LAND & WATER FLAGSHIP
www.csiro.au

# Milestone 4 - Report

# Synthetic wastewater composition for experimentation with entrained methane

Project Reference 10TR1

M. Toifl, G.Tjandraatmadja, J. Low, T. Muster, D. Beale

October 2014

This work was funded by Smart Water Fund and carried out by CSIRO Land & Water Flagship in conjunction with Melbourne Water.

## Trials on methane extraction - Sampling, analysis and Extraction Technologies

Synthetic wastewater compositions for experimentation with entrained methane

### Authors

M. Toifl, G.Tjandraatmadja, J. Low, T. Muster, D. Beale

### Business Contact:

**Steve Spencer**
Business Development Manager, Urban Water
CSIRO Land & Water Flagship
Ecosciences Precinct
GPO Box 2583, Brisbane, QLD 4001
Tel: 07 3833 5789, Mobile: 0467 807 253
Email: steve.spencer@csiro.au

### Copyright and disclaimer

© 2014 CSIRO To the extent permitted by law, all rights are reserved and no part of this publication covered by copyright may be reproduced or copied in any form or by any means except with the written permission of CSIRO.

### Important disclaimer

CSIRO advises that the information contained in this publication comprises general statements based on scientific research. The reader is advised and needs to be aware that such information may be incomplete or unable to be used in any specific situation. No reliance or actions must therefore be made on that information without seeking prior expert professional, scientific and technical advice. To the extent permitted by law, CSIRO (including its employees and consultants) excludes all liability to any person for any consequences, including but not limited to all losses, damages, costs, expenses and any other compensation, arising directly or indirectly from using this publication (in part or in whole) and any information or material contained in it.

### Acknowledgments

The authors would like to thank Jessica Yeung, Mark Trickey and Ken Baxter of Melbourne Water for continued guidance and the provision of samples.

# Contents

Figures 4

Tables 4

Executive summary.....5

1 Introduction .....6

2 Field Sampling .....7

2.1 Western Treatment Plant (raw wastewater) .....7

2.2 Eastern Treatment Plant (high-strength wastewater) .....8

3 Literature on compositions .....9

3.1 Low solids formulation .....10

3.2 High solids formulation (ETP) .....11

3.3 Assessment of particulate characteristics .....12

4 References.....13

5 References.....14

# Figures

Figure 1. Sampling location on the membrane cover of the Lagoon 25W at the WTP on 22 May 2014.....7

# Tables

Table 1. Selected characteristics of wastewater from 25W lagoon.....7

Table 2. Selected characteristics of wastewater for anaerobic digester effluent.....8

Table 3. Summary of wastewater recipes selected for further investigation. .....10

Table 4. Characteristics of various synthetic wastewater formulations. .....10

Table 5. Final formulation to replicate low-strength (raw) wastewater.....11

Table 6. Final formulation to replicate high-strength anaerobic digester centrate.....11

Table 7. TSS and particle scattering data for real and synthetic wastewater formulations. .....12

# Executive summary

Wastewater undergoing anaerobic treatment leads to the formation of methane, which may be collected and used for beneficial use. Where dissolved or entrained methane escapes to the environment it acts as a potent greenhouse gas.

There is a need to develop technologies to better manage the recovery of dissolved methane from wastewater as amounts released post-anaerobic digestion can be significant. The ability to develop such technologies would benefit from the design of synthetic wastewaters that can be used safely (avoiding the presence of microbial and pathogenic activity).

These wastewaters were designed to be free of organics and volatile substances, such that they remain stable over time, do not lead to unnecessary biofouling and can potentially be re-used with minor adjustment.

This report provides detail on the composition of both low-strength wastewaters, replicating raw wastewater processed in a lagoon, and a high-strength wastewater bearing resemblance to digested sludge from an anaerobic digester treating a mixture of thickened primary and secondary sludge.

Some uncertainty remains on the importance of methane adsorption onto suspended solids within the wastewater. Future experimental work will provide additional understanding on whether the proposed inert material (i.e. kaolin clay) has sufficient properties to replicate methane behaviour in practice.

# 1 Introduction

Melbourne Water's Western Treatment Plant (WTP) treats raw wastewater in large anaerobic lagoons (pots) and the Eastern Treatment Plant (ETP) treats primary and secondary sewage sludge in mesophilic anaerobic digesters. Methane produced during anaerobic treatment is captured and utilised for energy generation at both facilities. Previous sampling has showed that entrained methane concentration increases towards the exit of the lagoons at WTP and also with depth. There are financial and environmental incentives for developing technologies to enable this entrained methane to be captured more efficiently to both increase energy production, and to decrease greenhouse gas emissions to the environment.

**The primary objective of this work was to develop an appropriate synthetic solution that would effectively replicate both ETP and WTP anaerobic wastewaters to enable experimental studies on the extraction of methane from wastewater.**

Key parameters of WTP and ETP were provided by Melbourne Water. Additional assessments were carried out to investigate the total suspended solids (TSS) concentration and particle size characteristics of the individual wastewaters. Previous studies have demonstrated that microbes can generate supersaturated methane concentrations in wastewater under anaerobic conditions (Hartley and Lant, 2006; Souza et al., 2010). It follows that the retention of methane within wastewater compositions is thought to be a combination of gas contained within microbial cells (entrained methane) and that adsorbed to available surface area (Moraveji et al., 2013). The gas contained within microbial cells is not expected to be readily released upon the application of mild vacuum, agitation or sparging. Rather, these methods are thought to encourage physically adsorbed methane content to be released. In that case of physical adsorption, methane is thought to bind in an inert manner to a material within the wastewater. The composition of wastewater is complex due to it containing a range of organic and inorganic materials. Some experimental studies exist whereby the addition of solids to water has demonstrated increased methane solubility. For example, β-cyclodextrin, which presents both hydrophilic and hydrophobic characteristics have been explored for their ability to absorb methane (Mohammadi et al., 2011). The additional of the hydrophobic component only led to improved solubilities of around 10%. In other work, copper oxide nanoparticles added to water effectively doubled methane solubility (Moraveji et al., 2013). Heller and Zoback (2014) most recently showed that carbonaceous materials and clay materials exhibited high capacities for methane adsorption.

# 2 Field Sampling

## 2.1 Western Treatment Plant (raw wastewater)

Table 1 provides historical concentration ranges for influent into the WTP, along with recently determined wastewater characteristics in various parts of the 25W anaerobic lagoon (Tjandraatmadja et al 2014). Figure 1 provides a visual map of the location of location M, pond outlet and pumping station.

**Table 1. Selected characteristics of wastewater from 25W anaerobic lagoon.**

| Parameter | Historical range for 25W lagoon (Aug 2011 – Aug 2014)* | Location M (20m upstream of exit from cover) | Pond outlet | Pumping station |
|---|---|---|---|---|
| **COD** | 240-1100 | 2700 | 3900 | 2000 |
| **TKN** | 79±16 | 76.5 | 94 | 83 |
| **TP** | 13±3 | 13.5 | 18 | 16 |
| **SS** | 54-1,200 | 375 | 1950 | 295 |
| **VSS** | 84-1,200 | 285 | 920 | 225 |
| **TDS** | 590-1,200 | 820 | 710 | 740 |
| **TS** | 36-2,600 | 1500 | 2700 | 1400 |
| **Methane** | | 11.4 | 12.8 | 9.7 |

Note: *Historical data sourced from (Melbourne Water 2013, Tjandraatmadja et al., 2009); Location M, Pond outlet and pumping station were recent measurements reported in Tjandraatmadja et al., 2014)


**Figure 1. Sampling location on the membrane cover of the Lagoon 25W at the WTP on 22 May 2014.**

## 2.2 Eastern Treatment Plant (high-strength wastewater)

The Eastern Treatment Plant (ETP) operates eight anaerobic digesters, each having a volume of approximately 8000 $m^3$. The feed is comprised of 70-80 t (dry solids)/day primary sludge and 75 t (dry solids)/day waste activated sludge (WAS). The combined solids content is 5 wt% upon input into the digester. After treatment this is reduced to 2.4 wt%. The WAS starts at 0.9 wt %, which is thickened using dissolved air flotation (DAF) to 3.5-4 wt% solids. The primary sludge starts off at 4 wt% and gravity belt thickeners take it to 8 wt%. Organic loading is 3.5 kg/$m^3$/hr and temperature (held at approximately 37°C using heat exchangers in series with recirculating lines). The pH is measured regularly and is typically in the range of 6.0 – 7.9 (Melbourne Water, 2013). Table 2 provides additional wastewater concentrations of organic and inorganic components of digester effluent.

**Table 2. Selected characteristics of wastewater for anaerobic digester effluent.**

| Parameter | Anaerobic digester (ETP) [#1] | Anaerobic digester (ETP) [#2] | Digester Sludge [$] |
|---|---|---|---|
| **COD (mg/L)** | 26000 | 5450 | |
| **TDS (mg/L)** | | 3500 | 3500-4690 |
| **TS (mg/L)** | 210 | | |
| **Conductivity (µS/cm)** | | | |
| **Chloride (mg/L)** | | 120 | |
| **Calcium (mg/L)** | | 380 | |
| **Magnesium (mg/L)** | | 200 | |
| **Potassium (mg/L)** | | 50 | |
| **Sodium (mg/L)** | | 150 | |
| **pH** | | 6.0 – 7.9* | 6.3-6.5 |

[#] Analysis of ETP sludge collected on 18 Feb. 2014([#1]) and on 27 Nov.2013 ([#2]); *pH from historic records, Melbourne Water; [$] Additional data from Melbourne's domestic wastewater (Tjandraatmadja et al 2009).

# 3 Literature on compositions

In developing a synthetic solution to explore the extraction of methane from wastewater, desirable properties of the composition are:

- Ionic strength, salt and conductivity matching: salting out (i.e. release of methane) is encouraged at increased salt concentration. The pH of the solution can also influence the ionic strength, so should also be kept
- The use of non-volatile components: the incorporation of nitrogen the form of ammonia, for example, will lead to gaseous losses and an inability to store and/or re-use the synthetic wastewater.
- No biologically degradable contents: due to their ability to degrade and promote biological growth during storage and operation.
- Solids matching: the solids component of the wastewater should be matched in order that the available area for potential binding between methane and solid surfaces. This matching will be crude at most as solid surface area will be highly variable in practice.
- The composition should be made up of commonly available and if possible, affordable starting materials.

There are several literature formulations for synthetic wastewater. O'Flaherty and Gray (2013) provided a comparative analysis of the characteristics of a range of real and synthetic wastewaters. They found that the major discrepancies between synthetic and real wastewaters was in balancing BOD, COD and the ratio C:N:P. These differences mainly arise due to the specific way that the synthetic wastewater would be utilised. The vast majority of formulations that try to replicate the wastewater as a media for biological activity, and as such, make use of cheap organic substrates such as acetate, glucose, glycerol, yeast extract, milk products and beer to provide a suitable carbon source (i.e. ASTM D5905-98). Such formulations also try to ensure no deficiencies in micronutrients and as such, have a complex mixture of chemicals (Boeije et al., 1999). Inorganic materials are typically added as salts in specified quantities to balance nitrogen and phosphorus levels, along with pH, conductivity and alkalinity. Of the formulations covered by O'Flaherty and Gray (2013), solids (as measured by total suspended solids) were not consistently matched, varying from 5 mg/L up to 352 mg/L. Increased solids were achieved through the precipitation of multivalent cations (i.e. Ca, Mg, Al, Fe, Mn etc) with carbonates, phosphates and silicates, or, through the addition of inert filler materials such as diatomaceous earth, clay or fibres.

As mentioned above, one of the key characteristics in developing synthetic wastewater composition for methane extraction studies is to ensure that the solution will remain relatively unchanged and not degrade or react over time. As such, any of the literature compositions containing volatile components (i.e. milk, beer, ammonia etc.) were not favoured for their ongoing use in this work. The incorporation of these components would mean that the formulation could not be reused and would also lead to an increased chance of biofilm growth on the inside of the laboratory equipment, resulting in longer-term experimental complications.

Four compositions were chosen based upon the avoidance of volatiles, simplicity of their recipe, and scale of usage, as summarised in Table 3. The CSIRO recipe was a synthetic formulation used in non-related studies that was developed to investigate physical treatment methods (electrodialysis) for treated wastewater (Taylor, 2007).

**Table 3. Summary of wastewater recipes selected for further investigation.**

| Recipe base | Components | Advantages | Disadvantages |
|---|---|---|---|
| **Stasinakis (Stasinakis et al. 2003)** | Acetic acid, $NH_4Cl$, $K_2HPO_4$, $KH_2PO_4$ | Simple recipe | Contains acetic acid as a microbial food source. Contains ammonia as a volatile species. |
| **Tsang (Tsang et al. 2008)** | Glucose, $NH_4Cl$, $KH_2PO_4$ | Simple recipe | Contains glucose as a microbial food source. Contains ammonia as a volatile species. |
| **Lim (Lim et al., 2012)** | $NaHCO_3$, $(NH_4)_2SO_4$, $K_2H_2PO_4$, $KH_2PO_4$, yeast extract, $FeCl_3$, bactopeptone, Glucose, $MgSO_4$, NaCl, $CaCl_2$ | Sophisticated composition proven to enable microbial reactor to operate for over 3 months | Complex formulation |
| **CSIRO (Taylor, 2007)** | $NaHCO_3$, KCl, $MgCl_2$, $Ca(OH)_2$, NaCl | Simple recipe. No volatile components. | |

# 3 Conclusions and recommendations

## 3.1 Low solids formulation

Four solutions were initially prepared according to the formulations of Stasinakis et al. (2003), Tsang et al. (2008), Lim et al. (2012) and Taylor (2007). Analytical Grade Reagents were used in all preparations and determinations of pH, conductivity and total dissolved solids (TDS) were made for each preparation. Table 4 provides a summary of the desired range and those of the synthetic formulations.

**Table 4. Characteristics of various synthetic wastewater formulations.**

| | Desired range | Synthetic formulations | | | | |
|---|---|---|---|---|---|---|
| | | Tsang | Stasinakis | Lim | CSIRO | CSIRO Modified |
| pH | 6.0 – 7.9 | 6.39 | 4.4 | 7.56 | 9.33 | 8.16 |
| Conductivity (µS/cm) | 1200 – 2500 | 430 | - | 6000 | 954 | 2531 |
| TDS (mg/L) | 850 - 990 | 299 | - | 3912 | 620 | 823 |

The recipes based upon Stasinakis and Lim appeared to be unbalanced with regards to the desired ranges, whereas the formulations by Tsang et al. (2008) and Taylor (2007) were both found to have low conductivity and solids. It was therefore necessary to modify the initial formulations in order to match the synthetic wastewater properties. The CSIRO-base recipe of Taylor (2007) was chosen as a starting point, and the addition of $Ca(OH)_2$ was replaced with $CaCO_3$ with the thought to decrease the pH, and the amount of NaCl increased to increase electrical conductivity.  It was deemed important to ensure that conductivity was closely matched to the higher levels as the increased salt is known to 'salt out' methane from aqueous solutions (Serra et al., 2006).  The pH of the modified solution was slightly higher than that desired, however, with a molar concentration of Na ions exceeding 0.2 M, the small contribution of hydroxyl ions at pH 8.16 (i.e. approx $10^{-6}$) is negligible to influence salting out.  The final formulation is described in Table 5, which also shows that the addition of 0.38 g/L of Unimin clay provides sufficient replication of total suspended solids, as will be described in the section 3.3.

Unimin clay is Kaolin-rich was chosen based upon its prior use in developing a synthetic grey water solution (Diaper et al., 2005).  The clay is screened to possess a particle size <38 µm; it is inert, has a neutral pH (6.9) and modest surface area (26.2 $m^2/g$).  It has a reasonable specific gravity of 2.67 $g/cm^3$ which results in settling over modest timeframes (i.e. > 20 minutes).

**Table 5. Final formulation to replicate raw wastewater (WTP).**

| Chemical | Amount (g/L) |
|---|---|
| **$NaHCO_3$** | 0.2938 |
| **KCl** | 0.0593 |
| **$MgCl_2$** | 0.1015 |
| **NaCl** | 0.4510 |
| **$CaCO_3$** | 0.0813 |
| **Unimin clay** | 0.380 |

## 3.2 High solids formulation (ETP)

The high solids synthetic wastewater composition was based upon that used for low solids with two notable exceptions, magnesium and calcium salts are more prolific than sodium due to fact that it is a sludge stream, and secondly, the addition of a small amount of sulphuric acid was necessary to bring the formulation back down to the required pH level.

The initial formulation was developed in order to match a TDS of 3500 mg/L.  In matching total solids more closely, it was suggested that an extra addition of unimin clay was required in order to bring solids levels of the synthetic wastewater up to those of the real wastewater sample.

**Table 6. Final formulation to replicate high-strength anaerobic digester effluent.**

| Chemical | Formula 1 (g/L) | Formula 2 (preferred) (g/L) |
|---|---|---|
| **$NaHCO_3$** | 0.54 | 0.54 |
| **KCl** | 0.095 | 0.095 |
| **$MgCl_2$** | 0.1 | 0.1 |
| **$Mg(OH)_2$** | 0.42 | 0.42 |
| **$CaCO_3$** | 0.95 | 0.95 |
| **$H_2SO_4$ (mL)** | 0.2 | 0.2 |
| **Unimin clay** | 1 | 18 |

## 3.3 Assessment of particulate characteristics

The available area for physical adsorption of gases onto surfaces is hypothesized to influence the behaviour of methane in wastewater, however the extent to which this may influence practical application is not clear. As such, both the total suspended solids (TSS), light scattering intensity (reported as megacounts per second) and mean effective particulate diameter were assessed for both real and synthetic wastewater formulations. The characterisations are provided in Table 7.

TSS for both WTP and ETP were assessed by filtering and weighing the mass of a 0.45 µm Millipore filter paper; then filtering a known volume of wastewater, followed by evaluation of the dried sample mass at 110°C.

Light scattering studies were performed using a Brookhaven 90Plus dynamic light scattering instrument. Solutions were diluted with Millipore water and characterised in the scattering intensity range of 0.6 to 1.3 megacounts per second. The mean effective diameter and mean half-width was utilised to provide an understanding of the average size and size range of suspended solids in wastewater. The scattering intensity provided a means to match the suspended solids contents of the synthetic wastewater to those from ETP and WTP. This led to the preferred formulations of synthetic wastewater listed in Table 5 and Table 6.

**Table 7. TSS and particle scattering data for real and synthetic wastewater formulations.**

| Wastewater | Classification | TSS (mg/L) | Dilution | Scattering intensity (Mcps) | Mean effective diameter (nm) | Mean half-width (nm) | Age of sample |
|---|---|---|---|---|---|---|---|
| **WTP** | Low solids | 394 (300-2000) | 3:1 | 0.92 | 1543 | 946 | 1 week |
| **ETP** | High solids | 23450 | 110:1 | 1.3 | 5387 | 3382 | 1 week |
| **Synthetic** | Low solids | | 1:1 | 0.62 | 4361 | 3092 | 6 weeks |
| **Synthetic** | Low solids | 1363 | 3:1 (with unimin clay) | 0.87 | 4183 | 2745 | 6 weeks |
| **Synthetic** | High solids | 1606 | 20:1 | 1.2 | 4180 | 1866 | 6 weeks |
| **Synthetic** | High solids | 18000 | 110:1 (with additional unimin clay) | 1.3 | 2353 | 478 | 6 weeks, with fresh clay added |

The particle size of unimin clay, when dispersed effectively provides a mean effective diameter of approximately 2300 nm, however, when solutions are aged with time this diameter can increase (see difference between synthetic high solids samples).

The importance of matching particle surface areas, and also the choice of particles may need to be considered in more detail once further bench-scale testing done.

# 4 Conclusions

- There are numerous synthetic formulations that have been previously made to replicate wastewater. The large majority of these are tailored towards providing suitable substrates for biological activity.
- A synthetic wastewater formulation has been developed to explore the dissolution and extraction of methane. This composition is made such that it has good storage life, replicates the conductivity and dissolved solids content of real wastewater, and finally, attempts to match total suspended solids concentrations and range of particle sizes of these solids.
- Soon to be conducted experimental investigations will provide further understanding of the importance of suspended solids on the retention of methane within wastewater.

# 5 References


ASTM D5905-98 (2013) Standard practice for the preparation of substitute wastewater.

Boeije, G., Corstanje, R., Rottiers, A., Schowanek, D. (1999) Adaptation of the CAS test system and synthetic sewage for biological nutrient removal: Part I: development of a new synthetic sewage. Chemosphere 38(4), 699–709.

Diaper, C., Toifl, M., Storey, M. (2008) Greywater testing protocol. CSIRO Water for a Healthy Country report for Smart Water Fund.

Hartley, K., Lant, P. (2006) Eliminating non-renewable $CO_2$ emissions from sewage treatment: an anaerobic migrating bed reactor pilot plant study. Biotechnology and Bioengineering, 95(3), 384-398.

Heller, R., Zoback, M. (2014) Adsorption of methane and carbon dioxide on gas shale and pure mineral samples. Journal of Unconventional Oil and Gas Resources, 8, 14-24.

Lim S, Kim S, Yeon K-M, Sang B-I, Chun J, Lee C-H (2012) Correlation between microbial community structure and biofouling in a laboratory scale membrane bioreactor with synthetic wastewater. Desalination, 287, 209–215.

Melbourne Water (2013), Wade Mosse. Personal communication, September 2013.

Melbourne Water (2013), David Gregory, Mukundan Devadas, Deepak Joshi, October, 2013.

Mohammadi, A., Manteghian, M., Mirzaei, M. (2011) Effect of β-cyclodextrin on dissolution of methane in water. Chemical Engineering Research and Design, 89, 421-427.

Moraveji, M.K., Golkaram, M., Davarnejad, R. (2013) Effect of CuO nanoparticle on dissolution of methane in water. Journal of Molecular Liquids, 180, 45-50.

O'Flaherty, E., Gray, N.F. (2013) A comparative analysis of the characteristics of a range of real and synthetic wastewaters. Environmental Science and Pollution Research, 20, 8813-8830.

Serra, M.C.C., Pessoa, F.L.P., Palavra, A.M.F. (2006) Solubility of methane in water and in a medium for the cultivation of methanotrophs bacteria. J. Chem. Thermodynamics, 38, 1629-1633.

Souza, C.L., Chernicharo, C.A.L., Aquino, S.F. (2011) Quantification of dissolved methane in UASB reactor treating domestic wastewater under different operating conditions, 64(11), 2259-2264.

Stasinakis, A.S., Thomaidis, N.S., Mamais, D., Papanikolaou, E.C., Tsakon, A., Lekkas, T.D. (2003) Effects of chromium (VI) addition on the activated sludge process. Water Res., 37(9), 2140–2148.

Taylor, R., Goodman, N. (2007) CSIRO internal report. Work carried out within Smart Water Fund: Pilot plant demonstration of effluent desalination by electrodialysis at the Western Treatment Plant, Werribee.

Tjandraatmadja, G., Pollard, C., Gozukara, Y., Sheedy, C. (2009) Characterisation of priority contaminants in residential wastewater, CSIRO. Water for a Healthy Country National Flagship, http://www.clw.csiro.au/publications/waterforahealthycountry/2009/wfhc-characterisation-priority-contaminants-wastewater.pdf.

Tjandraatmadja, G., Beale, D., Goodman, N., Toifl, M., Marney, D. (2014) Trials on methane extraction - Sampling, analysis and Extraction Technologies, Method for sampling and analysis of dissolved methane in wastewater, CSIRO and Smart Water Fund.

Tsang, Y.F., Sin, S.N., Chua, H. (2008) Nocardia foaming control in activated sludge process treating domestic wastewater. Bioresource Technol., 99(9),3381–3388.

Yamamoto, S., Alcauskas, J.B., Crozier, T.E. (1976) Solubility of methane in distilled water and seawater. J. Chem. Eng. Data, 21(1), 78-80.

CONTACT US

**t** 1300 363 400
+61 3 9545 2176
**e** enquiries@csiro.au
**w** www.csiro.au

YOUR CSIRO

Australia is founding its future on science and innovation. Its national science agency, CSIRO, is a powerhouse of ideas, technologies and skills for building prosperity, growth, health and sustainability. It serves governments, industries, business and communities across the nation.

FOR FURTHER INFORMATION

**Dr Tim Muster**
**CSIRO Land and Water Flagship**
Gate 5 Normanby Road
Clayton Vic 3168
**t** +03 9545 7964
**e** tim.muster@csiro.au
http://www.csiro.au/people/tim.muster.html