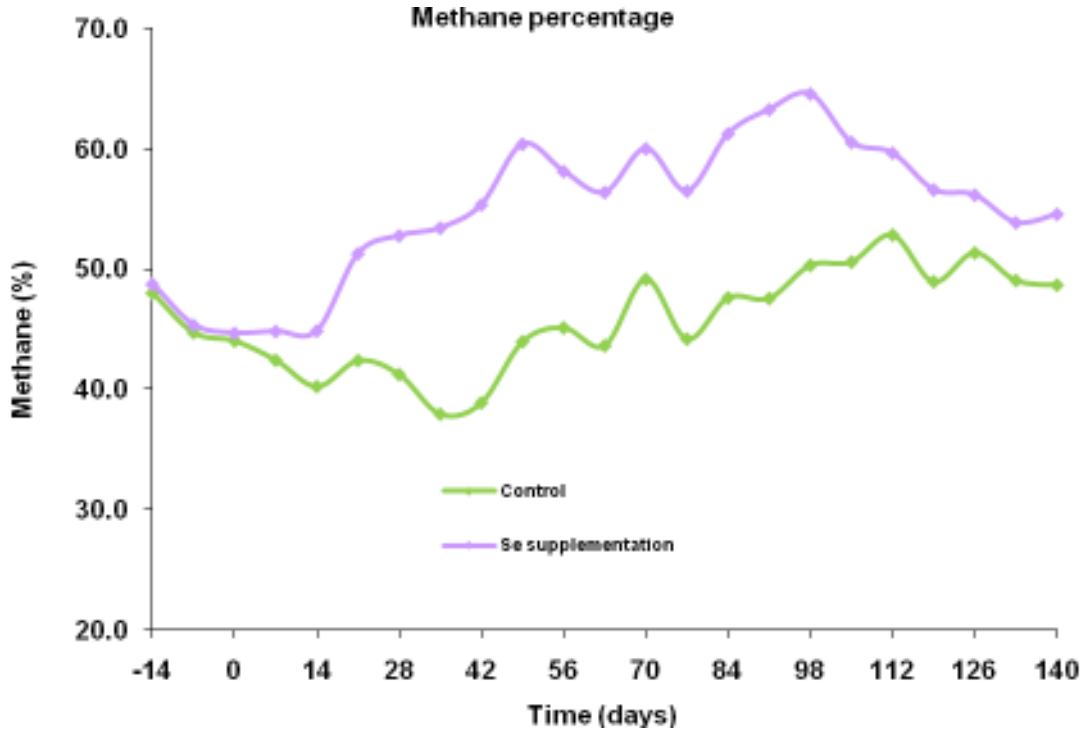


Figure 43 Weekly average methane content in biogas in the digester supplemented with Se and its control.

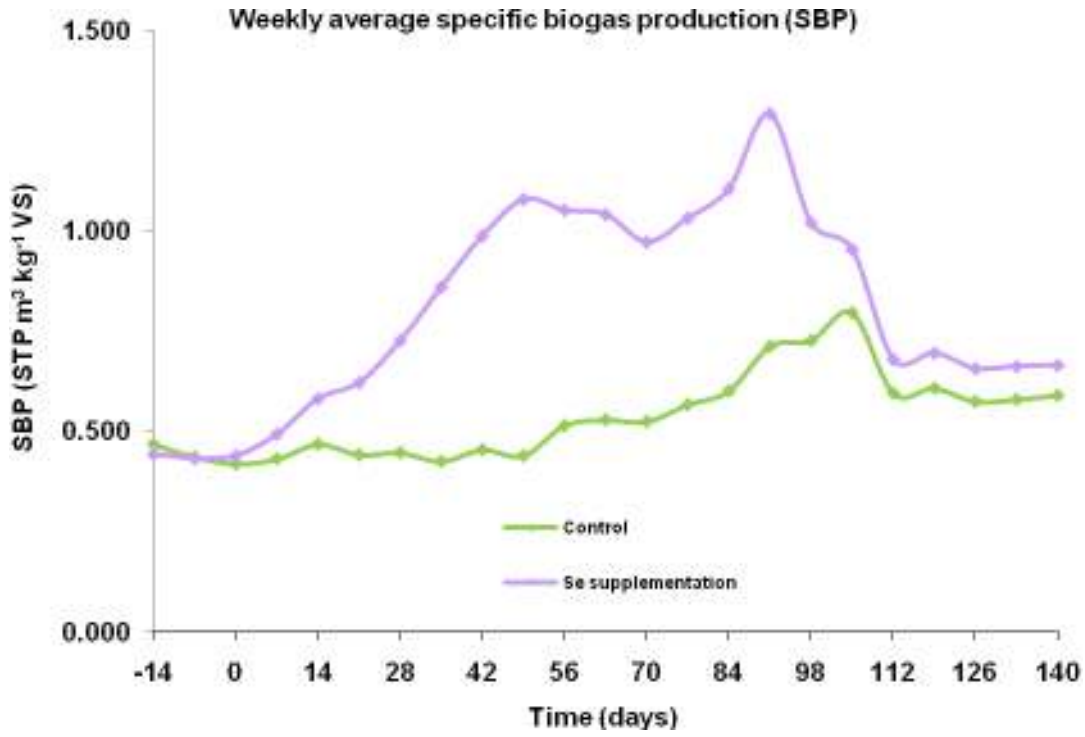


Figure 44 Weekly average specific biogas production in the digester supplemented with Se and its control.

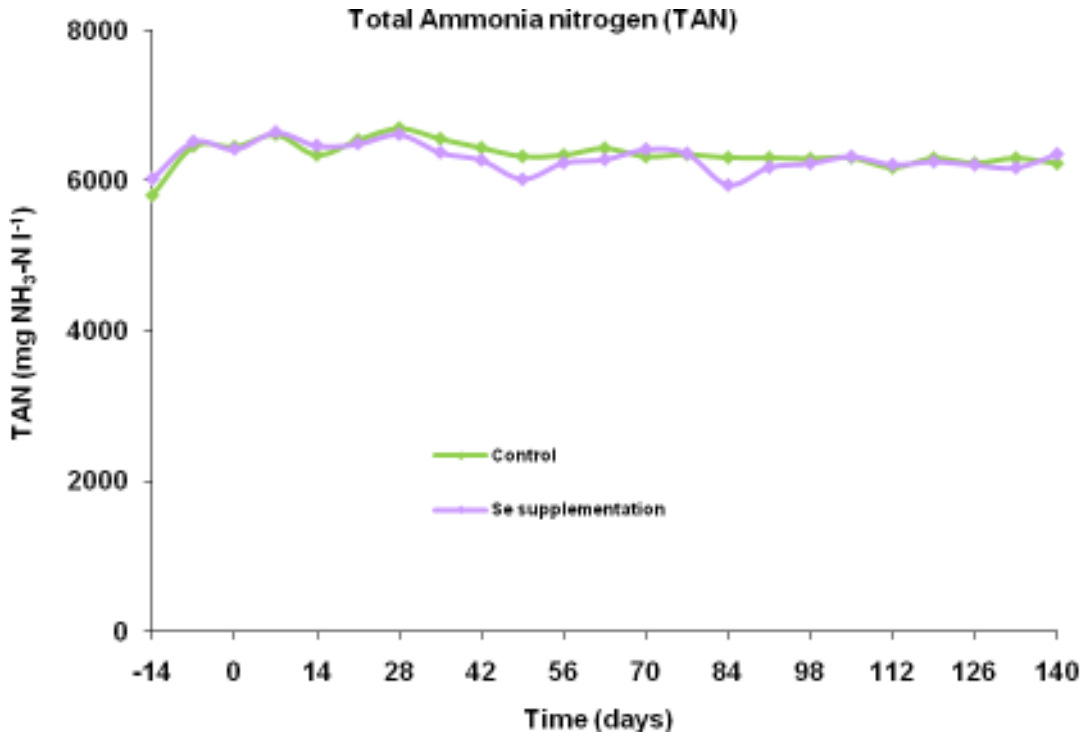


Figure 45 Total ammonia nitrogen in the digester supplemented with Se and its control.

6 Conclusions on trace element supplementation

From the results of experiments using trace element supplements it was concluded that among the 11 elements tested, selenium, cobalt and molybdenum are the key elements essential for the long-term stability of food waste digestion, which are unlikely to be present

in sufficient quantities in food waste.. The minimum concentrations of total selenium, cobalt and molybdenum in the food waste digesters should be around 0.16, 0.22, and 0.30 mg l^{-1} respectively at a moderate organic loading rate. As selenium is also known to be toxic to a wide range of organisms, batch experiments were carried out to investigate the concentration effect of Se supplementation on VFA degradation. The results indicated at the total selenium concentration less than 0.45 mg l^{-1} should be optimal for the VFA degradation, and there was evidence of high toxicity when its concentration was greater than 1.5 mg l^{-1}. No clear effect could be seen in Al, B, Cu, Fe, Mn, Ni, and Zn addition, mainly because food waste has a relatively high total concentration of these elements compared with the level of supplementation.

In semi-continuous trials the results showed that if a proper trace element supplementation strategy was followed food waste could be digested stably at an organic loading rate (OLR) of 5 kg VS m^{-3} d^{-1} over an experimental period of around 100 days (2.5 retention times) without any VFA accumulation: a much higher loading than achieved in previous laboratory and full-scale trials. The VFA concentration in the pair of digesters supplemented with Se, Mo, Co and W and in the pair of digesters with full trace element supplementation remained below 200 mg l^{-1} up until the time the project was completed. In these digesters the volumetric biogas production reached 3.8 STP m^3 m^{-3} d^{-1} and the specific biogas production was still stable at 0.76 STP m^3 kg^{-1} VS at the OLR of 5 kg VS m^{-3} d^{-1}.

The results also indicated that essential element addition, to a large extent, can only facilitate an increase in VFA degradation rate rather than initiate the VFA consumption process after digesters have been severely stressed by the accumulation of VFA for a period of time. As such, a strategy for stable food waste digestion should focus on the prevention of initial VFA accumulation in the digester by trace element supplementation, rather than the recovery of a severely VFA-laden digester.

7 Ammonia stripping - introduction

In the previous Defra-funded project WR0212 it was shown that the anaerobic digestion of food waste can suffer from process instability caused by the release of nitrogen in the form of ammonia during the breakdown of the protein fraction of the waste. This ammonia is toxic to methanogenic organisms, especially those responsible for the breakdown of acetic acid to methane and carbon dioxide; the acetoclastic methanogens. In this part of the research it was proposed to investigate the possibility of removing ammonia as a means to reduce this toxicity thus allowing the stable digestion of food waste. Gas stripping was chosen as the most suitable method of ammonia removal since biogas is available on site at anaerobic digestion plants, and this type of system can potentially be integrated into the AD process in a number of ways using existing technology and infrastructure.

Four possible process configurations were originally proposed: *in situ* ammonia removal, where the ammonia is stripped continuously from the digestate during digestion using a combined gas mixing and ammonia removal system; side-stream, where some digestate is removed from the digestion process, subjected to a stripping process and returned to the digester on a semi-continuous basis; post-hydrolysis, where ammonia removal is performed on food waste which has been subject to a short anaerobic hydrolysis process, with the reduced-ammonia food waste then going to normal anaerobic digestion; and post-digestion ammonia removal in conjunction with the post-pasteurisation stage performed at some AD

plants. The experimental work was designed to allow assessment of these four options as a basis for recommending the most appropriate ammonia removal system for practical use.

Nitrogen is present in food waste mainly in the form of proteins and upon their breakdown, through the process of anaerobic hydrolysis, ammonia is released. Ammonia is present in a digestate as both free ammonia (NH_3) and as the ammonium ion (NH_4^+). The distribution of ammonia into its two aqueous/liquid forms is governed by both pH and temperature, with increase of either leading to a higher proportion of free ammonia. Free ammonia is volatile and thus can be removed by gas stripping through conversion into gaseous ammonia. This system is summarised in Figure 46. It follows from this basic assessment that pH, temperature or gas flow rate could be used to control the amount of free ammonia present and its transfer into the gaseous form, and that an increase in any of these three quantities leads, in theory, to an increased rate of ammonia removal.

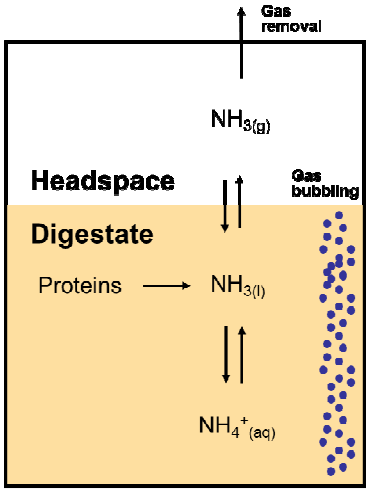


Figure 46 Schematic of the ammonia system in anaerobic digestion and gas stripping

The objective of the first part of the research was to look at the ammonia removal from food waste digestate using gas stripping; this involved a number of batch experiments to investigate the kinetics of the removal rate with regard to the important parameters of temperature, pH and gas flow rate. This work was performed on two different digestate samples, both acquired from commercial food waste digesters. The digestates contained large concentrations of both ammonia and volatile fatty acid, owing to the operating conditions and feedstock compositions of the facilities from which they were taken. The two samples were compared for their ammonia removal behaviour. This proved to be more complex than originally envisaged and appeared to be sensitive to digestate status in terms of chemical composition, alkalinity and volatile fatty acid content: additional time and resources were therefore dedicated to this part of the work in order to ensure a fuller understanding of these factors. Some changes were also made to the originally proposed experimental programme to allow modelling and prediction under a wider range of conditions that could be used in the design of an effective stripping device.

The experimental work also included semi-continuous digestion studies looking at some of the specific issues relating to the integration of ammonia stripping with anaerobic digestion. These comprised a trial of the side-stream stripping of ammonia during the mesophilic anaerobic digestion of food waste, and a study to quantify the ammonia release kinetics during a short hydrolysis process. The results from these experiments showed unexpected

trends, detailed in this report, which led to a shift in focus of the research onto the other two operating scenarios; *in situ* and post-digestion ammonia stripping. To further the research, a model was developed using data from the batch stripping experiments on the kinetics of ammonia removal to allow simulation of the ammonia concentration in a combined ammonia stripping/anaerobic digestion process. The purpose of this model was to allow informed recommendations to be made regarding the appropriate configuration and use of an ammonia removal system.

8 Batch ammonia stripping from food waste digestate

8.1 Aims and objectives

The aim of this part of the research was to gain a deeper understanding of the kinetics of ammonia removal from digestate using a gas stripping process. In initial experiments nitrogen was used as the stripping gas, but subsequently a standard solution of biogas (65% methane, 35% carbon dioxide) was used. The justification for the use of biogas was its availability on AD sites: furthermore it was found in the early stages of the research that stripping with nitrogen disturbs the pH by stripping carbonates from the digestate.

The specific parameters which were identified as potentially having a strong impact on the ammonia stripping characteristics were pH (and its modification by adding alkali), temperature of the digestate, and flow rate of gas. The justification behind the investigation of these three parameters comes from basic pH equilibrium and reaction kinetic theories: pH modifies the ammonia removal behaviour on a chemical basis, by shifting the equilibrium between free ammonia, the volatile form, and ammonium salts which are not volatile. Temperature alters the same equilibrium slightly, with an increase causing a greater fraction of free ammonia to be present in the digestate, but also has a physical effect in that it increases the saturated vapour pressure of the free ammonia, thus increasing the driving force which allows volatilisation into the gaseous form. Flow rate of gas has no chemical effect on the balance of free/ionic ammonia but instead changes the available surface interface between the liquid and gaseous phases within the stripping system, such that an increase in flow rate leads to an increase in reaction rate (in this case volatilisation and removal of ammonia).

The primary objective of this section of the project was to investigate the effect of these three parameters, which theoretically all have a strong influence on the removal of ammonia, in controlled laboratory experiments using real food waste digestate. Preliminary experiments allowed confirmation of the theoretical framework and initial definition of the parameter ranges which are of interest to the design of an ammonia stripping system, as well as familiarisation with and improvement of the purpose-built experimental equipment and the methods required satisfactorily to characterise the ammonia removal kinetics. The main set of experiments then focused on the testing of two different digestates, both collected from commercial AD plants using food waste as their primary feedstock. An additional objective was to compare the ammonia removal characteristics of these two samples.

As the experimental work progressed, other points of interest presented themselves, and investigations were made into: the effect of VFA on the stripping process, ammonia recovery and partitioning in the stripping system including ammonium salt crystal formation, foaming during the removal process and the alkali requirements for pH change. Each of these points is discussed in the following sections.

8.2 Experimental setup

The experimental setup was similar in all batch ammonia stripping experiments, although some minor alterations were made during the project to allow better data collection or investigation of specific areas of interest. The basic stripping experimental system is presented in Figure 47 and Figure 48. A heated ammonia stripping column of total volume three litres was connected to a sealed gas loop. Standard gas was pumped through the food waste digestate at flow rates of 0.125-0.75 litres of gas per litre of digestate per minute (l l^{-1} min^{-1}), and subsequently flowed through a series of traps. Initially two traps were used; one containing deionised water and a second containing 50-70% sulphuric acid. It was found that a weaker acid was sufficient and so in later experiments 0.25N sulphuric acid was used; a third trap was also added at the beginning of the sequence which was empty but collected any drops of condensed liquid. The two stripping systems, denoted reactors 1 & 2 (R1 & R2), were identical except for the type of peristaltic pumps used. R1 used a Watson Marlow 700 series pump which delivered bubbles in short bursts whereas R2 used a Watson Marlow 300 pump with multiple parallel heads, providing a more even flow rate. Both pumps were calibrated for their bulk flow characteristics, thus they provided equivalent volumes of gas per unit time over the periods of the experiments performed.

The ammonia concentrations and pH of digestates 1 and 2 were ~8000 and ~6000 mg l^{-1} and ~8.5-9.3 and 8.1-8.2 respectively. At the beginning of each batch experiment two litres of digestate were placed in the stripping column which was then sealed. The pump was used to fill the headspace and other parts of the gas loop with standard biogas. The pump was then set to the desired flow rate and the apparatus was left undisturbed, except to take periodic samples, until the end of the experiment. Sampling and analysis were performed in order to assess the kinetics of the ammonia removal and any pH change during the run. At the end of each experiment the ammonia concentration in the digestate, water, acid and condensate traps was measured to determine the distribution of ammonia within the system. In the later experimental runs, 10M NaOH was used to modify the pH of the food waste digestate.

Experimental runs are characterised by the reactor (R1 or R2), the temperature, the specific flow rate and the initial pH (where pH modification was performed). For example 1.1_55_0.125_N refers to run# 1, reactor 1 at 55˚C, 0.125 l l^{-1} min^{-1} and with no (N) pH addition. A list of experiments performed, including the run identifiers can be found in the results section Table 33.

Note: while it is expected that experimental conditions such as temperature and pH can be translated to full-scale plant, this is unlikely to be so for gas flow which is affected both by scale factors and specific design features of diffusers etc. Gas flow rates are therefore quoted for only for the purposes of comparison within the experimental work, and appropriate values will need to be determined by larger-scale experimentation. The gas flow rates used in experimental work ranged from 0.19 to 11.5 m^3 m^{-2} $hour^{-1}$ delivered through a fine bubble diffuser.

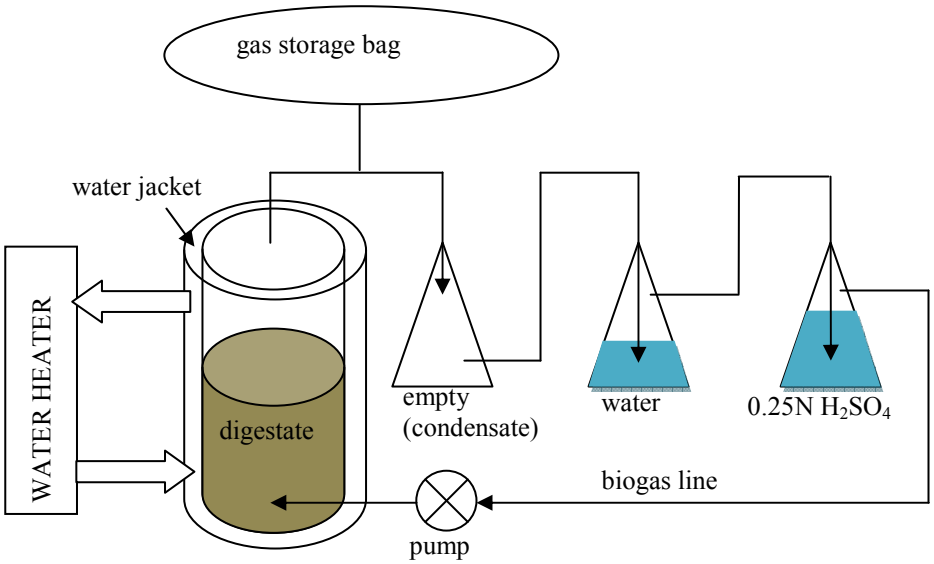


Figure 47 Schematic of ammonia stripping equipment

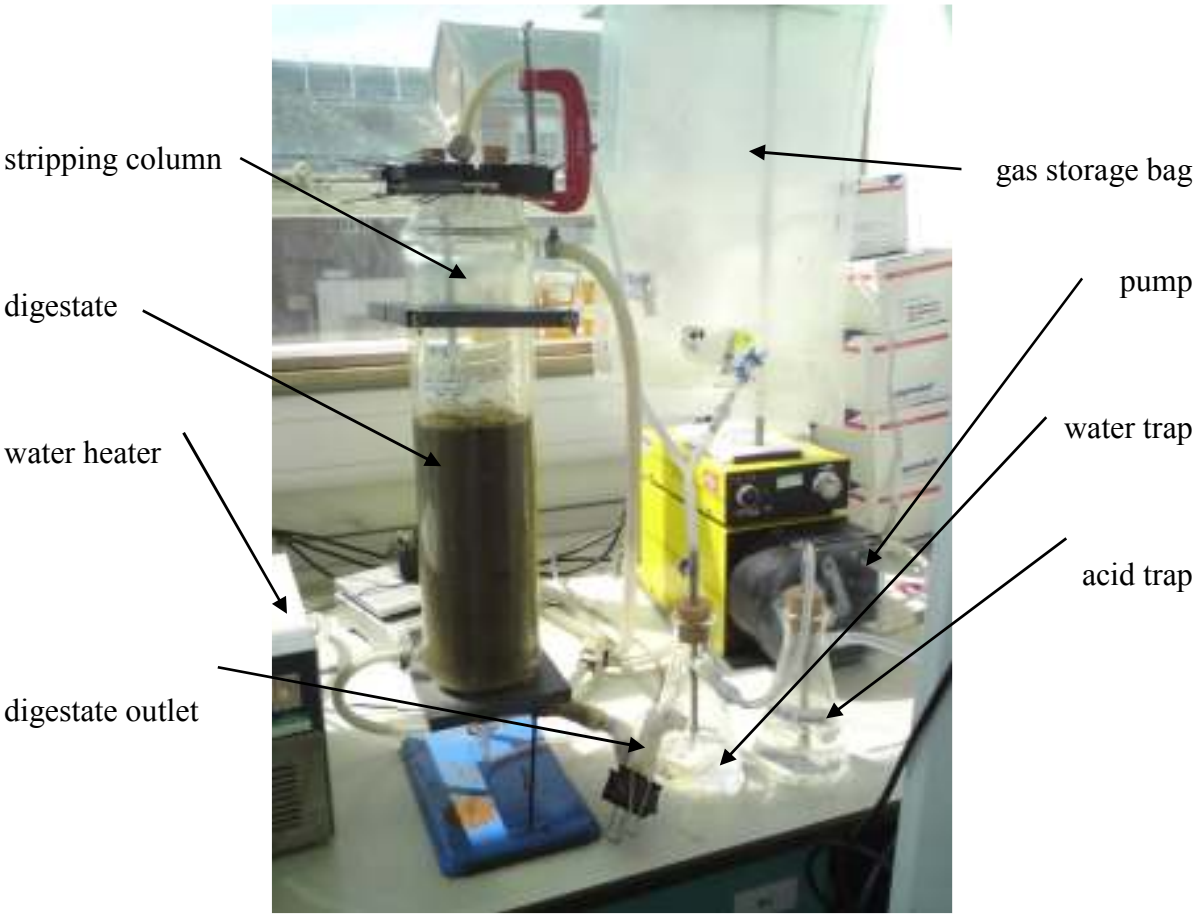


Figure 48 Ammonia stripping equipment (no condensate trap)

8.3 Results for batch stripping of ammonia from digestate

8.3.1 Preliminary experiments stripping with nitrogen and biogas

In these preliminary experiments the effect of nitrogen flow and temperature on ammonia removal and the effect of biogas flow and temperature on ammonia removal in a closed circuit were investigated using digestate 1. With nitrogen as the stripping gas the process was performed at temperatures of 35, 60 and 70 ºC at a gas flow rate of 0.375 l $l^{-1}min^{-1,}$ and the gas was vented to a fume cupboard. At 70 ºC an additional flow rate of 0.25 $l l^{-1}min^{-1}$ was investigated. For biogas, a closed gas loop was used. Digestate was sampled every few hours, or every day depending on the length of the experiment. The stripping process was performed at temperatures of 35, 60 and 70ºC at gas flow rates of 0.125, 0.25 and 0.375 $l l^{-1}$ min^{-1}.

8.3.1.1 Nitrogen Stripping

Figure 49 shows the main results from the nitrogen stripping experiments. The general trends were that higher temperatures and gas flow rates led to a greater removal rate of ammonia from the digestate; both of these effects were expected.

In all experiments there was an increase in pH from ~8.3 to ~9.3. It is thought that this is caused by carbonate removal. Under anaerobic conditions the digestates are in equilibrium with biogas with a carbon dioxide composition of around 40%; when this is replaced with nitrogen, as in these experiments, dissolved carbon dioxide and carbonates in the digestate are released as carbon dioxide gas as a result of the change in concentration gradient. It is expected that the removal of ammonia from digestate samples with high VFA concentrations will eventually cause a reduction in pH since the ammonium/ammonia ionic equilibrium provides buffering to a pH of around 9 (pKa = 9.23), and without this the effect of the VFA buffering will be to reduce the pH (e.g. acetic acid pKa = 4.75). In these experiments, however, the effect of dissolved carbonate/carbon dioxide is masking this effect and for this reason the following experiments were performed using biogas stripping.

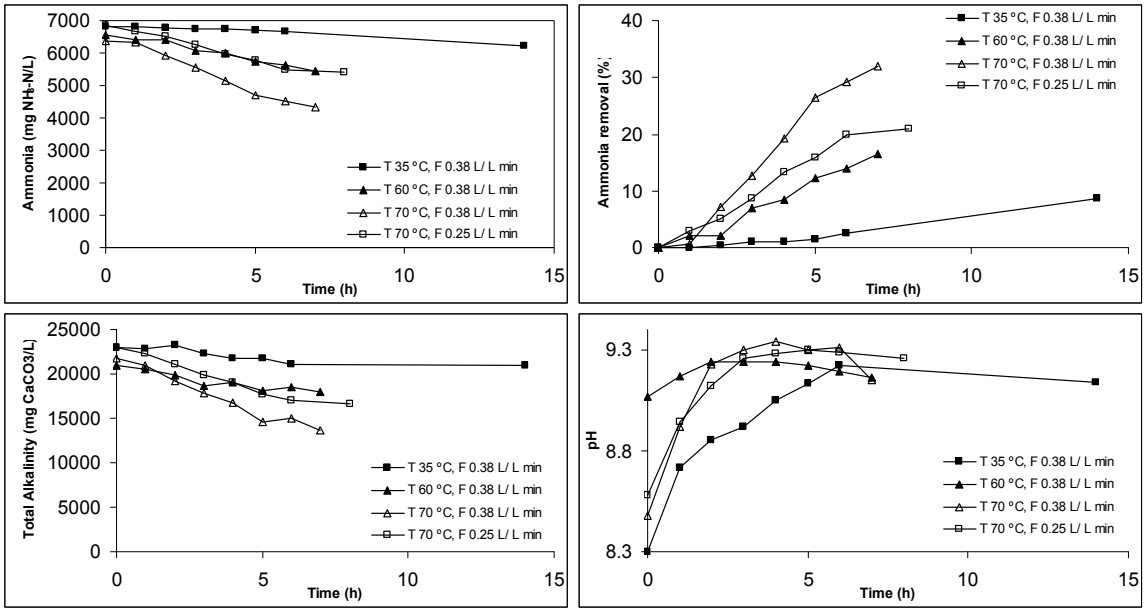


Figure 49 Ammonia stripping using Nitrogen

8.3.1.2 Biogas Stripping

The results from the initial ammonia stripping experiments at temperatures of 35, 55 and 70 ºC are shown in Figures 50, 51 and 52 respectively and summarised in Table 30. In all cases ammonia was removed from the digestate and captured in the acid traps. The biogas experiments were longer than the nitrogen stripping experiments as the experiments were continued until no further ammonia removal occurred. When stripping with biogas, a similar initial increase in pH was observed, probably caused by equilibrating carbonates between the biogas and digestate. In most cases the pH later decreased, showing the effect of the removal of ammonia.

At 35 ºC the ammonia removal rate was low relative to that in the other experiments. The rate of removal at both 0.125 and 0.25 $l l^{-1} min^{-1}$ was similar and the concentration of ammonia at the end of the experiments was 6370 and 5950 mg l^{-1} respectively. However at the increased flow rate the ammonia removal rate was approximately 4.5 times greater. The final ammonia concentration at the flow rate of 0.375 $l l^{-1} min^{-1}$ was 5670 mg l^{-1}. The initial increase, and later decrease, in pH were both gradual and the pH remained above 8 throughout all of the experiments. In all cases the partial alkalinity decreased during the experiments owing to the removal of both ammonia and carbonates which contribute to this measurement.

The results from ammonia removal at 55 ºC and 0.125 $l l^{-1} min^{-1}$, shown in Figure 51, did not follow the trends shown in the other experimental runs; the ammonia decreases initially and then increases to a concentration which is much higher than the initial value.

The two experiments at higher flow rates show similar trends to those at 35 ºC. Ammonia is removed faster at greater biogas flow rates but reaches similar final concentrations (5740 and 6160 mg l^{-1}). The pH trend is similar, with an initial increase followed by a subsequent fall; but the final pH is lower, decreasing to around 7.5 for both experiments. The fall in pH to around 7.5-8 appears to prevent further ammonia removal.

Operation of the stripping process at 70 ºC resulted in the greatest ammonia removal rates, as shown in Figure 52. The results are different from those in previous runs as the higher flow rate (0.375 $l l^{-1} min^{-1}$), although giving the fastest initial ammonia removal, removed much less ammonia in total over the experimental period than the lower flow rate (0.25 $l l^{-1} min^{-1}$).

At 70 ºC and at a flow rate of 0.375 $l l^{-1} min^{-1}$ the pH did not show the trend of an initial increase followed by a gradual decrease. pH decreased from the start of the experiment, possibly because of the high ammonia removal rate. The pH fell to around 6.5 and this was enough to prevent further ammonia removal since at this pH the ammonium ion prevails in solution. Another effect that occurs at high temperature is evaporation of the liquid in the digestate. At the highest temperature and flow rate approximately 25% of digestate (0.5 litres) was lost as evaporated moisture over the experimental period. This means that although ammonia is removed, the concentration in the digestate can remain the same or even increase as seen in Figure 51, defeating the purpose of removing ammonia in order to reduce 'in reactor' concentration. Furthermore the reduction in pH seen in this experimental run could cause problems in a semi-continuous anaerobic digester since this could disturb the methanogens and cause cessation of biogas production.

The conditions at 70 ºC and 0.25 $l l^{-1} min^{-1}$ show a greater removal of ammonia over the experimental period and a greater overall removal rate compared to the higher biogas flow

rate. This may be because the removal of ammonia is initially slower and therefore does not lead to a rapid decrease in pH which then prevents continued removal. The initial VFA concentration in this experimental run was ~9000 mg l^{-1}, however, compared with ~17,000 mg l^{-1} in the previous experiments. The lower VFA concentration may explain the stable pH despite removal of a large proportion of ammonia. This result is interesting since if the ammonia stripping process is used as a preventative measure to the build-up of VFA in a food waste digestate the VFA concentration would always be low and if the result holds for all flow/temperature combinations ammonia removal would therefore be more effective on a 'healthy' digestate.

Table 30 Summary of ammonia removal rates in initial ammonia stripping experiments using biogas

Temperature (ºC)	Flow rate (l_{biogas} $l^{-1}min^{-1}$	Ammonia removal (%)	Time (h)	Removal rate (% d^{-1})
35	0.125	15	196	1.84
35	0.25	15	194	1.86
35	0.375	27	78	8.31
55	0.125	-16	72	N/A
55	0.25	15	104	3.46
55	0.375	18	46	9.39
70	0.25	44	56	18.9
70	0.375	13	30	10.4

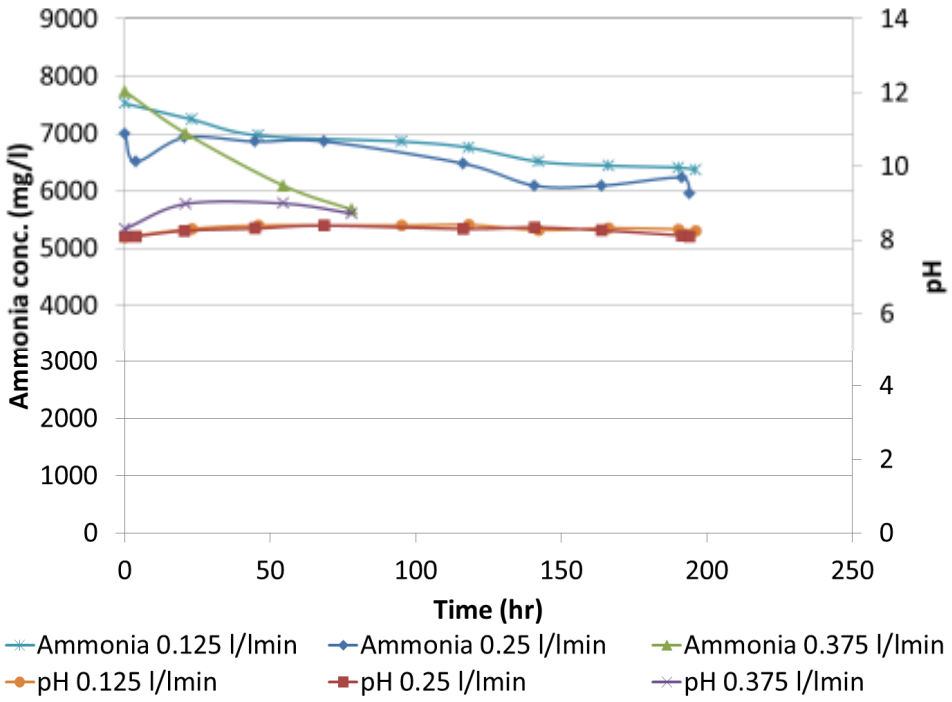


Figure 50 Initial ammonia stripping experiments using biogas at 35 ºC

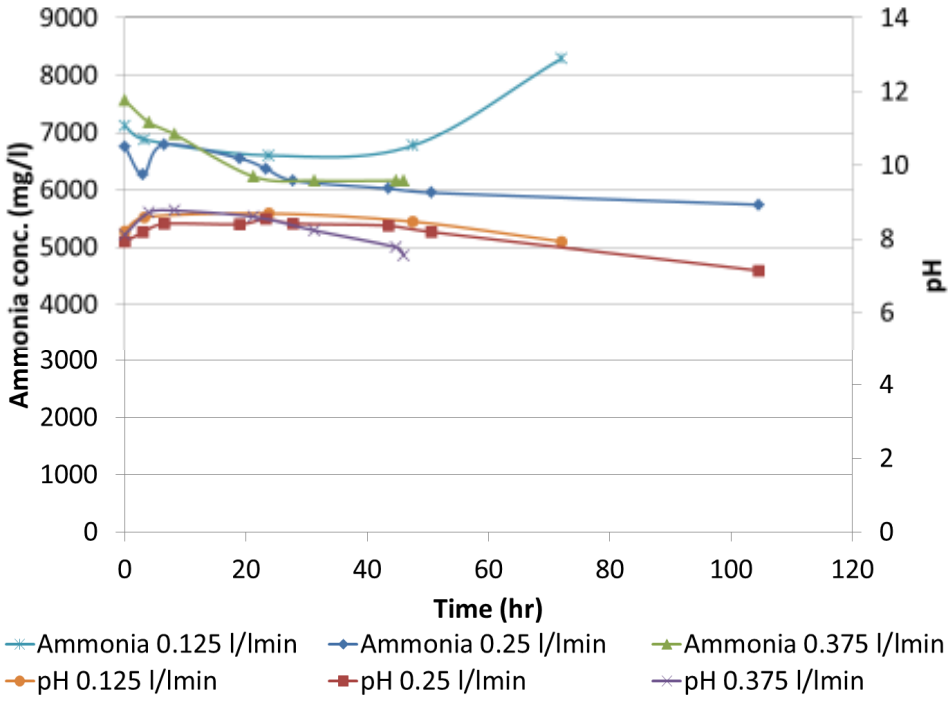


Figure 51 Initial ammonia stripping experiments using biogas at 55 ºC

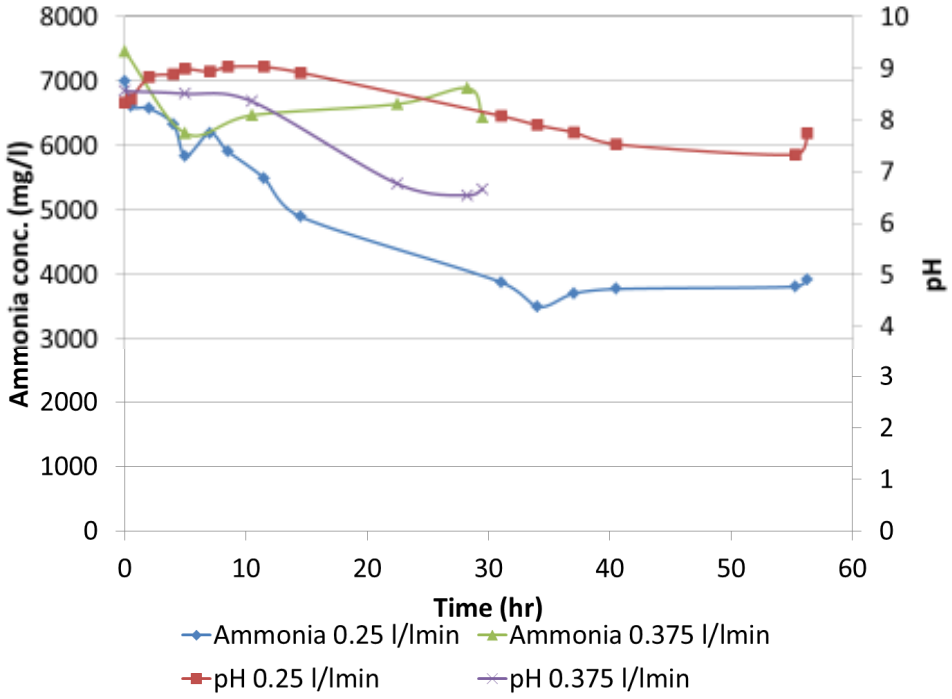


Figure 52 Initial ammonia stripping experiments using biogas at 70ºC

8.3.1.3 Outcomes of preliminary ammonia stripping experiments

Under conditions of high VFA concentration (~17,000 mg l^{-1}) and ammonia (~7000 mg l^{-1}) the range of temperatures and flow rates investigated led to a change in the ammonia removal rate of one order of magnitude between ~1.8-18 % day^{-1}. In general the predicted theoretical trends were followed, in that ammonia removal increased with both flow rate and temperature,

but there were some complicating factors. Too rapid ammonia removal resulted in a decrease in pH which led to a cessation of ammonia removal. Initial findings also suggested that VFA can have an influence on the removal process: if the VFA concentration is high, the decrease in pH caused by ammonia removal seemed to be more severe than at low VFA concentration. These findings are reported in de la Rubia *et al*. (2010). The results confirmed, however, that ammonia removal was possible using biogas stripping at least in some circumstances. Further experiments were therefore performed to provide a more detailed understanding of the factors affecting the effectiveness of the stripping process, and these are presented in the following two sections.

8.3.2 Ammonia stripping from digestate 1 using biogas

8.3.2.1 Introduction

In the previous section, preliminary experiments conducted as part of this project showed that the removal of ammonia from food waste digestate can be performed using biogas stripping. It was found that the removal rate was influenced positively by biogas flow rate and temperature, but that a number of other factors were significant. To obtain a further understanding of the relationship between these parameters this part of the work was extended from that envisaged in the original programme.

The batch experiments in this section were focussed on developing an ammonia removal process which could take place at the same time as the obligatory pasteurisation stage in an anaerobic digestion plant treating food waste, and therefore a temperature of 70 °C was used. In the previous work the time taken for ammonia removal was in the order of 50-100 hours which is much longer than that needed for pasteurisation (~1 hour) and therefore the processes were not yet obviously synergistic. In these experiments, the focus was on more rapid removal by a combination of increased flow rates of biogas and pH modification by alkali addition. To provide data for modelling, two further experiments were also performed at temperatures of 35 and 55 °C (runs 0 and 1).

In the experiments presented below, the ammonia was recovered by a combination of condensation, water and acid traps using 0.25N acid rather than stronger acid.

8.3.2.2 Results

A summary of all batch experiments is given in Table 33. For graphical presentation the ammonia removal kinetics have been separated into two groups; without alkali addition/pH modification (Figure 53), and with pH modification by alkali addition (Figure 54).

Ammonia stripping without alkali addition follows the previously observed trends that increases in flow rate and temperature both lead to an increase in the ammonia removal rate. However the range of flow rates used in these experiments was greater than previously used, up to 0.75 $l\,l^{-1}min^{-1}$, and it can be seen that increasing the gas flow rate above 0.375 $l\,l^{-1}min^{-1}$ has very little impact on the rate of removal; a saturation is reached where further increases in flow offer no process benefits. The timescales involved at 70 °C are between 30 and 80 hours for ammonia removal to cease.

In these experimental runs the pH decrease that was observed in the preliminary experiments was not encountered. Whereas previously the pH drop led to a cessation in ammonia removal

at concentrations of approx. 6000 mg l^{-1}, here the concentration in all cases decreased to below 1000 mg l^{-1}.

The repeatability and reproducibility of the experiments and equipment were both assessed; comparison of runs 2.1 and 3.1 for repeatability and runs 11.1 and 11.2 for reproducibility shows similar results. Additionally the effect of intermittent sampling was assessed by comparison of runs 12.1 and 12.2 where only R1 was sampled: the results for both reactors showed very similar ammonia concentrations thus confirming that the sampling process did not affect the experimental outcome strongly.

The repeatability between reactors 1 and 2 for runs 5.1 and 5.2 was less satisfactory; this was the first run where R2 was operated and the heating loop was connected in series with reactor 1 (i.e. heater → reactor 1 → reactor 2 → heater….) and therefore it is thought that reactor 2 had a lower working temperature during this run. After this the reactors were connected to the heater in parallel and their temperatures were checked to be the same at 70±0.1˚C. Further tests of reproducibility between the reactors gave better agreement.

Addition of alkali, to modify the initial pH, was shown to have a strong effect on the ammonia removal kinetics, as shown in Figure 54. The timescales for removal decreased from 30-80 hours to ~20 hours. This is again in agreement with the theoretical framework which was developed at the beginning of the project. Increasing the pH leads to a greater proportion of free ammonia and therefore a greater kinetic of removal. However with strong alkali dosage, experimental problems were encountered due to excessive foaming. Antifoaming agent (J-QUELL 19 mineral oil defoamer supplied by J1 Technologies Ltd, Trafford Park, Manchester) was successfully used to prevent this.

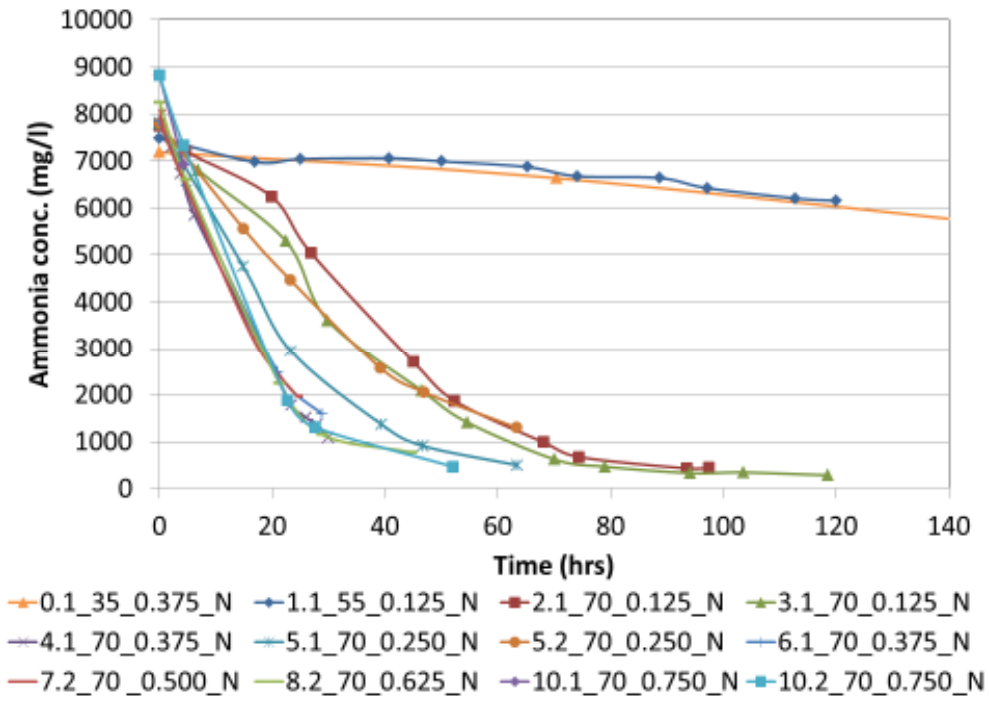


Figure 53 Ammonia stripping from digestate 1 with no pH modification

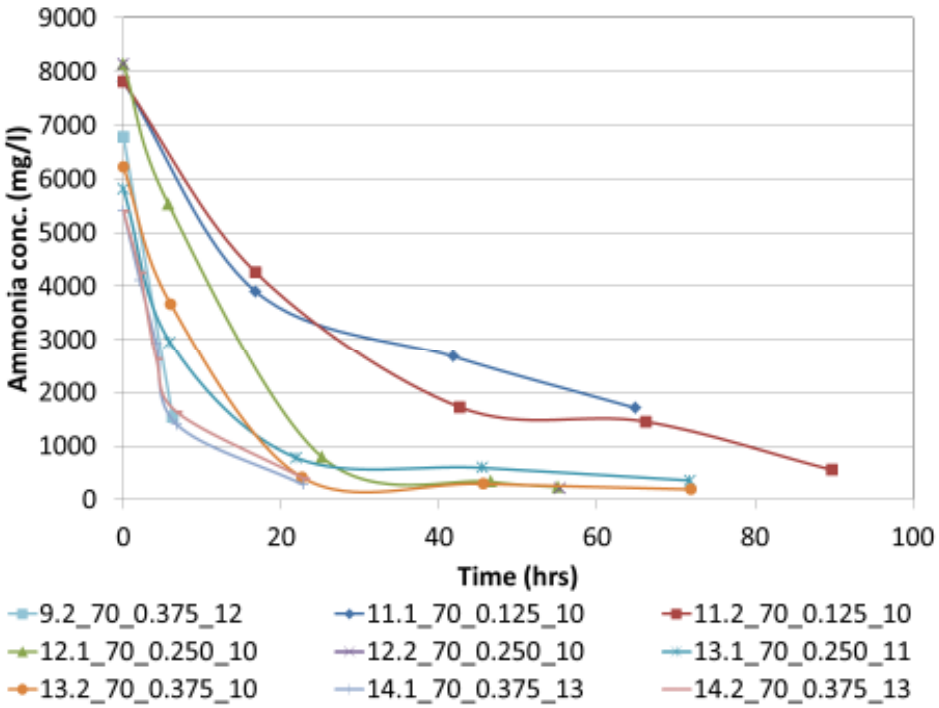


Figure 54 Ammonia stripping from digestate 1 with pH modification

8.3.3 Ammonia stripping from digestate 2 using biogas

The results of the ammonia stripping experiment on digestate 2 are presented according to the same structure as those for digestate 1. Figures 55 and 56 show the ammonia removal characteristics during experimental runs without and with pH modification respectively. In general all of the trends observed for digestate 1 were similar for digestate 2.

Inspection of Figure 55 shows that, as before, increasing the flow rate had the effect of increasing the ammonia removal rate. The change in ammonia concentration was from 6000 to ~1500 mg l^{-1} in all cases, corresponding to a removal of ~75% based on concentration, or 80-90% of the total mass of ammonia (see Table 33). The time taken for removal varied from 75-25 hours depending on flow rate and it can be seen that increasing the flow rate had a gradually decreasing positive effect on the removal rate in a similar way to digestate 1.

The timescale in Figure 56 is shorter than that in Figure 55 since the addition of alkali resulted in a sharp increase in ammonia removal rate. It can be seen that the pH has a larger effect on ammonia removal rate than the biogas flow rate, with pairs of runs at the same pH but with different flow rates showing almost identical ammonia removal kinetics.

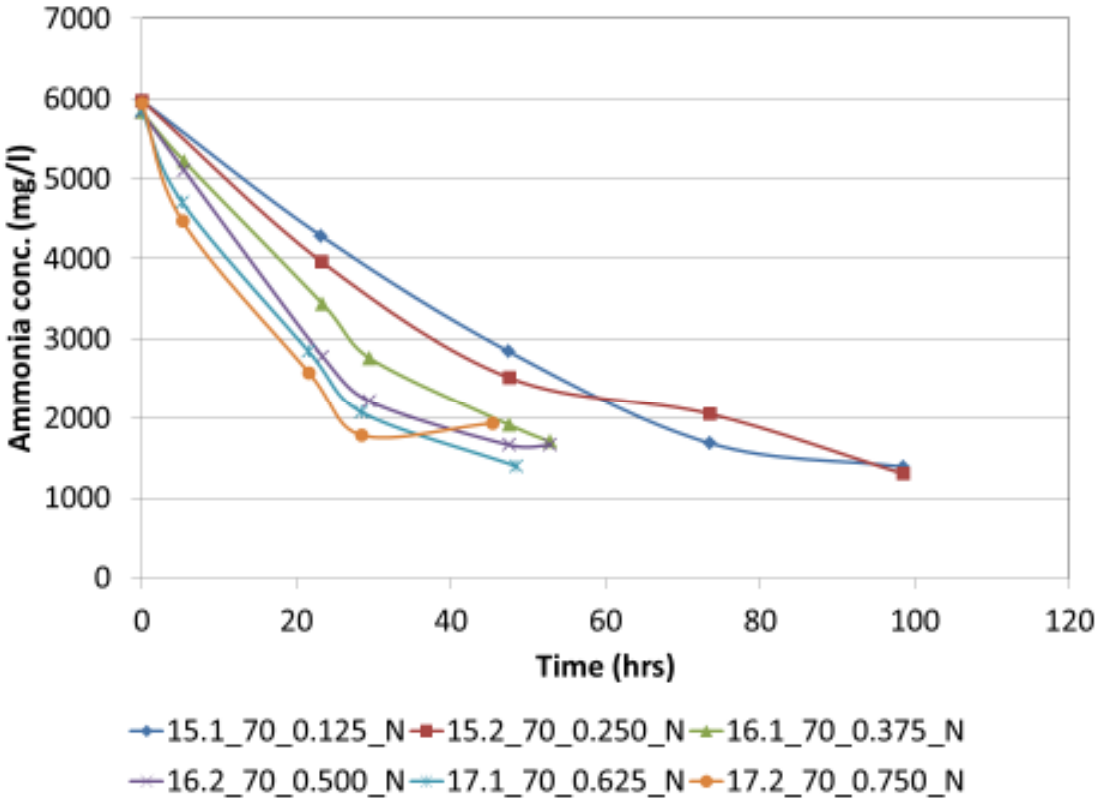


Figure 55 Ammonia stripping from digestate 2 with no pH modification

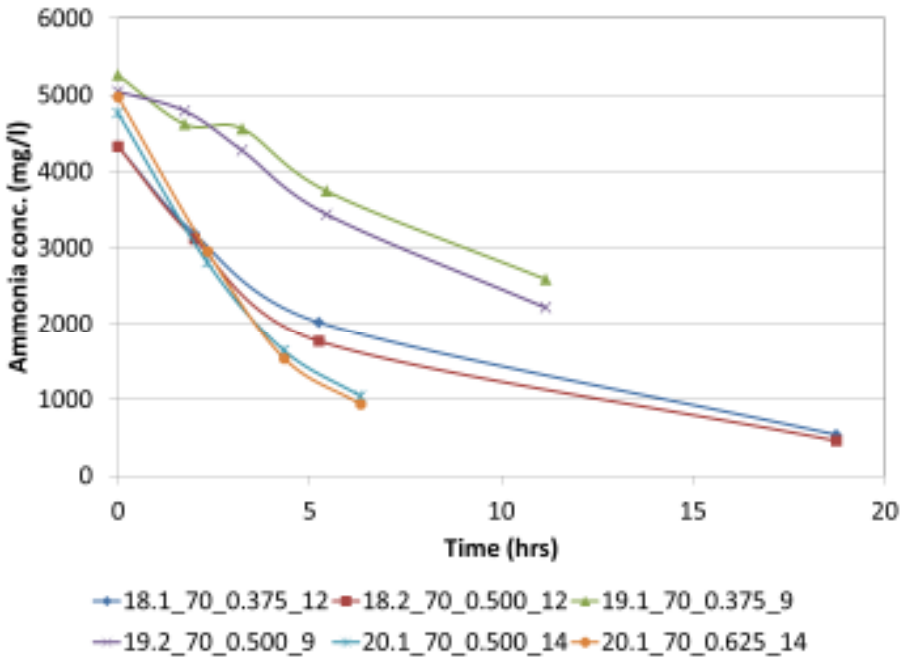


Figure 56 Ammonia removal from digestate 2 with pH modification

8.3.4 Comparison of ammonia stripping from two digestate samples

Table 33 shows a summary of the results from all of the ammonia removal experiments, including the flow, temperature and pH conditions, and the initial and final pH and ammonia concentrations allowing a comparison of all experimental runs. Also tabulated is the removal time constant and correlation coefficient (r^2) obtained by fitting an exponential decay curve to the ammonia removal data in the form;

$$C = C_0 e^{\frac{t}{\tau}} \qquad \textbf{Equation 1}$$

where C is ammonia concentration, C_0 is the initial ammonia concentration, t is time and τ is the removal time constant. The units of τ are hours and it gives the time (based on the fitted curve) for the ammonia concentration to reach 36.7% of its initial value. As can be seen in Table 33 the range of correlation coefficients for these curves is 0.73-1.00 but in most cases r^2 is above 0.95 indicating that an exponential decay function gave a satisfactory representation of the physical behaviour. The fit is not perfect, however, especially toward the end of the experiments since the ammonia concentration may reach a limiting value. This curve fit allows a quantitative comparison of the experimental runs which may have different initial and final conditions.

For runs without alkali addition the time constants were plotted against the biogas flow rate in Figure 57. It is clear that the removal of ammonia from digestate 1 was more rapid, in all cases, than digestate 2. The effect of biogas flow rate on the removal time constant shows similar behaviour for both digestates, albeit with a different absolute magnitude; an increase in flow rate produces an improvement in ammonia removal up until a flow of ~0.375 $l\,l^{-1}\,min^{-1}$, after which there is a saturation effect where a further increase in flow rate shows no appreciable improvement in removal rate.

In Figure 58 where the removal constants are plotted against initial pH, the effect of increasing the pH using NaOH is shown to have a stronger impact on the ammonia removal in digestate 2 compared with digestate 1, such that at high pH the removal rates of ammonia from both digestate are comparable, with time constants of around 4 hours. The reason for the difference in behaviour of the two digestates under similar ammonia stripping conditions is thought to have been caused by the higher VFA concentration in digestate 2. Additionally, digestates 1 and 2 were physically dissimilar: the solids contents were 5.50 and 3.14% of wet weight respectively meaning digestate 1 was much thicker. It is possible that some interaction of the physical characteristics of the digestate with the gas bubbles causes a difference in the removal behaviour but further investigation of this was outside the scope of the current work.

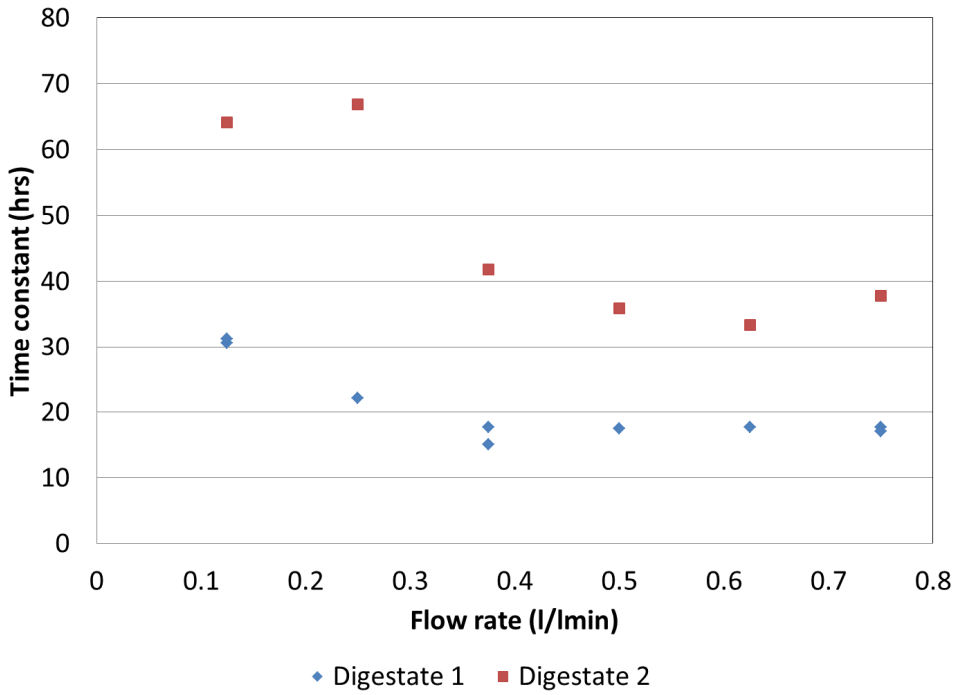


Figure 57 Effect of flow rate on ammonia removal constant for digestates 1 & 2 with no pH modification

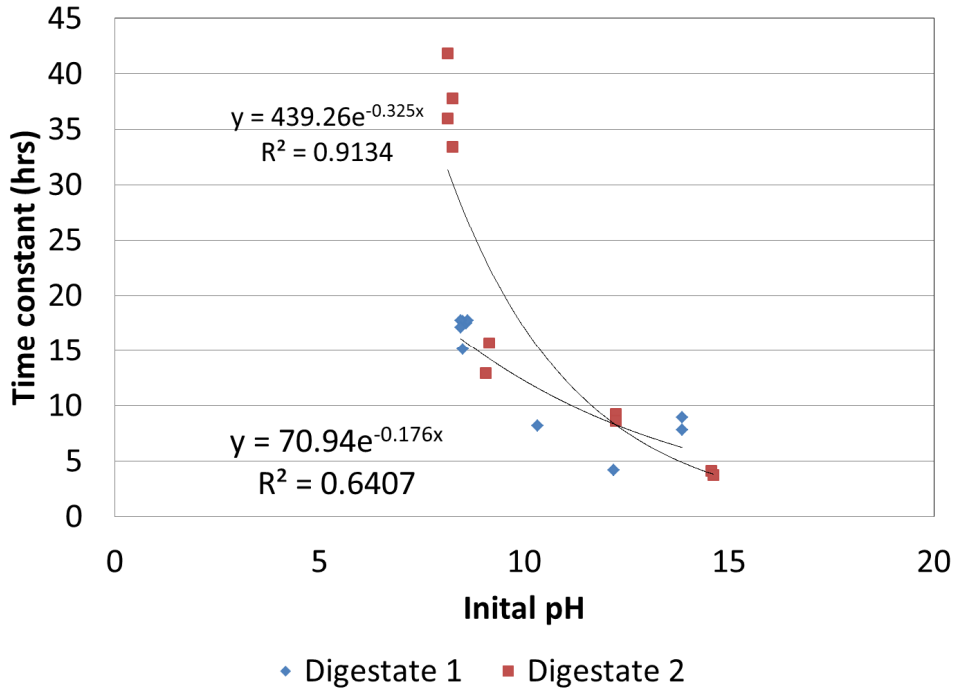


Figure 58 Effect of initial pH on ammonia removal rate constant for digestates 1 & 2

8.4 Further analysis, observations and discussion of batch ammonia stripping

8.4.1 Effect of VFA on ammonia stripping

The results from the preliminary ammonia stripping experimental runs were characterised by an initial increase in pH followed by a sharp swing to a lower pH, resulting in cessation of the

ammonia removal process. This characteristic behaviour was not reproduced in later experimental runs. It was hypothesised that this could be due to the high VFA concentration in digestate 1, which gradually decreased over time and therefore affected later experiments less. Table 31 shows VFA measurements during the early stages of the project, when digestate 1 was still fresh from collection, with a concentration in the range 13847-23880 mg l^{-1}. It was during this period that the initial ammonia removal experiments were performed. Later in the research, the same ammonia stripping apparatus was used but VFA concentrations were found to have reduced, probably due to natural anaerobic degradation and volatilisation, to a range of 1778-2826 mg l^{-1} as shown in Table 32. VFA are acidic in nature and, on removal of ammonia with the associated reduction in alkalinity or buffering capacity, will exert a strong influence on the pH of a digestate.

To consolidate the differing physical behaviour shown in results from different parts of the work and to give an indication of the likely response of digestates with different VFA concentrations to ammonia stripping, it was decided to investigate the influence of VFA on stripping behaviour. An ammonia stripping experiment was therefore performed using digestate 1 spiked with acetic and propionic acid up to the concentrations found on collection in June 2009. The experiment was performed under the conditions of 70°C, 0.375 l l^{-1} min^{-1} and without pH modification.

The ammonia removal and pH results are shown in Figure 59 and are compared with run 4.1 which had the same conditions without the added acetic and propionic acids. It can be seen that the effect of the high VFA concentration was to reduce the pH of the digestate, causing a pH swing as the ammonia was removed; and to inhibit the removal of ammonia below ~4300 mg l^{-1}, compared with a final ammonia concentration of 1090 mg l^{-1} without VFA addition. This explains the discrepancy between early and later findings and is an important result since it has implications for the use of ammonia stripping to recover food waste digesters that have already accumulated high concentrations of VFA: in these conditions removal is less effective and is unlikely to reduce ammonia concentrations to less than 4000 mg l^{-1}.

Table 31 VFA concentrations of digestate 1 shortly after collection

Date	01/07/2009 - 01/09/2009						
VFA (mg l^{-1})	17823	20816	13847	15741	21141	20723	23880

Table 32 Recent measurements of the VFA concentration of digestate 1

Date	14/04/2010	27/04/2010	04/05/2010	19/05/2010	02/06/2010	30/07/2010
VFA (mg l^{-1})	2826	1992	1786	2000	1781	1778

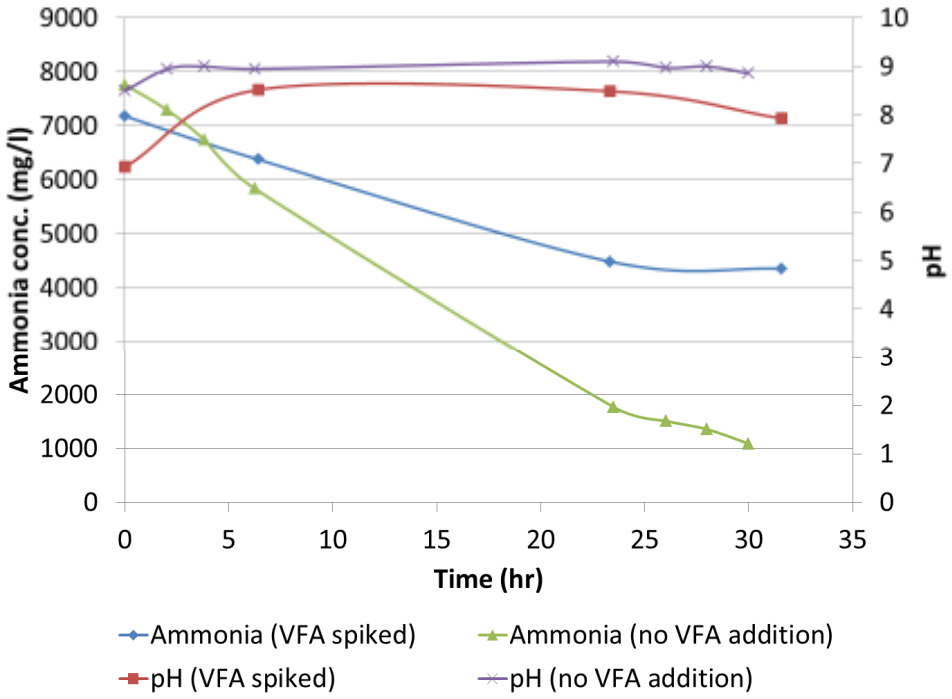


Figure 59 Ammonia stripping from digestate 1 spiked with acetic and propionic acids at conditions 70°C, 0.375 l l^{-1} min^{-1}

8.4.2 Ammonia recovery

Of interest is the form that the ammonia takes after recovery, it would be advantageous to have a product with a low water content and a high ammonia concentration since this would have value and thus improve the economics of AD combined with ammonia stripping..

In all of the experiments presented here, the ammonia was recovered in empty flasks or trapped in water or acid. The partitioning of this collection is important since it influences the value and possible uses for the resulting ammonia products. Table 33 shows the mass of ammonia found in each of the possible partitions at the beginning and end of a selection of runs. The condensation trap was added after run # 10.2. It can be seen that most of the ammonia is, in general, being transferred to the water trap, or condensate trap when present, with the acid trap only collecting a relatively small amount of ammonia. Additionally crystals were formed in the tubing on some runs which could be recovered by washing the tubes with water after the run.

Table 34 shows the partitioning of the ammonia on a concentration basis for runs 12.1/12.2_70_0.25_10, demonstrating that the solution captured in the condensation and water traps can reach very high concentrations of ammonia (35 and 21 g l^{-1} respectively). This is an advantage of the ammonia stripping process; that a more concentrated form of ammonia is produced which will subsequently have a higher value as a fertiliser. Additionally the results show that the acid trap is little used suggesting that it could be removed from the system without major impact of the process, and therefore reducing risks and cost associated with acid use on an industrial scale.

Table 33 Ammonia recovery and partitioning between traps for selected runs

Run #	Initial ammonia (mg)	Final ammonia (mg)					% Ammonia removal
	digestate	digestate	condensate	water	acid	crystal	
2.1_70_0.125_N	18874	650	NA	11710	2215	21	97
3.1_70_0.125_N	17105	547	NA	9651	3442	22	97
5.1_70_0.25_N	17132	799	NA	7878	3337	43	95
5.2_70_0.25_N	17217	1701	NA	9555	5091	57	90
7.2_70_0.5_N	17892	3432	NA	8925	437	91	81
8.2_70_0.635_N	17997	760	NA	12410	4049	0	96
9.2_70_0.375_12	10301	2033	NA	4462	0	0	80
10.2_70_0.75_N	19351	702	6483	4015	615	0	96
12.1_70_0.25_10	14247	351	6138	4073	2366	53	98
12.2_70_0.25_10	14247	319	7345	4472	2288	48	98

Table 34 Ammonia concentrations for run 12.1_70_0.25_10 and 12.2_70_0.25_10

Ammonia concentration (mg l^{-1})	R1	R2
Initial Digestate	8877	8877
Final Digestate	256	221
Acid trap	7681	7430
Water trap	19301	20996
Condensate trap	29227	34978
Crystals (with water)	330	240

8.4.3 Crystal formation

Crystals were formed on the tubing and connections, at least to some extent, on most runs. In some cases these were collected and analysed for ammonia content as shown in Table 33; in other cases the amount was so small it was difficult to quantify. During run 11.1_70_0.125_10 crystals were observed in the condensation trap (see Figure 60) and water addition was required after the run to dissolve these crystals to analyse their ammonia content.

It is thought that crystals form when the transfer of ammonia outperforms the removal of water from the digestate by evaporation or aerosol, which only occurs at the lowest flow rate considered (0.125 l l^{-1} min^{-1}). On entering the condensation trap the ammonia cools and becomes more likely to condense and precipitate as ammonium salts. At higher flow rates it is thought the same physical process occurs but since a larger volume of water is being transferred enough is present to dissolve the ammonium salts. Unfortunately where ammonium crystals are present in the condensate the low flow rate means the time constant is very long even with alkali addition (30-50 hours).

Figure 60 Crystals in the condensate flask for run 11.1_70_0.125_10

At the lower flow rate during run 2.1_70_0.125_N it was even possible to collect solid deposits from the tubing connections: these are shown in Figure 61. It is clear that any engineering solution will need the ability to flush the gas stripping system to remove these deposits and to recover the ammonium salts.

Figure 61 Crystals collected from tubing during run 2.1_70_0.125_N

8.4.3.1 Foaming

Excessive foaming was observed when alkali had been added to the digestate during the run, to such an extent that the volume of digestate added to the 3-litre column was reduced to 1.5 litres during runs 10-12. As can be seen in Figure 62, foaming can cause the digestate to expand to over twice its original volume. It is thought that the addition of alkali to the digestate causes the formation of soap-like substances (sodium salts of fatty acids), which lead to foaming. When working at high pH and flow rates it may be necessary to carry out control measures such as the use of antifoam or steam addition to prevent operational problems caused by excessive foaming.

Figure 62 Photo showing extent of foaming during run 9.2_70_0.375_12

8.4.4 A comparison of the pH behaviour of different digestates upon alkali addition

Three digestates were compared for their tendency for pH change with alkali addition. Digestate 1 was the commercial food waste digestate used for the other experiments in this section whereas digestates 3 and 4 were from laboratory-scale digesters fed on food waste and with trace element additions. The characteristics of these digestates can be found in Table 35 and the results showing pH change with addition of 10M NaOH are shown in Figure 63. It can be seen that the relative alkali addition needed for a given pH increases with the VFA concentration in the digestate, the reason for this being the weak acidity imparted by VFA.

An interesting result from these analyses is that pH changes rapidly between 12 and 13. pH 13 may deliver greater ammonia removal rates that 12 which come at low additional chemical use.

Table 35 Approximate characteristics of three food waste digestate samples

Digestate	VFA (mg l^{-1})	Ammonia (mg l^{-1})	10M NaOH added to pH 10	10M NaOH added to pH 12
1	~25000	~8000	1.89	4.89
3	~100	~5400	0.66	1.98
4	~15000	~5400	1.20	3.00

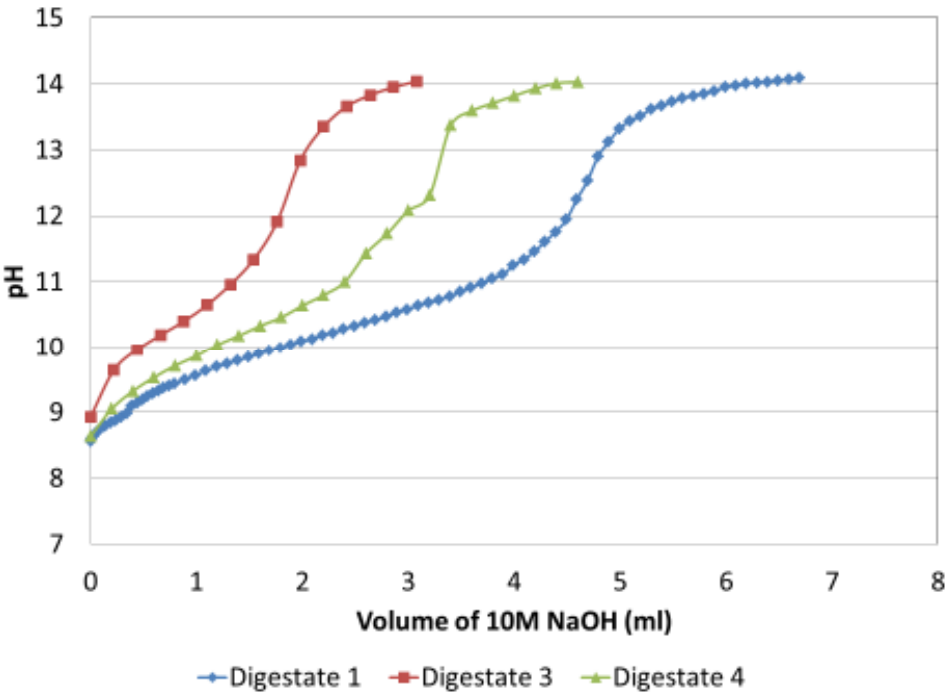


Figure 63 pH change caused by alkali addition; a comparison of three food waste digestates

8.5 Conclusions on batch ammonia stripping from digestate

The removal of ammonia from food waste digestate using biogas was explored in a number of batch experiments. Initial findings showed that digestate stripping with biogas removed ammonia and that increasing the operating temperature and gas flow rate increased the removal rate. Upon further investigation of the ammonia removal process, it was found that at modest flow rates (0.125-0.375 l l^{-1} min^{-1}) the removal rate was increased by an increase in flow, but that a saturation of removal rate was reached above these (0.5-0.75 l l^{-1} min^{-1}).

An exponential decay curve could be fitted to the ammonia removal data and allowed comparison of stripping experiments under different conditions and with different digestate samples. At 35 and 55 °C time constants were in the order of 600 hours, whereas at 70 °C ammonia concentrations could be reduced in 15-17 hours at or above a flow rate of 0.375 l l^{-1} min^{-1}. With pH adjustment by the addition of 10M NaOH the time constant could be further reduced to 3.9 hours at 70°C, 0.375 l l^{-1} min^{-1} and initial pH 12.

Ammonia stripping experiments performed on a second digestate sample showed similar qualitative behaviour with respect to ammonia removal when compared with those of digestate 1. Increasing biogas flow rate up to 0.375 l l^{-1} min^{-1} increased the removal rate of ammonia. Few gains are realised by increasing the flow rate further, but addition of alkali to increase the pH greatly increases the rate of ammonia removal. However, quantitative analysis of the ammonia removal kinetics show that for the same conditions the removal of ammonia from digestate 2 required approximately double the amount of time, except at extreme pH (12-14) where the behaviour was very similar, with minimum time constants of around 4 hours for 63% removal.

High VFA concentrations were shown to have a negative impact on the ammonia removal process, in that the VFA caused the pH of the digestate to be lower, and also to decrease as ammonia is removed. This appears to impose a limit on the amount of ammonia that can be removed from digestates with extremely high VFA concentrations (~20,000 mg VFA l^{-1}) to around 4000 mg l^{-1}. This has implications for recovery of anaerobic digestion plants where the process is already operating at these high VFA concentrations as it will limit the effectiveness of ammonia removal by stripping with biogas.

Ammonia is effectively trapped in condensation and water traps and during the stripping processes ammonia salt solutions are obtained with concentrations of the order 20-35 g l^{-1} of ammonia. This is advantageous since these products could have a value greater than that of the digestate itself; furthermore the fact that acid is not required to trap ammonia presents further advantages from an engineering, risk and cost point of view. Whilst working at a low flow rate (0.125 l l^{-1} min^{-1}) produces only modest rates of ammonia removal and time constants in the order of 100 days, crystals formed in the room temperature condensate trap could easily be separated from the collected liquid leaving a solid product.

Table 36 Summary of all batch ammonia stripping experiments

Run #	Reactor #	Temperature (°C)	Flow Rate (l l^{-1} min^{-1})	Alkali addition	Length of Run (hrs)	Initial		Final		Time constant (hrs)	r^2	% Ammonia Removed
Digestate 1						pH	Ammonia (mg l^{-1})	pH	Ammonia (mg l^{-1})			
0.1	2	35	0.375	N	306.25	8.43	7189	8.87	4318	575.4	0.98	45%
1.1	1	55	0.125	N	120.07	8.46	7479	8.89	6155	699.6	0.91	21%
2.1	1	70	0.125	N	97.50	8.70	7743	8.49	446	30.7	0.96	96%
3.1	1	70	0.125	N	118.50	8.49	7798	9.36	285	31.3	0.96	96%
4.1	1	70	0.375	N	30.00	8.50	7764	8.86	1090	15.1	0.99	89%
5.1	1	70	0.25	N	63.48	8.65	7810	8.89	497	22.1	0.99	95%
6.1	1	70	0.375	N	28.83	8.50	7847	8.99	1585	17.7	1.00	83%
7.2	2	70	0.5	N	24.40	8.59	8076	9.04	1963	17.5	1.00	80%
8.2	2	70	0.625	N	44.68	8.62	8245	7.98	773	17.7	0.97	95%
9.2	2	70	0.375	Y	6.25	12.18	6783	10.99	1539	4.2	1.00	78%
10.1	1	70	0.75	N	22.72	8.45	8821	9.03	6925	17.8	0.97	-
10.2	2	70	0.75	N	52.00	8.45	8821	8.01	470	17.1	0.97	96%
11.1	1	70	0.125	Y	64.88	10.19	7815	10.36	1706	45.2	0.93	78%
11.2	2	70	0.125	Y	89.80	10.19	7815	10.12	551	36.0	0.91	93%
12.1	1	70	0.25	Y	55.10	10.25	8134	10.30	235	15.3	0.96	97%
12.2	2	70	0.25	Y	55.30	10.25	8134	10.18	202	15.0	1.00	98%
13.1	1	70	0.25	Y	71.78	11.43	5816	11.18	357	27.8	0.73	95%
13.2	2	70	0.375	Y	71.85	10.32	6232	10.41	191	8.2	0.74	98%
14.1	1	70	0.375	Y	22.78	13.86	5404	11.28	281	7.8	0.96	95%
14.2	2	70	0.375	Y	22.88	13.86	5404	11.36	391	8.9	0.95	94%
Digestate 2												
15.1	1	70	0.125	N	98.48	8.20	5978	8.57	1389	64.2	0.99	81%
15.2	2	70	0.25	N	98.48	8.20	5978	7.63	1302	66.9	0.98	88%
16.1	1	70	0.375	N	52.87	8.13	5834	8.82	1701	41.8	1.00	82%
16.2	2	70	0.5	N	52.87	8.13	5834	8.13	1664	36.0	0.95	82%
17.1	1	70	0.625	N	48.50	8.24	5849	7.86	1395	33.4	0.98	85%
17.2	2	70	0.75	N	45.33	8.24	5948	7.85	1937	37.8	0.80	90%
18.1	1	70	0.375	Y	18.75	12.24	4328	11.18	537	9.2	0.99	91%
18.2	2	70	0.5	Y	18.75	12.24	4328	11.28	458	8.6	0.98	93%
19.1	1	70	0.375	Y	11.17	9.15	5258	9.96	2587	15.7	0.99	49%
19.2	2	70	0.5	Y	11.17	9.06	5045	9.93	2214	13.0	0.98	64%
20.1	1	70	0.5	Y	6.33	14.56	4764	12.08	1044	4.1	1.00	78%
20.2	2	70	0.625	Y	6.33	14.61	4976	11.84	940	3.7	0.99	83%

9 Integration of ammonia stripping with anaerobic digestion

9.1 Aims and objectives

This section details two laboratory-scale semi-continuous experiments which were performed in order to further understand how ammonia stripping could be integrated with the anaerobic digestion process.

9.1.1 Side-stream ammonia stripping

In this experiment a laboratory-scale side-stream stripping process was operated for a period of 100 days in order to assess the interaction of the ammonia stripping and anaerobic digestion processes. Mesophilic digestion combined with both mesophilic and thermophilic stripping were investigated. These conditions were chosen based on the need to avoid subjecting the active biomass in the digester to a temperature that would eradicate many of the organisms present: although digestion can occur at extreme thermophilic temperatures there is little or no experience in operating commercial digesters in this temperature range and 70 °C was deemed unsuitable. For similar reasons (not subjecting the biomass to extreme conditions) it was decided that no pH modification would be performed. Of the gas flow rates investigated in batch experiments 0.375 l l^{-1} min^{-1} was chosen since it was the minimum flow rate that gave maximum ammonia removal rate.

9.1.2 Ammonia released during hydrolysis

The aim of the hydrolysis experiment was to investigate the ammonia released during the hydrolysis stage of the anaerobic digestion of food waste. The context of this within the current research was that after the hydrolysis, an ammonia removal step could be performed followed by anaerobic digestion. This process configuration is advantageous, since the ammonia is recovered before the anaerobic digestion and therefore cannot cause in-digester toxicity. The primary object of this experiment was to assess the performance of this hypothetical system in terms of ammonia removal, and secondly to investigate the optimal length of time needed for the hydrolysis removal in terms of ammonia released and required size of digester. The experiment took the form of a kinetic study, with digesters fed on food waste at a range of retention times or organic loading rates.

9.2 Ammonia stripping in a side-stream process to semi-continuous anaerobic digestion of food waste

9.2.1 Experimental setup and procedure

The apparatus used in this part of the project consisted of two separate pieces of equipment: the digesters and the stripping system, shown in Figures 64 and 65 respectively. The four digesters had a working volume of 3.6 litres and were continuously stirred. Temperature was controlled to 37˚C using a thermocirculating pump which circulated water through copper coils surrounding the digesters. Biogas volume was

measured using a low flow gas meter and the biogas was subsequently collected in impermeable (Tedlar) bags for calibration and analysis.

The stripping system was made up of 0.36-litre stripping reactors, a pump, acid traps and water traps. The stripping reactors were temperature controlled by submersion in water baths. Two of the stripping reactors were operated and mesophilic temperature (37˚C) and two at thermophilic temperature (55˚C). The pump was used to circulate biogas around the stripping system between the stripping reactors and the acid trap. The thermophilic stripping loops also contained a water trap after the stripping reactor to prevent excess condensation into the acid trap.

Figure 64 Digester system

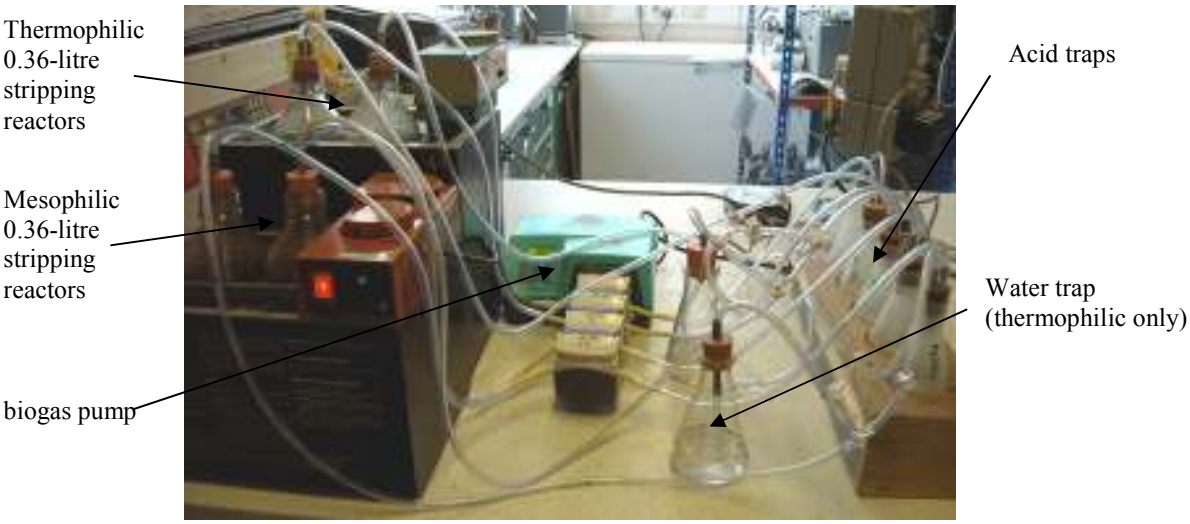


Figure 65 Stripping system

A schematic of the experimental procedure is shown in Figure 66. The mesophilic digesters were fed on food waste at an OLR of 2g VS l^{-1} d^{-1}. On a daily basis 0.36 litres of the digester contents (10%) were removed and placed into the corresponding stripping reactor. The contents of the stripping reactor from the previous day were replaced into the main digester. The volume in the main digesters was kept constant by removing excess digestate for analysis.

The stripping system was flushed daily with biogas and operated continuously to circulate the gas between the stripping reactor and the traps at a rate of 0.375 $l l^{-1}$ min^{-1} (based on the stripping reactor volume). The experiment consisted of two duplicate digester/stripping systems, the only difference being the stripping temperature. The nomenclature of the digesters and stripping reactors is shown in Table 37, digesters were named according to the stripping temperature (i.e. M=mesophilic, T=thermophilic).

Start-up of the experiment involved inoculating the digesters with 4 litres of food waste digestate as described in section 4.2.2, followed by an acclimatisation period of 16 days where the digesters were only fed without stripping. Stripping started on day 17 and the experiment lasted 100 days in total.

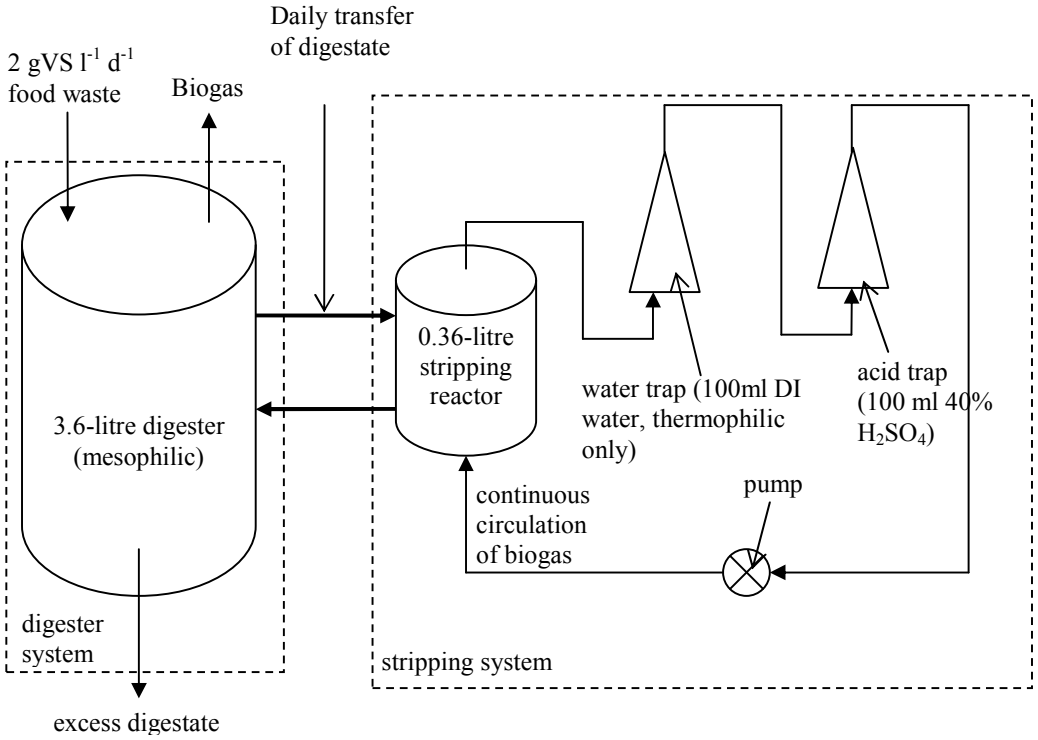


Figure 66 Summary of the continuous side-stream stripping experiment

Table 37 Summary of experimental conditions of the continuous side-stream stripping experiment

Digester	Digester temp.	Stripping reactor	Stripping temp.	Loading rate
DT1	Mesophilic	ST1	Thermophilic	2g VS l^{-1} d^{-1}
DT2	Mesophilic	ST2	Thermophilic	2g VS l^{-1} d^{-1}
DM1	Mesophilic	SM1	Mesophilic	2g VS l^{-1} d^{-1}
DM2	Mesophilic	SM2	Mesophilic	2g VS l^{-1} d^{-1}

9.2.2 Results and discussion for side-stream ammonia removal

Results from the side-stream stripping experiment are shown in Table 38 along with those for a pair of control digesters (described in section 4.1.1), which were operated in a similar manner but without ammonia stripping. Also presented are daily methane production, pH, and ammonia concentrations in Figures 67, 68 and 69 respectively.

It can clearly be seen in Table 38 and Figure 67 that the supposedly duplicate digester/stripping systems did not behave as such. Digester DM1 showed poor performance in terms of low methane production, low pH and a high IA:PA suggesting incipient failure of the digester. Its counterpart DM2 showed healthy digestion, however. This may have been in part due to operational problems with DM1 which lost some digestate early in the run; but a similar degree of divergence was visible between DT1 and DT2 at the end of the period.

Table 38 Summary of the results of the continuous side-stream stripping experiment (averaged over the 7 day period 21/11/09-29/11/09)

Quantity	DT1/ST1	DT2/ST2	DM1/SM1	DM2/SM2	Control
Specific methane production (STP l g^{-1} VSadded)	0.362	0.469	0.201	0.330	0.414
Digester pH	7.70	7.84	7.36	7.63	7.92
Stripper pH	7.95	8.14	7.53	7.78	NA
Digester ammonia-N concentration (mg l^{-1})	4546	4783	4688	4776	4808
Stripper ammonia-N concentration (mg l^{-1})	4415	4636	4576	4855	NA
Digester total alkalinity (mg l^{-1})	23251	25240	21046	23236	23535
Digester partial alkalinity (mg l^{-1})	11716	12861	7767	10620	15352
Digester intermediate alkalinity (mg l^{-1})	9617	10577	10587	10499	8182
Digester intermediate:partial alkalinity	0.82	0.83	1.37	0.99	0.54

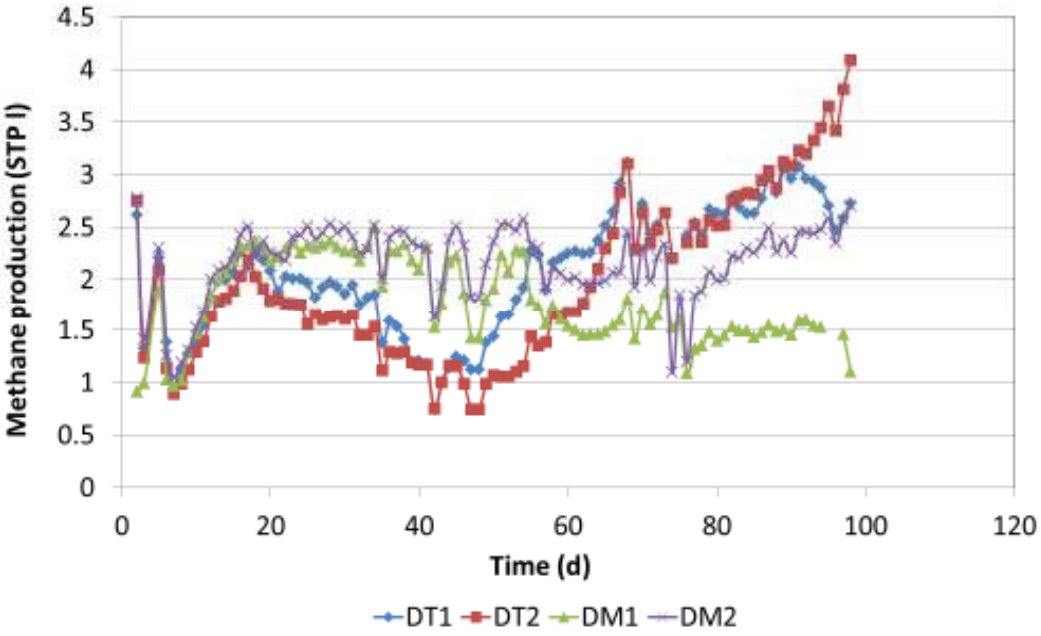


Figure 67 Daily methane production of the continuous side-stream stripping digesters

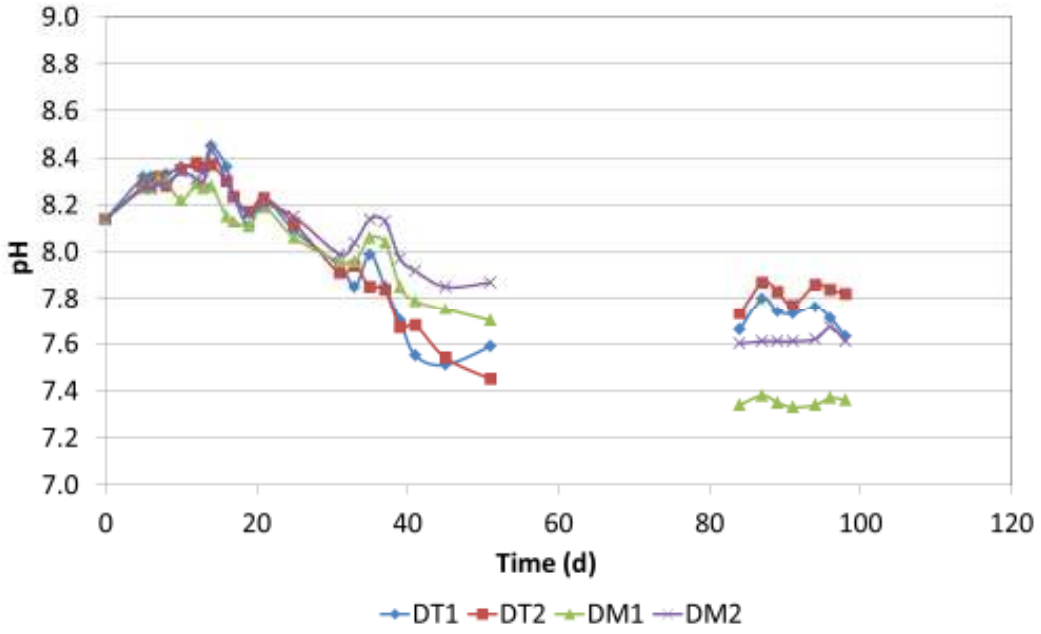


Figure 68 pH of the continuous side-stream stripping digesters

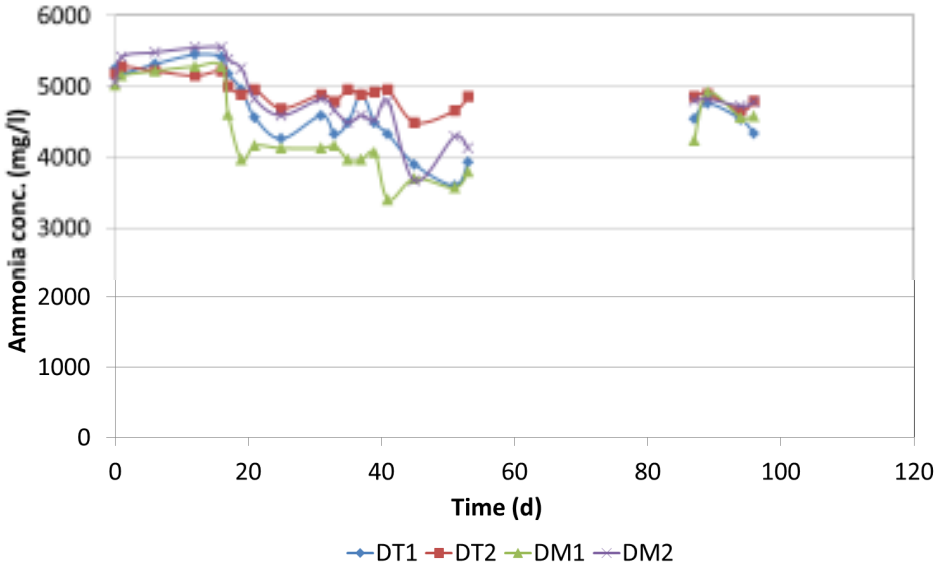


Figure 69 Ammonia concentration in the continuous side-stream stripping digesters

The methane production of all systems showed a gradual increase during the first 20 days of the experiment as the digestate became acclimatised. After this DM1 showed a decline from approximately day 60, while DM2 showed recovery from day 75 onwards. DT1/2 showed a different pattern: after stripping was commenced there was a reduction in methane production until around day 45-50 followed by an increase for the next 50 days. It is possible that the period of decreased methane production in DT1/2 was the result of a second acclimatisation period for these digesters to the temperature changes experienced by the microorganisms in the thermophilic stripping. Towards the end of the experiment the thermophilic stripping appeared to be delivering a process advantage, in that these digesters produced the largest volume of methane (DT2 produced 0.469 litres g^{-1} VS day^{-1} c.f. 0.414 for the control). There are a number of feasible explanations for this; that the increased temperature of the stripping resulted in a greater degree of hydrolysis of the food waste; or that the temperature shifting regime naturally selected a different population of microorganisms more able to degrade the waste under a regime of temperature change. Another explanation of this difference could be due to the experimental setup; biogas production in the stripping system was not measured and may have been higher in the mesophilic stripping reactors leading to an apparent deficit in the digesters.

The ammonia concentration in the digesters remained steady throughout the experiment and was similar to that in the control reactor. The simplest conclusion was that the stripping system was not removing a measurable quantity of ammonia. The higher specific gas production in DT2 indicates a higher degree of organic matter breakdown, however, which is associated with greater release of ammonia nitrogen. A nitrogen mass balance around the system was not carried out, but it is possible that ammonia removal was taking place down to the limiting concentration of the system. By the end of the experiment the VFA concentration in the stripped digesters was around 14000 mg l^{-1}, and

as shown earlier the presence of VFA may determine the minimum achievable ammonia concentration. This view is supported by the fact that when stripping started on day 17 there was a reduction in the ammonia concentration in the digesters accompanied by a pH drop from 8.4 to 8.1.

9.3 Ammonia released during the hydrolysis of food waste

9.3.1 Experimental setup and procedure

A total of 8 digesters, the design of which is shown in Figure 70, were used in the experiment. The digesters had a working weight of 600 g (~600 ml working volume) and were seeded with anaerobic digester sludge from Millbrook Wastewater Treatment Works, Southampton. They were then fed on food waste in duplicate at retention times of 10, 8, 7, 6 days. The digesters were continuously stirred, and maintained at an operating temperature of 37 ˚C in a water bath, with gas collection in 1-litre storage (Tedlar) bags. Daily, the digesters were removed from the water bath, weighed and the contents homogenised. After this, digestate was removed and the appropriate quantity of food waste was added. Samples were taken for pH, ammonia concentration, gas volume (production) and composition in order that the performance of the system could be assessed. No liquid was added to any digesters and therefore the retention times were 'natural', meaning that they were defined by the feed rate as summarised in Table 39. Following this first run the digester contents were mixed, homogenised and redistributed equally between the digesters and feeding restarted at retention times of 5, 4, 3 and 2 days. The whole experiment lasted a total of 65 days, 43 of which were spent at the greater retention times (10, 8, 7, 6 days) and 22 at the lesser (5, 4, 3, 2 days) reflecting the time required for the digesters to reach stable operating conditions based on the parameters measured.

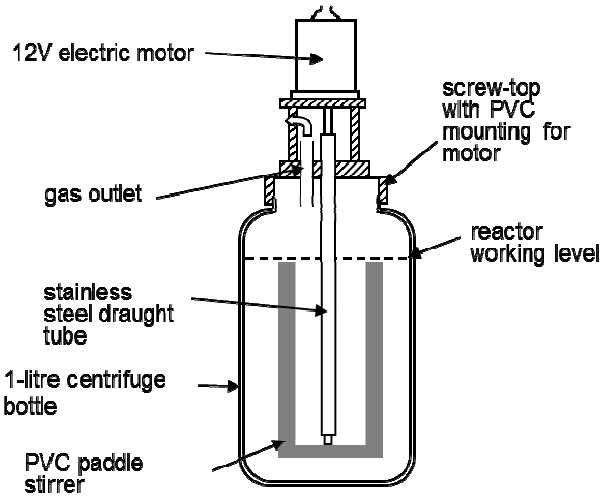


Figure 70 Design of 600 ml digesters used in hydrolysis experiment

Table 39 Hydrolysis experiment summary of experimental conditions

Retention time (d)	# digesters	Digestate removed daily (g)	Food waste added daily (g)	Temp (˚C)	Working weight (g)
10	2	60	60	37	600
8	2	75	75	37	600
7	2	85	85	37	600
6	2	100	100	37	600
5	2	120	120	37	600
4	2	150	150	37	600
3	2	200	200	37	600
2	2	300	300	37	600

9.3.2 Results and discussion for ammonia release during hydrolysis

A summary of the main experimental results, based on the average of 4 values taken when each of the hydrolysis reactors was deemed to have reached stable operation, is given in Table 40. It can be seen that the ammonia concentration in all digesters is around 1000 mg l^{-1} indicating that only ~15% of the hydrolysable ammonia-containing organics were being degraded and that changing the retention time of the hydrolysis digester had no effect on this parameter. This has negative implications for post-hydrolysis ammonia stripping without pH control since only a small quantity of ammonia could be removed whilst the rest would still be released during the main methanogenic digestion stage and could therefore still inhibit acetoclastic methanogenesis.

Figure 71 shows the pH evolution through the experiment and Figure 72, the final steady state pH of the digesters. It can be seen that low pH was observed in all cases, but that below a retention time of 5 days, a step change in pH occurs. Low pH was expected in reactors operated at low hydraulic retention times since slow-growing acetogens and methanogens, which work together to remove the acidic VFA in the digesters, are washed out leaving a population of mainly hydrolytic and fermentative organisms which produce acids. At such low values of pH, hydrolysis can become partially inhibited which may explain the low concentrations of ammonia in the reactors.

Table 40 Summary of results from the hydrolysis reactors at steady state

Retention time (d)	pH	σ	Carbon dioxide production (l d^{-1})	σ	Total ammonia concentration (mg N l^{-1})	σ
10	4.72	0.03	0.403	0.045	1052	27
8	4.72	0.03	0.529	0.060	1024	31
7	4.72	0.03	0.581	0.078	1026	20
6	4.71	0.02	0.703	0.051	1017	20
5	4.03	0.04	0.744	0.029	1084	31
4	4.01	0.04	0.949	0.033	1072	53
3	3.99	0.05	1.234	0.049	1084	57
2	3.89	0.02	1.818	0.043	1060	49

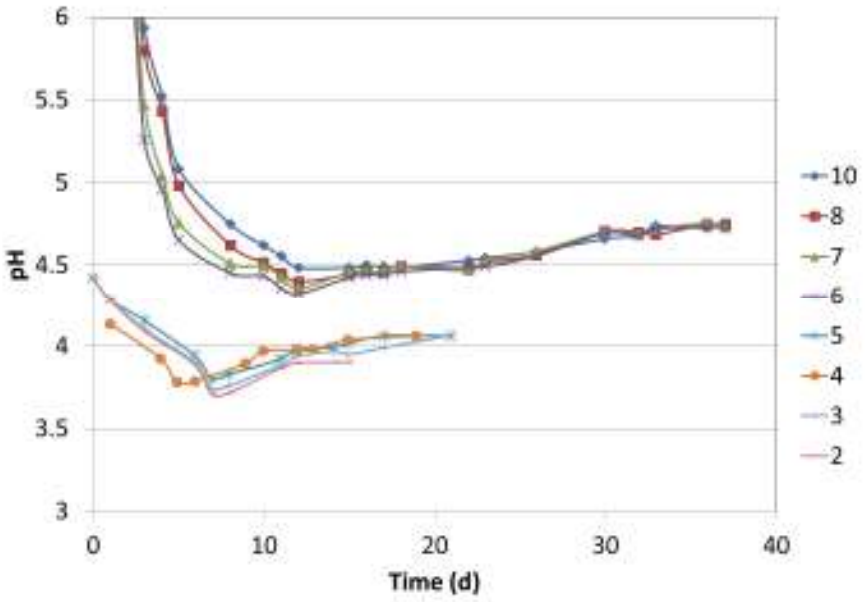


Figure 71 pH of hydrolysis reactors

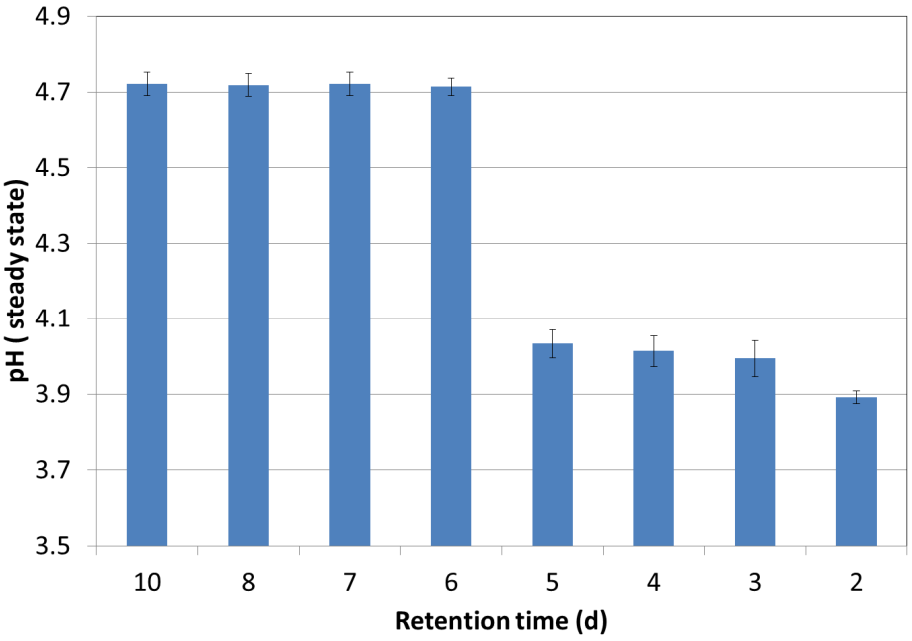


Figure 72 pH of hydrolysis reactors at steady state

The inhibition of the hydrolysis/fermentation processes can also be seen in the digester gas production, which is shown in Figure 73. Gas composition was measured on all samples: no methane was found and the main component was carbon dioxide. The trend was that carbon dioxide production increased with decreasing retention time; this is

expected since at the shorter retention times the quantity of food waste fed to the digesters was greater. Carbon dioxide is a product of fermentative reactions and therefore at increased loading rates a larger quantity of carbon dioxide is produced. The specific gas production was similar for all of the digesters. This suggests that hydrolysis and fermentation are proceeding to a similar extent on the food waste and that these processes occur rapidly (<2 days), after which any further fermentation is inhibited by the digestion conditions.

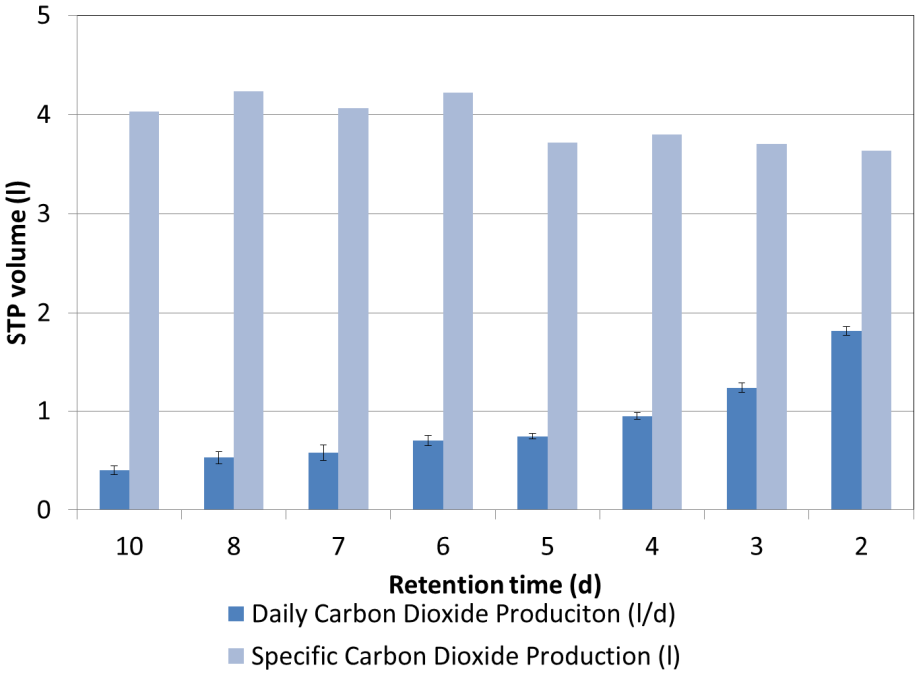


Figure 73 Gas production from hydrolysis reactors

Figure 74 shows the evolution of ammonia in the digesters throughout the experiment. During the initial stages, before day 20 when the pH was higher, a slightly increased ammonia concentration was found whereas once the pH stabilised around 4 then it decreased in all cases to around 1000 mg l^{-1}. The steady state ammonia concentrations are shown in Figure 75.

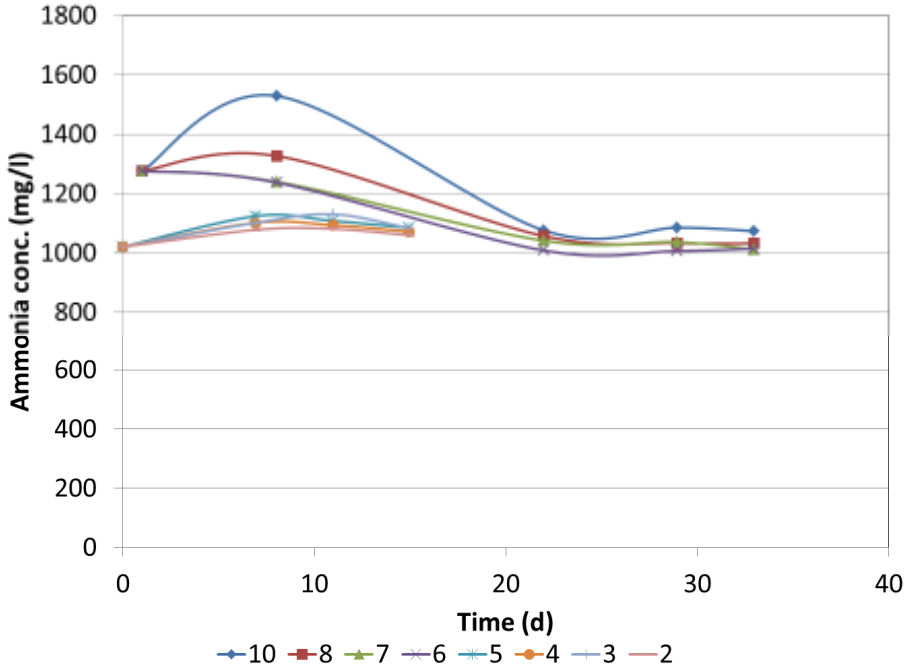


Figure 74 Ammonia concentration in hydrolysis reactors

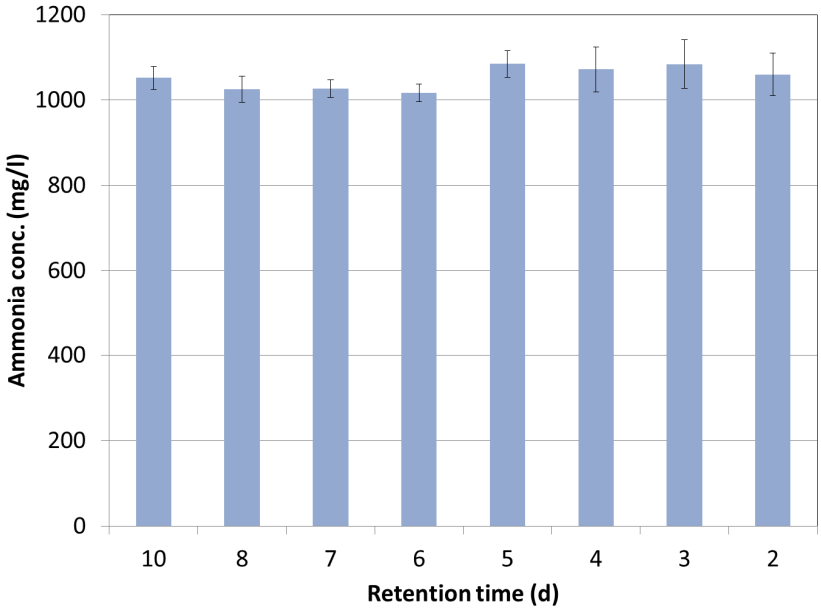


Figure 75 Ammonia concentration in hydrolysis reactors at steady state

All of the parameters measured during this experiment point towards inhibition of the hydrolysis/fermentation in the digesters beyond a nominal level (15% for N-containing species) and also suggest that increasing the residence time of the food waste in the hydrolysis stage does not have any impact on the degree of hydrolysis, and therefore ammonia production, taking place. The results indicate that without pH control the pre-

digestion removal of ammonia from hydrolysate will not be effective in reducing the 2nd stage (acetogenic/methanogenic) by more than than 15%. It is possible that, with pH modification, an increased rate/amount of hydrolysis would occur which could increase the ammonia production in a short hydrolysis stage: this is an area for further investigation.

9.4 Conclusions on integration of ammonia stripping with anaerobic digestion

9.4.1 Side-stream ammonia stripping

The continuous side-stream ammonia stripping experiment was operated for 100 days during which the digesters continued to show transient behaviour, possibly due to the interaction of VFA accumulation and ammonia stripping. Ammonia concentrations in the digesters with stripping systems were similar to the control case where no stripping was performed. Under the experimental conditions used the side-stream process was not successful in preventing the accumulation of volatile fatty acids, and this in turn limited the effectiveness of the ammonia removal process. A more extensive programme of experimentation is therefore needed to optimise the system, particularly in order to maintain the system at low ammonia concentrations in the initial stages.

9.4.2 Ammonia released during hydrolysis

The envisaged process of a hydrolysis step followed by ammonia removal then by anaerobic digestion is unlikely to provide any process benefits of stability due to a reduction in the ammonia concentrations to which the methanogens are subjected. The experiment into the hydrolysis of food waste showed that without pH control only a small proportion (~15%) of the bio-available ammonia was released during this first stage, and there is evidence to suggest that hydrolysis/fermentation was inhibited after a certain point. This was probably due to the low pH observed in all hydrolysis reactors.

10 Modelling ammonia removal in an anaerobic digestion plant

The aim of this part of the work was to use the experimental data obtained as a basis for modelling ammonia removal and to give guidance on the options for industrial application of ammonia stripping in various full-scale plant configurations. The model was developed to simulate the two most promising modes of *in situ* and post digestion ammonia removal.

10.1 Model description

The model relies on certain simplifying assumptions in order to allow the development of a flexible tool. These are as follows:

- Ammonia is removed exponentially, that is the removal rate relative to the ammonia concentration is constant, and independent of all other parameters within the model. This function has been shown experimentally to provide an adequate model of ammonia removal in a gas stripping system.
- The model is dimensionless, therefore any units of mass, length etc. can be substituted: this is inherent in the model but also makes the assumption that the laboratory-based experiments can be scaled up to full-size.
- Ammonia is released into the digester immediately by the incoming food waste; in reality this is not the case, as there is some delay while proteins are hydrolysed; but this time is short relative to the typical retention times in anaerobic digestion.
- Bio-available ammonia is released at a fixed concentration which can be set by the user (e.g. 7000 mg l^{-1}). The concentration of ammonia in a digester has been shown to be feedstock-specific, and independent of organic loading rate so long as the process is not inhibited.
- The digester, mixing tank and pasteuriser are completely mixed.

The parameters that must be specified in order to simulate the ammonia removal process are as follows: bio-available ammonia concentration (mg l^{-1}), organic loading rate (kg VS m^{-3} d^{-1}), initial ammonia concentration (mg l^{-1}), VS content of the food waste (g kg^{-1}), ammonia removal time constant (hrs) and the amount of time the stripper is on per day (hrs).

The model has been built for two specific scenarios: the first represents removal of ammonia in the pasteuriser at 70°C, with some digestate recycle. This is presented diagrammatically in Figure 76. The overall retention time of the whole digestion system is set by the organic loading rate, but the digester retention time is a variable and can be altered by adjusting the digestate recycle.

For maximum ammonia removal in the digester it is preferable to recycle most of the digestate, i.e. adding something with low ammonia concentration to the incoming food waste. This presents a problem, however, since the recycled digestate has been pasteurised and therefore does not return active anaerobic biomass to the system. The limitation is the minimum digester retention time, which sets the maximum amount of

digestate that can be recycled. For process stability a value of 30 days has been used in the simulation for the target digester retention time (maximising the digestate recycle).

The second scenario is shown in Figure 77 and represents *in situ* ammonia removal during the mesophilic anaerobic digestion stage, by combining gas mixing with a biogas ammonia stripping system. In this case the overall retention time is simply set by the incoming food waste since there is no recycling of digestate.

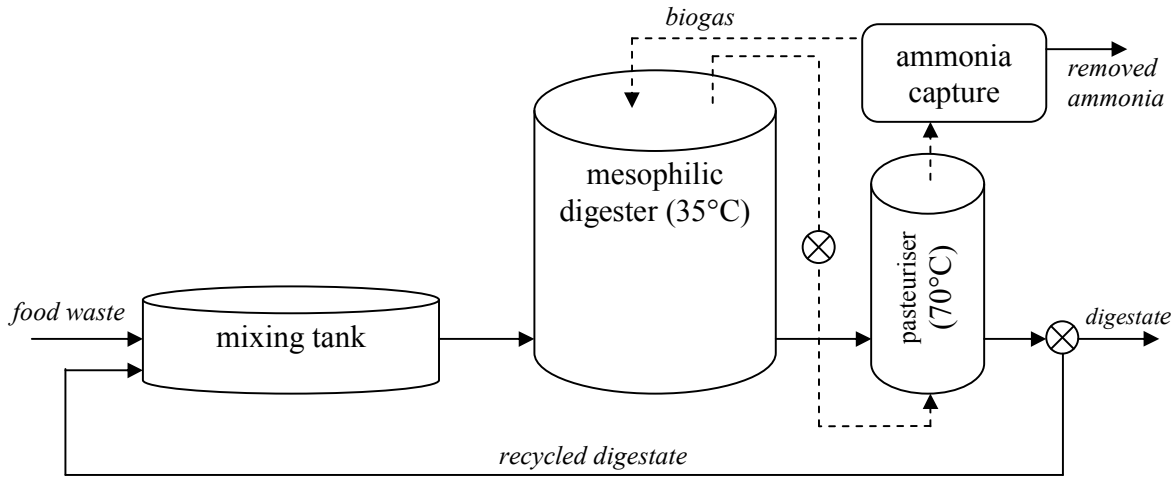


Figure 76 Scenario 1 – Post digestion ammonia removal during pasteurisation step

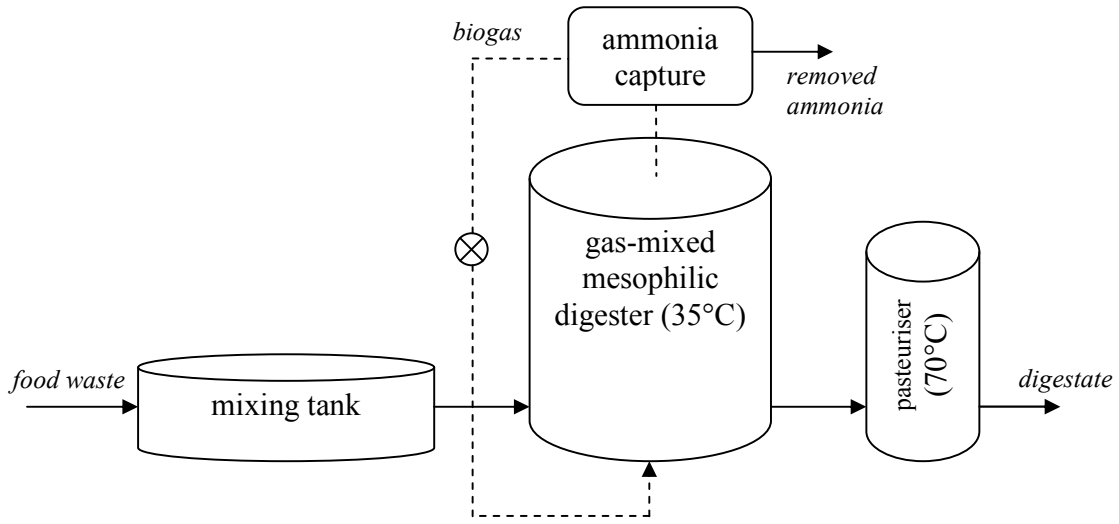


Figure 77 Scenario 2 – In situ ammonia removal during mesophilic digestion

10.2 Results and discussion on modelling ammonia removal

For both scenarios the following conditions were simulated;

- Organic loading rates of 2 and 5 kg VS m^{-3} d^{-1} representing a modest and high loading rate plant respectively.
- Initial ammonia concentrations of 500 and 6000 mg l^{-1} representing a freshly inoculated and mature food waste digester respectively.
- Bio-available ammonia in the food waste 6000 mg l^{-1}.
- VS content of the incoming food waste 217 g kg^{-1}.
- Ammonia strippers operated 24 hours a day
- Mesophilic ammonia stripping with a time constant of 575 hours as per run 0.1 (Table 36)
- Ammonia stripping at 70°C with a time constant of 4 hours as per runs 20.1 and 20.2 (Table 36)

For scenario 1 with digestate recycling a hydraulic retention time (HRT) in the digester of 30 days was simulated to avoid potential biomass washout, thus setting the ratio of recycled digestate : incoming food waste.

Figure 78 shows the in-digester ammonia concentration during the simulation of scenario 1, the post-digestion stripping during pasteurisation. It can be seen that the final ammonia concentration is independent of the initial concentration, which is as expected since the inoculum material is eventually diluted out of the digester. At 2 kg VS m^{-3} d^{-1} the final ammonia concentration is 1661 mg l^{-1} corresponding to a 72% ammonia reduction. At 5 kg VS m^{-3} d^{-1} the final ammonia concentration is much higher at 4149 mg l^{-1}, corresponding to a 31% reduction relative to no intervention.

In the high rate system, the amount of recycled digestate is small since the natural retention time is only 43.4 days, and in this case the recycle ratio (recycled digestate : incoming food waste) is only 0.45. At the lower loading rate the recycle ratio is much higher at 2.62, meaning the recycled digestate which has had ammonia removed dilutes the incoming food waste to a greater degree.

Figure 79 shows the results of the simulations for scenario 2; again the final ammonia concentration is independent of the initial concentration. In this case, despite the ammonia removal time constant being two orders of magnitude higher, the final ammonia concentrations at both loading rates are lower than in scenario 1. At 2 and 5 kg VS m^{-3} d^{-1} the ammonia removed equates to a 81 and 63% reduction respectively relative to no intervention. On this basis the recommended ammonia removal method would be scenario 2, i.e. *in situ* mesophilic ammonia stripping by gas mixing.

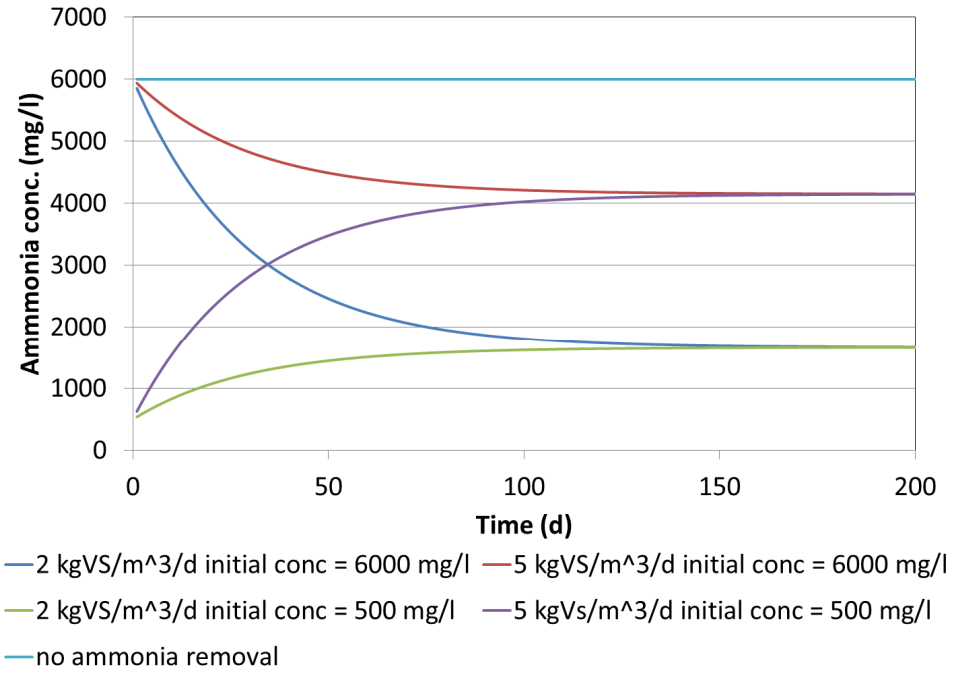


Figure 78 Simulated ammonia removal for scenario 1 – gas flow 0.375 l l^{-1} min^{-1}, 70°C, continuous stripping, working to a digester retention time of 30 days at loading rates 2 and 5 kg VS m^{-3} d^{-1} and initial ammonia concentrations of 6000 and 500 mg l^{-1} (time constant = 4 hours, see table 36)

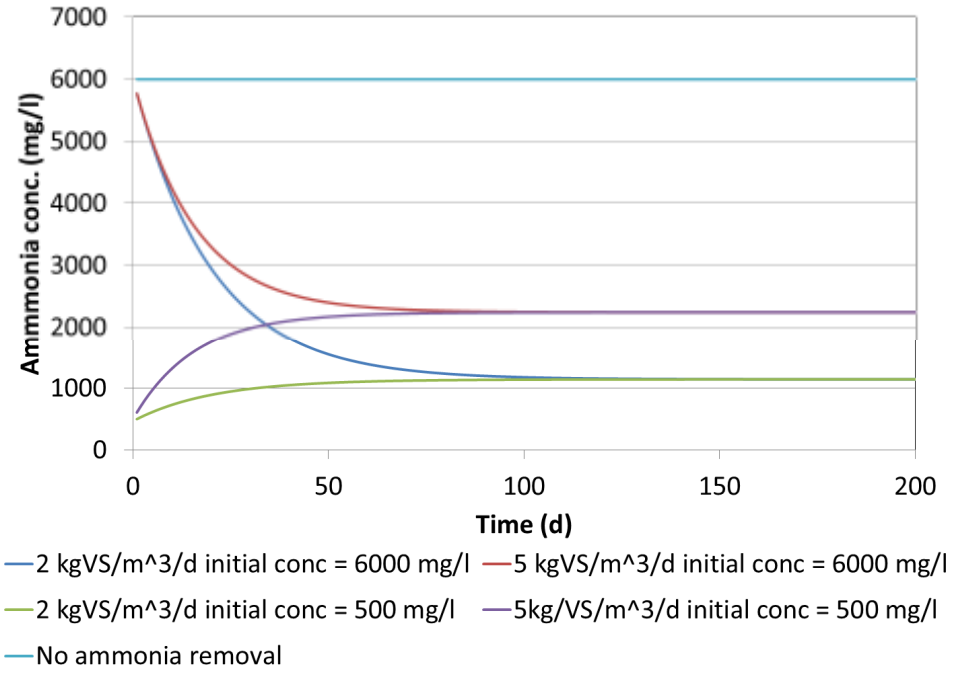


Figure 79 Simulated ammonia removal for scenario 2 – gas flow 0.375 l l^{-1} min^{-1}, 35°C, continuous stripping and gas mixing at loading rates 2 and 5 kg VS m^{-3} d^{-1} and initial ammonia concentrations of 6000 and 500 mg l^{-1} (time constant = 595 hours, see table 36)

10.2.1 Energetic considerations

It should be noted that although scenario 2 appears to be advantageous for ammonia removal during food waste digestion, this is only part of the story: energetically both scenarios have strengths and the decision on which method to use may depend on the overall energy balance.

Post-digestion stripping has the advantage of a lower gas pumping requirement since the biogas flow rate is relatively low at $1/30^{th}$ of that in the gas mixed system: this is because the volume of the pasteuriser is $1/30^{th}$ of the digester based on a 30-day digester retention time. In this scenario, however, more digestate is pasteurised than is required depending on the recycle ratio and therefore the heat use is high. This may not be a problem if there is excess waste heat on site. The situation is reversed for *in situ* ammonia removal; gas mixing energy is high, but pasteurisation will only be performed on the digestate leaving the plant so no heat is wasted.

It is clear that the situation is not so simple that one method can always be recommended. Furthermore a decision may be made based on the available plant and infrastructure, process capacity and configuration that exists at a particular facility.

10.2.2 Conclusions on modelling ammonia removal

The simulation of the ammonia concentration in a food waste anaerobic digester suggests that *in situ* mesophilic stripping combined with gas mixing will lead to the lowest in-digester ammonia concentrations. A more thorough energetic analysis is needed, however, before firm recommendations can be made, and best practice in terms of the overall energy balance may be situation specific depending mainly on the availability of waste heat.

11 Conclusions on ammonia stripping

11.1 Batch ammonia stripping

It was found that the removal of ammonia by stripping with biogas was possible and that the effectiveness depended strongly on the physical and chemical conditions at which the process was operated. Ammonia could be effectively trapped in condensate and water traps, at room temperature, and during the stripping process solutions of ammonia salts were obtained with concentrations of the order 20-35 g l^{-1} of ammonia.

The relationship of ammonia removal kinetics with the important process parameters of temperature, gas flow rate and pH was investigated in a number of batch experiments using two food waste digestate samples collected from commercial anaerobic digestion plants. The relationships followed trends which fitted the theoretical framework developed in the early stages of the project; Temperature, pH and flow rate all had a positive effect on the removal rate of ammonia; in the case of gas flow rate a threshold value was observed after which no further increase in removal rate occurred.

An exponential decay curve could be fitted to the ammonia removal data and allowed comparison of stripping experiments under different conditions and digestate samples. At 35 and 55 °C removal time constants were in the order of 600 hours, whereas at 70 °C this could be reduced to around 15-17 hours at a suitable flow rate. With pH adjustment by the addition of 10M NaOH the time constant could be further reduced to 3.9 hours at 70˚C.

High VFA concentrations were shown to have a negative impact on the ammonia removal process, in that the VFA caused the pH of the digestate to decrease during the stripping process. This appears to impose a limit on the amount of ammonia that can be removed from digestates with high VFA concentrations (~20,000 mg VFA l^{-1}) to an ammonia concentration of around 4000 mg l^{-1}. This has implications for recovery of anaerobic digestion plants where the process is already operating at these high VFA concentrations as it will limit the effectiveness of ammonia removal by stripping with biogas.

11.2 Integration of ammonia stripping with anaerobic digestion

Two semi-continuous laboratory experiments were performed to investigate aspects of the integration of ammonia stripping with an anaerobic digestion plant. Removal of ammonia in a side-stream linked to semi-continuous digesters was found to be a complex process and a more extensive programme of experimentation is needed to optimise the system, particularly in the initial stages in order to maintain the system at low ammonia concentrations.

The second experiment investigated a hydrolysis step, which could be followed by ammonia removal, and then by anaerobic digestion. It was found that without pH control this process configuration would not provide any process benefits of stability due to a

reduction in the ammonia concentrations to which the methanogens are subjected. It was shown that only a small (~15%) proportion of the bio-available ammonia was released during this stage, and there is evidence to support that hydrolysis/fermentation is being inhibited.

11.3 Modelling ammonia removal

The simulation of the ammonia concentration in a food waste anaerobic digester suggests that *in situ* mesophilic stripping combined with gas mixing will lead to the lowest in-digester ammonia concentrations. A more thorough energetic analysis is needed, however, before firm recommendations can be made, and the best practice may be situation specific depending mainly on the availability of waste heat.

12 Conclusions

- Source segregated food wastes from Luton and Hackney and those used at the Ludlow digestion plant were very similar in their physico-chemical properties.
- Selenium and cobalt are the key trace elements that are needed for the long-term stability of food waste digestion, but that are likely to be lacking in food waste. The minimum concentrations recommended for selenium and cobalt in food waste digesters at moderate organic loading rates (~2-3 kg VS m^3 day^{-1}) are around 0.16 and 0.22 mg l^{-1} respectively. A total selenium concentration greater than 1.5 mg l^{-1} is likely to be toxic to the microbial consortium in the digester. Mo, W, and Ni are present in food waste in sufficient quantities for moderate loadings, but may have to be supplemented in digestion at a high organic loading rate (~5 kg VS m^3 day^{-1}). The potential for synergistic effects involving Mo and W has yet to be clarified. Food waste has sufficient Al, B, Cu, Fe, Mn and Zn.
- Food waste digesters can be operated stably with low VFA concentrations at an organic loading rate (OLR) of 5 kg VS m^{-3} d^{-1} with a volumetric biogas production of 3.8 STP m^3 m^{-3} d^{-1} and specific biogas production of 0.76 STP m^3 kg^{-1} VS.
- Prevention of VFA accumulation in the digester by trace element supplementation is necessary, as recovery of a severely VFA-laden digester is not a rapid process even when supplements are added.
- Increases in temperature, gas flow rate and pH had a positive effect on the ammonia removal rate. In the case of gas flow rate a threshold was observed above which no further increase in removal rate occurred. At 35 and 55 °C the decay constants at the optimum flow rate were in the order of 600 hours, whereas at 70 °C this reduced to 15-17 hours. With pH adjustment the time constant could be further reduced to 3.9 hours at 70 ˚C.
- High VFA concentrations were shown to have a negative impact on ammonia removal. This has implications for recovery of anaerobic digestion plants where the process is already operating at high VFA concentrations.
- Removal of ammonia in a side-stream linked to semi-continuous digesters is a complex process and a more extensive programme of experimentation is needed to optimise the system, particularly in the initial stages in order to maintain the system

at low ammonia concentrations. The stripping process should also be used in conjunction with trace element supplementation to prevent VFA accumulation.

- Post-hydrolysis ammonia removal was found to be unfeasible without pH control as only a small proportion (~15%) of the bio-available ammonia was released.
- Simulation of the ammonia concentration in a food waste anaerobic digester suggested that *in situ* mesophilic stripping combined with gas mixing will lead to the lowest in-digester ammonia concentrations, especially at high organic loading rates. A more thorough analysis of system energy requirements is needed, however, and best practice may be situation specific depending on the availability of waste heat.

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