COOPERATION

SEVENTH FRAMEWORK PROGRAMME
THEME ENERGY.2009.3.2.2
Biowaste as feedstock for 2nd generation

VALORGAS

Project acronym: **VALORGAS**
Project full title: **Valorisation of food waste to biogas**
Grant agreement no.: **241334**

D4.5: Final recommendations for trace element and nutrient supplementation for stable operation of digesters receiving food waste

Due date of deliverable: Month 40
Actual submission date: Month 42

Project start date: 01/03/2010 Duration: 42 months

Lead contractor for this deliverable
University of Southampton (Soton)

Revision [1]

D4.5 Final recommendations for trace element and nutrient supplementation for stable operation of digesters receiving food waste

Lead contractor for this deliverable
University of Southampton (Soton)

Main contributors:
Yue Zhang, Charles Banks, Ying Jiang, Sonia Heaven (Soton) [a]
David Bolzonella (UNIVR) [b]

[a] University of Southampton, Faculty of Engineering and the Environment, Southampton SO17 1BJ, UK
[b] Dipartimento Biotecnologie, Università Degli Studi Di Verona, Strada Le Grazie 15, 37134 Verona, Italy

Acknowledgements

Some early work at Soton on trace element requirements in mesophilic digestion was carried out in conjunction with Project WR1208 'Optimising Processes for the Stable Operation of Food Waste Digestion', funded by the Department for Environment, Food and Rural Affairs (Defra), UK.

Revisions
Amendments to tabulated values and supporting explanation

Table of Contents

D4.5 Final recommendations for trace element and nutrient supplementation for stable operation of digesters receiving food waste

1 Introduction

Prior research has shown that when domestic food waste is treated by anaerobic digestion without any process intervention it will start to accumulate volatile fatty acid (VFA) (Banks et al., 2008; Banks et al., 2011; Climenhaga and Banks (2008); Neiva Correia et al., 2008; Zhang et al., 2012). The time span over which VFA accumulates occurs can be more than a year, but this will depend on a number of factors. In severe cases the accumulation of VFA will overcome the digester buffering capacity leading to process failure. Digester VFA accumulation has also been seen (intentionally) in a number of trials in the VALORGAS project (Deliverable D3.3 and D3.7). The research has shown conclusively that supplementation with selected trace elements can prevent VFA accumulation in mesophilic food waste digesters when this is linked to high ammonia concentrations. It is, however, unable to prevent VFA accumulation in thermophilic food waste digesters in similar circumstances.

2 Mesophilic food waste digestion

A hypothesis why trace element supplementation can prevent VFA accumulation were put forward at the beginning of the VALORGAS project and was subsequently reported in Banks et al (2012). The back ground to this hypothesis and evidence to support it are summarised below:

The observation is that when a digester is seeded with sludge from a municipal wastewater treatment digester and then fed food waste with a high TKN (> 7g $kg(ww)^{-1}$ then VFA accumulates after a period of months. This takes the form of an initial increase in acetic acid concentration reaching a reaching a peak which then declines. Following this there is a longer term accumulation of propionic acid which shows no decline. The time span over which these accumulations occur depends on the process loading, but typically it may be more than a year before the accumulated acids in the digester overcomes the buffering capacity causing a sharp drop in pH and causing the process to fail.

The hypothesis was: The first peak in acetic acid is a consequence of inhibition of the acetoclastic methanogens when the ammonia concentration reaches a threshold concentration (Karakashev et al., 2006; Schnurer and Nordberg, 2008). The current work indicates that this threshold is ~4.0g l^{-1} at mesophilic temperature. Even though the ammonia concentration continues to rise a decline in acetic acid concentration and its stabilisation at a low value is observed, this was thought to indicate a shift in the dominant methanogenic activity from acetoclastic to hydrogenotrophic and the oxidation of acetic acid to hydrogen and carbon dioxide to feed this pathway. There is a growing amount of evidence which indicates that the hydrogenotrophic methanogens have higher tolerance to ammonia (Angelidaki and Ahring, 1993; Hansen et al., 1998; Schnürer and Nordberg, 2008). The current work has now established that the threshold of toxicity to the hydrogenotrophic methanogens is ~8.0g l^{-1} in a urea supplemented food waste digester.
The non-reversible accumulation of propionic acid was postulated to occur because of a deficiency of selenium which is required for synthesis of the enzymes needed in syntrophic hydrogenotrophic methane production. Selenium (Se) has been reported as being important in formate oxidation because of a requirement for it in the enzyme formate dehydrogenase (Böck, 2006). An accumulation of formate, a breakdown product of propionic acid, had been reported as possibly triggering a feedback inhibition in propionic acid oxidation (Dong, 1994). There are further reports

regarding the importance of molybdenum (Mo) and tungsten (W) in these metabolic pathways and both of these trace elements were also tested.

Analysis of source segregated domestic food waste in the UK found both Selenium and Cobalt to be only present at very low concentrations (Table 1) although it both elements were typically present in inoculum taken from a municipal wastewater biosolids digestion. Both these elements would therefore be diluted out of an operational food waste digester over a period of time and only when critical concentrations are reached, and after ammonia concentrations have reached the inhibition threshold do VFA start to accumulate.

The conclusions reached in this deliverable are based on the results of batch and long-term continuous digestion trials carried out with differential supplementation of trace elements, together with assays carried out using fluorescent in-situ hybridisation (FISH), ^{14}C radiolabelling experiments, gene pyrosequencing to identify the methanogenic groups and metabolic pathways which are present in anaerobic digesters operating at high ammonia concentrations.

Results from experiments

A wide range of trace element supplements have been recommended for anaerobic digesters and a review of the requirement for these in energy crop and manure digesters is given by Demirel and Scherer, 2011. There are also a number of trace element formulations specified for the growth of methanogens in culture medium or for adding to batch tests such as the biochemical methane potential rest. Work in the VALORGAS project thus adopted a precautionary principle and added a comprehensive trace element supplement to digesters which were not specifically being used to determine the critical requirement for selected trace elements or their critical concentrations. The authors do not believe that it is necessary to dose all of these trace elements to food waste digesters, indeed the concentration of some of these elements in food waste is already far higher than that in the supplement e.g Fe. The concentration of those elements which we have found to be critical (Se and Co) have been raised in the mix to ensure oversupply, and the same is true for Ni because of its known importance in anaerobic digestion systems. In dilute out trials we have never found a requirement for iron, molybdenum, tungsten, aluminium, boron, copper, manganese or zinc when using source segregated food waste as a digester feed. But as we added this full set of trace elements to digester trials operating at very high loadings (as we had insufficient time to check individual requirements across the full range of loadings used) we are unable to eliminate the possibility that one of more of these may become important at high loading.

We are much more certain about the requirement for Selenium because we ran many experiments against appropriate controls where selenium was the only trace element added. A dilute out experiment carried out quite early on in the project (Figure 1) established the critical concentration in the digester to be 0.16 mg l^{-1}

When a food waste digester is dosed to maintain this concentration we have every reason to believe that it can function stably provided the process loading does not increase above ~3kgVS m^3d^{-1}. The experimental programme has shown, however, that at higher loadings the digesters also have a requirement for cobalt. It is still unclear why this requirement is not needed at the lower loading as the quantity of cobalt entering the digester naturally with the food waste is a constant proportion to the load, in other words the more food given the more cobalt is received. Because of this load dependent variable demand it is very difficult to establish a finite requirement and our recommendation is based on washout experiments carried out whilst Se concentrations were

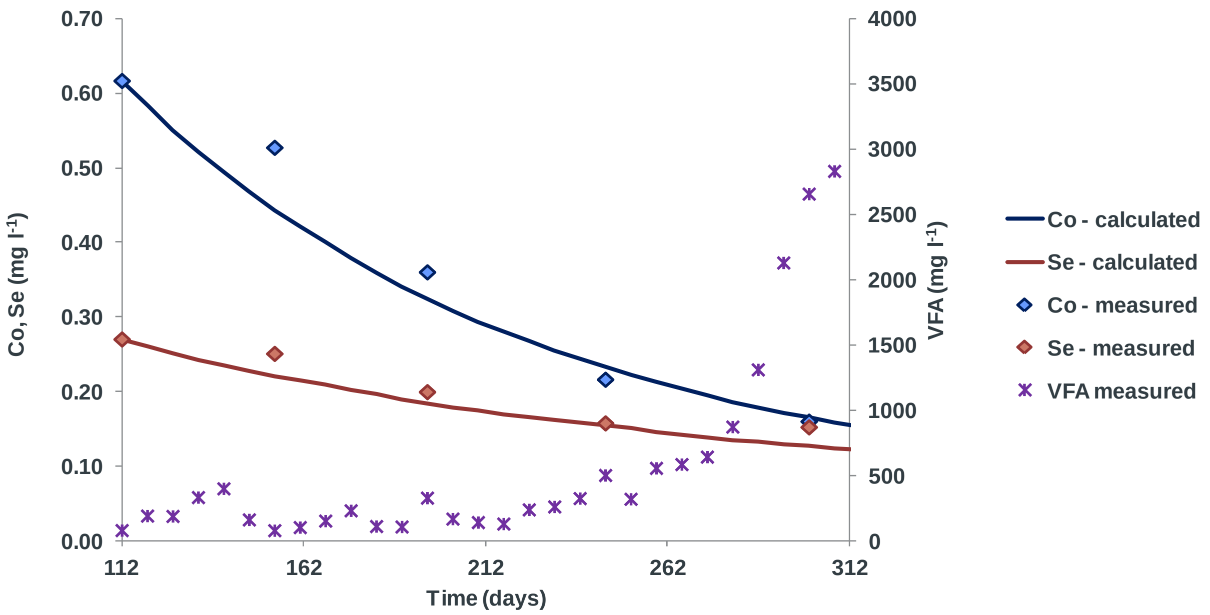

Figure 1 Cobalt and selenium dilute out curves in the pair of digesters where Se, Mo, Co, W, Fe, and Ni supplementation ceased on day 112. (By day 245 the VFA concentration in the digesters had risen above 500 mg l^{-1}.)

maintained constant until a point where VFA accumulated. We have then considered the concentration of Co that has been required to return to an equilibrium, this is considerably higher than the washout concentration. Based on these dilute/recovery experiments we believe the minimum necessary concentration of Co at a loading of 5.0 kgVS m^3d^{-1} is 0.35 mgl^{-1} in the digester

Our recommendation for the minimum trace element addition to a food waste digester where the total ammonia nitrogen concentration is likely to rise above 4.0gl^{-1} and the loading is ≥5.0kgVS m^3d^{-1} is:

Selenium	**0.2**	**mg l^{-1}**
Cobalt	**0.35**	**mg l^{-1}**

These are the concentrations required in the digestate and the base line concentrations should be established in the food waste prior to make final decisions on the dosing strategy. Because of the known proven importance of nickel in the digestion process we also recommend a minimum concentration in the digester of 1 mg l^{-1}, in our experience this concentration is usually present in food waste digestate even without supplementation (Table 2).

It should also be noted that overdosing trace elements may cause harmful effect to digesters. A total selenium concentration greater than 1.5 mg l^{-1} is likely to be toxic to the microbial community in the digesters.

We have operated mesophilic digesters at an organic loading rate of 8 kg VS m^{-3} day^{-1}, but we have not attempted to do this using Se and Co as the only supplements. Digesters fed at this loading have received a trace element supplementation as shown in Table 3

Table 1. Trace element concentrations (mg l^{-1} fresh matter) in food waste streams.

Element	Luton, UK	Hackney, UK	Ludlow, UK	Eastleigh, UK
Selenium (Se)	0.28	0.10	< 0.07	0.11
Cobalt (Co)	0.02	0.09	< 0.06	0.04
Nickel (Ni)	0.41	0.35	1.66	0.76
Molybdenum (Mo)	0.26	0.31	0.11	0.76
Tungsten (W)	0.26	0.26	< 0.24	-
Iron (Fe)	35	45	54	30
Aluminium (Al)	-	-	-	-
Boron (B)	-	-	-	-
Copper (Cu)	1.3	1.7	1.7	1.3
Manganese (Mn)	23	24	20	23
Zinc (Zn)	8.6	11.6	7.8	6.1

Table 2. Trace element concentrations (mg l^{-1} fresh matter) in food waste digestates in soton lab without trace element supplementation.

Element	Digestate 1	Digestate 2	Digestate 3	Digestate 4
Selenium (Se)	0.02	0.05	0.04	0.07
Cobalt (Co)	0.05	0.08	0.04	0.04
Nickel (Ni)	0.70	2.9	1.1	1.3
Molybdenum (Mo)	0.05	0.29	0.17	0.21
Tungsten (W)	-	< 0.04	-	-
Iron (Fe)	92	174	80	39
Aluminium (Al)	50	63	26	32
Boron (B)	3.5	2.5	2.0	2.1
Copper (Cu)	1.9	5.8	2.2	1.8
Manganese (Mn)	5.7	19	10	15
Zinc (Zn)	7.1	8.1	3.6	5.1

Table 3. Trace element supplementation used in high load mesophilic food waste digesters (N.B not all of the elements shown have been proven to be essential in this study).

Element	Compound used	Supplementation concentration (mg l^{-1})
Selenium (Se)	Na_2SeO_3	0.2
Cobalt (Co)	$CoCl_2 \cdot 6H_2O$	1
Nickel (Ni)	$NiCl_2 \cdot 6H_2O$	1
Molybdenum (Mo)	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	0.2
Tungsten (W)	$Na_2WO_4 \cdot 2H_2O$	0.2
Iron (Fe)	$FeCl_2 \cdot 4H_2O$	5
Aluminium (Al)	$AlCl_3 \cdot 6H_2O$	0.1
Boron (B)	H_3BO_3	0.1
Copper (Cu)	$CuCl_2 \cdot 2H_2O$	0.1
Manganese (Mn)	$MnCl_2 \cdot 4H_2O$	1
Zinc (Zn)	$ZnCl_2$	0.2

3 Thermophilic food waste digestion

The trace element supplementation strategies were tested on thermophilic food waste digesters, following its success in mesophilic digesters. A number of studies showed that the supplementation of trace elements could only delay to a limited extent the onset of VFA accumulation, but VFA would eventually accumulate in the thermophilic food waste digesters leading to process failure (Yirong et al. 2013a and b). Therefore, no effective trace element supplementation strategy has been identified for thermophilic conditions, and other process intervention approaches are required for stable long-term thermophilic digestion of food waste: these may include feedstock dilution using water (VALORGAS Deliverable D4.6) and ammonia stripping (VALORGAS Deliverable D3.6), both of which were demonstrated to be promising approaches according to the results obtained in the project.

References

Note: Papers marked * are outputs from the FP7 VALORGAS project

Angelidaki, I. and Ahring, B. K., 1993. Thermophilic anaerobic digestion of livestock waste: the effect of ammonia. Appl. Microbiol. Biot. 38, 560-564.

Banks C. J., Chesshire M. and Stringfellow A. (2008) A pilot-scale comparison of mesophilic and thermophilic digestion of source segregated domestic food waste. Water Science and Technology 58, 1475-1480.

Banks C. J., Chesshire M., Heaven S. and Arnold R. (2011) Anaerobic digestion of source-segregated domestic food waste: Performance assessment by mass and energy balance. Bioresource Technology 102, 612-620.

*Banks C. J., Zhang Y., Jiang Y., Heaven S. (2012) Trace element requirements for stable food waste digestion at elevated ammonia concentrations. Bioresource Technology 104, 127-135.

Böck, A. 2006. Selenium Proteins Containing Selenocysteine. Encyclopedia of Inorganic Chemistry. John Wiley & Sons, Published online: DOI: 10.1002/0470862106.ia215

Climenhaga, M.A. and Banks C.J., 2008. Anaerobic digestion of catering wastes: effect of micronutrients and retention time. Wat. Sci. Technol. 57(5), 687-692.

Demirel, B and Scherer, P. (2011) Trace element requirements of agricultural biogas digesters during biological conversion of renewable biomass to methane. Biomass and Bioenergy, 35, 992–998

Dong X., Plugge C.M. and Stams A.J.M., 1994. Anaerobic degradation of propionate by a mesophilic acetogenic bacterium in coculture and triculture with different methanogens. Appl. Environ. Microb. 60(8), 2834-2838.

*Facchin V., Cavinato C., Fatone F., Pavan P., Cecchi F., Bolzonella D., (2013). Effect of trace element supplementation on the mesophilic anaerobic digestion of foodwaste in batch trials: the influence of inoculum origin. Biochemical Engineering Journal, 70, 71-77.

Hansen, K.H., Angelidaki, I. and Ahring, B.K., 1998. Anaerobic digestion of swine manure: Inhibition by ammonia. Water Res. 32(1), 5-12.

Karakashev D., Batstone D. J., Trably E. and Angelidaki I., 2006. Acetate oxidation is the dominant methanogenic pathway from acetate in the absence of Methanosaetaceae. Appl. Environ. Microbiol. 72(7), 5138-5141.

Neiva Correia C., Vaz F. and Torres A. (2008) Anaerobic digestion of biodegradable waste – operational and stability parameters for stability control. 5th IWA International Symposium on AD of Solid Wastes & Energy Crops, Tunisia.

Schnurer, A. and Nordberg, A., 2008. Ammonia, a selective agent for methane production by syntrophic acetate oxidation at mesophilic temperature. Wat. Sci. Technol. **57**(5), 735-740.
*Yirong C., Banks, C.J. and Heaven, S. (2013a) Effect of ammonia nitrogen on thermophilic anaerobic digestion of food waste. Proceedings of the 21st EU Biomass Conference and Exhibition, Copenhagen, 3-7 June 2013.
*Yirong C., Banks, C.J. and Heaven, S. (2013b) Comparison of mesophilic and thermophilic anaerobic digestion of food waste. Proceedings of the 13th World Congress on Anaerobic Digestion, Santiago de Compostela, 25-28 June 2013.
*Zhang Y., Banks C. J. and Heaven S. (2012) Co-digestion of source segregated domestic food waste to improve process stability. Bioresource Technology 114, 168-178.