Increasing biogas quantity and quality from anaerobic digestion of wastewater sludge using nutrient supplementation

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Introduction

A key factor in reducing global CO<sub>2</sub> emissions is recovering energy from waste material. Anaerobic digestion is already the most widespread technology for treatment of wastewater sludge in the UK and is also being promoted as a key process to recover energy from organic material such as supermarket or agro-industrial wastes. The current drive to maximise energy recovery from waste means that the biogas energy from anaerobic digestion is increasingly harnessed by means of combined heat and power (CHP) technology. However, in many cases sludge digesters are still operated to ensure sludge stabilisation, rather than to maximise biogas output. One method of enhancing biogas potential is the supplementation of anaerobic digesters with small amounts of trace inorganic nutrients, e.g. nickel; cobalt; manganese; iron, which stimulate bacterial activity. Previous research on this topic suggests that targeted nutrient supplementation could enhance the methane content and volume of digestion biogas. The research that exists lacks information on the bioavailability of the added metals within the anaerobic digestion environment, without which it is impossible to quantify cause and effect. For example, addition of a certain quantity of trace metal might be recorded to increase biogas yield by a certain percentage, but if much of this metal was immediately precipitated and was hence biologically unavailable, this would not be a true relationship and could lead to expensive overdosing of digesters.

This research seeks to increase our understanding of how biosupplementation could be used to optimise the microbiological performance of anaerobic digesters, so enhancing biogas production. A key focus of the research will be furthering our understanding of the relationship between metal bioavailability in anaerobic environments and microbiological performance in anaerobic digesters. This will be achieved by a combination of laboratory anaerobic digestion experiments combined with metal fractionation analysis.

Research hypothesis

It is hypothesised that anaerobic sludge digesters supplemented with selected trace metals will produce more methane, either by producing more biogas or by producing biogas with a higher percentage of methane, primarily by stimulation of methanogenesis and possibly by stimulation of the hydrolytic and acidogenic phases. The extent of biogas enhancement is expected to be proportional to the concentration of the trace nutrient that remains bioavailable in the digester.

**Research Aims** 

• To investigate the potential of inorganic nutrient supplements to enhance energy recovery from anaerobic digestion by increasing both the quality and quantity of the biogas output.

• To further the understanding of the relationship between metal bioavailability and biogas output in digesters, to enable identification of the most bioavailable forms of nutrient supplements.

## **Specific Objectives**

- Modification of existing sequential extraction methods to enable identification of metal fractions of interest to this research, i.e. bioavailable versus unavailable fractions.
- Short-term batch anaerobic digestion studies to investigate:
  - The potential of trace nutrients (identified from literature review) to increase biogas quantity and/or quality.
  - o The potential to increase trace nutrient bioavailability (and hence biogas) by adding different chemical forms of trace elements (e.g. FeCl<sub>2</sub> versus Fe-citrate).
  - The effect/s of different levels of anions (carbonate, sulphide and phosphate) on trace nutrient bioavailability in the digesters.
  - Which biochemical stage of anaerobic digestion, i.e. hydrolysis, acidogenesis and/or methanogenesis, benefits from nutrient supplementation.
- Longer-term, continuous, bench-scale anaerobic digestion studies on those inorganic nutrients with the most practical potential to enhance biogas output, incl. methods to increase bioavailability.
- Quantification and costing of nutrient bioavailability versus biogas production and energy recovery.

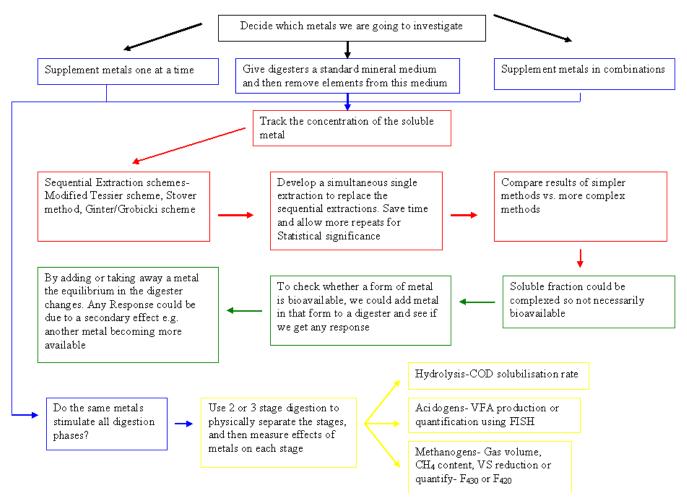
## Literature Review

Literature documenting the effecting of nutrient supplementation on anaerobic digestion is summarised in the table below:

Reference	Type of Digester	Substrate	Supplements	Bioavailability	Effect
Scherer P et al. 1983	N/A Pure cultures	№A	N∕A	Methanogenic bacteria require phosphate, carbonate and sulphide. These can cause precipitation of trace elements. This is potential source of error	Elemental composition of 10 methanogenics pecies was determined. Levels of the following trace elements found are given with lowest and highest values. Fe 750-2850ppm, Ni 65-180ppm, Co 10-120ppm, Mo 10-70ppm, Zn 50-630ppm, Cu 10-160ppm and Mn 5-25ppm.  Fe levels discovered in much greater concentrations than the other trace elements of interest.
Schonheit et al 1979	N/A Pure culture of Methanobacterium thermoautotrophicum	H₂ and CO₂	Ni, Co, Mo, Fe, Cu. Mn, Zn, Ca, Al and B		10,000nM Fe, 20nM Co, 20nM Mo and 150nM Ni required for the synthesis of 1g cells (dry weight).  A dependence of growth on Cu. Mn, Zn, Ca, Al and B could not be demonstrated
Speece RE and Parkin GF 1987*	Full-scale and laboratory investigations		Fe	If Fe is complexed with a chelator stronger than those produced by the MO's it becomes unavailable just as it's been precipitated.	Researcher collated number of studies in which Fe addition was beneficial. In all cases high concentrations of VFA's were reported to occur which, after Fe supplementation, decreased to very low levels with a concomitant increase in methane production.  Also addition of Fe as an EDTA chelate was shown to increase soluble Fe levels but yet not have a stimulatory effect.

Hoban D J and van den Berg L 1979*	Enriched mixed culture.  Municipal anaerobic sewage digesters.  Anaerobic digesters fermenting food plant wastes	Culture in a defined substrate solution with acetic acid as the sole carbon source	Fe as ferrous chloride	Large percentage of Fe was found to precipitate as carbonate. Ferrous carbonate strongly related to production of CO₂ during digestion.  Often limiting factor is found to be soluble Fe.	Initially batch reactors (serum bottles) were carried out. Addition of iron markedly increased the rate of acetic acid conversion to methane. Optimum concentrations (in respect to methane production) of Fe were 5-10 mM. Even 20mM Fe increased activity however at such high levels Fe was often slightly inhibitory for the first 2 to 4 d. Continuous-flow reactors also showed stimulatory effect of Fe. The activity was increased by 100% in municipal sewage treating digesters. Researchers experienced difficulty maintaining soluble Fe concentrations as precipitate readily as ironcarbonate.
Pfeffer J T and White J E 1964*	Continuously-fed unmixed laboratory digesters		Fe, Ca, Al	High Fe decreased soluble phosphate levels and/or supernatant had low sus pended solids i.e. Fe may have coagulated the microorganisms and prevented them from being dispersed to maintain adequate contact with SOM.	Research mainly on Fe. 5 digesters run with differing concentrations of Fe: 0, 200, 400, 600 and 800 mg/l. Iron supplementation (200 and 400) stimulated digester activity measured by VFA degradation and methane production. Whereas Digesters fed 600 and 800ml/l Fe showed a decrease in activity.  Ca and Al supplementation gave similar results. This brings up the question as to whether Fe itself is physiologically important or whether its principal function is that of precipitant and coagulant.
Jansen S <i>e</i> f al. 2007	Methanosarcina sp. enriched culture	Methanol	Ni and Co	Speciation of metals in absence of MO's studied. Ni did not precipitate, Fe and Co precip. was observed. Fe precip. more slowly and stayed at higher conc.	Methanogenic activity increased with total Co and Ni concentrations and decreased with increasing sulphides conc. Increase in activity related to increased conc. of dissolved Co as Ni stayed same after raising added conc. of both metals.
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Gonzalez-Gil G et al. 1999	Methyltrophic- methanogenic biomass. Lab s cale reactors	Mainly methanol	Nickel and Cobalt	Continuous addition of metals better than spiking. Precipitation-dissolution kinetics if metal sulphides believed to be responsible for micronutrient limitations	Three methane production rate phases recognized. 1) Exponential increase 2) temporary decrease 3) arithmetic increase. Increased Ni and Co acceleretaed phase 1 and 3 and reduced 2. Phase 2 was eliminated when Ni and Co added continuously rather than all in one go
Gonzales-Gil G <i>et al.</i> 2002	Methanosarcina sp. Culture a full-scale anaerobic reactor treating wastewater from a chemical factory that produces formaldehyde from methanol.	Medium was supplemen ted with methanol	Co and Ni	Bioavailability of these trace elements was greatly increased by the addition of yeast extract. This is due to the formation of dissolved bioavailable complexes, which favors the dissolution of metals from sulphides.	The presence of sulphides, metals seem to be limiting the rate of methanogenesis. Yeast extracts seem to overcome limitations. Ashed (inorganic fraction) yeast did not have any stimulatory effect whereas hydrolyzed yeast has stimulatory effect but it's weaker than that of intact yeast extract- organic fraction has stimulatory effect. The use of cysteine instead of sulphides as sulphur source also helped avoid metal limitations. Trace doses of yeast extract may be effective in keeping additions of essential metals to anaerobic reactors at a minimum.
Murray W D and Berg L V D1981	Fixed-film digesters	Food processing waste- bean blanching waste	Nickel, Cobalt and Molybdenum		Stimulated by the addition of 100nM Ni and 50nM Co especially when in combination. Mo only had slight effect when in combination with Ni and Co. Trace nutrients allowed accumulation of a thicker methanogenic fixed film.

## Increasing biogas using nutrient supplementation – initial experimental approach



## Acknowledgements

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