UNIVERSITY OF SOUTHAMPTON

FACULTY OF ENGINEERING AND PHYSICAL SCIENCES

THE IMPACT OF NITROGEN CONTROL STRATEGIES AND OF BIOPACKAGING DEGRADATION ON THE IMPLEMENTATION OF THE ANAEROBIC DIGESTION OF SELECTED MSW FRACTIONS

by

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ABSTRACT
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Anaerobic digestion (AD) offers a sustainable route to resource recovery from management of municipal solid waste (MSW) in the form of biogas as a renewable fuel and digestate as source of plant nutrients. The thesis presents set of papers describing work carried out to investigate some specific issues in AD of some selected fraction of the municipal solid waste stream, such as source segregated food waste (SSFW), compostable bioplastics present in SSFW streams and residual MSW. Highlights include:

The first long-term comparative study of thermophilic and mesophilic digestion of source segregated domestic food waste in a parallel trial supported by compositional analysis and stability and performance data, which identifies the ammonia inhibition thresholds in these conditions.

The first demonstration of stable thermophilic operation with an undiluted SSFW substrate, using biogas stripping to control digestate ammonia concentrations below the inhibitory threshold.

The first reported study on co-digestion of FW and card packaging with a range of compostable bioplastics. The results provide performance data and indicate that plastics degradation performance may be less good than expected. The study is also the first to note that the physical operating parameters of the digester may influence the retention time of plastic materials, and to highlight the potential effects of plastic density (floating and sinking).

The first reported study on residual MSW degradation with feed addition and removal designed to simulate practice in a commercial AD plant that is facing the issue of low OLR. The addition of sewage sludge digestate as a co-substrate provided a novel and effective solution.

Keywords: Anaerobic digestion; source segregated domestic food waste; ammonia inhibition; side-stream stripping; compostable bioplastics; residual municipal solid waste

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1. Yirong, C., Zhang, W., Heaven, S. and Banks, C. J. (2017). Influence of ammonia in the anaerobic digestion of food waste. *Journal of Environmental Chemical Engineering 5*(5): 5131-5142.

2. Zhang, W., Heaven, S. and Banks, C. J. (2017). Continuous operation of thermophilic food waste digestion with side-stream ammonia stripping. *Bioresource Technology* 244(Pt 1): 611-620.

3. Zhang, W., Heaven, S. and Banks, C. J. (2017). Thermophilic Digestion of Food Waste by Dilution: Ammonia Limit Values and Energy Considerations. *Energy & Fuels* 31(10): 10890-10900.

4. Zhang, W., Heaven, S. and Banks, C. J. (2018). Degradation of some EN13432 compliant plastics in simulated mesophilic anaerobic digestion of food waste. *Polymer Degradation and Stability* 147: 76-88.

5. Zhang, W., Torrella, F., Banks, C. J. and Heaven, S. (2019). Data related to anaerobic digestion of bioplastics: Images and properties of digested bioplastics and digestate, synthetic food waste recipe and packaging information. *Data in Brief* 25: 103990.

6. Zhang W., Venetsaneas N., Heaven S. and Banks C. J. (2020) Impact of low loading on digestion of the mechanically-separated organic fraction of municipal waste. *Waste Management* 107 (2020) 101-102

ABBREVIATIONS

AD	Anaerobic digestion
BMP	Biochemical methane potential
FAN	Free ammonia nitrogen
FW	Food waste
HRT	Hydraulic retention time
GHG	Greenhouse gas
MS-OFMSW	Mechanically separated organic fraction of municipal waste
MSW	Municipal solid waste
OFMSW	Organic fraction of municipal solid waste
OLR	Organic loading rate
PAS 110	Publicly available specification 110
PTE	Potential toxic element
SSFW	Source segregated food waste
TAN	Total ammonia nitrogen
VFA	Total ammonia nitrogen
VS	Volatile solids

DECLARATION OF AUTHORSHIP

I, Wei Zhang declare that this thesis and the work presented in it is my own and has been generated by me as the result of my own original research.
The Impact of Nitrogen Control Strategies and Biodegradable Biopolymers Degradation on the Implementation of the Anaerobic Digestion of Selected MSW Fractions

I confirm that:

- This work was done wholly or mainly while in candidature for a research degree at this University;
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- Where I have consulted the published work of others, this is always clearly attributed;
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- I have acknowledged all main sources of help;
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  Yirong, C., Zhang, W., Heaven, S. and Banks, C. J. (2017). Influence of ammonia in the anaerobic digestion of food waste. *Journal of Environmental Chemical Engineering 5*(5): 5131-5142.

  Zhang, W., Heaven, S. and Banks, C. J. (2017). Continuous operation of thermophilic food waste digestion with side-stream ammonia stripping. *Bioresource Technology* 244(Pt 1): 611-620.

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Signature:
Date:

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COMMENTARY

1. Introduction

With the growth of population and rise in average living standards over the world, this is a period of unprecedented human impact on our planet. Issues include climate change, biodiversity loss and contamination of the environment from the consumption of goods and energy as well as the generated waste products and pollutants. In the UK, for example, the average amount of municipal solid waste (MSW) generated per person was calculated as 468 kg per year in 2017. This has dropped slightly since 2008 when it was 541 kg per person-year (Eurostat 2019); however, the population of the United Kingdom is growing steadily and is expected to exceed 70 million by 2026 (Statistics 2017). The total amount of waste generated has therefore not fallen significantly, and this exerts high pressure on the landfill capacity, which was historically the conventional method of municipal solid waste treatment (Sosnowski, Wieczorek et al. 2003).

The European Union is the major source of environmental legislation and guidance in relation to waste management in the UK. The Landfill Directive (1999/31/EC) is the main item of European legislation that UK waste policy has to meet, and it requires that the amount of biodegradable municipal solid waste sent to landfill in the UK to be reduced to 35% of 1995 levels by 2020 (Bioenergy 2018). Methane emission from landfill have been defined as a major source of greenhouse gas (GHG) (IPCC 1996). Development of alternative sustainable methods of municipal solid waste management is therefore of high importance. On the other hand, growing awareness of need for more sustainable use of resources has driven a more circular economy to the top of the agenda, in which materials and energy are recovered and returned to the cycle of utility rather than becoming waste. A Clean Growth strategy (BEIS,2017) has been set out by the UK government to help protect the climate and environment upon which we and our future generations depend (Government 2018). The Strategy includes measures such as recycling, composting, valorisation or energy recovery.

In 2009 the UK Government published a renewable energy (RE) strategy, which recognises that the biodegradable fraction of waste is a renewable resource for generating energy (Bioenergy 2018). Waste-to-energy technologies utilise three main pathways: thermochemical, physicochemical and biochemical processes, as shown in Fig. 1.1 (Ouda, Raza et al. 2016). Anaerobic digestion is often considered a more sustainable route to resource recovery than other

waste treatment technologies, particularly when dealing with high moisture content materials (McKendry 2002). It normally offers a net energy gain, as the parasitic energy requirements are lower than the energy value contained in the biogas produced (Burnley, Phillips et al. 2011). It has therefore been used for a number of years for treatment and recovery of energy and nutrients from a wide range of waste resources (Digman and Kim 2008).

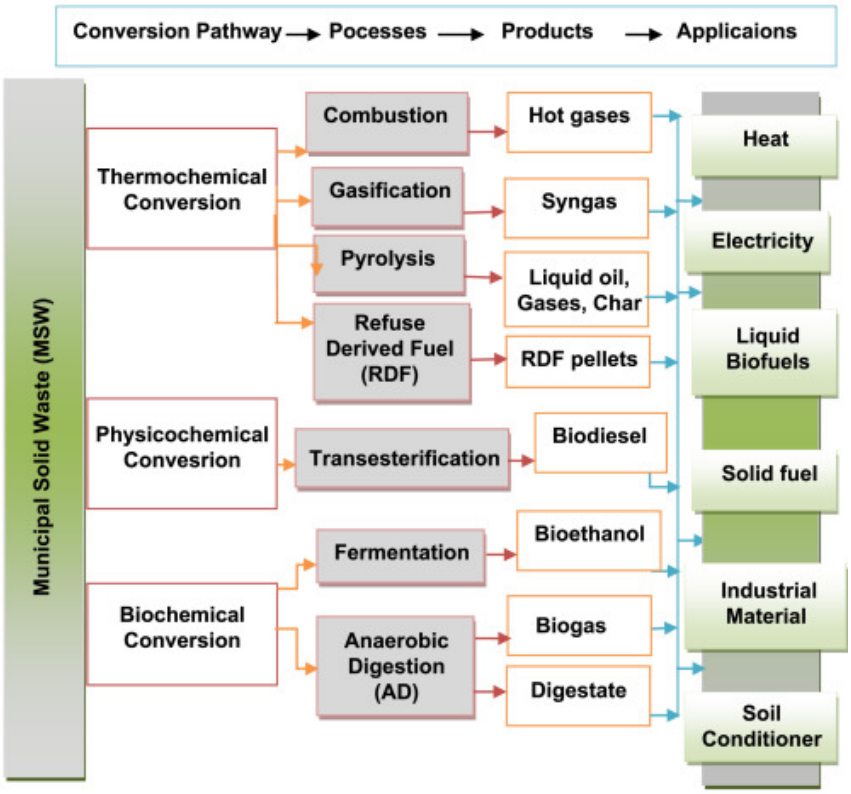

Fig. 1.1 Waste to energy technologies based conversion process (Ouda, Raza et al. 2016)

Municipal solid waste is defined as household waste collected by local authorities, and waste from businesses which has a composition similar to household waste (Bioenergy 2018). In the U.S., food waste is estimated to make up 15% or more of the municipal waste stream (Thyberg, Tonjes et al. 2015), while in European countries this figure is typically 20−25%, and in China the proportion may be as high as 50% (Zhang, Su et al. 2014). This material is therefore available in substantial quantities. If handled improperly it can cause a range of adverse environmental impacts, from greenhouse gas (GHG) emissions to groundwater pollution; and can also lead to transmission of diseases either by director microbial contamination or by encouraging encourage insect and rodent vectors. On the other hand, if properly treated it represents a valuable source of plant nutrients, and a potential substrate for bioenergy recovery and/or bio-refinery processes. Thus, the treatment of organic wastes such as food waste has a major role to play in waste management and subsequent recovery of energy and resources.

Anaerobic digestion is an effective technology for recovering value from food wastes in the form of biogas as a renewable fuel and nutrients for recycling back to agriculture. Digestion of source segregated domestic food waste is now a popular approach in many areas of the world (Bernstad, Malmquist et al. 2013, Deng, Liu et al. 2017), with almost 100 plants in the UK alone contributing 250 MW to the electricity grid in 2016 (ADBA 2016). The UK was one of the first countries to focus on this material, but the path to commercialization was not entirely smooth. One of the major problems initially encountered was high ammonia concentrations in the digester that could lead to inhibition and ultimately failure of the process. The problem of inhibition arises because most domestic food wastes have a relatively high content of proteinaceous material, which on hydrolysis may lead to elevated concentrations of total ammonia nitrogen (TAN). Solutions to this problem are needed for all high nitrogen wastes and are particularly critical for digestion in thermophilic conditions, where toxicity thresholds are lower but there may be other potential gains in terms of more rapid processing, greater solids degradation or avoidance of the need for additional pasteurisation and sanitisation steps.

This thesis consists of a set of published papers on the topic of the anaerobic biological treatment of organic fractions of municipal waste. The work was carried out as part of a series of distinct projects and covers a number of different aspects but is linked by some common themes, as outlined in this commentary.

2. Coherence between materials

The work presented in the five published papers (including one data article) and one submitted manuscript covers some different but related aspects of the effective treatment and recovery of value from MSW via the anaerobic digestion process.

Three of the papers (Yirong, Zhang et al. 2017; Zhang, Heaven et al. 2017; Zhang, Heaven et al. 2017) consider SSFW as a fraction of the municipal waste stream, with a specific focus on the effects of ammonia nitrogen on digestion performance and stability. The main purpose of the work presented in Yirong, Zhang et al. (2017) was to investigate ammonia toxicity in both mesophilic and thermophilic conditions and to establish a limit of ammonia toxicity in thermophilic conditions. The work presented in Zhang, Heaven et al. (2017) tested the effect of dilution of the substrate with water to mitigate the inhibition caused by high TAN concentrations. It allowed the determination of critical threshold concentrations for TAN, and for free ammonia

nitrogen (FAN) by calculation, and monitoring of the pattern of volatile fatty acid (VFA) production; it was also used as the basis for comparative energy balance calculations (carried out by others). The research reported in Zhang, Heaven et al. (2017) applied a side stream biogas stripping process initially developed by others for mesophilic digestion to demonstrate for the first time the successful stable digestion of SSFW at a thermophilic temperature. These published materials thus share a common interwoven theme of the effect of ammonia in anaerobic digestion systems and of different options for dealing with it.

The fourth paper Zhang, Heaven et al. (2018) used synthetic food waste as substrate, under operating conditions where ammonia toxicity is known not to be an issue, in order to look at the fate of nine different plastic films (7 biodegradable and 2 non-biodegradable controls) in conventional anaerobic digestion. A combination of testing strategies was used to assess the degree of degradation both under batch conditions, and in a simulation in which the individual plastics and food waste were fed daily to laboratory-scale digesters for a period of 147 days. Use of digestate is a key issue in the valorisation of food waste through anaerobic digestion, due to its importance as a means of nutrient recycling. The presence of plastics and other contaminants in digestate could put the land application route at risk through failure to comply with quality assurance regulations or simply through lack of public acceptability. The work thus has close links to that on digestate ammonia concentrations through a common theme of controlling digestate quality to allow utilisation and recovery of value.

The fifth paper (data article) Zhang, Torrella et al. (2019) is related to the fourth one, as it presents supporting material and further details and explanations of the work carried out. This includes quantification of residual materials from preparation of a synthetic food waste feedstock; photographic images of the physical appearance of the test plastics after prolonged exposure to microbial degradation in a continuously-operated anaerobic digestion trial; microscopic images of selected plastics after anaerobic biodegradation; test data and results for a Biochemical Methane Potential (BMP) assay for the plastics; analytical data for potentially toxic elements in the plastics; and values for residual biogas potential of the digestate. Additional data on experimental methods is given, including a recipe for a synthetic food waste specifically designed for use in anaerobic digestion simulation studies; and details on adjustment of calculations after amendment of the digestate sampling methodology used in the main study are provided. The article is thus closely linked to the rest of the research studies presented.

The final paper Zhang, Venetsaneas et al. (2020) examines the effect of low organic loading rates in digestion of ms-OFMSW. It presents the results of long-term studies of this material as a mono-substrate diluted with water, and in co-digestion with sewage sludge digestate. Although it uses a different main substrate from the previous papers, the scenarios considered are a potential result of successful implementation of source segregation schemes for OFMSW, with a consequent reduction both in overall volumes of residual waste and in the high-energy food waste component. It is thus linked to the rest of the work through the common overall issue of the best technologies and operating strategies to manage the resources present in organic municipal waste streams.

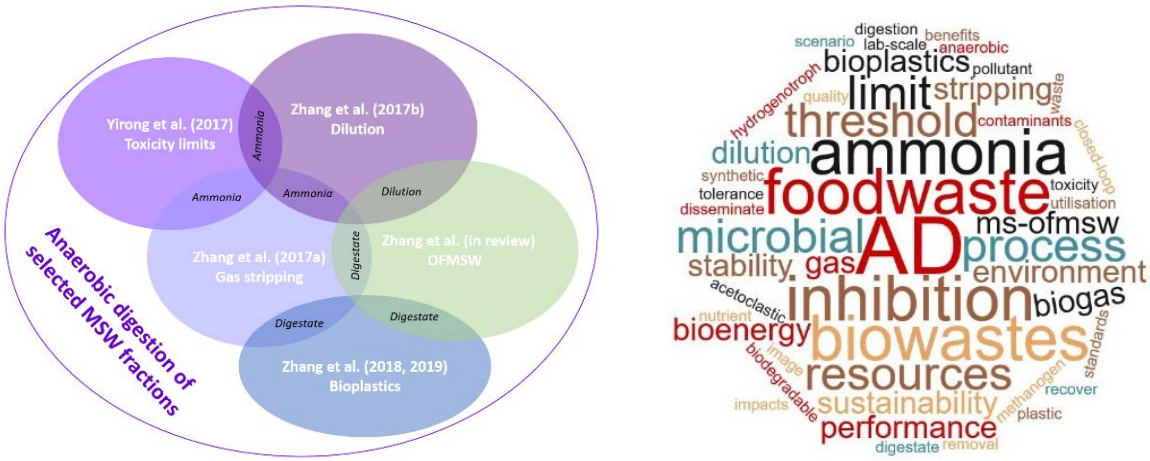

Fig. 1.2 Schematic for coherence between materials. *Left*: Venn diagram of topics. *Right*: Word cloud

3. How the materials presented in the thesis fit within the context of other work in the field

3.1 Anaerobic digestion of municipal solid waste

There has been a lot of work done in this area since the pioneering research started in the 1930s (Cecchi 1988). Anaerobic biological treatment of MSW is effective in terms of waste volume reduction and stabilisation as well as bioenergy production (Sroot 2001). Since 1980s special emphasis has initially been focused on anaerobic digestion (AD) of MSW for energy recovery (Den Braber, de Ruijter et al. 1995; Tanji 1998). Nasir (2012) carried out a comprehensive review of the studies on AD of MSW taking both operational and process performance parameters into account, as shown in Table 1.2. As can be seen from Table 1.2 these have investigated different types of digesters operating across various ranges of parameters such as temperature, OLR and

hydraulic retention time (HRT). The effects of these operational parameters are of high importance for the performance of the anaerobic digestion process. The current work adds to our knowledge of these systems in operating modes not previously considered by the studies shown.

The work presented in Zhang, Venetsaneas et al. (2020) specifically considered a number of scenarios where MS-OFMSW digestion is carried out at relatively low OLR due to an important case where the plant is oversized. One possible factor that is likely to have an increasing impact on OLR in future is the adoption of alternative technologies for recovery of materials and energy from the general waste stream, which leave a reduced volume of residual MSW for digestion. Plant operators will therefore need strategies to accommodate such changes in loading, and these will have different impacts depending on the operating mode and plant configuration. The study presented was carried out to simulate an operating mode used in a number of full-scale plants, based on data provided (in confidence) by a major company in the UK waste management sector.

Table 1.1 Operational and performance data for different bioreactor designs applied for solid wastes (based on Muhammad Nasir et al. (2012))

Reactor	Reactor type and volume	Feed	Temp. (°C)	OLR (kg VS m^{-3} $days^{-1}$)	HRT (days)	Efficiency VS_{RED} (%)	OLR (kg VS m^{-3} $days^{-1}$)	Biogas yield (m^3 kg^{-1} VS)	$\%CH_4$
Rao et al. (2000)	Batch	MSW	25 and 29	NA	NR	85	NR	NR	72
Rao and Singh (2004)	Batch (3.25L)	MSW	25	NA	15	76.3	NR	0.560	70
Lopez and Espinosa (2008)	Batch (1L)	OFMSW	25	NA	NR	94	0.15	NR	NR
Elango et al. (2007)	Semi-cont., Batch (5L)	MSW + domestic sewage	26-36	0.5-4.3	25	88.1	NR	0.36	68-72
Fernandez et al. (2008)	Batch (1.7L)	OFMSW	35	NA	NR	NR	0.11 (20% TS); 0.007 (30% TS)	NR	NR
Fernandez et al. (2010)	Batch (1.7L)	OFMSW	35	NA	15 (20% TS); 35 (30% TS)	NR	NR	NR	80 (20% TS)
Guendouz et al. (2010)	High solid batch (40L)	MSW	35	NA	15	40	0.211	NR	NR
Parawira et al. (2004)	Batch (0.5L)	Potato waste/potato waste+ beet leaves	37	NA	14	NR	0.42/0.68	NR	62/84
Macias-Coral et al. (2008)	UAF (222L)	OFMSW+CM/CGW+CM	NR	NR	141/151	NR	0.1/0.19	NR	72

Table 1.1 (continued)

Reactor	Reactor type and volume	Feed	Temp. (°C)	OLR (kg VS m^{-3} $days^{-1}$)	HRT (days)	Efficiency VS_{RED} (%)	OLR (kg VS m^{-3} $days^{-1}$)	Biogas yield (m^3 kg^{-1} VS)	$\%CH_4$
Fernandez et al. (2005)	Semi-conti. Batch (14L)	OFMSW	37	0.97	17	73	0.3	0.8	58
Nguyen et al. (2007)	Batch (375L)	Leachate	37	NR	60	61	0.26	NR	55
Hartmann and Ahring (2005)	CSTR (4.5L)	OFMSW+CM	55	4	18	74	0.460	0.710	64
Linke (2006)	CSTR	Potato processing waste	55	0.8-3.4	NR	NR	NR	0.65-0.85	58
Glass et al. (2005)	CSTR and AF	Steam-treated OFMSW	NR	NR	12	20% COD, 86% COD (CSTR, AF)	NR	0.02-0.29, 0.04-0.47 (CSTR, AF)	NR
Sosnowski et al. (2003)	2-stage CSTR and UASB	Sewage sludge + OFMSW	56,36 (CSTR, UASB)	0.669 g VSS dm^{-3} day^{-1}	17.3, 44.2 (CSTR, UASB)	NR	0.024	NR	60
Fongsatitkul et al. (2010)	2-stge	OFMSW +RAS	35	NR	28	78	NR	0.73	NR
Bouallagui et al. (2003)	Tubular reactor (18 L)	FVW	35	6% TS	20	75.9	NR	0.707	57

Table 1.1 (continued)

Reactor	**Reactor type and volume**	**Feed**	**Temp. (°C)**	**OLR (kg VS m^{-3} $days^{-1}$)**	**HRT (days)**	**Efficiency VS_{RED} (%)**	**CH4 yield (m^3 kg^{-1} VS added)**	**Biogas yield (m^3 kg^{-1} VS)**	**%CH_4**
Bouallagui et al. (2004)	2-phase system (18 L)	FVW	35/55	7.5 KG COD m^{-3} day^{-1}	20	96% COD	NR	0.705, 0.997 (35 and 55°C)	64, 61 (35 and 55°C)
Zhang et al. (2007)	Batch system	Food waste	50	NA	10/28	81	0.348, 0.435 (10, 28 days)	NR	73
Forster-Carneiro et al. (2007b)	Batch	FW	35	NR	20-60	NR	NR	0.49	NR
Bouallagui et al. (2009)	ASBR (2 L)	Abattoir waste + FVW	55	2.56	20	86.2	NR	0.73	62
Alvarez and Liden (2008)	Semi cont. (2 L)	FVW + SW + manure	35	1.3	30	NR	0.320	1.36	56
Schober et al. (1999)	1–stage and 2-stage (30 L)	KR	35/55	6	11	72,80 (35 and 55°C)	NR	0.8, 0.830 (35 and 55°C)	NR
Parawira et al. (2006)	UASB (0.84 L) and APB	PW leachate (UASB), PW(APB)	37	6.1, 4.7 (UASB, APB)	13.2, 10 (UASB, APB)	NR	NR	NR	59, 66 (UASB, APB)

Table 1.1 (continued)

Reactor	Reactor type and volume	Feed	Temp. (°C)	OLR (kg VS m^{-3} $days^{-1}$)	HRT (days)	Efficiency VS_{RED} (%)	CH4 yield (m^3 kg^{-1} VS added)	Biogas yield (m^3 kg^{-1} VS)	$\%CH_4$
Angelidaki et al. (2006)	CSTR (4.5 L)	SS-OFMSW	55	11.4	15	30	0.430	0.71	64
Forster-Carneiro et al. (2008a)	Batch (5 L)	SS-OFMSW/MS-OFMSW	55	NA	60	56	NR	NR	53.4
Maroun and EL Fadel (2007)	CSTR (10.4 L)	SS-OFMSW	35	2.03	90	NR	NR	0.2-0.56	40-65
Kim et al. (2006)	3-stage semi cont.	Food waste	50	NR	12.4	NR	NR	NR	67.4
Forster-Carneiro et al. (2008c)	Batch (1.1 L)	FW/SH-OFMSW/OFMSW	55	NR	90	32.4/73.7/79.4	0.18/0.05/0.08	NR	NR
Forster-Carneiro et al. (2007)	Batch (1.1 L)	SS-OFMSW, food waste	55	NA	90	74,32.4 (SS-OFMSW, FW)	0.5, 0.180 (SS-OFMSW, FW)	NR	68.5, 76.7 (SS-OFMSW, FW)
Sharma et al. (2000)	PFR (1350 L)	SSW	37	40	33.7	71	0.7	1.05	NR
Lastella et al. (2002)	PFR (1350L)	SSW	37	60	22.5	72	NR	NR	68

Table 1.1 (continued)

Reactor	**Reactor type and volume**	**Feed**	**Temp. (°C)**	**OLR (kg VS m^{-3} $days^{-1}$)**	**HRT (days)**	**Efficiency VS_{RED} (%)**	**CH4 yield (m^3 kg^{-1} VS added)**	**Biogas yield (m^3 kg^{-1} VS)**	**%CH_4**
Bolzonella et al. (2006)	Full scale (2200 m^3)	SS-OFMSW mixture	36-39	4-6	40-60	78	0.4	NR	56
Zupancic et al. (2008)	Full scale (2200 m^3)	OW + sludge	35	0.8	20	NR	0.39-0.6	NR	NR
(Dhar, Kumar et al. 2016)	**Batch (2L)**	**OFMSW**	**38**	**5.1, 10.4 and 15.2 g/L COD**	**5-13**	**NR**	**0.084, 0.101 and 0.168**	**0.277, 0.303 and 0.323**	**NR**

Semi cont. semi-continuous, *CSTR* continuous stirred tank reactor, *MSW* municipal solid waste, *FVW* fruit and vegetable waste, *SW* slaughter house waste, *SSW* semisolid waste, *CGW* cotton gin waste, *CM* cattle manure, *KR* kitchen refuse, *PW* potato waste, *RAS* return activated sludge, *SSW* semisolid waste, *SS-OFMSW* source sorted organic fraction of municipal solid waste, *OW* organic waste, *Temp.* temperature, *OLR* organic loading rate, *HRT* hydraulic retention time, VS_{RED} volatile solids reduction, VS_a volatile solids added, *NR* not reported, *NA* not applicable

3.2 Source-segregated organic fraction of municipal solid waste

Source segregated collection of different fractions of municipal waste is becoming increasingly popular. Positive separation of food waste can have benefits in that it produces a very 'clean' feedstock with low levels of contamination from plastics, metals, glass and other MSW components (VALORGAS 2013). The presence of such contaminants may be a limiting factor on disposal options for the digestate. In some European countries (Portugal, Italy), regulations effectively prevent the land application of MSW-derived digestates, while in the UK digestate quality standards are determined in accordance with PAS110 (BSI, 2014) to enable recovery of nutrients by land application. Some authors maintain that source segregation into multiple categories (paper and card, metals and glass, plastics, putrescible organics etc.) is the best solution for resource recovery from MSW and the only means of obtaining 'clean' materials (Seadi et al., 2013). Others have argued that the cost of separate collection is an unreasonable and unnecessary burden, and favour mixed collections with mechanical recovery of different fractions, at the expense of greater contamination, although this point of view is increasingly disputed (Seyring et al., 2015). In either case, however, there is likely to be a residual MSW fraction that is still rich in organics but of a lower quality than conventional SSFW. In the longer-term other methods capable of recovering value from mixed wastes may be developed, such as the Fiberight process (https://fiberight.com) or other thermo-chemical and biorefinery-type approaches (Sadhukhan and Martinez-Hernandez 2017). At present these are not operational at a fully commercial scale commercial scale; and as waste management infrastructure typically has a life expectancy of several decades, it is likely that methods of dealing with the current range of fractions of OFMSW will be needed for years to come.

Gunaseelan (1999) discussed AD of MSW including source-sorted and mechanically sorted MSW. The digestion of unsegregated or mechanically-recovered waste is becoming less popular due to issues of contamination with plastic, glass, metal etc. leading to difficulties in beneficial utilisation of digestate (Den Braber, de Ruijter et al. 1995). Moreover, reported methane yields (0.11 – 0.36 STP m^3 CH_4 kg^{-1} VS) (Hartmann and Ahring 2006, Zhang 2010, Zhang, Banks et al. 2012) from AD of MS-OFMSW are lower than the methane yields from SS-OFMSW (0.43 – 0.63 STP m^3 CH_4 kg^{-1} VS) (Hansen, Jansen et al. 2007, Zhang 2010, Zhang, Banks et al. 2012, Bernstad, Malmquist et al. 2013). In another study (Bolzonella, Pavan et al. 2006) investigated anaerobic digestion of differently sorted organic municipal solid waste and concluded that the strategy of waste

collection significantly altered the characteristics of the organic waste and subsequent biogas yields even under similar operational conditions.

The work described in two of the papers (Yirong, Zhang et al. 2017; Zhang, Heaven et al. 2017) presented in this thesis was carried out as part of the VALORGAS project (www.valorgas.soton.ac.uk), which had the overall aim of determining the feasibility and energy and resource implications of collection and processing source segregated food waste.

3.3 Biopackaging

Anaerobic digestion is becoming increasingly popular worldwide as a means of processing food waste for energy and fertiliser recovery. Positive separation of food waste can have benefits in that it produces a very 'clean' feedstock with low levels of contamination from plastics, metals, glass and other MSW components (VALORGAS 2013). Even a high-performing SSFW collection scheme will contain some contaminants, however, while some components of the organic municipal waste stream, such as supermarket wastes, are disposed of still wrapped and thus require mechanical de-packaging. Meanwhile there has been a huge surge in public awareness of the impact of plastics, and in particular plastic packaging wastes, on the environment. This with other factors is driving the development of biodegradable plastics, and a move towards more readily biodegradable packaging that could be included in the fraction of waste for bioprocessing. It is the commercial food retailing and catering sectors that are driving growth in the development and use of biodegradable polymers as companies seek to meet sustainability goals (Meeks, Hottle et al. 2015).

The inclusion of biodegradable catering films, food wraps and card packaging in the feedstock stream would greatly simplify collection and processing, and eliminate the need for a depackaging stage for input materials such as supermarket wastes and other packaged food materials. It is now recognised that the biodegradability of plastic films is dependent on process conditions, with significant differences reported between aerobic and anaerobic systems (Ishigaki, Sugano et al. 2004, Massardier-Nageotte, Pestre et al. 2006, Mohee, Unmar et al. 2008, Cho, Moon et al. 2011). There are also known disparities between different methods for assessing anaerobic biodegradability, leading to questions as to whether batch testing methods can adequately predict what will happen to plastic packaging materials under real operating conditions in a full-scale bioprocessing plant (Castro-Aguirre, Auras et al. 2017).

There has been considerable interest in developing biodegradable films designed for disposal via composting or anaerobic digestion. These plastics, generally referred to as 'bioplastics', can be produced from conventional petrochemicals or from renewable biological resources. In the latter case they are termed bio-based plastics. Bio-based plastics can be synthesised from bio-based chemical building blocks, e.g. lactic or succinic acids; through modification of natural polymers, such as starch, cellulose or chitin; or through fermentation to produce microbial polymers such as polyhydroxyalkanoates.

According to European Bioplastics a plastic material is defined as a bioplastic if it is either biobased, biodegradable, or features both properties (European Bioplastics, N.D.). Bioplastics can be biobased, biodegradable or both. Current standardization on testing of bioplastics in Europe includes CEN/TS 16137:2011 which applies to biobased plastics, EN 13432:2000 applying to compostable packaging and EN 14995:2006 applying to compostable plastics. The CEN/TS 16137 provides a standardised set of methods to determine and calculate biobased carbon content in monomers, polymers and plastic materials and products. The standards EN 13432 and EN 14995 define the technical specification for the compostability of bioplastics products. The EN 13432 applies to compostable packaging materials and EN 14995 covers compostable plastics (European Bioplastics).

The work presented in Zhang, Heaven et al. (2018) in this thesis was conducted to assess the extent to which selected bioplastic films were broken down in a mesophilic digester treating food waste. These bioplastic films are EN 13432 compliant materials and produced from cellulose and starch etc. Therefore, they are also biobased plastics, however, their anaerobic biodegradability, biogas production potential and whether the resulting digestate would meet relevant quality standards for use in agriculture had not previously been tested. The results of the study were intended to provide comparative information on the degradation of selected biopolymers under anaerobic conditions, and to inform stakeholders on whether AD is a suitable treatment method for a waste stream containing packaged food material that includes carton and renewable plastic film. Both semi-continuous and batch trials indicated that even the most degradable materials would not break down sufficiently to meet the physical contaminant criteria of the UK PAS 110 specification for anaerobically digested material, if fed to a digester at 2.0% of the input load on a volatile solids basis. On the other hand, the presence of undegraded materials in digestate is a potential issue. PAS110 (BSI, 2014) specifies that total glass, metal, plastic and any ‘other’ non-stone, man-made fragments > 2 mm must not exceed 0.5 % m/m dry matter. The work carried

out for this thesis showed that even the most degradable materials tested would not degrade sufficiently to meet this criterion, if fed to a digester at 0.5% of the input load on a volatile solids basis. This partly reflects the high degradability of food waste feedstock, where the residual dry matter content is low; as well as the incomplete disappearance of the tested bioplastic materials. If digestate containing residual compostable bioplastics is applied to land, it is possible these will degrade in an acceptably brief period in these conditions: but this was not investigated in the current work. It should also be noted that some of the materials tested appeared to break down physically without necessarily being mineralized. This behaviour may enable compliance with PAS110 (BSI, 2014) requirements but does not reduce the amount of micro-plastics entering the environment and with growing awareness of this issue the purpose of the original criterion may therefore need to be re-visited.

Worldwide there are a number of standards for the use of bioprocessed waste materials in agriculture and horticulture, but the UK has adopted separate specifications for aerobically and anaerobically processed materials. The UK's PAS 110 Specification for anaerobic digestates contains criteria (PAS 110) for pathogen content, Potentially Toxic Elements (PTE), stability and physical contaminants, and was used as a reference in the work on the biodegradable biopolymers presented as part of the thesis. PAS 110 is non-statutory document and does not set regulatory limit values for the quality and use of digestated materials. However, it creates an industry specification against which producers can check that the digested materials are of consistent quality and fit for purpose.

PAS 110 specifies that physical contaminants must not exceed a given proportion of the wet weight of digestate, with the proportion increasing as the digestate nitrogen concentration increases: the logic behind this is that land spreading is often limited by nitrogen load, and hence the amount of contaminant applied per unit area of land area should be the same at a given load. With regard to these criteria, the apparent disappearance of the plastic is of more importance than whether it in fact undergoes ultimate biodegradation to gaseous products.

Even when source separated, food waste used as an anaerobic digestion typically contains a mixture of materials and components with different biodegradability, ranging from sugars and fatty acids (either naturally present or produced by breakdown during storage and collection) to lignin and lignin-bound components in plant products (Banks et al., 2018). In certain conditions, e.g. high-rate systems, this variability may pose a challenge with respect to selection of the

optimal loading rate and retention time for maximum degradation and specific methane productivity. As a result there has been continuing interest in the potential of approaches such as pre-treatment (Kondusamy and Kalamdhad, 2014; Ren et al. 2018) and or addition of enzymes (Rajin et al., 2020; Meng et al., 2017) to accelerate the degradation rate of more recalcitrant fractions. The physico-chemical properties of food waste and in particular its moisture content mean, however, that conventional digesters typically operate at relatively long hydraulic retention times sufficient to allow degradation of all components. At an organic loading rate of 5 kg VS m^{-3} day^{-1}, typical of that which might be applied in a well-operated commercial AD plant, a food waste with a VS content of 22 % on a wet weight basis will have an HRT of 44 days. According to the FP7 VALORGAS project, the maximum organic loading rate that could be applied in conventional laboratory-scale digesters before a reduction in specific methane yield was observed was 8 kg VS m^{-3} day^{-1}, corresponding to a HRT of around 27.5 days (VALORGAS 2013). Despite its complex composition, in a well-operated digestion process food waste is capable of achieving a very high proportion of its theoretical methane yield (Zhang et al., 2020). This suggests that addition of other materials such as bioplastics should not pose a particular challenge provided that they have similar degradability to other food waste components.

Banks and Zhang (2010) also carried out work on co-digestion of food waste and card packaging, a material which may appear in the food waste stream in small quantities or may be deliberately chosen as a co-substrate. Data from biochemical methane potential tests of the packaging as a sole substrate indicated that the majority of degradation had occurred within the first 30 days (Zhang et al., 2020), while testing of the digestate from semi-continuous trials showed a low residual biogas potential confirming effective degradation of the co-substrates (Zhang et al., 2012b). This adds further support to the view that addition of other packaging substrate bioplastics that are genuinely anaerobically degradable should not pose a particular challenge in conventional anaerobic digestion.

3.4 History of anaerobic digestion of food waste

As noted in the introduction, food waste makes up a large proportion of MSW in both developing and developed countries. Anaerobic digestion as a promising sustainable means of food waste treatment has therefore been widely used all over the world. It is reported in the UK there are now 94 plants producing biogas from mixed commercial and residential food waste, the largest proportion of which is used to generate 250 MW of electricity in CHP units (Bioenergy 2017). The Scandinavian countries were also early adopters of food waste digestion and plants can also be

seen in parts of Spain and Portugal(Bioenergy 2018). For various historical reasons such as specific local bio-waste collection schemes different food waste digestion systems have been developed, there are typically either 'wet' digester designs in which water or digestate can recycled or a plug flow 'dry' digestion system (Bioenergy 2018) (Fig. 1.3).

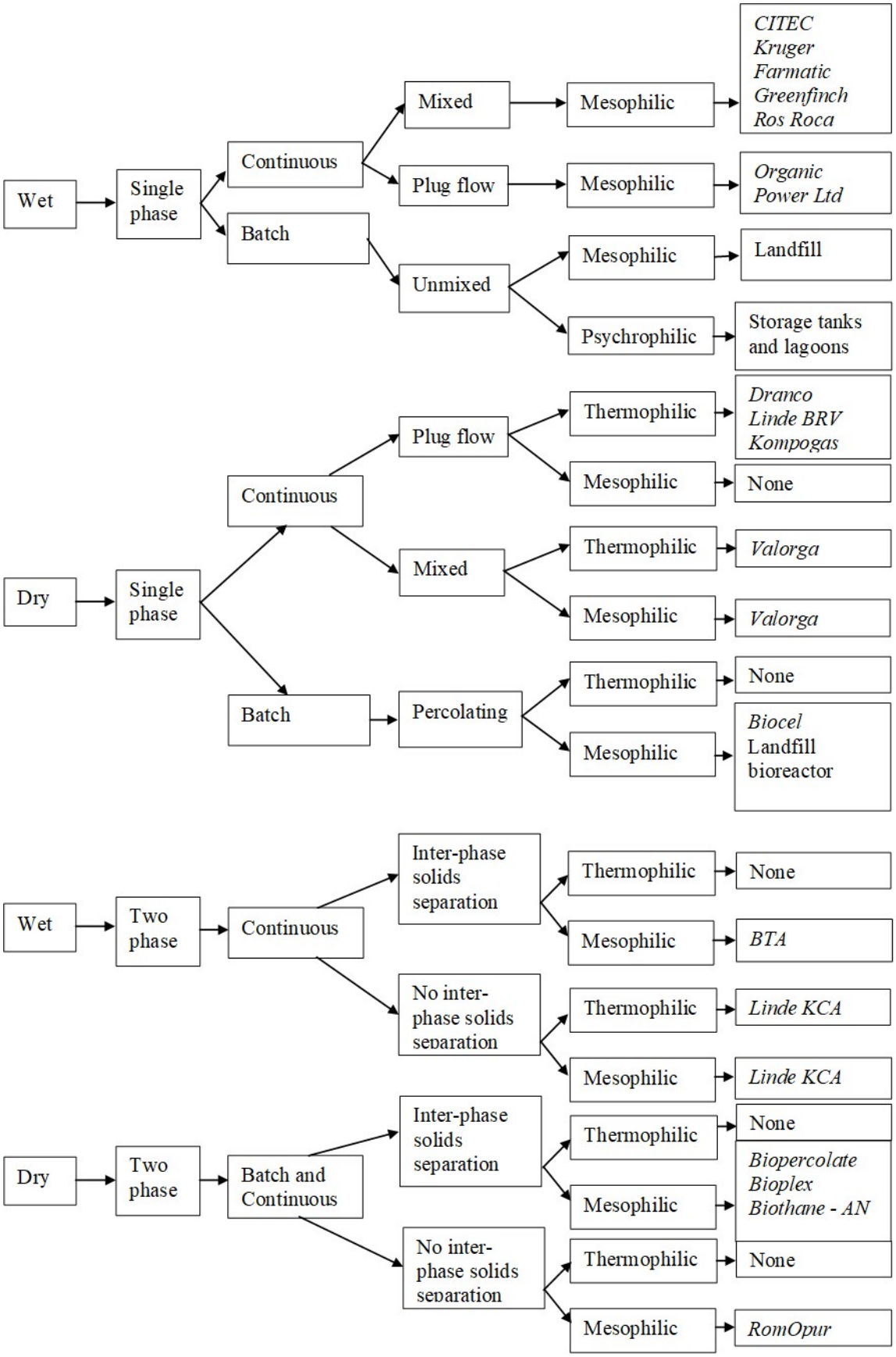

Fig. 1.3 Classification of AD process alternatives (Banks and Stentiford, 2007)

3.5 Mechanisms of ammonia inhibition in anaerobic digestion

Anaerobic digestion is a microbial fermentation process facilitated by a series of microorganisms and reactions in an anoxic environment in which complex organic materials are degraded and biogas is produced. This process is accomplished via four successive stages, which are hydrolysis, acidogenesis, acetogenesis and methanogenesis. Optimal ammonia concentrations are of high importance to permit microbial growth and ensure sufficient buffer capacity of cultures in anaerobic digestion. However high ammonia concentrations may cause severe disturbance in performance of the overall process (Sung 2002, Zhang, Zamudio Canas et al. 2011). The last stage of anaerobic digestion where biogas is formed is carried out by a highly specialised group of microorganisms called methanogens that rely on a limited range of feedstocks and methanogenesis is the only way that they can obtain energy for growth (Thauer, Kaster et al. 2008). Methanogens are more sensitive to high ammonia concentrations compared to other groups of microorganisms in AD and the issue of ammonia toxicity has been recognised for many years (Chen, Cheng et al. 2008, Rajagopal, Masse et al. 2013, Yenigün and Demirel 2013). Inhibition of the AD process is usually indicated by accumulation of VFA, subsequent pH drop and eventual process failure (Calli, Mertoglu et al. 2005, Zhang, Heaven et al. 2017).

Food waste that has been source segregated in the home or collected from restaurants, cafeterias and supermarkets has been shown to have fairly similar properties in a number of studies and typically has a C: N ratio of∼15 and a TKN of 3–4% on a total solids basis (Capson-Tojo, Rouez et al. 2016) due to its association with high protein content. During anaerobic digestion the protein contained in food waste is rapidly hydrolysed to release ammonia which can be inhibitory or toxic to the process at concentrations above the relevant critical threshold (Chen, Cheng et al. 2008, Rajagopal, Masse et al. 2013). If SSFW is used directly into a digester the TAN concentration will typically equilibrate between 4.5 and 5.5 g N L−1 (Banks, Chesshire et al. 2008), which can be tolerated in mesophilic systems but is inhibitory under thermophilic conditions.

It is difficult to quote absolute values for the threshold of ammonia inhibition/toxicity as this depends on a number of factors, including temperature and pH. In operational terms, tolerance to ammonia has been variously reported in the literature with a wide range of values quoted (Chen, Cheng et al. 2008, Rajagopal, Masse et al. 2013). Inhibition is a particular problem in thermophilic conditions as the equilibrium between ammonia in its ionic form and the more toxic free ammonia shifts in favour of the latter at higher temperatures. The high TAN also leads to a high pH environment which again favours a shift in the equilibrium to FAN.

The mechanism of ammonia inhibition still remains unclear, however, consideration of the chemical interaction of ammonia and cells could lead to further understanding (Jiang et al. 2019). Kayhnian (1999) proposed a physical model to describe the entrance of the NH_3 molecules into cells and subsequent accumulation of ammonia based on the understanding of trans-membrane electrical and pH gradient theory. According to the model, free ammonia molecules will diffuse through cell membranes into the cells of methanogens, whereas ammonium does not readily diffuse through cell membranes. Thus, the intracellular and extracellular concentrations of ammonium are dependent on ammonia concentration and the local pH and temperature (Capson-Tojo et al. 2020). Experimental work to support this hypothesis is very limited, however, due to the complicated approaches to measure intracellular pH and cation concentrations (Jiang et al. 2019).

Once ammonia has diffused into cells, the inhibition of methanogens will occur. Only a few mechanisms have been postulated for this inhibition, of which two are favoured (Jiang et al. 2019). One is the direct inhibition of the activity of cytosolic enzymes by un-ionized ammonia (Kadam et al 1996); the other is intracellular accumulation of ammonium (Jiang et al. 2019). In the latter case, when ammonia molecules enter the cell the lower intracellular pH drives the conversion of part of the ammonia molecules into ammonium by absorbing protons in the cell. The elevated energy requirement for the potassium pump to balance the increased numbers of protons potentially causes inhibition of specific enzyme reactions (Gallert et al. 1998).

In terms of relative sensitivity to ammonia toxicity, this has been intensively investigated on methanogens like Methanosaeta and Methanosarcina etc. It is broadly recognized that Methanosarcina are much more resistant to ammonia toxicity than Methanosaeta probably due to their mixotrophic capacity i.e. the ability to consume both acetate and hydrogen (Capson-Tojo et al. 2020). The irregular multi-cocci shape of Methanpsarcina could also contribute to protect the cell against various environmental shocks including ammonia toxicity, pH fluctuation etc. Although Methanosaeta belong to the same order as Methanosarcina do, they are the most vulnerable genus to ammonia toxicity (Rajagopal et al 2013). In comparison to Methanosarcina, they can only consume acetate to produce methane. As Methanosaeta are able to perform a more efficient acetate conversion to methane they are often found to be dominant at low ammonia concentrations (Jiang et al 2019).

Three papers presented in this thesis consider SSFW as a fraction of the municipal waste stream, with a specific focus on the effects of ammonia inhibition on digestion performance and stability under either mesophilic or thermophilic conditions.

3.6 Mitigation means on ammonia toxicity

It has been reported (Chen, Cheng et al. 2008, Yenigün and Demirel 2013, Tian, Fotidis et al. 2018) that microbial populations can acclimatise to higher ammonia concentrations. Bio-augmentation of high ammonia tolerant methanogenic species in anaerobic digesters is also an effective solution to ammonia inhibition (Westerholm, Leven et al. 2012, Fotidis, Wang et al. 2014); but may also require repeated supplementation with an associated increase in operating costs. The alternative is to reduce the ammonia concentration, and the two main approaches are based either on stripping ammonia from the liquor (Serna-Maza, Heaven et al. 2014, Serna-Maza, Heaven et al. 2017) or more commonly on dilution to below the toxicity threshold. The latter approach, however, results in an increase in the volume of material to be treated, which in principle can make the process economically unattractive (Kelleher 2002) and energetically less favourable. As an alternative to water addition, co-digestion with a low nitrogen material also serves to "dilute" the TAN: this strategy was also demonstrated by Nielson and Angelidaki (Nielsen and Angelidaki 2008) as a means of recovery from ammonia inhibition in the thermophilic digestion of cattle manure. Co-digestion has the benefit of gaining further energy from the added carbon and is therefore likely to be preferable in terms of the overall energy balance.

The study by Zhang, Heaven et al. (2017) in this thesis used diluted municipally collected SSFW firstly to assess the performance of the digestion process under these conditions, and secondly to make a preliminary assessment (carried out by others) of the energy implications of adopting this type of strategy. The work by Yirong, Zhang et al. (2017) outlined in the thesis was adopting an acclimatisation strategy to compare mesophilic and thermophilic anaerobic digestion of SSFW in parallel. Another paper (Zhang, Heaven et al. 2017) presented in this thesis was a demonstration that a side-stream ammonia stripping process used in conjunction with thermophilic food waste digestion could allow successful long-term operation.

3.7 Ammonia stripping

Walker, Iyer et al. (2011) discussed the advantages and disadvantage of biogas stripping in various operating modes and from different locations in the plant flowsheet or using additional process

stages. Of the options considered, side-stream stripping was shown to be able to reduce TAN concentrations in a mesophilic digester without apparent detriment to the process (Serna-Maza et al., 2014). The system described involved a simple 'bolt-on' stripping column in which a proportion of the digestate is stripped of its ammonia under alkaline conditions, with recovery as a concentrated ammonium sulphate solution by dissolution into sulphuric acid. Side-stream stripping appeared to offer the greatest promise (Serna-Maza, Heaven et al. 2015, Serna-Maza, Heaven et al. 2017) . The experimental results in these previous studies showed that with in-situ biogas stripping at gas mixing rates typical of full-scale commercial digesters the reduction in total ammonia nitrogen concentrations was insufficient to allow stable performance under mesophilic conditions, or to mitigate total inhibition of methanogenic activity in thermophilic food waste digestion (Serna-Maza, Heaven et al. 2017).

The work presented in (Zhang, Heaven et al. 2017) in this thesis was first to successfully adopt a side-stream ammonia stripping strategy in anaerobic digestion of source segregated food waste under thermophilic conditions, using biogas as the stripping agent.

4. Aims and objectives

4.1 Aims and objectives

The aim of the research described in the following sections and papers was to address some specific issues in processing of municipal waste streams, in particular:

Aim 1. To provide confirmation of and supporting evidence on the impact of high ammonia concentrations encountered during the anaerobic digestion of source segregated food waste (SSFW) under both mesophilic and thermophilic conditions, and demonstrate the strategies to mitigate these effects;

Objective 1: To carry out semi-continuous studies on high nitrogen FW with suitable trace element additions under mesophilic conditions in order to demonstrate that the material itself contained no inherently toxic or inhibitory components at the loading used and establish a baseline level of digestion performance.

Objective 2: To feed an acclimated stable thermophilic inoculum on high-N FW to demonstrate the effect of the increased nitrogen content.

Objective 3: To find the threshold for ammonia toxicity in the digesters fed on low-N FW by increasing the TAN, by adding urea both gradually and as a single dose.

Objective 4: To demonstrate dilution is an effective means to control the TAN concentrations below inhibitory threshold under thermophilic conditions.

Objective 5: To carry out semi-continuous studies to demonstrate the TAN can be controlled below inhibitory concentrations using side-stream stripping under thermophilic conditions.

Aim 2. To demonstrate the fate of compostable bioplastics present in SSFW and related wastes streams during digestion;

Objective 1: To carry out semi-continuous studies to assess the extent to which selected bioplastics were broken down under anaerobic conditions in a mesophilic digester treating FW.

Aim 3. To assess potential effects of responses by commercial plant operators to reductions in organic loading in organic loading during the digestion of residual MSW such as might occur due to the successful introduction of source segregation schemes.

Objective 1: To provide a baseline for thermophilic digestion of a particular ms-OFMSW feedstock.

Objective 2: To simulate the effect of a low OLR, such as might occur in an existing plant operated with partial recycling of the liquid fraction of digestate plus water addition with a long-term shortfall in waste feedstock.

Objective 3: To investigate the effect of replacing water addition with addition of digestate from municipal wastewater biosolids as a potential strategy for alleviation of load reduction.

4.2 Nature of the research

The research involved extended laboratory-experimental studies using real and simulated waste streams under either mesophilic or thermophilic conditions, as follows:

(i) The work presented in Yirong, Zhang et al. (2017) was carried out to compare thermophilic and mesophilic anaerobic digestion of source segregated domestic food waste in a parallel trial supported by compositional analysis and stability and performance data. This work was begun by Dr Chaowana Yirong, first author on the paper, and part of it was presented in her PhD thesis.

(ii) The research presented in Zhang, Heaven et al. (2017) was conducted to demonstrate that a side-stream ammonia stripping process used in conjunction with thermophilic FW digestion could allow successful stable long-term operation. The work was therefore carried out over an extended period in order to provide steady state data on digester performance and stability with side-stream stripping, and to compare this with an unstripped control.

(iii) The work presented in Zhang, Heaven et al. (2017) was designed to test the effect of dilution of a SSFW feedstock to below the expected threshold for ammonia inhibition; and to gather data on process performance and stability for energy balance calculations (carried out by others) in order to assess the advantages and disadvantages of this as an operating mode to avoid ammonia inhibition. It also provided an opportunity to re-confirm the threshold and effects of ammonia toxicity in thermophilic conditions.

(iv) The work presented in Zhang, Heaven et al. (2018) was designed to assess the extent to which selected bioplastic films were broken down under anaerobic conditions in a mesophilic digester treating food waste. In addition to the bioplastics, card packaging was added as part of the digester feedstock, to simulate the case where a biodegradable composite packaging is co-digested with food residues in a bio-treatment process. The feedstock in the trial was formulated to contain food waste, card packaging and bioplastic at volatile solids (VS) ratios of 80:18:2 based on a likely composition for segregated waste streams arising either from homes, or from supermarkets if biodegradable packaging is included at source.

(v) The published data article Zhang, Torrella et al. (2019) is related to the research article entitled ‘Degradation of some EN13432 compliant plastics in simulated mesophilic anaerobic digestion of food waste’ (Zhang, Heaven et al. 2018). It includes visual data on the physical appearance of plastics after digestion, which can be used in comparative evaluation of degradation performance and in assessment of degradation mechanisms; microscopy images that may offer researchers supporting evidence for theories on degradation and attack mechanisms; biochemical methane

potential (BMP) values, potential toxic element (PTE) content and residual biogas potential that provide comparative data for alternative methods and other research; a synthetic food waste recipe that can be used in other investigations; and data on reject materials from the synthetic food waste that can be used in research on food-related packaging waste generation rates.

(vi) The work presented in Zhang, Venetsaneas et al. (2020) was designed to consider a number of scenarios where digestion of the mechanically-separated organic fraction (MS-OFMSW) is carried out at relatively low organic loading rates (OLR). One objective was to provide a baseline for thermophilic digestion of a particular MS-OFMSW feedstock for comparison with alternative energy recovery options, including integrated pyrolysis and anaerobic digestion (Yang et al. 2018b). Another was to simulate the effect of a lower OLR such as might occur in an existing plant with a long-term shortfall in waste feedstock.

Table 1.2 summarises the key elements of each research study listed above.

Table 1.2 Summary of the key elements of five research studies listed above

Study	Duration (days)	Mesophilic	Thermophilic	Source segregated domestic food waste	Simulated waste	MS-OFMSW	Compostable bioplastics	Specific issues
Influence of ammonia in the anaerobic digestion of food waste (Yirong, Zhang et al. 2017)	**875**	✓	✓	✓	✓			**Ammonia toxicity**
Continuous operation of thermophilic food waste digestion with side-stream ammonia stripping (Zhang, Heaven et al. 2017)	**382**		✓	✓	✓			**Ammonia toxicity**
Thermophilic Digestion of Food Waste by Dilution: Ammonia Limit Values and Energy Considerations (Zhang, Heaven et al. 2017)	**238**		✓	✓				**Ammonia toxicity**
Degradation of some EN13432 compliant plastics in simulated mesophilic anaerobic digestion of food waste (Zhang, Heaven et al. 2018)	**147**	✓			✓		✓	**Compostable bioplastics**
Impact of low loading on digestion of mechanically-separated OFMSW	**525**	✓	✓			✓		**Low organic loading rate (OLR)**

5. Methods and data analysis

5.1 Methods

The analytical procedures and reactor operation protocols used were as summarized in the respective papers and are based on our standard laboratory procedures. The main procedures used are presented in Appendix 1.

5.2 Data analysis

Table 1.3 Details of controls and replicates in the studies presented in this thesis

Paper: Influence of ammonia in the anaerobic digestion of food waste (Yirong, Zhang et al. 2017)
Mesophilic digesters M1&2 and M3&4 (all with working volumes of 4 L) were operated as duplicate pairs throughout the study. Thermophilic digesters T1&2 and T3&4 (all with 4-L working volumes) were operated as duplicates until day 384, then conditions in T1 and T2 were modified with respect to urea addition. T1 was the first to receive urea while T2 continued under the same conditions acting as a control; then T2 received a different pattern of urea addition for comparison with T1.
Paper: Continuous operation of thermophilic food waste digestion with side-stream ammonia stripping (Zhang, Heaven et al. 2017)
The 35-L working volume digesters were operated without duplicates and the experiment was internally controlled in that in Stage 1 all four digesters were running under the same baseline conditions (and therefore should produce closely similar results, as was in fact shown to be the case). In Stage 2 the control was digesters T3 and T4, in which the conditions remained unchanged from those in stage 1, thus providing a control for the effects of increasing the amount of digestate stripped in T1 and T2. In Stage 3, operation of T1 and T3 continued as in Stage 2 and these digesters therefore acted as controls for the changes introduced in this stage: namely, doubling of the amount stripped in T2 and cessation of stripping in T4. This allowed T4 without stripping to be compared with its control reactor T3, where stripping continued under the same conditions as in Stage 1 and 2. T3 therefore also provided a consistent control as the original stripping regime remained constant throughout the entire experiment. T1 also provided a control for comparison with T2. The nature of the material and operating conditions did not allow use of an unstripped reactor as control, as the ammonia concentration would be inhibitory (as shown by the response of T4

to cessation for stripping). Thus, only when successful operation with ammonia removal had been established was the stripping stopped in one digester to demonstrate ammonia accumulation and verify the resulting process inhibition in unstripped conditions.
Paper: Thermophilic Digestion of Food Waste by Dilution: Ammonia Limit Values and Energy Considerations (Zhang, Heaven et al. 2017)
For the first 61 days all six digesters (working volumes 4-L) were operated under identical conditions on a feedstock diluted at a 2:1 (water: food waste) ratio on a wet weight basis, to demonstrate acclimatisation and replicability of performance. After day 62 the feeding regime was modified so that in one pair of digesters (T1&2) feed was added without water (dilution 0:1); in one pair (T3&4) dilution was reduced to 0.5:1; and in one pair (T5&6) dilution remained at 2:1 as before. By day 164 T5&6 had completed more than 4 HRT at a 2:1 dilution, providing a control for the other digesters and a clear baseline value for this set of conditions. The dilution in these digesters was then reduced to 1:1 to provide a further set of operating conditions for comparison of digestion performance and monitoring parameter values.
Papers: Degradation of some EN13432 compliant plastics in simulated mesophilic anaerobic digestion of food waste (Zhang, Heaven et al. 2018); plus Data related to anaerobic digestion of bioplastics: Images and properties of digested bioplastics and digestate, synthetic food waste recipe and packaging information (Zhang, Torrella et al. 2019).
The work used 12 no. digesters each with a working volume of 4 L. In view of the extremely labour-intensive nature of the work (a total of 63,400 plastic tokens counted into the digesters, and 42,418 undigested pieces carefully recovered from digestate and washed and dried before counting), the experiment was run on single digesters without replicates. The experiment ran for 147 days and some support for the statistical validity of the data on plastic degradation is provided by mathematical modelling of the observed trends according to the methodologies described in Zhang, Torella et al. (2019)
Paper: Impact of low loading on digestion of mechanically-separated OFMSW (Zhang, Venetsaneas, Heaven et al. 2018)
Mesophilic digesters M1&2 (working volumes 35 L) were operated as a duplicate pair until performance diverged under stressed conditions, when different conditions were applied to recover the more seriously affected replicate. Thermophilic digesters T1&2 (working volumes 35 L) were operated as a duplicate pair throughout the study.

Where replicate digesters were available, values are either reported for each individual digester or as averages with range or standard deviation, as reported in each paper. The low number of

replicates makes further statistical analysis of the results difficult; but this is common in the majority of experimental work of this type due to the labour and resource-intensive nature of digester operation, especially when using larger-scale laboratory experimental reactors.

Regarding analytical results, where measurements were undertaken to establish basic characteristics of feedstocks these were carried out at least in duplicate or triplicate and reported as means with standard deviations or ranges, as shown in each paper.

Routine monitoring of digestion parameters such as pH, solids, TAN, alkalinity, VFA and gas composition etc was normally based on single samples, with occasional repeat testing of any individual samples appearing to diverge strongly from the established trend. This again is common practice in this field, and is justifiable where the aim is to determine changes or trends over time. It should also be noted that, while the individual data points in series of monitoring parameter values are occasionally treated as if they are independent, this is not strictly so as the conditions in the digester on a given day depend on those in the preceding days and weeks; it is, however, possible to use data series of this type to consider rates of change over time and between paired control and experimental reactors as shown in Table 1.3.

6. Nature and extent of original contribution

6.1 The work presented in Yirong, Zhang et al. (2017) is the first long-term comparative study of thermophilic and mesophilic digestion of source segregated domestic food waste in a parallel trial supported by compositional analysis and stability and performance data, and provides confirmation of the ammonia inhibition thresholds in these conditions.

6.2 The work presented in Zhang, Heaven et al. (2017) is the first time that stable thermophilic operation has been achieved with an undiluted SSFW substrate of this type, using biogas stripping to control digestate ammonia concentrations.

6.3 The work presented in Zhang, Heaven et al. (2018) is the first reported study on bioplastics degradation kinetics in a co-digestion study with feed addition and removal designed to simulate practice in a commercial AD plant. The results provide performance data and indicate that degradation performance may be less good than expected. The study is also the first to note that the physical operating parameters of the digester may influence the retention time of plastic materials, and to highlight the potential effects of plastic density (floating and sinking).

6.4 The research presented in Zhang, Venetsaneas et al. (2020) is the first reported study on residual MSW degradation in a co-digestion study with feed addition and removal designed to simulate practice in a commercial AD plant that is facing the issue of low OLR. The results provide useful insights for operators of full-scale plant facing current or potential changes in MS-OFMSW feedstock availability, and on benefits that might arise from substrate blending with digestate from municipal wastewater biosolids treatment. The use of pre-digested sewage sludge as a co-substrate provides a novel and effective solution.

7. Conclusions

7.1 Impact of ammonia inhibition

(i) Long term stable operation of digesters fed on high-N FW without dilution was not possible. Very sharp increases in VFA concentration were observed as the TAN concentration exceeded 3.5 g N L^{-1} and, although this could be partially overcome in the short term, there was no long-term solution to the accumulation of propionic acid.

(ii) It was possible to run the digesters over long periods on a low-N FW with good methane production and VS destruction. it was possible to operate without significant VFA accumulation at a TAN concentration of≤ 2.5 g N L^{-1} but propionic acid started to appear as the TAN rose above 3.0 g N L^{-1} and showed irreversible accumulation at a concentration of 3.5 g N L^{-1}. Despite different strategies for increasing the ammonia concentration, applied in over relatively long periods, no clear sign of adaptation or acclimatisation was seen in terms of the overall digestion performance.

(iii) Diluting the feedstock proved a reliable method for establishing the critical TAN concentration at which instability was first observed (2.5 g of N L^{-1}) and also the point where incremental accumulation of propionic and other longer chain VFA began (3.5 g of N L^{-1}). Stable digestion without loss of specific or volumetric biogas production could be maintained at a 0.5:1 water/FW dilution. The results indicated that the impacts of dilution were relatively small for this energy-rich substrate where mesophilic digestion requires pasteurization and can easily be met from the energy available from use of the biogas in a CHP plant even at the highest dilutions, assuming there is no other economic use for the heat. Considering the other potential advantages of thermophilic systems in terms of improved rheology and dewaterability

and the enhanced potential for advanced forms of nutrient recovery, dilution may be an acceptable operating strategy.

(iv) Thermophilic food waste digestion was possible using a side-stream stripping process at 70 °C with initial pH>10. Ammonia inhibition thresholds were established for this substrate, and the process could control TAN below these without detrimental effects. The pattern of VFA accumulation without stripping suggested that the acetate oxidation pathway failed as TAN approached 5 g N L^{-1}, although progressive instability was noted at>2.5 g N L^{-1}. Stripping achieved 54% TKN removal, which allowed recovery of 3.5 g N kg^{-1} substrate. This means nutrient recovery by this method is not likely to provide a viable income stream in most circumstances because the quantity produced both at individual sites and nationally is small relation to the scale of industrial demand. The ammonia mitigation strategies adopted were therefore judged to be successful, and the research carried out confirmed the results of our previous work which demonstrated that thermophilic digestion of food waste as a mono-substrate without dilution was not possible. The strategies of dilution and ammonia stripping tested allowed stable long-term operation with good gas production and performance parameters; the result for ammonia stripping is particularly interesting as this was the first demonstration of a technique which does not require water addition.

7.2 Biopackaging degradation in anaerobic digestion

(i) Of the nine biopackaging materials tested only the four cellulose-based materials showed extensive biodegradation in the static BMP assay. This verified that both polylactic acid film (PLAF) and cellulose diacetate film (CDF), which were shown to be removed in the simulation trials, were initially disrupted but not degraded; it was likely that only the PLAF showed biodegradation over a longer period.

(ii) None of the materials inhibited or destabilised the digestion process, which ran for 177 days in total and provided some useful insights into issues relating to the physical properties of the plastic materials that are likely to affect the behavior of full-scale systems.

(iii) Although the digestion trial was run with a solids retention time of 50 days, the degree of breakdown of even the most biodegradable of the polymers tested was unlikely to meet more stringent environmental requirements for the exclusion of physical contaminants, such as those specified in the UK PAS110 (BSI, 2014) for digestate utilization.

7.3 Impact of low loading on digestion of the ms-OFMSW

(i) Thermophilic CSTR digesters fed on mechanically-separated OFMSW at a moderate OLR of 2 kg VS m^{-3} day^{-1} and operated to simulate a full-scale plant with combined digestate recycling and water addition showed stable operation with a specific methane production of 0.296 m^3 CH_4 kg^{-1}VS, equivalent to 87 m^3 CH_4 per tonne of waste input. VS destruction was estimated at 82% based on the weight of biogas produced.

(ii) Operating in the same mode but at a lower OLR of 1 kg VS m^{-3} day^{-1} and constant HRT had no adverse effect on performance, with specific methane production of 0.290 m^3 CH_4 kg^{-1} VS (86 m^3 CH_4 $tonne^{-1}$ OFMSW). Under mesophilic conditions at OLR 1 kg VS m^{-3} day^{-1} with the same operating mode, however, the specific methane yield was lower at 0.256 m^3 CH_4 kg^{-1} VS (77 m^3 CH_4 $tonne^{-1}$ OFMSW); and signs of reduced operational stability were seen especially when at incremental increases in OLR were attempted. This was probably due to the low TAN concentrations, which stabilized at around 0.2 g N kg^{-1} WW and led to limited digester buffering capacity. In practice if the OLR in such a plant is to be reduced steps should be taken to maintain TAN and buffering capacity, e.g. by reducing water addition and allowing an increase in HRT. The strategy of replacing water with municipal biosolids digestate did address this problem and offered an alternative potential strategy for plants where reduction of water addition is not feasible for operational reasons.

8. Ongoing and future work

Since the completion of the above papers my own work has continued and extended in this area. In particular:

- I have completed a study of the transition in the dominant metabolic pathway in mesophilic anaerobic digestion of SSFW from acetoclastic the hydrogenotrophic methanogenesis in parallel with rising digester ammonia concentrations. The work involved start-up and operation of digesters at OLR of 3 and 5 g VS L^{-1} day^{-1}, with and without the trace element supplementation needed to allow stable operation at the expected digestate TAN concentrations. This is believed to be the first paper systematically to monitor the transition period, using both ^{14}C isotope labelling experiments and the results of 16s rRNA sequencing. (The manuscript has been submitted, the abstract of the work is presented in Appendix 2).

- In addition, I completed a long-term experiment looking at both mesophilic and thermophilic anaerobic digestion of SSFW, with and without (i) ammonia stripping and (ii) hydrogen addition for in situ biomethanisation of the biogas CO_2.

- Other work on biomethanisation has also been carried out using wastewater biosolids and synthetic substrates. This work is not yet published and not presented as part of the current PhD submission, but is mentioned here as it provides additional context on how the materials presented fit with other work being carried out in this field.

- Currently I am working on a 12-month project to upgrade biogas production in-situ from a pair of 3-litre fermenters fed on thickened sewage sludge.

- Future work is still needed to fully illustrate the mechanism of ammonia inhibition probably by developing approaches on intracellular pH and cation concentration measurements.

- The future work could focus on intensive molecular biology techniques (such as metagenomics, metatranscriptomics etc.) to provide clearer images on dynamic changes of microbial populations in anaerobic digestion. Although an increasing number of studies report the microbial community structure, our knowledge and understanding of the links between this and functionality is still in its infancy. Rapid progress will depend on the development of tools and methods of data analysis capable of elucidating these relationships.

- More comprehensive approaches such as FISH-MAR (Microautoradiography combined with fluorescence in situ hybridization) and DNA-SIP (DNA stable-isotope probing) are needed to be developed to provide further understanding of microbial communities by utilizing combined microbial identity and functional information. In the first piece of ongoing work mentioned above I used C-14 tracer technique and 16s rRNA sequencing to show clearer images on the responses from some of high-ammonia sensitive methanogens to the elevating ammonia concentrations until the extreme high conditions had reached. However, the independent information on either microbial identification or function are unable to illustrate the syntrophic relationship between SAOB and methanogens, which is key in understanding ammonia inhibition. Therefore, more

comprehensive techniques such as DNA-SIP are needed to answer the question who (what microbes) is doing what (what substrate is being consumed to produce methane), and how? This is the ultimate answer to solve various inhibition problems in anaerobic digestion.

- Further evaluation protocols on anaerobic degradability of biodegradable biopolymers are needed to improve and expand applications on anaerobic degradation of biopolymers.

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APPENDICES

Appendix 1. Analytical procedures, digester construction and operation

Total Solids (TS) and Volatile Solids (VS)

TS and VS determination was based on Standard Method 2540 G (APHA, 2005). After thorough agitation, approximately 25-50 g of sample was transferred into a weighed crucible by pipetting (digestate samples) or spatula (substrate samples). Samples were weighed to an accuracy of ± 0.001 g (Sartorius LC6215 balance, Sartorius AG, Gottingen Germany) and placed in an oven (Vulcan laboratory oven, LTE Scientific Ltd., Oldham UK) for drying overnight at 105 ± 2 °C. After drying the samples were transferred to a desiccator to cool for at least 40 minutes. Samples were then weighed again with the same balance, transferred to a muffle furnace (Carbolite Furnace 201, Carbolite, UK) and heated to 550 ± 10 °C for two hours. After this ashing step, samples were again cooled in a desiccator for at least one hour before weighing a third time.

After all analyses, crucibles were washed with detergent, rinsed with deionised water, and stored in an oven until required for the next analysis. Crucibles were transferred from the oven to a desiccator for cooling to room temperature before each analysis. Total and volatile solids were calculated according to the following equations:

$$\%\ \mathrm{TS}\ = \frac{W_3 - W_1}{W_2 - W_1} \mathrm{x}\ 100 \qquad \text{Equation 1.1}$$

$$\%\ \mathrm{VS\ (on\ a\ wet\ weight\ basis)} = \frac{W_3 - W_4}{W_2 - W_1} \mathrm{x}\ 100 \qquad \text{Equation 1.2}$$

$$\%\ \mathrm{VS\ (on\ a\ TS\ basis)} = \frac{W_3 - W_4}{W_3 - W_1} \mathrm{x}\ 100 \qquad \text{Equation 1.3}$$

Where:

W_1 = weight of empty crucible (g)

W_2 = weight of crucible containing fresh sample (g)

W_3 = weight of crucible and sample after drying at 105 °C (g)

W_4 = weight of crucible and sample after heating to 550 °C (g)

pH

pH was measured using a Jenway 3010 pH meter (Jenway Ltd., Essex UK) with a combination glass electrode, calibrated in buffers at pH 4, 7 and 9.2. The pH meter was temperature compensated and had a sensitivity of ±0.01 pH unit and accuracy of 0.01±0.005 pH units. Buffer solution used for calibration was prepared from buffer tablets (Fisher Scientific, UK) prepared according to the supplier's instructions. During measurements, the sample was stirred to ensure homogeneity. In addition, the pH probe was rinsed with DI water in between measurements and placed into a mild acid solution to avoid cross-contamination. Digestate samples were measured immediately after sampling to prevent changes in pH due to the loss of dissolved CO_2.

Alkalinity

Alkalinity was measured by titration based on Standard Method 2320B for Alkalinity (APHA, 2005). Digestate was sieved to obtain a homogenous sample and 2-5g of this was added to 40 ml of DI water. Titration was done using a Schott Titroline Easy automatic digital titration burette system (Schott, Mainz, Germany), with the samples being magnetically stirred while the titration was carried out. A 0.25 N H_2SO_4 titrant was used to determine endpoints of pH 5.7, 4.3 and 4.0, allowing calculation of total (TA), partial (PA) and intermediate alkalinity (IA) (Ripley *et al.*, 1986). PA is a measurement of bicarbonate buffering while IA is attributed to the buffering capacity of Volatile Fatty Acids (VFA).

The pH probe was calibrated before titration using buffers as described before and washed with DI water between subsequent samples to avoid cross contamination. Alkalinity was calculated according to the following equations:

$$\mathrm{TA} = \frac{(\mathrm{V}_{4.0} + \mathrm{V}_{4.3} + \mathrm{V}_{5.7})\ \mathrm{x\ N\ x\ 50000}}{\mathrm{V}} \qquad \text{Equation 1.4}$$

$$\mathrm{PA} = \frac{\mathrm{V}_{5.7}\ \mathrm{x\ N\ x\ 50000}}{\mathrm{V}} \qquad \text{Equation 1.5}$$

$$\mathrm{IA} = \frac{\mathrm{V}_{4.3}\ \mathrm{x\ N\ x\ 50000}}{\mathrm{V}_\mathrm{s}} \qquad \text{Equation 1.6}$$

Where:

TA = total alkalinity (mg $CaCO_3$ l^{-1})

PA = partial or bicarbonate alkalinity (mg $CaCO_3$ l^{-1})

IA = intermediate or volatile fatty acid alkalinity (mg $CaCO_3$ l^{-1})

V_s = volume of sample (ml)

$V_{subscript}$ = volume of titrant required to reach the pH value indicated in the subscript (ml)

N = normality of the H_2SO_4 titrant, or the theoretical normality multiplied by a correction factor for the specific batch of titrant

Total Ammonia Nitrogen (TAN)

Total ammonia nitrogen (TAN) analysis was based on Standard Method 4500-NH3 B and C (APHA, 2005). A sample aliquot of between 2-3g was weighed (i201, My Weigh Europe, Huckelhoven Germany) into a digestion tube and 50 ml of DI water added. Blanks (50 ml DI water) and standards (containing 10 ml of 1000 mg l^{-1} NH_4Cl with 40 ml DI water) were also prepared in digestion tubes. 5 ml of 10 M sodium hydroxide (NaOH) was added to each digestion tube to raise the pH above 9.5 and the samples were distilled using either a Foss Tecator Kjeltec system 1002 distillation unit (Foss Tecator A-B, Hoganas, Sweden) or a Büchi K-350 Distillation Unit (Büchi, UK). Erlenmeyer flasks previously filled with 25 ml of boric acid as an indicator were used to collect the distillate and progress of the distillation was indicated by a colour change from purple to green. The distillate was titrated manually with 0.25N H_2SO_4 using a digital titration system (Schott Titroline, Gerhardt UK Ltd) until an endpoint was reached as indicated by a colour change to purple at which point the volume of titrant added was recorded. Standards and blanks were distilled in the same way. The TAN concentration was calculated according to the following equation:

$$\mathrm{TAN} = \frac{(\mathrm{A} - \mathrm{B}) \text{ x } 14.0 \text{ x } \mathrm{N} \text{ x } 1000}{\mathrm{V_s}} \qquad \text{Equation 1.7}$$

Where:

TAN = total ammonia nitrogen (mg l^{-1})

A = volume of titrant used to titrate the sample (ml)

B = volume of titrant used to titrate the blank (ml)

N = normality of the H_2SO_4 titrant, or the theoretical normality multiplied by a correction factor for the specific batch of titrant

V_s = weight of sample (g)

Total Kjeldhal Nitrogen (TKN)

Total Kjeldhal Nitrogen (TKN) analysis was carried out on duplicate samples alongside blanks and controls as follows: 3-5 g (weighed to ± 1 mg) of sample was placed in a glass digestion tube. Two Kjeltab Cu 3.5 catalyst tablets were added to facilitate acid digestion by lowering the activation energy of the reaction. 12 ml of low nitrogen concentrated H_2SO_4 was added carefully to each

digestion tube and agitated gently to ensure that the entire sample was completely exposed to acid. The digestion tubes were then placed into the heating block with exhaust system using either a Foss Tecator 1007 Digestion System 6 (Foss Analytical, Hoganas Sweden) or a Büchi K-435 Digestion Unit (Büchi, UK) for approximately two hours until the solution colour became a clear blue-green. Both systems operated at 420 ± 5 ^{o}C and once the reaction was completed the tubes were cooled to around 50 ^{o}C and 40 ml of DI water slowly added to the digestion tube to prevent later crystallisation on further cooling. Samples, blanks and standards were then distilled and titrated as for Total ammonia nitrogen.

$$\mathrm{TKN} = \frac{(\mathrm{A} - \mathrm{B}) \text{ x } 14.0 \text{ x N x } 1000}{\mathrm{W_s}} \qquad \text{Equation 1.8}$$

Where:

TAN = total ammonia nitrogen (mg kg^{-1} wet weight)

A = volume of titrant used to titrate the sample (ml)

B = volume of titrant used to titrate the blank (ml)

N = normality of the H_2SO_4 titrant, or the theoretical normality multiplied by a correction factor for the specific batch of titrant

W_s = wet weight of sample (kg)

Gas Chromatograph determination of volatile fatty acid (VFA)

The method used was based on SCA (1979): Determination of Volatile Fatty Acids in Sewage sludge (1979). Samples were prepared for analysis by centrifugation at 14,000 g (micro-centrifuge, various manufacturers) for 15 minutes. 0.9 ml of the supernatant was transferred by pipette to vials with 0.1 ml formic acid to give a final concentration of 10% formic acid. Where dilution was necessary, deionised water was used and formic acid was added to give a concentration of 10% of the total volume for analysis. If the samples at this point were turbid they were centrifuged again at 14,000 rpm to obtain a clearer supernatant. The supernatant after acidification and centrifugation was transferred into the vials and loaded onto the GC auto-sampler ready for the VFA measurement.

A standard solution containing acetic, propionic, iso-butyric, n-butyric, iso-valeric, valeric, hexanoic and heptanoic acids, at three dilutions to give individual acid concentrations of 50, 250 and 500 mg l^{-1} respectively, was used for calibration and also loaded onto the GC.

Quantification of the VFA was by a Shimazdu GC-2010 gas chromatograph (Shimadzu, Milton Keynes, UK), using a flame ionization detector and a capillary column type SGE BP-21. The carrier gas was helium at a flow of 190.8 ml min^{-1} and a split ratio of 100 to give a flow rate of 1.86 ml min^{-1} in the column and a 3.0 ml min^{-1} purge. The GC oven temperature was programmed to increase from 60 to 210°C in 15 minutes with a final hold time of 3 minutes. The temperatures of injector and detector were 200 and 250°C, respectively.

Gas composition

The gas produced during anaerobic digestion of wastes contains methane and carbon dioxide (CO_2) as its major components with minor quantities of hydrogen (H_2), hydrogen sulphides (H_2S), nitrogen (N_2), and oxygen (O_2).

Methane and carbon dioxide

Biogas composition was quantified using a Varian Star 3400 CX gas chromatograph (Varian Ltd, Oxford, UK). The GC was fitted with a Hayesep C column and used either argon or helium as the carrier gas at a flow of 50 ml min^{-1} with a thermal conductivity detector. The biogas composition was compared with a standard gas containing 65 % CH_4 and 35% CO_2 (v/v) for calibration. A sample of 2 ml was taken from a Tedlar bag used for sample collection and was injected into a gas sampling loop. The small amount of air in the sample normally caused by atmospheric is corrected by excluding the volume of air from the total sample volume.

Gas volume

Unless noted, biogas was collected in a gas-impermeable sampling bags. Gas bag volumes were measured using a weight-type water displacement gasometer (Walker et al. 2009). The measurement procedure was as follows: the initial height of solution in the gasometer (h_1) was recorded before the collected gas was introduced into the column through the top valve. After the bag was empty, the final height (h_2) and the weight of water (m) were recorded, as well as the temperature (T) and pressure (P) in the room. All gas volumes reported are corrected to standard temperature and pressure of 0°C, 101.325 kPa as described by Walker et al. (2009) according to the following equations:

Height Gasometer Governing Equation Equation 1.9

$$V_{stp} = \frac{T_{stp} A}{T_{atm} p_{stp}} \left(\left(p_{atm} - p_{H_2O}(T_{atm}) - \rho_b g \left(h_{t2} - h_{c2} \right) \right) h_{c2} - \left(p_{atm} - p_{H_2O}(T_{atm}) - \rho_b g \left(h_{t1} - h_{c1} \right) \right) h_{c1} \right)$$

Weight Gasometer Governing Equation Equation 1.10

$$V_{stp} = \frac{T_{stp}A}{T_{atm}p_{stp}}\left[\left(\left(P_{atn} - p_{H_2O}(T_{atm}) + \rho_b g\left(H - h_1 - \frac{m_b}{A\rho_b}\right)\right)\left(h_1 + \frac{m_b}{A\rho_b}\right)\right) - \left(p_{atn} - p_{H_2O}(T_{atm}) + \rho_b g(H - h_1)\right)h_1\right]$$

Where:

V = gas volume (m^3)

P = pressure (Pa)

T = temperature (K)

H = total height of column (m)

h = distance to liquid surface from a datum (m)

A = cross-sectional area of gasometer (m^2)

m_b = mass of barrier solution (kg)

ρ = density pf barrier solution (kg m^{-3})

g = gravitational acceleration (m s^{-2})

1, 2, stp, atm, b, t, c subscripts refer to condition 1 (before addition of gas to column), condition 2 (after gas addition to column), standard temperature and pressure, atmospheric, barrier solution, collection trough and column respectively.

Digester construction and operation

The digesters had a total volume of 5 litres and were operated at a working volume of 4 litres. A schematic drawing of a pair of digesters is shown in Figure 2.1. The digesters were constructed in PVC with a top flange to which a top plate was secured using stainless steel bolts and wing nuts. A gas tight seal between the top plate and the digester flange was maintained using a closed pore neoprene gasket. The top plate was fitted with a gas outlet connector and a feed port sealed with a rubber bung. On the top plate a DC motor was mounted which coupled to the digester stirrer through a draught tube water gas seal, the draught tube itself being secured in a gas tight compression seal. Digestate was removed from the digester via a 15mm diameter outlet port at the base of the digester. The contents of the digesters were continuously stirred by means of an asymmetric stirrer at 40rpm. Temperature was maintained at 35 ^oC +/- 0.5 (or as noted) by water circulating through an external heating coil that surrounded the digesters. When assembled, and before filling, each digester was tested for gas leaks by applying a positive pressure to the digester and submerging in water to ensure there was no gas escape when all ports were sealed. The digesters were connected to gas counters, which continuously measured gas production throughout the digestion period; the gas counters operated by the alternate filling and

discharging of a calibrated cell which logged each discharge via a labjack (labjack ltd) computer interface. (Walker et al, 2009). The calibration of each gas counter was checked approximately weekly by attaching a gas-impermeable collection bag (e.g. Tedlar SKC 232, SKC Ltd, Blandford Forum, UK) to the gas vent of gas counter.

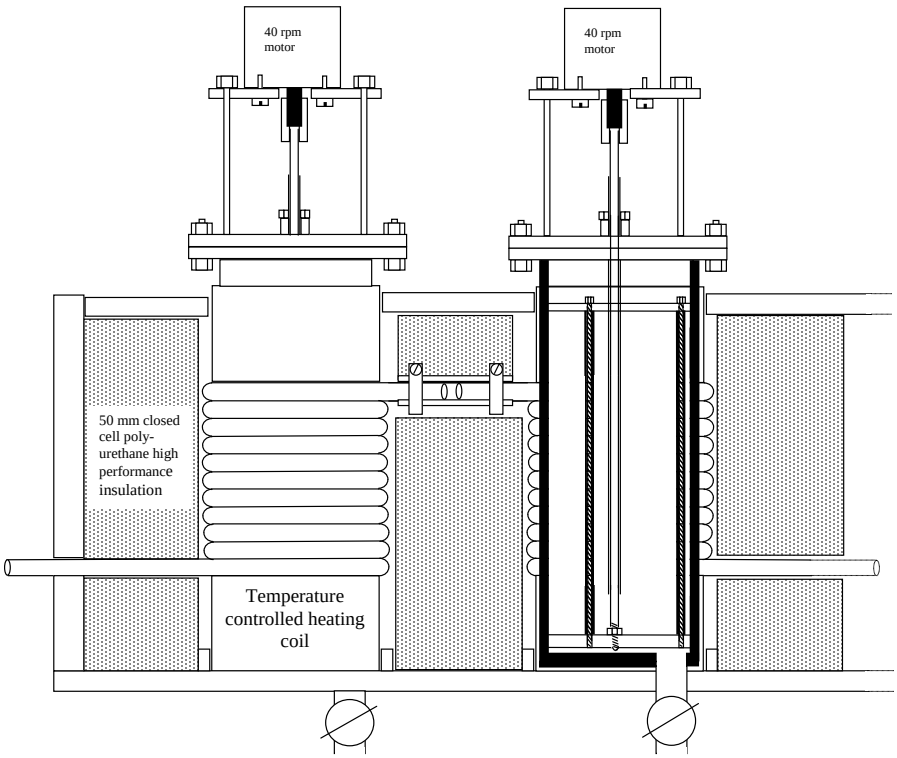

Figure 2.1 Schematic of 5-L CSTR digester used with cross-section showing details of heating and stirring systems

Digester operation and calculations

The digesters were operated in a semi continuous mode i.e. fed daily fed with a specific amount of feedstock and digestate removed to maintain a constant volume in the digesters. The organic loading rate (OLR) was determined according to Equation 1.11.

$$OLR = \frac{mVS_{substrate}}{V_{reactor}} \qquad \text{Equation 1.11}$$

Where:

m is the mass of substrate daily added to the reactor (g d^{-1})

$VS_{substrate}$ is the volatile solid content of feedstock (% wet weight)

$V_{reactor}$ is the volume of reactor (l)

The Hydraulic Retention Time (HRT) of the digester is expressed in Equation 1.12.

$$HRT = \frac{V_{reactor}}{Q}$$ Equation 1.12

Where:

$V_{reactor}$ is the working volume of each reactor (ml)

Q is the daily flow of material (substrate added and digestate removed) through the reactor (ml d^{-1})

The amount of substrate and digestate was measured in g but for ease of calculation it was assumed that both the substrate and digestate had a specific gravity of 1.0. Therefore, 1g of substrate and digestate was considered to be equivalent to 1ml.

The performance of digesters was monitored in terms of specific biogas and methane production which were calculated using equations 1.13 and 1.14,

$$\text{Specific biogas production} = \frac{V_{biogas}}{OLR \times V_{reactor}}$$ Equation 1.13

Where:

V_{biogas} is the volume of biogas produced daily (ld^{-1})

OLR is the organic loading rate ($gVSl^{-1}d^{-1}$)

$V_{reactor}$ is the volume of reactor (l)

$$\text{Specific methane production} = \frac{V_{CH4}}{OLR \times V_{reactor}}$$ Equation 1.14

Where:

V_{CH4} is the volume of methane produced daily (ld^{-1})

OLR is the organic loading rate ($gVSl^{-1}d^{-1}$)

$V_{reactor}$ is the volume of reactor (l)

Appendix 2. Abstract of the manuscript submitted

Transitions in metabolic pathway and microbial community structure in response to increasing ammonia concentrations were determined by detailed monitoring of mesophilic anaerobic digesters seeded with a predominantly acetoclastic methanogenic community taken from a sewage sludge digester. Ammonia concentration was raised by switching the feed to source segregated domestic food waste and controlling feed rate to give two different organic loading rates (OLR) and hydraulic retention times (HRT) in paired digesters. One of each pair was dosed weekly with trace elements (TE) known to be essential to the transition, with the other unsupplemented digester acting as a control. Samples taken during the 180-day trial were used to determine the metabolic pathway to methanogenesis using ^{14}C labelled acetate. Partitioning of ^{14}C between the product gases was interpreted via an equation to indicate the proportion produced by acetoclastic and hydrogenotrophic routes. Archaeal and selected bacterial groups were identified by 16S rRNA sequencing, to determine relative abundance and diversity. Acclimatisation for digesters with TE was relatively smooth, but OLR and HRT influenced both metabolic route and final community structure. The ^{14}C ratio could be used quantitatively and, when interpreted alongside archaeal community structure, showed that at longer HRT and lower loading *Methanobacteriaceae* were dominant and hydrogenotrophic activity accounted for 77% of methane production. At the higher OLR and shorter HRT, *Methanosarcinaceae* were dominant with the ^{14}C ratio indicating simultaneous production of methane by acetoclastic and hydrogenotrophic pathways: the first reported observation of this in digestion under

mesophilic conditions. Digesters without TE supplementation showed similar initial changes but, as expected, failed without completing the transition.

Appendix 3. Bibliography of all the published papers and submitted manuscript

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Research Paper

Influence of ammonia in the anaerobic digestion of food waste

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ABSTRACT

Ammonia toxicity was investigated in mesophilic (37 °C) and thermophilic (55 °C) digesters using high and low-nitrogen food wastes (FW). Mesophilic inoculum was successfully acclimated to thermophilic conditions by a step change in temperature followed by incremental increases in organic loading rate (OLR). Digestion performance and stability were monitored via volatile fatty acid (VFA) profiles, alkalinity, specific methane production (SMP) and volatile solids (VS) destruction. High-nitrogen mesophilic digesters stabilised by day 70 and responded well to increases in OLR, with a SMP of 0.45 L CH_4 g^{-1} VS, stable pH, and VFA < 0.2 g L^{-1}. Thermophilic digesters fed on high and low-nitrogen FWs showed almost identical responses to acclimatisation. Behaviour then deviated, with high-nitrogen digesters accumulating VFA. Stable pH could be maintained for up to 310 days before eventual failure at total ammonia nitrogen (TAN) concentration > 5.0 g N L^{-1}, although accumulation of propionic and other longer-chain VFA began at TAN ~3.5 g N L^{-1}. The low-nitrogen digesters showed no VFA accumulation, and had a SMP of ~0.39 L CH_4 g VS L^{-1} day^{-1} with 91% VS destruction. After 384 days the TAN concentration was increased from ~0.7 g N L^{-1} by urea addition. This resulted in progressive VFA accumulation in one digester when TAN reached ~3.5 g N L^{-1}, while stable operation at very low VFA was possible at up to ~2.5 g N L^{-1} in the second digester. The results confirmed acclimatisation to thermophilic conditions was possible on a far shorter timescale than to high TAN concentrations.

1. Introduction

Anaerobic digestion is an effective technology for recovering value from food wastes in the form of biogas as a renewable fuel and nutrients for recycling back to agriculture. These wastes arise at various points in the production and distribution chain: their characteristics and composition reflect this, and digestion of a number of relatively homogeneous wastes and effluents from food processing has been practiced for a long time [1]. Despite some regional differences, the composition of food waste from domestic properties and catering establishments is relatively similar in many parts of the world [2]; but it is only recently that source segregated collection of this material has become popular, meaning that larger volumes are available for processing. Pilot-scale studies carried out with this material in 2003 considered both mesophilic and thermophilic operation [3] and based on these studies the first full-scale commercial demonstration plant was designed as a continuously stirred tank reactor (CSTR) operated at mesophilic temperature [4]. Since then a number of alternative technologies for food waste digestion have been suggested including two phase systems [5] and leach bed reactors [6,7]. Digestion of source segregated domestic food waste is now a popular approach in many areas of the world [8,9], with 400 plants in the UK alone contributing 480 MW to the electricity grid in 2016 [10]. Operation of food waste digesters at thermophilic temperatures remains challenging, however, and is only possible through interventions to reduce inhibition such as dilution [11,12] or ammonia removal [13], both of which require additional engineering and control systems. A detailed understanding of the threshold limits of inhibition is therefore important to establish the design and operating criteria for implementation of these interventions.

The problem of inhibition arises because most domestic food wastes have a relatively high content of proteinaceous material, which on hydrolysis may lead to elevated concentrations of total ammonia nitrogen (TAN). A proportion of this TAN, depending on temperature and pH, is present as free ammonia nitrogen (FAN). Even under mesophilic conditions this can cause operational problems during digestion [14–16] and in thermophilic conditions it has led to severe inhibition, accumulation of volatile fatty acids (VFA), and eventual process failure [13,17]. A substantial amount of information is now available on threshold concentrations for TAN inhibition in mesophilic conditions [18–20], with reported values generally in the range of 3–5 g N L^{-1}. The uncertainty in this value is due to several factors that may influence the onset of process instability or loss in digestion performance, such as

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the pH, operating temperature and microorganism adaptation. With the development of new genetic and molecular tools, some new insights are now emerging into how communities might adapt or acclimatise to high ammonia environments [21,22].

Under thermophilic conditions a greater proportion of TAN is present as the more inhibitory free ammonia as the equilibrium is temperature-dependent [23]; but less information is available on the toxic thresholds in thermophilic systems, and virtually none concerning food waste digestion. The problem is a circular one in that, firstly, there are few sources of thermophilic inoculum that has been 'acclimatised' to high-nitrogen feedstock; secondly, the process of acclimatisation to thermophilic temperatures can itself lead to signs of instability [24]. Hence, when a mesophilic inoculum is adapted to thermophilic conditions using a typical domestic food waste as the feedstock, fully stable operation may not have been established at the higher temperature before instability starts to occur due to the build-up of ammonia. This situation can lead to uncertainty regarding which stress factor leads to digester instability, as monitored by VFA accumulation, loss of biogas production and other key indicators. To ensure that these two factors could be clearly separated and therefore accurately reported, the current work had the following specific objectives: i) to run digesters on high nitrogen (high-N) food waste (FW) under mesophilic conditions in order to demonstrate that the material itself contained no inherently toxic or inhibitory components at the loading used, and establish a baseline level of digestion performance; ii) to acclimate inoculum from the same source to thermophilic conditions using a low-nitrogen (low-N) FW to demonstrate that the acclimatisation method was successful; iii) to feed an acclimated stable thermophilic inoculum on high-N FW from the same source to demonstrate the effect of the increased nitrogen content; and iv) to find the critical threshold for ammonia toxicity in the digesters fed on low-N FW by increasing the TAN, by adding urea both gradually and as a single dose. A further purpose of the final objective was thus to give an insight into the mechanism of adaptation to high TAN concentrations by differentiating between a gradual growth-mediated response and that to a shock load. In all cases the onset of instability was monitored by reference to VFA concentrations and profiles, and changes in alkalinity ratio, pH and biogas productivity and composition.

The current work is thus the first long-term comparative study of thermophilic and mesophilic digestion of source segregated domestic food waste in a parallel trial supported by compositional analysis and stability and performance data.

2. Materials and methods

2.1. Food wastes

The high-N FW was source segregated domestic waste collected commercially by Veolia Environmental Services (UK) Ltd from households in Eastleigh, Hampshire, UK. The waste is collected in biodegradable plastic bags, and a representative sample of these with a weight of around 300 kg was prepared for use throughout the experimental work. The FW was taken out of the bags, and any obvious non-food contamination removed along with any large bones and seeds. The sample was then ground (S52/010 Waste Disposer, IMC Limited, UK) to a homogeneous pulp, mixed thoroughly in a single batch and frozen at −18 °C in snap-top plastic containers in ~3 kg aliquots. When needed, the feedstock was thawed and stored at 4 °C and used within a period of a few days.

The low-N FW was made using mainly vegetables and fruits with a small amount of meat, dairy products and bread (see Supplementary materials for recipe). The ingredients were chopped, mixed and then ground before freezing as above. Before use the thawed material was mixed with cellulose powder (α-cellulose C8002, Sigma-Aldrich) to give a volatile solids (VS) concentration similar to that of the high-N FW.

2.2. CSTR digesters

Four pairs of 4-L working volume anaerobic digesters of a continuously-stirred tank reactor (CSTR) design were used. These were constructed of PVC tube with gas-tight top and bottom plates. The top plate was fitted with a gas outlet, a feed port sealed with a rubber bung, and a draught tube liquid seal through which an asymmetric bar stirrer was inserted with a 40 rpm motor mounted directly on the plate. Digester temperature was maintained at 37 ± 1 °C (mesophilic) or 55 ± 1 °C (thermophilic) by circulating water from a thermostatically-controlled bath through heating coils around the digesters. Biogas was measured using tipping-bucket gas counters with continuous datalogging. Gas counter calibration was checked weekly by collecting the gas produced over a one-day period in a gas-impermeable bag and measuring its volume in a weight-type gasometer [25]. All gas volumes reported are corrected to standard temperature and pressure (STP) of 0 °C, 101.325 kPa.

2.3. Digester set-up, operation and monitoring

Eight digesters were inoculated with digestate taken from a mesophilic digester treating municipal wastewater biosolids (Millbrook wastewater treatment works, Southampton, UK). The digesters were fed semi-continuously by addition of substrate on a daily basis with removal of digestate to maintain a constant volume. During operation all digesters were supplemented with the 5-element TE stock solution (Table 1) at the rate of 1 mL kg^{-1} wet weight (WW) of feedstock added, unless otherwise noted.

Four of the digesters (T1-T4) were acclimated to thermophilic conditions by increasing the temperature to 55 °C in one step and then not feeding for 6 days. One pair of these (T1 and T2) was fed on low-N FW and the other pair (T3 and T4) on high-N FW. Feeding was started at an organic loading rate (OLR) of 0.5 g VS L^{-1} day^{-1} and was increased daily by 0.05 g VS L^{-1} day^{-1} until 2 g VS L^{-1} day^{-1} was reached on day 39. T1–T4 were then run at OLR 2 g VS L^{-1} day^{-1} for the duration of the experiment, except when failure conditions were apparent, at which point feeding was stopped to allow recovery.

The other four digesters (M1-M4) were maintained at mesophilic temperature and fed on high-N FW at an OLR of 2 g VS L^{-1} day^{-1} for a period of 97 days to ensure stable operation. The OLR on M3 & 4 was then increased to 3 g VS L^{-1} day^{-1} by raising the loading by 0.05 g VS L^{-1} day^{-1} every two days over a 3-week period. Starting on day 177, the OLR was increased over a 5-week period to 3 g VS L^{-1} day^{-1} in M1 & 2 and to 4 g VS L^{-1} day^{-1} in M3 & 4. These OLRs were then

Table 1
Trace element solutions.

Cations	Compound used	Compound concentration in stock solution, g L^{-1}	TE concentration in 5 and stock solutions, g L^{-1}	
			5-element	11-element
Aluminium (Al)	$AlCl_3 \cdot 6H_2O$	0.895	–	0.1
Boron (B)	H_3BO_3	0.572	–	0.1
Cobalt (Co)	$CoCl_2 \cdot 6H_2O$	4.038	1.0	1.0
Copper (Cu)	$CuCl_2 \cdot 2H_2O$	0.268	–	0.1
Iron (Fe)	$FeCl_2 \cdot 4H_2O$	35.597	–	10.0
Manganese (Mn)	$MnCl_2 \cdot 6H_2O$	4.258	–	1.0
Nickel (Ni)	$NiCl_2 \cdot 6H_2O$	4.050	1.0	1.0
Zinc (Zn)	$ZnCl_2$	0.417	–	0.2
Oxyanions				
Molybdenum (Mo)	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	0.368	0.2	0.2
Selenium (Se)	Na_2SeO_3	0.438	0.2	0.2
Tungsten (W)	Na_2WO_4 $2H_2O$	0.359	0.2	0.2

Table 2
Planned operating conditions during experimental period.

	Day	M1 & 2	M3 & 4	
Feedstock		high-N FW	high-N FW	
Temp °C		37	37	
OLR (gVS L^{-1} day^{-1})	0 – 97	2	2	–
	98–116	2	2–3	–
	117–176	2	3	–
	177–209	2–3	3–4	–
	210–296	3	4	–
		T1	T2	T3 & 4
Feedstock		low-N FW	low-N FW	high-N FW
Temp °C		55	55	55
OLR (gVSL^{-1} day^{-1})	0 – 6	0	0	0
	7–39	0.5–2	0.5–2	0.5–2
	40 on	2	2	2
Urea: Target TAN (g N L^{-1})	384	2.5	0	–
	441 on	–	0–2.5	–
	464 on	2.5–3.5	0–2.5	–
	750 on	4	3	–

maintained until the end of the experiment on day 296.

In the second part of the study the ammonia concentration in the thermophilic digesters receiving low-N FW (T1 and T2) was raised by adding urea. This was added to T1 on day 384 as a single dose of 20.0 g aimed at increasing the TAN concentration to ~2.5 g N L^{-1}. T1 was then left for 80 days without further urea addition to allow acclimatisation, after which the TAN content was raised gradually to ~3.5 g N L^{-1} by adding urea in the daily feed to give this target concentration. The TAN concentration was further increased between day 750 and 875 to a final value of around ~4.2 g N L^{-1}. In T2 the TAN concentration was increased to ~2.5 g N L^{-1}, but this was done gradually by adding an initial dose of 7.7 g of urea to the T2 digester on day 441and then adding urea to the daily feed. This allowed comparison with the effect of the shock urea load applied to T1. The TAN concentration in T2 was then raised to ~3.0 g N L^{-1} between day 750–875 in order to provide a detailed profile of the stability parameters around the threshold ammonia toxicity threshold.

Digester operational modes during the experimental period are summarised in Table 2.

2.4. Analytical methods

Total and volatile solids (TS and VS) were measured according to Standard Method 2540 G [26] using a Heraeus Function Line Series oven and a 201/301 Carbolite muffle furnace. pH was determined using a Jenway 3010 meter (Bibby Scientific Ltd, UK) with a combination glass electrode calibrated in buffers at pH 4, 7 and 9.2 (Fisher Scientific, UK). Alkalinity was measured by titration with 0.25N H_2SO_4 to endpoints of pH 5.75 and 4.3 using an automatic digital titration burette system (SCHOTT titroline easy), to allow calculation of total (TA), partial (PA) and intermediate alkalinity (IA) [27]. Total Kjeldahl Nitrogen (TKN) was determined after acid digestion, by steam distillation and titration. This used a BÜCHI Digestion Unit K-435 with H_2SO_4 and K_2SO_4 as the reactants and $CuSO_4$ as the catalyst to convert amino-nitrogen and free ammonia (NH_3) to ammonium (NH_4^+). This was then measured as total ammonia nitrogen (TAN) using a BÜCHI Distillation Unit K-350 with NaOH addition, followed by collection of the distillate in boric acid indicator and titration with 0.25 N H_2SO_4. VFA concentrations were determined by gas chromatography (Shimadzu GC-2010), with a flame ionisation detector and a capillary column (SGE BP-21) and helium as carrier gas. Samples were acidified to 10% using formic acid and measured against mixed standards of 50, 250 and 500 mg L^{-1} of acetic, propionic, isobutyric, *n*-butyric, isovaleric, valeric, hexanoic and heptanoic acids. Biogas composition (CH_4 and CO_2) was determined using a Varian star 3400 CX Gas Chromatograph fitted with a packed stainless steel SUPELCO 80/100 mesh porapack-Q column and a TCD detector. The GC was calibrated with a standard gas containing 65% CH_4 and 35% CO_2 (v/v) (BOC, UK).

Further characterisation was carried out on samples prepared by air drying to constant weight and then milled to a particle size ≤0.5 mm in a micro-hammer mill (Retsch, Germany). Calorific values (CV) were determined using a bomb calorimeter (CAL2k-ECO, South Africa). Carbohydrates were determined after preliminary acid hydrolyis using 72% sulphuric acid in an orbital shaker (1 h at 150–200 rpm) [28]. The hydrolysate was autoclaved at 121 °C for 1 h and analysed using a Dionex HPLC with an EC-400 detector and fitted with a Carbopac PA1 column (250 × 4 mm) in combination with a Carbopac guard column (25 × 4 mm) (Dionex Corp, Sunnyvale, USA). Lipids were measured after Soxhlet extraction using *n*-hexane [29]. Inorganic elements were extracted in nitric acid and the extract filtered and diluted to 50 mL with deionised water (Milli-Q Gradient, Millipore, Watford, UK). Phosphorus was measured by the ammonium molybdate spectrometric method [30]. Digestate samples for trace element determination (Co, Fe, Ni, Mo, Se) were sent to an external laboratory for analysis by ICP-MS (LGC, Teddington, UK). Fibre analysis (hemi-cellulose, cellulose and lignin) for low-N FW was done using the Fibercap method [31] in a FOSS kit FibretecTM 2023 (Hillerød, Denmark). Characterisation of the FW for trace element and fibre content and elemental composition was carried out by MTT Agrifood Research, Finland. Biochemical methane potential (BMP) was determined as described in [16] with a test duration of 28 days.

2.5. Calculation

Ammonia toxicity thresholds are expressed as TAN concentrations at the temperature and pH as measured, and this data is then used to calculate the equivalent FAN concentrations [32]. Theoretical CV was calculated based on the elemental composition, using the Dulong equation according to the method in Combustion file 24 [33]; and on the biochemical composition according to the values for protein, lipid and carbohydrate suggested by Angelidaki and Sanders [34]. The maximum theoretical methane production (ThMP) and biogas methane content was calculated from the elemental composition using the Buswell equation in conjunction with Avogadro's law [34,35]. For calculation of energy recovery the calorific value (higher heat value) of methane was taken as 39.84 MJ m^{-3} CH_4 at STP. VS destruction was calculated using a mass balance approach based on digestate VS concentration and taking into account the reduction in digestate volume.

3. Results and discussion

3.1. Feedstock and inoculum characteristics

The characteristics of the two types of FW are shown in Table 3, and of the inoculum in Table 4. The low-N FW had a TKN content of 1.45% on a TS basis, reflecting its ingredients which were mainly fruit and vegetables. The TKN content of the high-N source segregated domestic food was 3.09% TS; in this and other respects it was typical of source segregated food wastes of this type [36]. The C/N ratios of the low and high-N FWs based on elemental composition were 16.5 and 46.8 respectively. The measured calorific values of the feedstocks were in good agreement with calculated values based on the Dulong equation, providing support for the accuracy of the elemental analysis. Calculated values based on biochemical composition were slightly lower value than the measured values.

3.2. Mesophilic digestion

The experiment ran for 296 days, equivalent to a cumulative total of

Table 3
Food waste characteristics.

Parameter	Source segregated kerbside collected domestic food waste	low-N synthetic food waste
Basic characteristics for anaerobic digestion		
TS (% wet weight)	23.91	22.48
VS (% wet weight)	21.64	21.88
VS (% TS)	90.51	97.33
Nutrients value as fertiliser substitute		
TKN (% TS)	3.09	1.45
TP (P) (g kg^{-1} TS)	3.80	–
TK (K) (g kg^{-1} TS)	12.87	–
Essential trace elements (mg kg^{-1} TS)		
Cobalt (Co)	0.086	*ND
Iron (Fe)	121.1	38.2
Manganese (Mn)	90.05	–
Molybdenum (Mo)	0.506	0.23
Selenium (Se)	0.127	*ND
Tungsten (W)	< 0.015	–
Biochemical composition (g kg^{-1} VS)		
Carbohydrates	525	555
Lipids	151	13
Crude proteins	213	91
Hemi-cellulose	66	49
Cellulose	68	324
Lignin	16	5
Elemental analysis(%VS)		
C	54.89	47.52
H	6.89	6.94
N	3.32	1.02
S	0.25	–
Calorific Value (kJ g^{-1} VS)		
Measured CV	23.2	18.0
Calculated CV (Du Long)	22.6	19.0
Calculated CV (Biochemical)	21.2	17.8

* ND: not detected.

Table 4
Mesophilic inoculum characteristics.

Parameters	Value
pH	7.26
TS (% wet weight)	3.46
VS (% wet weight)	2.31
TAN (mg N kg^{-1} wet weight)	1393
Total alkalinity (mg kg^{-1} wet weight as $CaCO_3$)	7027
Intermediate alkalinity (mg kg^{-1} wet weight as $CaCO_3$)	2238
Partial alkalinity (mg kg^{-1} wet weight as $CaCO_3$)	4789
Total VFA (mg L^{-1})	53

3.1 and 4.0 HRT based on the total volumes of feedstock added to digesters M1 & 2 and M3 & 4, respectively. Results for digestion performance are presented in Fig. 1.

Biogas production started immediately on adding feed to the inoculum, and over the course of the experiment volumetric biogas production (VBP) (Fig. 1a) mirrored changes in loading. The specific methane production (SMP) stabilised at around 0.460 L CH4 g^{-1} VS day^{-1} (Fig. 1b) although it was lower and less stable over the first 70 days of operation. Methane content varied between 55 and 60%, with the lower percentage in the period between days 40–70. Although there appeared to be no long-term performance issues with acclimatisation a sharp increase in total VFA (TVFA) concentrations can be seen around day 40 (Fig. 1c), which peaked at day 50 and had returned to baseline values by day 85. This pattern has been noted several times in the past when using an inoculum from this source and switching to a new substrate [37]. The reason for it is unknown but its regularity of appearance has earned it the name 'the 40 day bump'. Individual VFA profiles are shown in Supplementary materials, and show that the VFA peaks were mainly composed of acetic acid with a small increase in isovaleric concentrations. The increase in TVFA is mirrored by the sharp increase in the IA/PA ratio (Fig. 1d), although the pH remained above 7 (Fig. 1e) and finally stabilised around 7.9–8.0. As anticipated the TAN in the digestate increased (Fig. 1f) reaching an equilibrium value of ~4.5 g L^{-1} by day 290. This provided strong buffering to the system and accounted for the elevated pH and high partial alkalinity (PA) which gradually increased from 4 g $CaCO_3$ L^{-1} at the beginning of the experiment to above 15 g $CaCO_3$ L^{-1} around day 130. The initial IA/PA ratio of 0.45–0.48 decreased to ≤ 0.3 even when the OLR was increased to 3 and 4 g VS L^{-1} day^{-1}, within the suggested range for stable digestion [27]. Digestate solids content had also stabilised by the end of the run, with a slightly higher proportion of VS as %TS and % WW in the digesters at the higher OLR (Fig. 1g and h).

From day 70 all of the digesters had a high and reasonably stable gas production, low VFA and a low IA/PA ratio confirming that successful acclimatisation had occurred and the high-N FW had no apparently toxic components. These results for mesophilic digestion of food waste are in good agreement with those of Banks et al. [15] and Zhang and Jahng [38].

3.3. Thermophilic digestion

3.3.1. Acclimatisation to thermophilic conditions

T1 & 2 were fed with low-N FW and T3 & 4 with high-N FW, but otherwise the conditions and feeding regime in these two pairs of digesters were the same. Temperature was raised on day 0 and feeding began on day 6. The sudden increase in temperature is a shock to the system and this was reflected in the analytical results for process stability parameters over the following 60 days (Fig. 2). SMP was initially low (Fig. 2a) with a biogas methane content of around 20% (Fig. 2b). Once substrate was added this was primarily converted to VFA (Fig. 2c) which rose to between 3.5–5.0 g L^{-1} irrespective of feed type. There was a corresponding increase in the IA/PA ratio (Fig. 2d) in response to the VFA production, although the moderate rate of feed addition prevented the pH dropping to an inhibitory value (Fig. 2e). From day 15 the digesters started to recover and this can be seen by the increase in biogas methane content (Fig. 2b), the reduction in TVFA (Fig. 2c), a fall in the IA/PA ratio (Fig. 2d) and an increase in the SMP (Fig. 2a). VS content in T3 & 4 rose slightly but the VS/TS ratio in all four digesters remained similar (Fig. 2g and h). By day 20 digestion appeared to be reasonably stable although the TVFA concentration fluctuated until around day 60: this may represent a thermophilic version of the '40 day bump', but other factors such as the temperature change and rising OLR are also present. Individual VFA profiles are shown in Supplementary materials, and are closely similar to those reported by Yirong et al. [36] for start-up on a similar FW feedstock. The only major deviation between the digesters over this period was in the TAN concentration (Fig. 2f) which gradually decreased in the low-N fed digesters T1 & T2 and increased in the high-N fed digesters T3 & T4. The results clearly showed that both pairs of digesters responded in a similar way to the heat shock and had acclimatised to the applied load by day 60, with pH around neutral, IA/PA ratio between 0.4–0.5 and TVFA generally below 500 mg L^{-1}. These values are within the limits suggested by Ferrer et al. [39] who proposed the following to prevent failure in thermophilic digesters: acetic acid < 600 mg L^{-1}, TVFA < 3700 mg L^{-1}, intermediate alkalinity < 1800 mg $CaCO_3$ L^{-1}, IA/PA < 0.9, and biogas methane content > 55%.

3.3.2. Thermophilic operation on low-N FW

Fig. 3 shows some key results over the 383-day operational period during which all performance and stability indicators settled within an acceptable range, with pH around 7.4 (Fig. 3a), IA/PA ratio between 0.4–0.5 (Fig. 3b), and TVFA generally below 500 mg L^{-1} (Fig. 3c). There were some minor deviations: for example VBP was less stable for

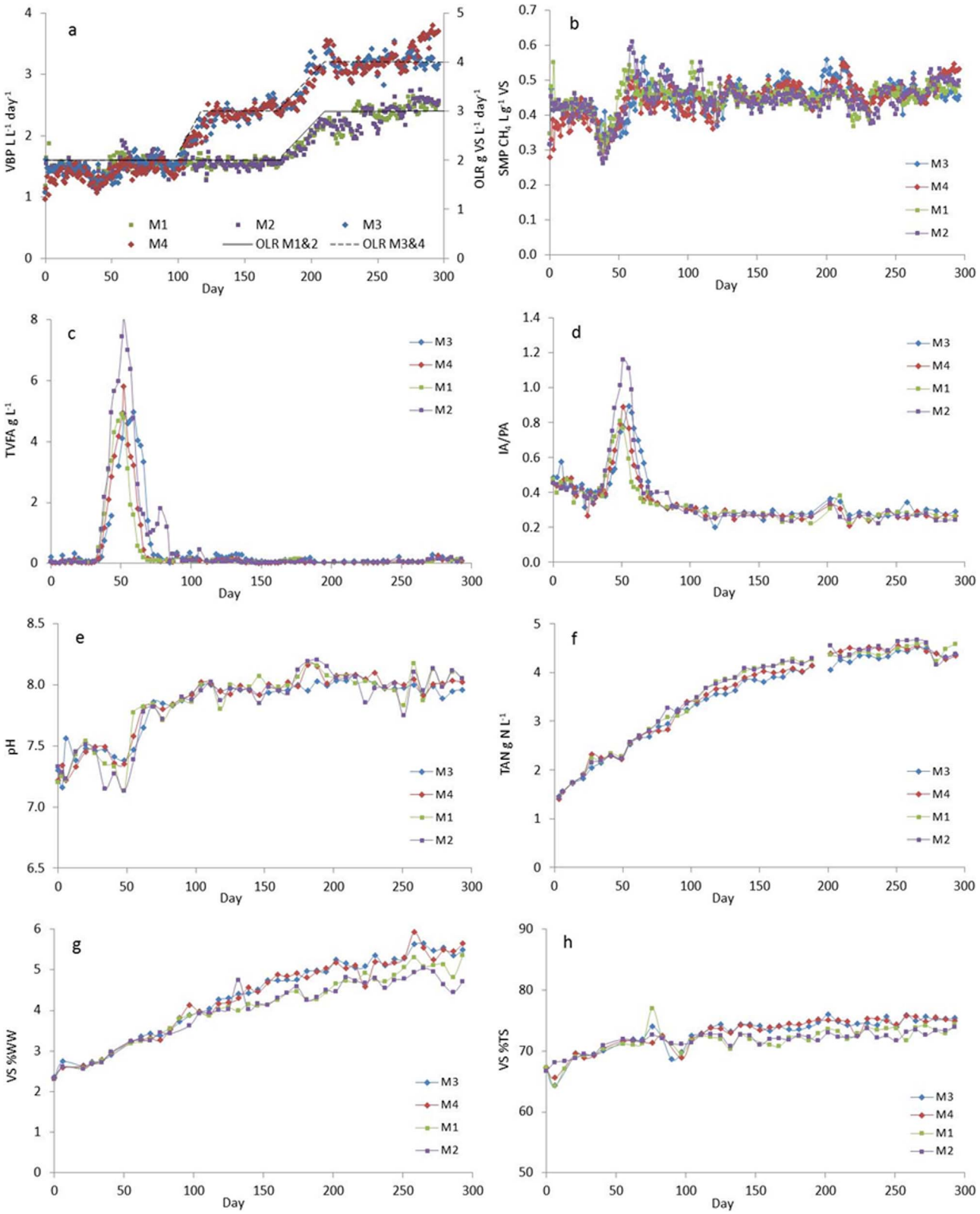

Fig. 1. Selected monitoring parameters during mesophilic digestion of high-N FW. (a) VBP, (b) SMP, (c) TVFA (d) IA/PA ratio, (e) pH, (f) TAN content, (g) VS %WW (h) VS %TS. Vertical dotted lines indicate changes in OLR as noted in Table 2.

short periods around days 133 and 297 (Fig. 3d), but this was due to short-term heater failures causing temporary cooling of the digesters, and production rapidly recovered when the operating temperature was restored. The average SMP in both T1 and T2 between days 283–383 was 0.386 L CH_4 g^{-1} VS, corresponding to recovery of 85% of the measured calorific value as methane. The digestate VS concentration was around 2.5%, corresponding to around 90% VS destruction of the low-N FW on a mass balance basis. It can be seen that the low-N feed allowed successful and stable long-term operation, and as 3 HRT had been achieved the digesters were considered to be in a suitable state for

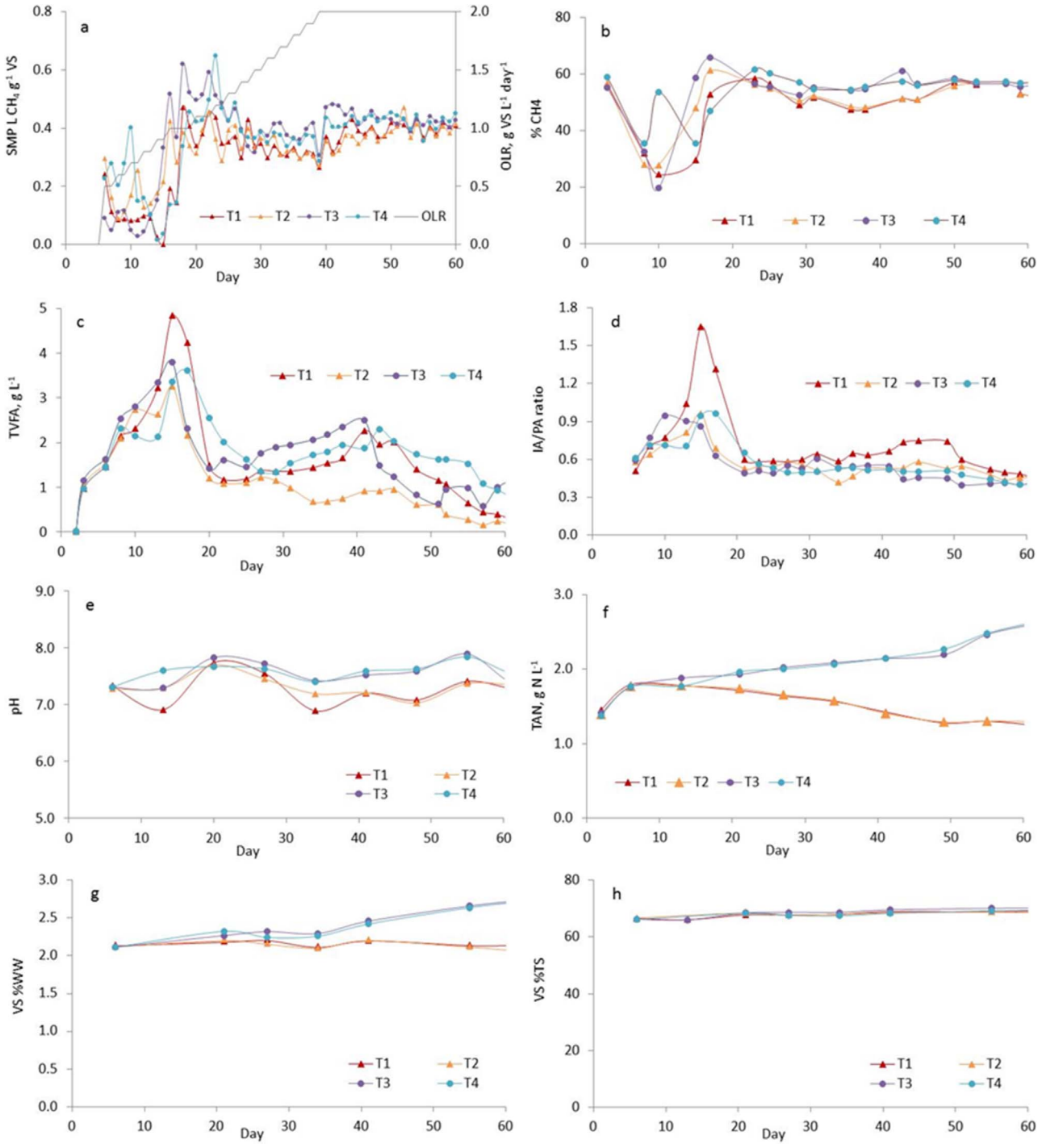

Fig. 2. Selected monitoring parameters during acclimatisation of thermophilic digesters (day 0–60) (a) SMP, (b) biogas methane content, (c) TVFA (d) IA/PA ratio, (e) pH, (f) TAN, (g) VS as %WW and (h) VS as %TS.

the N augmentation study using urea.

3.3.3. Thermophilic operation on high-N

Fig. 4 shows the results over the experimental period for the pair of digesters fed on high-N FW (T3 & 4). The digesters began to show signs of stress as the TAN concentration rose above ~2.5 g N L^{-1} (Fig. 4a) with both digesters showing a very rapid increase in VFA (Fig. 4b) and a fall in specific methane production (Fig. 4c). In an attempt to address this additional doses of selected trace elements (Table 1, 11-element recipe) were added but without noticeable benefit. Digester T3 was more severely affected than T4: its VFA concentration had risen to ~30 g L^{-1} before feeding was stopped on day 153, by which time the pH had fallen to < 6.0 and the biogas methane content to < 20% (Fig. 4d and e). The digester was considered to have failed by this point. It was, however, decided to try and recover it by re-seeding it using waste digestate from digesters T1, T2 and T4 to gradually dilute out the accumulated VFA and enrich the failed methanogenic population. Feeding of T3 started again on day 231 after a 78-day pause, at which point the IA/PA ratio was around 0.5.

The feed to T4 continued uninterrupted and the rapid increase in TVFA peaked at 12 g L^{-1} on day 132 without breaking the buffering capacity of the digester, hence the pH did not fall to a point where

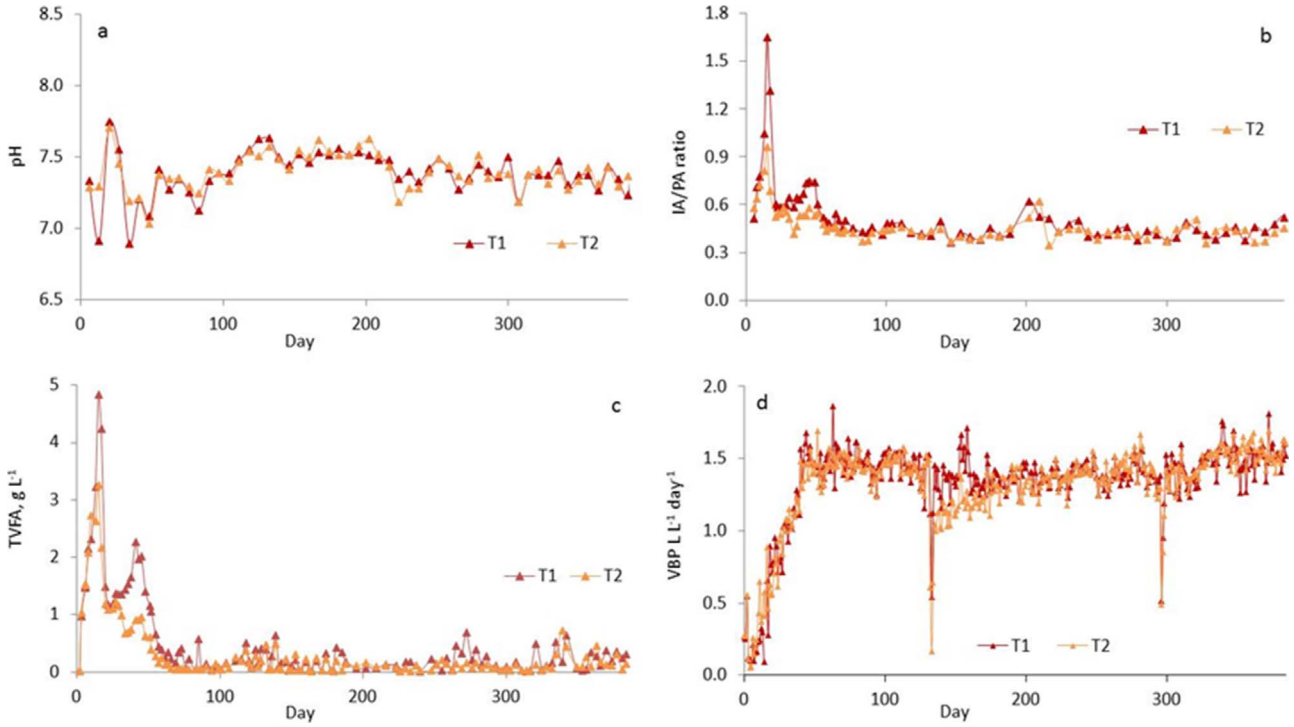

Fig. 3. Selected monitoring parameters during thermophilic digestion of low-N FW. (a) pH, (b) IA/PA ratio, (c) TVFA (d) VBP.

methanogenesis was inhibited (Fig. 4d). TVFA concentration fell over the next several days before starting to increase again from day 160, but more gradually than before, reaching ~19 g L^{-1} by day 279. At this point there was again a very sharp increase in the rate of VFA accumulation with the concentration reaching > 33 g L^{-1} on day 307. This increase was sufficient to overcome the buffering capacity of the digestate and the pH dropped sharply to < 6 by day 307 (Fig. 4d) while the IA/PA ratio rose to 26.5 (Fig. 4f). At this point the TAN in T4 had risen to > 5 g N L^{-1}, and feeding to this digester was stopped on day 310. TVFA concentrations, however, continued to rise to a peak of > 46 g L^{-1} by day 325 before decreasing over the next 56 days to around 18 g L^{-1}. This was a sufficient reduction to allow the pH to return to > 8 and the IA/PA ratio to fall to 1.3. On day 661, however, almost a year after feeding had finished, the TVFA concentration was still ~11 g L^{-1} (data not shown). The VFA profile (Fig. 4h) shows the final rapid VFA accumulation to be in the form of acetic acid: this could be due to any of a range of factors, including inhibition of syntrophic acetate oxidisers, some of which are reported to be more sensitive than the methanogens to ammonia toxicity [40]. This acetic peak was subsequently removed after feeding ceased, but the 'fixed' VFA was propionic acid and its rate of removal was only very slow even under starvation conditions.

When feeding was resumed to digester T3 after a 78-day period of reseeding, a similar pattern of VFA accumulation was recommenced from day 231. A second sharp increase in TVFA occurred after the TVFA concentration reached about 18 g L^{-1} (Fig. 4b), which again peaked at 45 g L^{-1} with an IA/PA ratio of 51.7. The final sharp rise in VFA could again be attributed to acetic acid accumulation (Fig. 4g). Feeding was stopped on day 434 and the same pattern of partial recovery was seen as in T4, with a drop in acetic acid and a return to a pH 7 with the IA/PA ratio falling to 0.9. The results indicate that the period of reseeding did not help the population to acclimate and the point at which acetate conversion to methane failed was at around the same TAN concentration of ~3.5 gL^{-1}. This value is similar to that reported by Hendriksen and Ahring [41] who showed initial inhibition between 3 and 4 g N L^{-1}. TAN itself is not the most critical parameter, as the toxicity is due mainly to free ammonia and the equilibrium is pH and temperature dependent. In the current trial the pH in digesters T3 and T4 was about 8.0, and the FAN was thus in the same range as the 700–1100 mg N L^{-1} inhibitory concentration suggested by Angelidaki and Ahring [42]. Methane production continued up until the point that the pH buffering capacity of the digester was broken and the pH dropped to a point known to be inhibitory to methanogens. It should be noted that the incremental accumulation of propionic and other longer chain VFA started after the TAN reached ~2.5 g L^{-1} and indicates that the ammonia toxicity occurs through disruption of syntrophy.

3.3.4. *Effect of urea addition to low-N digesters*

In the first part of the trial the low-N digesters T1 & 2 had shown a decreasing TAN concentration due to washout of the original inoculum TAN over 3 HRT, reaching a stable concentration by ~day 280 (Fig. 5a). Urea addition began on day 384, with a single dose added to T1 to raise the TAN concentration to ~2.5 g N L^{-1}. There was then a slight decline, as no further urea was added while the reactor responded to this input and TAN washed out between day 385 and 464. Urea was then added incrementally as part of the daily feed to T1 to take the concentration to ~3.5 g N L^{-1}, and then finally added incrementally from day 700 to take the concentration to ~4.2.g N L^{-1}. In T2 no urea was added until day 441, allowing this digester to act as a control against which the response of T1 to the shock load could be measured. Incremental urea addition then started and the TAN increased from that point to its target value of 2.5 g N L^{-1} which was reached around day 625 (Fig. 5a). The TAN concentration was then increased incrementally from day 690 with a target of 3 g N L^{-1}.

Calculated values for FAN based on the TAN, pH and digester temperature are shown in Fig. 5b.

The response to these increases in TAN can be seen in the alkalinity and VFA profiles in Fig. 5c and d. In T1 there was an immediate increase in VFA to around 4 g L^{-1} when the initial urea spike was added, which declined to < 0.5 g L^{-1} as the TAN concentration fell to ~2.2 g N L^{-1}. This VFA peak was buffered by the increased TAN, resulting in a rise in pH (Fig. 5e) and there was little or no change in the IA/PA ratio which remained below 0.5, or in the SMP which continued at ~0.38 m^3 CH_4 kg^{-1} VS (Fig. 5f). Addition of urea in the feed to T1

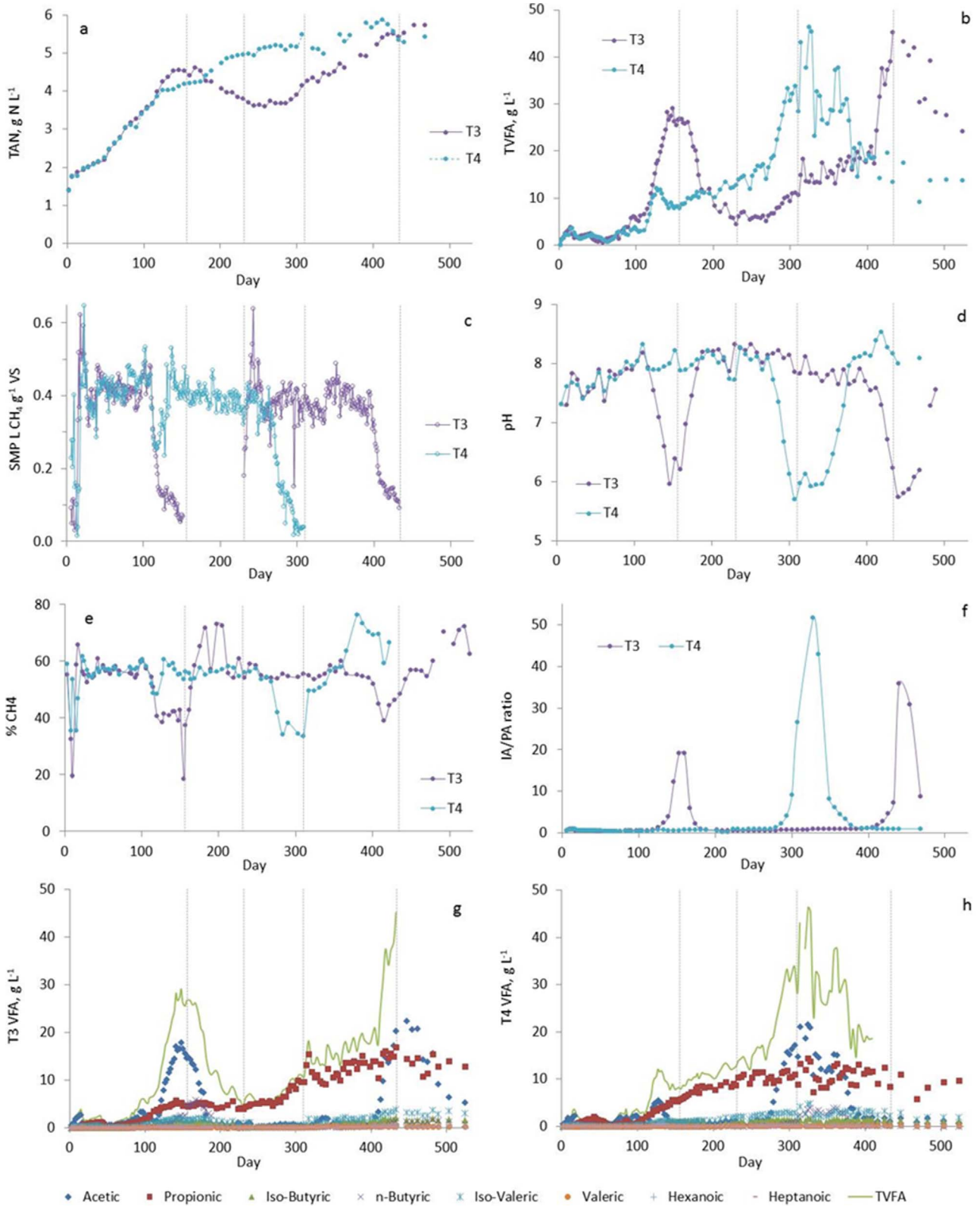

Fig. 4. Selected monitoring parameters during thermophilic digestion of high-N FW between days 0–530. (a) TAN, (b) TVFA (c) SMP, (d) pH, (e) biogas CH_4 content, (f) IA/PA ratio, and VFA profiles in (g) T3 and (h) T4. Vertical dotted lines indicate a change in feeding in response to digester conditions.

from day 464 led to a gradual increase in TAN and once the concentration reached ~2.5 g N L^{-1} VFA peaks of up to 3.3 g L^{-1} again began to appear. These were characterised by sharp increases in propionic acid, followed by even sharper falls (Fig. 5 g); acetic acid concentrations were also slightly elevated but the fluctuations were less pronounced. A slight reduction in TAN to below 3.5 g N L^{-1} between day 687–737 was accompanied by a fall in propionic acid concentration. When the TAN rose above ~3.5 g N L^{-1} after day 750 the magnitude of the VFA peaks increased, and at a concentration of 4 g N L^{-1} there was no further decline in propionic acid and peaks in *n*- and

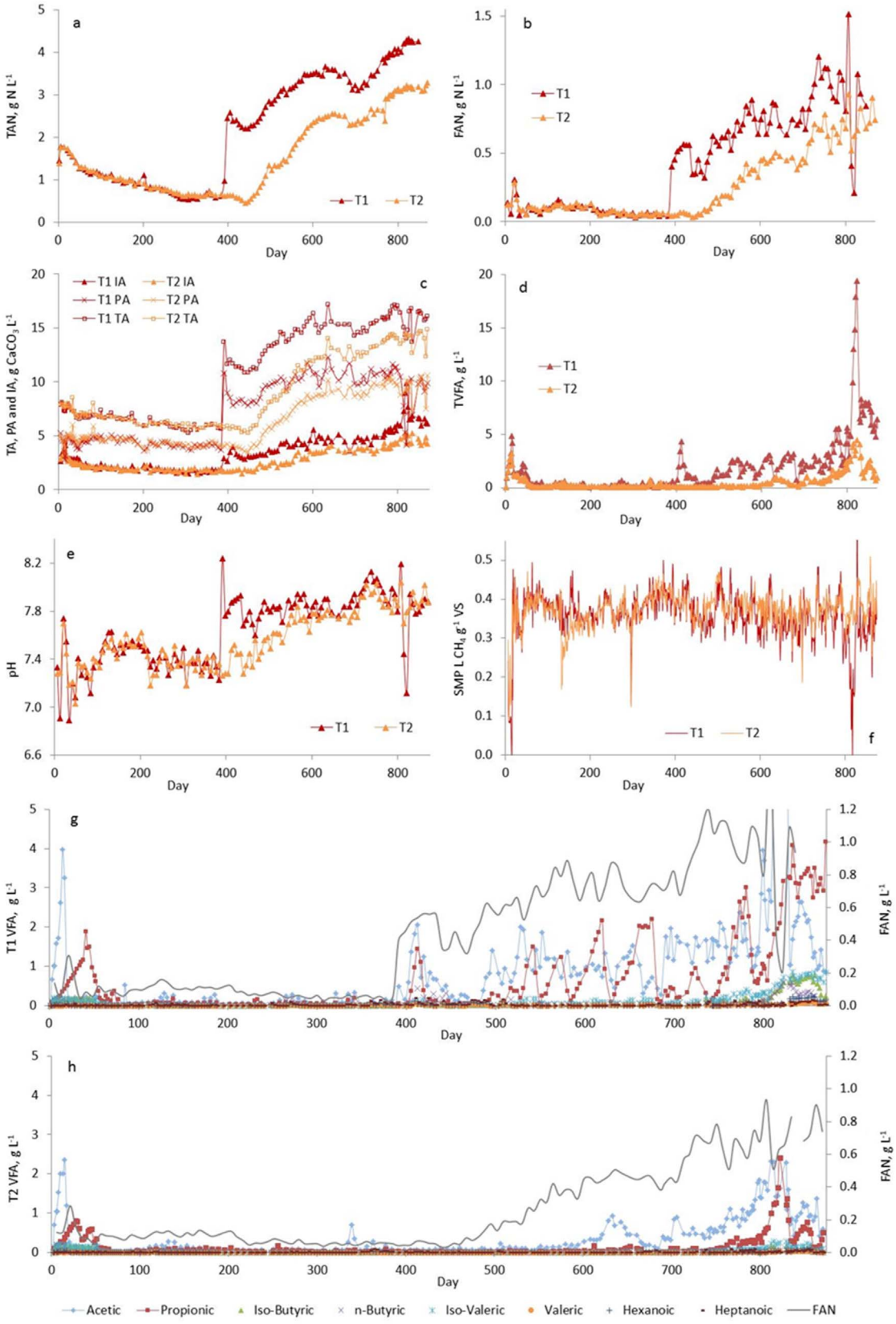

Fig. 5. Selected monitoring parameters during thermophilic digestion of low-N FW. (a) TAN, (b) FAN, (c) alkalinity, (d) TVFA, e) pH, (f) SMP and VFA profiles and FAN in (g) T1 and (h) T2 during whole experiment including period with urea addition.

isobutyric appeared, along with a rise in isovaleric concentration to around 0.8 g L^{-1}. The appearance of longer chain VFA (C3–C5 and above) indicates some blockage in the process of chain reduction and acetogenesis, as a direct or indirect effect of the increasing TAN concentration and its interaction with other digestion parameters.

The more gradual increase in TAN in digester T2 had no effect on total VFA concentration until the TAN reached around 2.5 g N L^{-1} when VFA peaks of ~1 g L^{-1} began to appear, which were mainly composed of acetic acid (Fig. 5 h). A further increase in TAN concentration to around 3.0 g N L^{-1} led to an increase in VFA and the appearance of propionic acid peaks with the characteristic saw-tooth fluctuation observed in T1. This cyclic fluctuation could be due to the sensitivity of FAN to pH: as the VFA increases a small associated fall in pH may occur which shifts the ammonia equilibrium slightly away from the more toxic FAN. This in turn may reduce inhibition of methanogens and/or propionate degraders, causing a short-term fall in VFA and an increase in pH which subsequently leads to an increase in FAN and the start of the next cycle. Some support for this explanation is provided by Fig. 5g and h where peaks in VFA and FAN appear to be in anti-phase.

In both T1 and T2 digestate pH increased to around 7.8 in response to the urea addition (Fig. 5e), while the average SMP showed little change (Fig. 5f). The methane concentration in the biogas averaged around 54% throughout the experiment, in agreement with the value predicted by the Buswell equation.

The results clearly showed the initial onset of instability when digester TAN concentrations reached 2.5 g N L^{-1}, in agreement with the values obtained when using the high-N FW. There was no noticeable improvement in ammonia tolerance (i.e. no evidence of acclimatisation or adaptation in terms of digestion performance) in T2 despite the more gradual increase in TAN concentration, which remained around the lower threshold for onset of inhibition for over 100 days: a similar pattern of VFA accumulation is seen in T2 between days 700–830 in response to the increase in TAN and FAN concentrations as in T1 between days 390–470 after the shock increase in TAN. The digesters could, however, continue to perform without noticeable loss in SMP until the TAN concentration reached 3.5 g N L^{-1} where stability was seriously compromised, characterised by a sharp increase in acetic acid and an irreversible increase in the concentration of longer chain length VFA.

3.4. Energy conversion efficiency

Measured BMP values are shown in Table 5 and compared with theoretical BMP values from the Buswell equation and equivalent CVs; values for VS destruction are also shown. In the BMP test, the calorific value of the methane produced by the high-N FW was 18.8 kJ g^{-1} VS, equal to 81% of the measured CV; the equivalent values for low-N FW were 15.6 kJ g^{-1} VS and 87%, reflecting its lower protein and lipid content but slightly higher degradability. In the mesophilic digestion trial with high-N FW the SMP achieved was only slightly lower than the BMP value, equivalent to around 79% of the measured CV and 97% of the BMP, again confirming the rapid degradability and good energy yield of this substrate. The high percentage of BMP may also reflect the long retention time at this OLR. The value of 79% of CV also corresponds well to the VS destruction of around 81% and to the 81% of ThMP for M3 and M4. In thermophilic conditions the SMP for high-N FW was lower and less consistent, averaging around 70% of measured CV for T3 and 75% for T4 during periods of apparent stability. Many authors have suggested that thermophilic digestion may give higher methane yields than mesophilic. For the current FW, however, the results indicate that even if the potential for degradation is higher in thermophilic conditions, this is not sufficient to make up for the inhibitory effects of TAN, as indicated by the relative proportions of BMP, ThMP and measured CV achieved in the mesophilic and thermophilic trials with high-N FW (Table 5).

For the low-N FW the SMP in thermophilic conditions was around 85% of the measured CV, in reasonable agreement with the VS destruction of ~90%. The SMP of 15.6 kJ g^{-1} VS was over 98% of the measured BMP value of 15.6 kJ g^{-1} VS added. As the BMP test was conducted in mesophilic conditions this could indicate slightly greater conversion at 55 °C. In general the results confirm the very high degree of conversion and energy recovery achievable with substrates of this type. More details of the BMP test and results are given in Supplementary materials.

Table 5
Energy recovery values for methane production from low-N and high-N FW.

	L CH_4 g^{-1} VS	kJ g^{-1} VS	% BMP	% ThMP	% measured CV	%VS destruction
High-N FW						
ThMP[a]	0.563	22.4	–	–	–	–
BMP	0.473	18.8	–	84.0%	81.2%	–
SMP mesophilic	0.460	18.3	97.2%	81.7%	78.9%	81.2%
SMP thermo – T3[b]	0.408	16.3	86.3%	72.5%	70.1%	–
SMP thermo – T4[b]	0.436	17.4	92.2%	77.4%	74.9%	–
Low-N FW						
ThMP[a]	0.476	19.0	–	–	–	–
BMP	0.392	15.6	–	82.4%	86.8%	–
SMP thermo – T1[b]	0.386	15.4	98.4%	81.0%	85.4%	90.6%
SMP thermo – T2[b]	0.386	15.4	98.4%	81.0%	85.4%	91.0%

[a] Theoretical methane potential calculated from the Buswell equation.
[b] Measured SMP during stable operation: average of M1-4 for days 77–296 for SMP mesophilic; average for days 284–386 for SMP thermo T1 and T2; average of days 70–100 for SMP thermo T3 and T4.

3.5. Discussion

The results clearly show that acclimatisation of a mesophilic inoculum to thermophilic conditions can reach a stable state in a period of less than 60 days, and the approach used of a step increase in temperature was an effective alternative to the step-wise changes in temperature that are sometimes recommended [43]. The sharp rise in VFA early in the acclimatisation process is a strong indication that the load in the early stages must be moderated to ensure that pH does not fall below a critical value. The pattern of acclimatisation between two quite dissimilar feedstocks (low and high-N) was remarkably similar. The high-N FW was readily digestible in mesophilic conditions indicating that the substrate itself was not likely to be inhibitory to the digestion process, which could tolerate a digestate TAN concentration of at least 4.5 g N L^{-1}, equivalent to a FAN of 0.45 g N L^{-1}. Unfortunately the range of tolerances quoted in a recent review [20] is so wide that comparison is difficult, especially given the many different substrates that have been used. The current result is very similar to that in previous work carried out using this type of substrate in mesophilic conditions where TAN concentrations as high as 5.4 g N L^{-1} have been tolerated without significant loss of performance [15]. The digesters fed on low-N FW stabilised at a very low TAN concentration and were never in danger from ammonia toxicity. Ammonia toxicity thresholds in thermophilic conditions have been reported for a number of different substrates, with general agreement that these are below values seen in mesophilic systems. Hashimoto [44] observed that ammonia inhibition began at about 2.5 g N L^{-1} and 4 g N L^{-1} for unacclimatised and acclimatised thermophilic methanogens, respectively, and a number of other studies have demonstrated acclimatisation is possible [42,45–47]; but it is unclear whether this is as a result of a metabolic transition in the existing microbial population or from the growth of new cultures

adapted to different ammonia concentrations [19]. In the current work, no real evidence of adaptation or acclimatisation was seen in the digestion performance despite the prolonged operating periods at high TAN concentrations.

The work using low-N FW with urea addition clearly established the threshold concentrations where instability could be observed (2.5 g N L^{-1}) and the critical point at which irreversible failure was likely at a TAN 3.5 g N L^{-1}, equivalent to a FAN concentration of 0.85 g N L^{-1}. The TAN and FAN concentrations for this critical point were almost identical for both the high-N FW and the urea-supplemented low-N FW, despite the contrasting strategies of shock loading versus slow accumulation, and again no evidence of adaptation or acclimatisation was observed in the digestion performance.

This study is believed to be one of the first to identify different inhibition thresholds, from the onset of mild instability through to progressive failure, and to suggest an explanation for the phenomenon of saw-tooth VFA profiles observed in meta-stable conditions below the critical TAN and FAN concentrations for progressive VFA accumulation. The results thus contribute towards clarifying the wide range of inhibition values quoted in previous literature.

4. Conclusions

The mesophilic digestion of a source segregated domestic food waste with a typical 'high' nitrogen content was possible without any signs of system instability or loss of performance at increasing loadings. There was clearly no component of the food waste itself which under these conditions was toxic or inhibitory to the anaerobic process. A step change in temperature from mesophilic to thermophilic temperatures followed by a period of starvation and then a gradual increase in load was shown to be an effective means of acclimating to thermophilic conditions. Running digesters on high-N FW without dilution was not, however, possible in the long term. Although gas production continued even at high VFA concentrations, the increase in VFA eventually overcame the buffering capacity, resulting in a rapid decrease in pH and catastrophic failure. Very sharp increases in VFA concentration were observed as the TAN concentration exceeded 3.5 g N L^{-1} and, although this could be partially overcome in the short term, there was no long term solution to the accumulation of propionic acid. It was possible to run the digesters over long periods on a low-N FW with good methane production and VS destruction. Raising the TAN of this feed material with urea provided a method of establishing the critical TAN concentration. The results showed it was possible to operate without significant VFA accumulation at a TAN concentration of $\leq$ 2.5 g N L^{-1} but propionic acid started to appear as the TAN rose above 3.0 g N L^{-1} and showed irreversible accumulation at a concentration of 3.5 g N L^{-1}. Digester failure was as a result of the pH buffering capacity of the digester being broken causing a rapid fall in pH to sub-optimal conditions for methanogens. This fall was preceded by a sharp increase in acetic acid concentration indicating that all routes for conversion of acetate to methane were compromised. The steady accumulation of proprionate and other longer chain VFA indicated that ammonia also inhibits the syntrophy between methanogens and acetogens. Despite different strategies for increasing the ammonia concentration, applied in over relatively long periods, no clear sign of adaptation or acclimatisation was seen in terms of the overall digestion performance.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jece.2017.09.043.

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Continuous operation of thermophilic food waste digestion with side-stream ammonia stripping

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ABSTRACT

Digesters fed on food waste (high nitrogen content) were operated successfully over an extended period using sidestream biogas stripping to control total ammonia nitrogen (TAN) below inhibitory concentrations. This is the first time biogas stripping has been used to achieve stable thermophilic operation with undiluted substrate of this type. Stripping columns operated batch-wise treated the equivalent of 1.7–4.1% of digester contents daily at pH > 10 and 70 °C, with no detrimental effect on digestion. TKN removal was 54%, with potential to recover 3.5 kg N tonne^{-1} substrate. When stripping was stopped in one digester TAN increased, accompanied by rising propionic acid concentrations with progressive instability observed from 2.5 g N L^{-1}. Eventual failure as TAN approached 5 g N L^{-1} was due to rapid acetic acid accumulation, resulting in a fall in pH to below 6.5. The pattern of VFA accumulation indicated failure of both acetoclastic methanogenesis and acetate oxidation.

1. Introduction

Anaerobic digestion is often considered a more sustainable route to resource recovery than other waste treatment technologies particularly when dealing with high moisture content materials (McKendry, 2002). It normally offers a net energy gain, as the parasitic energy requirements are lower than the energy value contained in the biogas produced (Burnley et al., 2011). It has therefore been used for a number of years for treatment and recovery of energy and nutrients from a wide range of organic waste resources, including food processing wastes (Digman and Kim, 2008). More recently it has become popular for treating source segregated food wastes from municipal sources (Bernstad et al., 2013; ADBA, 2016). Anaerobic digestion of this type of waste is not without difficulties, however, mainly associated with its high protein content. This is potentially problematic, as during digestion the protein is rapidly hydrolysed to release ammonia which is inhibitory or toxic to the process (Chen et al., 2008; Rajagopal et al., 2013). Food waste that has been source segregated in the home or collected from restaurants, cafeterias and supermarkets has been shown to have fairly similar properties in a number of studies (Capson-Tojo et al., 2016) and typically has a C:N ratio of ~15 and a TKN of 3–4% on a total solids basis. If used directly into a digester the total ammonia nitrogen (TAN) concentration will typically equilibrate between 4.5 and 5.5 g N L^{-1} (Banks et al., 2008), which can be tolerated in mesophilic systems but is inhibitory under thermophilic conditions.

Yet there may be some advantages in using thermophilic systems for this type of material. Thermophilic treatment offers a higher degree of pathogen destruction, potentially allowing operation without a separate pasteurisation step (Al Seadi et al., 2013). Digestate from thermophilic operation may in some cases be easier to dewater and less prone to foaming (Coelho et al., 2011; Suhartini et al., 2014). Higher specific methane yields and solids destruction have been reported (Labatut et al., 2014), while increased rates of reaction may allow the process to operate at shorter retention times and higher loadings (Cavinato et al., 2013). Inhibition is a particular problem in these conditions, however, as the equilibrium between ammonia in its ionic form and the more toxic free ammonia shifts in favour of the latter at higher temperatures. The high TAN also leads to a high pH environment which again favours a shift in the equilibrium to free ammonia nitrogen (FAN). There have therefore been no successful long-term examples of thermophilic anaerobic digestion of undiluted source segregated food waste.

It is difficult to quote absolute values for the threshold of ammonia inhibition/toxicity as this is dependent on a number of factors, including temperature and pH. It has been widely reported (Chen et al., 2008; Yenigün and Demirel, 2013) that microbial populations can acclimatise to higher ammonia concentrations, but the mechanism by which this occurs is less clear. Inhibition studies specifically related to food waste digestion (Yirong et al., 2013) suggest, however, that under thermophilic conditions (55 °C, pH ~8) stable operation at very low VFA concentrations was possible at up to ~2.5 g N L^{-1} while the onset of irreversible VFA accumulation is likely occur when the TAN reaches 3.5 g N L^{-1}, corresponding to a FAN concentration of around

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0.8 g N L^{-1}.

Where thermophilic anaerobic digestion of food waste has been practiced at a large scale, one approach taken to avoid toxicity has been to reduce the TAN concentration in the digester by dilution (Neiva Correia et al., 2008). This has both resource and energy implications, but if the advantages of thermophilic operation can be shown to outweigh these it may offer an effective strategy. Co-digestion to increase the C/N ratio is also possible, and its benefits have been widely demonstrated (Mata-Alvarez et al., 2011, 2014); but the practicality of this approach depends on the availability of a suitable low nitrogen co-substrate. Reducing the ammonia in the digester or its feed are also potential solutions. Approaches considered include the development of ion exchange or zeolite bed reactors (Milán et al., 1997; Zheng et al., 2015), and the use of membrane contactors for *in situ* removal or as a post-treatment step with stripped liquor recycle (Lauterböck et al., 2014; Du Preez et al., 2005). Gas stripping has been most widely used, both as a pre-treatment to reduce the substrate nitrogen content (Zhang et al., 2012; Markou, 2015; Yabu et al., 2011); and to remove ammonia from the digester mixed liquor using air (Pedezzi et al., 2017), nitrogen (Nielsen et al., 2013), steam (Resch et al., 2011), biogas (De la Rubia et al., 2010; Abouelenien et al., 2010), and flue or exhaust gases (Bousek et al., 2016) as the stripping agent. Many of these studies were based on short-term laboratory-scale batch testing, but Pintucci et al. (2017) operated a 3 m^3 pilot-scale system with side-stream air stripping for co-digestion of swine manure and vegetable wastes, while Pedezzi et al. (2017) ran digesters coupled to a side-stream air stripping column on the same feedstock for over 700 days. Sun et al. (2014) operated digesters for a 90-day period, on stillage derived from ethanol fermentation of food wastes, both with and without biogas stripping of ammonia.

Walker et al. (2011) discussed the advantages and disadvantage of biogas stripping in various operating modes and from different locations in the plant flowsheet or with additional process stages. Of these options, side-stream stripping appears to offer the greatest promise (Serna-Maza et al., 2015, 2017) and was shown to be able to reduce TAN concentrations in a mesophilic digester without apparent detriment to the process (Serna-Maza et al., 2014). The system described involved a simple 'bolt-on' stripping column in which a proportion of the digestate is stripped of its ammonia under alkaline conditions, with recovery as a concentrated ammonium sulphate solution by dissolution into sulphuric acid. The work concluded that to reduce TAN below threshold toxicity concentrations in a thermophilic food waste digestion process a minimum stripping temperature of 70 °C would be required (Serna-Maza et al., 2014)

The aim of the current study was to demonstrate that a side-stream ammonia stripping process used in conjunction with thermophilic food waste digestion could allow successful long-term operation. The work was therefore carried out over an extended period in order to provide steady state data on digester performance and stability with side-stream stripping, and to compare this with an unstripped control.

2. Materials and methods

2.1. Digester and stripping column design

Four continuously-stirred tank reactor (CSTR) digesters (T1-4) were used in the study, each with a total capacity of 40 L and a working volume of 35 L. These were constructed from 36 cm ID PVC pipe sealed at the top and bottom by plates incorporating feed and drainage ports. The digesters are sealed from the outside atmosphere by a draught tube through which an offset bar stirrer is inserted to allow low-speed mixing at 26 rpm by geared motors (Parvalux, UK). Digester temperature was controlled at 55 °C by recirculating water from a thermostatic bath through an internal heating coil. Biogas production was measured using continuous gas flow meters, and is reported at standard temperature and pressure (STP) of 0 °C and 101.325 kPa (Walker et al., 2009). Biogas was also periodically collected in gas-impermeable bags to check gas counter calibrations and determine the biogas composition.

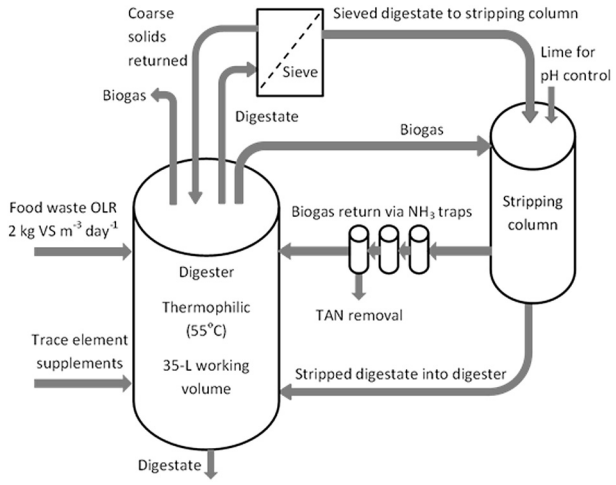

Fig. 1. Schematic of the coupled anaerobic digestion and side-stream ammonia stripping process.

The digesters were coupled to ammonia stripping columns C1-C4 made from stainless steel tube with a height of 56 cm and 10 cm internal diameter. Temperature in the columns was maintained at 70 °C using externally mounted thermostatically-controlled electrical heating mats (Non Adhesive Wire Wound Heater 104 Dia × 200 P 230 V, Holroyd, UK). Ammonia stripping was carried out as a semi-batch process with biogas recirculated around the system by a peristaltic pump (505 s, Watson Marlow, UK). The biogas enters the stripping column at a controlled flow-rate through a sintered-glass diffuser. After leaving the column it is then passed through traps to remove ammonia: this was achieved by provision of a condensate trap followed by bubbling through deionised water and then through 0.25 N H_2SO_4 before recirculation to the stripping columns. The system configuration is shown in Fig. 1.

2.2. Inoculum, feedstock and digester operation

The inoculum used was digestate from a mesophilic digester operated by Southern Water Plc for treatment of municipal wastewater biosolids (Millbrook, Southampton, UK). This was placed in the digesters and the temperature was raised to 55 °C in a single step, after which the digesters were left without feeding for 27 days to allow acclimatisation to the new operating temperature.

From day 0 to 20 the digesters were fed on a low-nitrogen food waste that has previously been used in thermophilic digestion experiments (Yirong et al., 2013): this was to avoid any rapid build-up of ammonia during the acclimatisation period. Feeding started on day 0 at an organic loading rate (OLR) of 0.5 kg volatile solids (VS) m^{-3} day^{-1} and was increased in equal increments up to 1.5 kg VS m^{-3} day^{-1} on day 20.

On day 21 the feed was switched to source separated domestic food waste and the OLR was raised to the final target value of 2.0 kg VS m^{-3} day^{-1}. The food waste used was collected commercially by Veolia Environmental Services (UK) Plc from households in Eastleigh, UK and was typical of this type of material (Yirong et al., 2015). Samples of 200–300 kg were taken and any obvious contaminants, large bones and stones were removed. The material was homogenised to a pulp by passing it through a macerating grinder (S52/010, IMC Limited, UK), then mixed, subdivided into portions and frozen at −20 °C. Portions were defrosted as needed prior to use. During the course of the experiment three batches of waste were prepared in this way.

Digestate was removed twice per week and sieved to remove any large solids, which were returned to the digester. A proportion of the sieved digestate was wasted, and the remainder was added to the stripping column after pH adjustment by addition of lime (CaO), and removal of the stripped digestate. The stripped digestate was returned to the main digester to maintain its working volume. The digesters were monitored on a regular basis for pH, TAN, alkalinity, total and volatile solids and volatile fatty acid (VFA) concentrations.

A trace element solution was added as noted below to give an additional working concentration in the digestate of the following metals: (mg L^{-1}) Cobalt 1.0, Nickel 1.0, Molybdenum 0.2, Selenium 0.2, Tungsten 0.2.

The experiment was conducted in three stages. In Stage 1 all four digesters were run under the same conditions, to demonstrate effective acclimatisation to thermophilic conditions and confirm the repeatability of the response to stripping. In Stage 2 the quantity of digestate stripped was increased for two digesters, while two continued under the same conditions as before; in Stage 3 the quantity stripped was doubled for one digester and in another stripping was stopped. The purpose of Stages 2 and 3 was to demonstrate that stable operation could be achieved by stripping with control over the digestate TAN concentration. Table 1 summarises the key operational and other changes.

2.3. Analytical methods

Total solids (TS) and volatile solids (VS) were determined according to Standard Method 2540 G (APHA, 2005) using a Heraeus Function Line Series oven and a 201/301 Carbolite muffle furnace. pH was measured using a Jenway 3010 meter (Bibby Scientific Ltd, UK) with a combination glass electrode calibrated in buffers at pH 4, 7 and 9.2 (Fisher Scientific, UK). Alkalinity was measured by titration with 0.25 N H_2SO_4 to endpoints of pH 5.75 and 4.3 using an automatic digital titration burette system (SCHOTT titroline easy) to allow calculation of total (TA), partial (PA) and intermediate alkalinity (IA) (Ripley et al., 1986). Total Kjeldahl Nitrogen (TKN) was determined after acid digestion by steam distillation and titration. This used a BÜCHI K-435 Digestion Unit with H_2SO_4 and K_2SO_4 as the reactants and $CuSO_4$ as the catalyst to convert the amino-nitrogen and free ammonia (NH_3) to ammonium (NH_4^+). TAN was measured using a BÜCHI Distillation Unit K-350 with NaOH addition followed by collection of the distillate in boric acid indicator and titration with 0.25 N H_2SO_4. FAN concentrations were calculated from TAN, pH and temperature as in Hansen et al. (1998). Volatile fatty acid (VFA) concentrations were determined by gas chromatography (Shimadzu GC-2010), with a flame ionization detector and a capillary column (SGE BP-21) and helium as carrier gas. Samples were acidified to 10% with formic acid and measured against mixed standards of 50, 250 and 500 mg L^{-1} of acetic, propionic, isobutyric, n-butyric, iso-valeric, valeric, hexanoic and heptanoic acids. Biogas composition (CH_4 and CO_2) was determined using a Varian star 3400 CX Gas Chromatograph fitted with a packed stainless steel SUPELCO 80/100 mesh porapack-Q column and a TCD detector. The GC was calibrated with a standard gas of 65% CH_4 and 35% CO_2 (v/v) (BOC Ltd, UK).

Table 1
Stages and changes in key operational conditions.

Stage	Day	Operational change
1		All digesters operated under the same conditions
	0	Start of feeding on low N food waste at 0.5 kg VS m^{-3} day^{-1}
	0–20	Incremental loading increase to 1.5 kg VS m^{-3} day^{-1}
	21	Feed switched to source segregated domestic food waste at 2.0 kg VS m^{-3} day^{-1} Ammonia stripping started at 2.1 kg of digestate twice a week for each digester T1–4 (equivalent to 1.7% of digester volume per day).
2	108	Stripping regime in T1 and T2 changed to 2.5 kg twice a week (equivalent to 2.0% of digester volume per day); T3 and T4 continue as Stage 1.
	120	New batch of source segregated domestic food waste
	178	One-off dose of trace element solution added to T4
3	210	Stripping regime changed: T2 increased to 5.0 kg twice a week (using 2 stripping towers; equivalent to 4.1% of digester volume per day). Stripping stopped for T4; T1 and T3 continue as Stage 2.
	245	New batch of source segregated domestic food waste
	346	Feeding and ammonia stripping stopped in all digesters
4	370	End of monitoring

Table 2
Physico-chemical characteristics of first batch of substrate.

Parameter	Units	Value		SD
Total solids	g TS kg^{-1} WW	238.5	±	1.2[a]
Volatile solids	g VS kg^{-1} WW	206.8	±	2.1[a]
TKN	g N kg^{-1} WW	7.0	±	0.12
Elemental C	% of TS	50.28	±	0.75
Elemental H	% of TS	6.37	±	0.07
Elemental N	% of TS	3.68	±	0.09
Carbohydrate	g kg^{-1} VS	492.1	±	12.5
Lipid	g kg^{-1} VS	197.0	±	2.2
Crude protein	g kg^{-1} VS	211.2	±	3.7
Calorific value	MJ kg^{-1} TS	22.0	±	0.06
	MJ kg^{-1} VS	25.4	±	0.06

SD = standard deviation for triplicate samples unless noted.
[a] 8 samples.

3. Results and discussion

3.1. Feedstock characteristics

Results of a detailed characterisation of the first batch of feedstock are given in Table 2, and confirm that its properties are closely similar to those reported elsewhere for source separated domestic food wastes (e.g. Yirong et al., 2015). Between days 120–244 and 245–345 new batches of source segregated domestic food waste were used, with characteristics similar to those of the original batch but slightly different moisture contents. This led to small changes in the hydraulic retention time (HRT), as the OLR was maintained at 2 kg VS m^{-3} day^{-1}.

3.2. Acclimatisation and start of stripping (Stage 1, day 0–107)

It was necessary initially to acclimate the inoculum to thermophilic conditions, then to avoid toxicity it was necessary to strip ammonia from the digesters almost from the outset to remain below inhibitory concentrations. During stage 1 all digesters were operated under the same conditions. Feeding began on day 0 with low-nitrogen food waste at an OLR of 0.5 kg VS m^{-3} day^{-1} and was incrementally raised to 1.5 kg VS m^{-3} day^{-1} by day 20. On day 21 the feed was switched to source segregated domestic food waste at 2.0 kg VS m^{-3} day^{-1} and ammonia stripping commenced. For this purpose 2.1 kg of digestate was taken from each digester twice per week, and stripped at a gas flow rate of 0.15 m^3 $m^{-3}_{digestate}$ min^{-1} or 0.04 m^3 m^{-2} min^{-1}, corresponding to violent mixing (Perry and Green, 1999). These conditions continued until the end of this stage on day 107.

Fig. 2 shows the process monitoring and stability parameters during stage 1. The pH remained fairly steady, averaging around 7.8 in all digesters from day 21 onwards (Fig. 2a). TAN concentrations rose after the switch from low-nitrogen feedstock to normal source segregated domestic food waste on day 21, but remained below the lower stability threshold of 2.5 g N L^{-1} (Yirong et al., 2013) in all digesters apart from T4, where TAN was slightly higher from day 94 onwards (Fig. 2b). The reason for this small difference is not known but may be due to minor differences in stripping efficiency, which then affects other parameters.

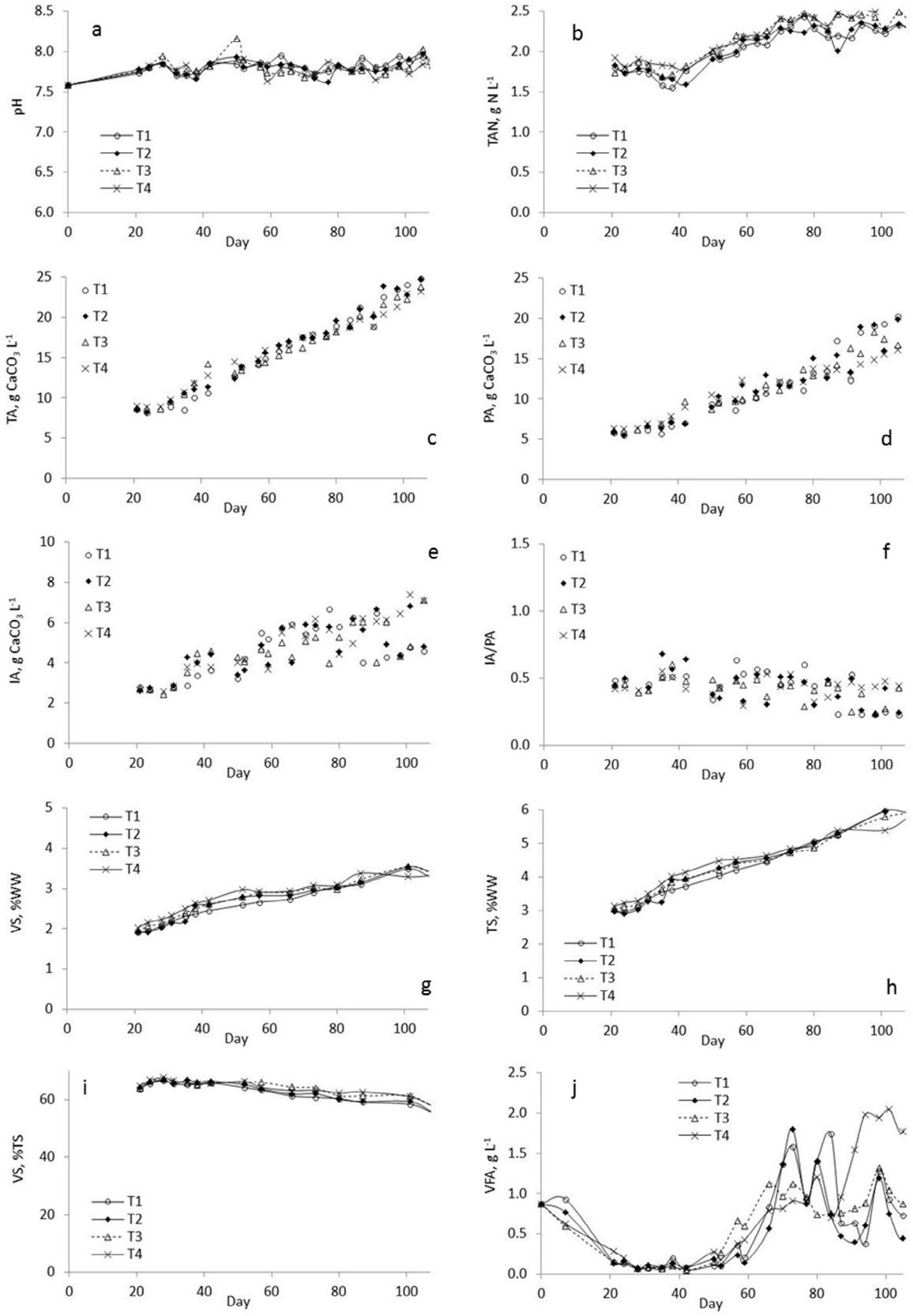

Fig. 2. Monitoring parameters during stage 1 of the experimental period: (a) pH, (b) TAN, (c) TA, (d) PA, (e) IA, (f) IA/PA, (g) VS as %WW, (h) TS as % WW, (i) VS as %TS, (h) total VFA concentrations.

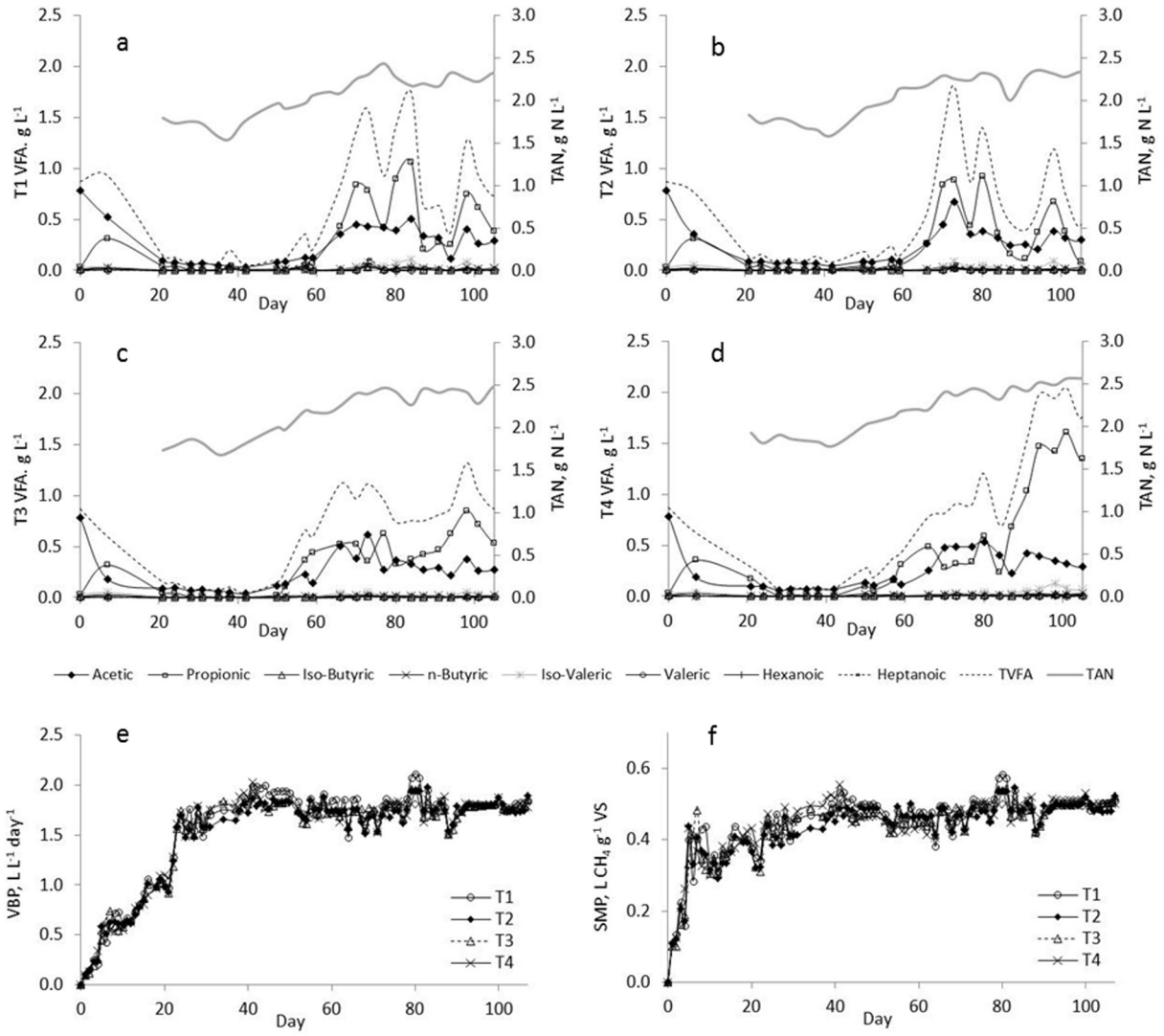

Fig. 3. Monitoring parameters during stage 1 of the experimental period: Individual VFA species and TAN concentrations in (a) T1. (b) T2, (c) T3, (d) T4, and (e) VBP and (f) SMP in all 4 digesters.

Total, partial and intermediate alkalinity (Fig. 2c, d and e) rose throughout the period, reflecting the addition of lime for pH control in the stripping columns as well as the initial rise in ammonia concentration. The ratio of intermediate to partial alkalinity (IA/PA) fluctuated but showed a downward trend (Fig. 2f): this parameter is considered a good indicator of digestion stability (Ripley et al., 1986). Digestate volatile solids content had stabilised by day ~100 (Fig. 2g), but total solids (Fig. 2h) continued to rise while the VS/TS ratio fell (Fig. 2i) as a result of the lime addition. Total VFA concentrations (Fig. 2j) remained low until day 50 but then increased slightly as TAN concentrations rose towards 2.5 g N L^{-1}: the higher VFA concentration in T4 mirrored the higher TAN in this digester. Fig. 3 shows individual VFA species for each digester with total VFA and TAN. The appearance of occasional peaks of propionic acid of around ~1 g L^{-1} is similar to that previously observed in reactors running on synthetic low-nitrogen food waste spiked with urea to achieve this TAN concentration (Yirong et al., 2013). The slightly higher propionic acid concentration in T4 reflects the higher TAN concentration, as well as the range of natural variability seen in biological systems of this type.

Digester performance was assessed based on the volumetric biogas production (VBP) and the specific methane production (SMP) for each digester. Differences between the digesters were negligible (Fig. 3e and f). The average SMP for the first batch of food waste from day 50 to 107 was 0.480 m^3 CH_4 kg^{-1} VS added. This is at the higher end of the expected range for typical source segregated domestic foodwaste, but may reflect both the lipid content of this batch, which was slightly above average, and possibly an enhanced degree of degradation due to the thermophilic conditions and/or high-temperature alkaline hydrolysis occurring in the stripping column.

3.3. Increasing ammonia removal by increased stripping (Stage 2, day 108–209)

In stage 2 the quantity of digestate stripped was increased in digesters T1 and T2 to 2.5 kg twice per week. The gas flow rate remained the same, giving gas mixing rates of 0.126 m^3 $m^{-3}_{digestate}$ min^{-1} or 0.04 m^3 m^{-2} min^{-1} (violent mixing). Feeding with the second batch of food waste began from day 120, and a one-off dose of trace element solution was added to T4 on day 178. From day 108 TAN concentrations in T1 and T2 began to fall more rapidly than in T3 and T4 as a result of the increased stripping (Fig. 4a). This was accompanied by an increase in TA and PA (Fig. 4b and c) as proportionately more lime was added. The extra lime addition also increased the TS content in T1 and T2 above that in T3 and T4 (Fig. 4d), but VS content during this period was stable at around 3.4% of wet weight (WW) (Fig. 4e) leading to a fall in the VS/TS ratios (Fig. 4f). In T1 and T2 the TAN was gradually

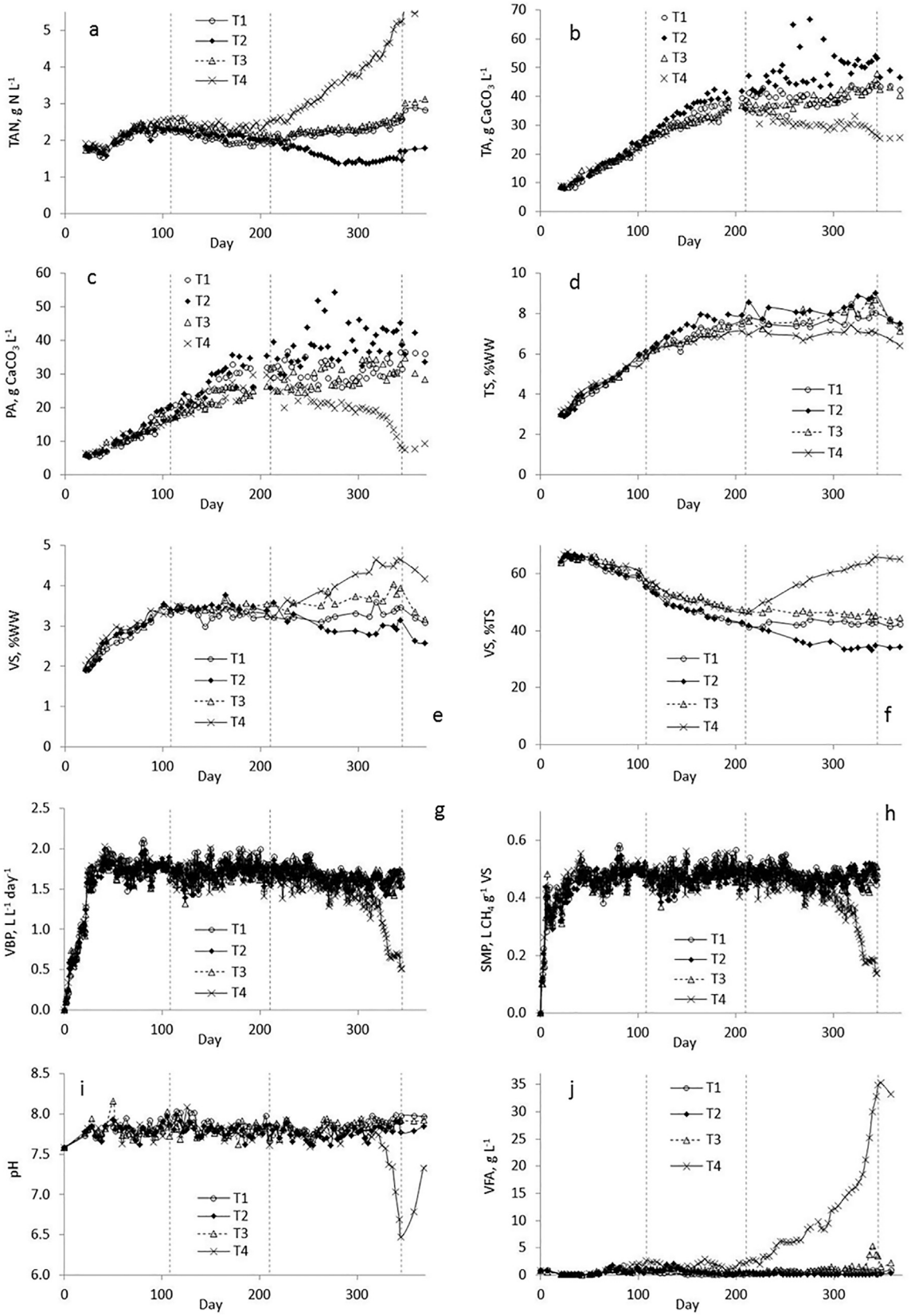

Fig. 4. Monitoring parameters during the whole experimental period: (a) TAN, (b) TA, (c) PA, (d) TS as % WW, (e) VS as % WW, (f) VS as % WW, (g) VBP, (h) SMP, (i) pH and (j) total VFA concentrations. Vertical dotted lines indicate ends of stages.

reduced to around 2.0 g N L^{-1} and the previous signs of mild instability, as indicated by slightly elevated VFA concentrations at the end of stage 1, gradually decreased. VFA concentrations in T3 and T4, however, continued to show fluctuations up to ~1 g L^{-1} as the TAN concentration in these digesters remained slightly higher. In all 4 digesters there was no apparent loss in performance as both VBP and SMP remained more or less constant during this period (Fig. 4g and h), with average values of 1.72 L L^{-1} day^{-1} and 0.479 L CH_4 g^{-1} VS, respectively.

3.4. Comparison of stripped and unstripped digesters (Stage 3, day 210 on)

This stage was designed to assess the effectiveness of the ammonia stripping system as a means of producing different conditions in the digesters. In digester T4 stripping was stopped and the ammonia concentration allowed to increase above the critical threshold at which instability and VFA accumulation were expected to occur. In digester T2 the ammonia concentration was further reduced by doubling the volume stripped to 5.0 kg twice per week (using stripping columns C2 and C4 in parallel). The other two digesters continued to operate under the same stripping conditions as in stage 2 (2.5 kg in T1 and 2.1 kg in T3 stripped twice per week). Feeding with the third batch of food waste started from day 245.

At the beginning of stage 3 TAN in digesters T1-3 was close to 2.0 g N L^{-1} while that in T4 was slightly higher at 2.5 g N L^{-1}. For the rest of the experimental period the TAN concentration in T4 increased steadily (Fig. 4a), reaching 5.2 g N L^{-1} by day 345. In T2, where the amount of digestate stripped was doubled, TAN reduced over the next 70 days and stabilised at an average value of 1.5 g N L^{-1}, well below any inhibitory threshold (Yirong et al., 2013). In T1 and T3, where the stripping regimes remained the same as in the previous stage, TAN concentrations rose slightly reflecting a slight increase in the TKN of the new batch of feedstock, and were close to the threshold value of 2.5 g N L^{-1} where early signs of instability may be observed. Process stability parameters during this period can be seen in Fig. 4. The pH in all of the digesters except T4 remained stable during the whole stage (Fig. 4i), averaging around 7.8. In T4 the pH remained close to that in the other digesters until day 322 after which it fell sharply to below 6.5 on day 345, at which time feeding was stopped. This sharp fall in pH can be attributed to the buffering capacity in the digester being overcome by the increasing VFA concentration (Fig. 4j). Changes in total alkalinity (Fig. 4b) reflected the degree of alkali addition for stripping purposes. In T4 the TA dropped after stripping ceased; whereas in T1 and T3 it increased slightly, and in T2 there was a sharper rise due to the double stripping. There were some problems in obtaining consistent alkalinity measurements for T2, especially after double stripping was introduced, probably due to insufficient mixing of samples; but these were resolved by the end of the run with stable values achieved. PA (Fig. 4c) followed a similar trend to TA until around day 325 when the PA value in T4 began to fall dramatically, from ~18 to ~8 g $CaCO_3$ L^{-1} by day 345. At the same time the IA in T4 rose from day 300 onwards, leading to a peak in IA/PA ratio of 2.3 by day 345. TS concentrations in all four digesters (Fig. 4d) reflected the degree of alkali addition for stripping purposes. VS concentrations both as a proportion of wet weight and of TS content (Fig. 4e and f) clearly indicated, however, that VS conversion in T4 decreased after stripping ceased; while conversion in T2 (double stripping) appeared to be slightly higher than in T1 and T3 (single stripping).

The changes in pH and alkalinity were linked to changes in VFA concentrations in the digesters (Fig. 4j). In T2 where the TAN concentration was reduced to 1.5 g N L^{-1}, the total VFA concentration between days 220 and 345 was very low, averaging 0.15 g L^{-1}. In T1 (2.5 kg stripped) total VFA showed a slight increase when TAN concentrations reached ~2.2 g N L^{-1}, averaging around 0.7 g L^{-1}. In T3 (2.1 kg stripped) total VFA concentrations were similar to those in T2, apart from during a brief peak around day 330 which may have been due to a short-term temperature rise in T3 to 57 °C.

The VFA species are shown in Fig. 5 together with calculated FAN concentrations. In T1 and T3 the main acids present were acetic and propionic, with elevated levels appearing when FAN concentrations approached 0.5 g N L^{-1}. In T4 immediately after stripping ceased there was a gradual but steady increase in propionic acid concentration which reached around 11 g L^{-1} by day 345. Acetic acid also rose to around 2.2 g L^{-1} by day 241, leading to a short-term reduction in FAN, but then fell over the next 10 days. From day 300 onwards other VFA species began to appear; and from day 329 there was a rapid linear increase in acetic acid of around 0.95 g L^{-1} day^{-1} until feeding ceased on day 345, by which time the concentration had reached 17 g L^{-1}.

SMP of the stripped digesters was very close to that in the previous period (Fig. 4h), with average values of 0.472, 0.474 and 0.472 L CH_4 g^{-1} VS for T1, T2 and T3, respectively. VBP fell by around 7–10% in comparison with stage 1 (Fig. 4g), possibly due to the effect of lime addition on the carbonate equilibrium leading to an increase in CO_2 dissolution: this was reflected in a small increase in biogas methane content from around 55% to 59%, resulting in the SMP remaining constant. In T4 gas production declined slowly from day ~250 onwards, and sharply from day ~300, reaching 0.16 L CH_4 g^{-1} VS by day 345. Biogas methane content in T4 had fallen to 53.8% by the end of the run, well below the average of 59.2% for the other digesters.

After feeding and stripping stopped on day 345, monitoring of selected digestion parameters continued at a reduced frequency until day 382. TAN concentrations rose slightly in all reactors, probably indicating a reduction in and hydrolysis of the active microbial biomass. In T4 the pH rose, IA/PA ratio fell and VFA concentrations reduced slightly, reflecting a fall in acetic acid concentration to around 15 g L^{-1}. Concentrations of other VFA species were unaffected, however, while the FAN concentration rose in response to these changes.

The VFA profiles, VBP and SMP results provided a clear indication of the stability and performance of the digesters at each of the targeted TAN concentrations. As the TAN was allowed to increase in T4 the digester became unstable, resulting in loss of methane production, a sharp drop in pH and a rapid rise in IA/PA ratio as the TAN approached 5 g N L^{-1} (FAN 0.8 g N L^{-1}); but increasing propionic acid concentrations indicated the onset of progressive instability as the TAN exceeded 2.5 g N L^{-1}. Digesters T1 and T3 showed signs of the onset of mild instability in the form of fluctuating VFA concentrations at a threshold TAN concentration of 2.2 g N L^{-1}, or FAN of around 0.5 g N L^{-1}. It is therefore difficult to specify a precise TAN (or FAN) concentration where ammonia toxicity occurs, as this manifests itself in different forms. Fluctuating VFA concentrations with the appearance of VFA of predominantly C3 and longer chain length indicate some mild interference with the flow of carbon through to methane once the TAN exceeds a threshold of 2.5 g N L^{-1}. This could directly affect the activities of the propionate-degrading acetogens, which may be more sensitive to ammonia than methanogenic *Archaea* (Calli et al., 2005). It is also possible that ammonia inhibition of acetoclastic methanogenesis results in the channelling of carbon to CH_4 via acetate oxidation and hydrogenotrophic methanogenesis. This, however, may lead to an increase in the partial pressure of H_2 and a consequent reduction in propionate degradation as changes in the thermodynamic equilibrium make it a less desirable substrate (Müller et al., 2010). This could explain the consistently low concentrations of acetic acid observed until the TAN concentration approached 5.0 g N L^{-1}, at which point a rapid increase in acetic acid was observed, indicating that both the acetoclastic and acetate oxidation routes to methane formation had been compromised. The fall in pH resulting from the increased acid load takes this to below an optimum value for methanogenesis and the digester becomes 'stuck' (McCarty and McKinney, 1961), a condition from which recovery is difficult.

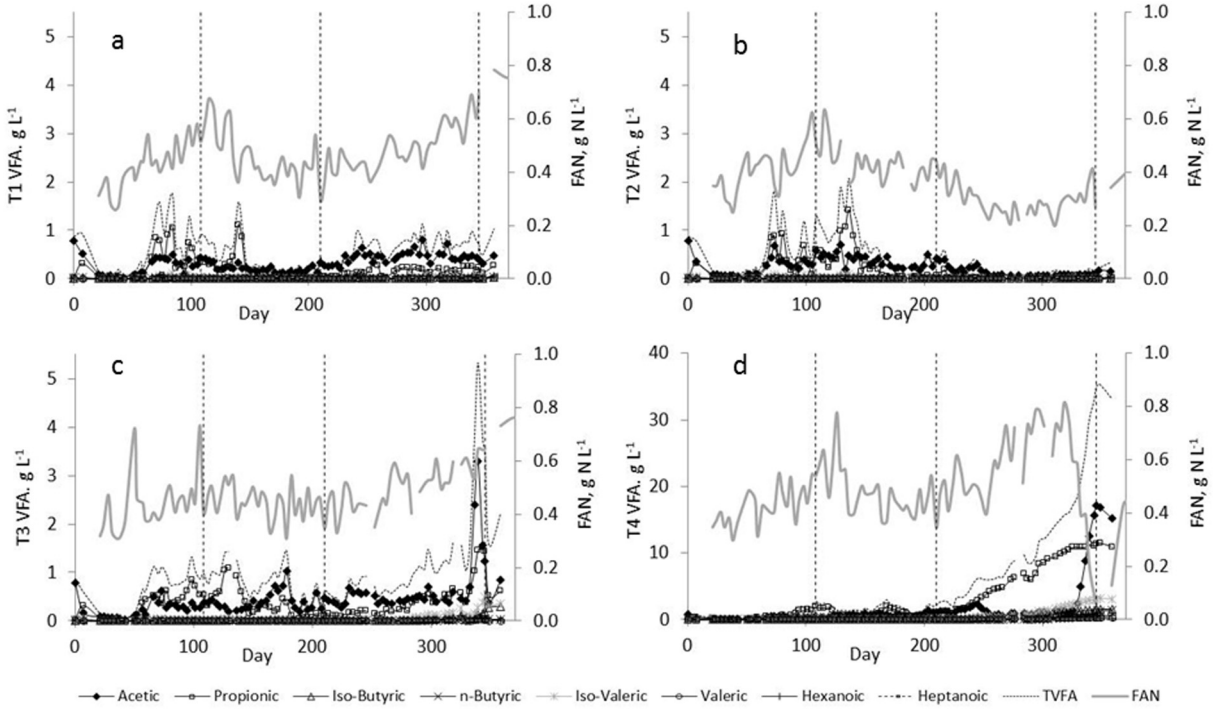

Fig. 5. Individual VFA species and FAN concentration in (a) T1, (b) T2, (c) T3, (d) T4, during the whole experimental period (note change of axes for VFA in T4). Vertical dotted lines indicate ends of stages.

3.5. Stripping parameters and performance

The purpose of sidestream stripping is to allow an increase in the temperature and pH of a proportion of the digestate to facilitate removal of ammonia in the gaseous phase: in this case the aim was to increase the temperature to 70 °C and the pH to above 10 by lime (CaO) addition, while recirculating biogas at a fixed flow rate. The lime dose required was around 14 g CaO kg^{-1} WW of digestate, which was lower than the 18.6–21.4 g CaO kg^{-1} WW needed by Serna-Maza et al. (2014) in a previous study with food waste of the same type digested under mesophilic conditions. The lime dose used was sufficient to raise the initial pH above 10, and on some occasions even above 11. The pH of the stripped sample declined during the stripping process to final values which were generally between 8.5 and 9.5.

Fig. 6a shows the TAN concentration in the stripped digestate at the end of each 3.5-day stripping period, while Fig. 6b shows the removal efficiency. During the first ~50 days of operation, when TAN concentrations were increasing as a result of the introduction of a normal food waste feedstock, removal efficiencies decreased (Fig. 6b). It can be seen that during stage 2 the final TAN concentration was slightly lower in C1 and C2 (2.5 kg stripped) than in C3 and C4 (2.1 kg stripped); while the removal efficiency in C1 and C2 was slightly higher, at 79% compared to 73% in C3 and C4, perhaps due to the greater depth of digestate in stripping columns C1 and C2. In stage 3 the final TAN concentrations for the two columns (C2 and C4, 2.5 kg stripped) used for digestate from digester T2 were closely similar, indicating that both were performing equally well. A fall in stripping efficiency in C1 during stage 3 could have been due to partial blockage of the gas sparger, after a temporary interruption to gas recirculation on day 213.

Fig. 6c shows TAN removal kinetics over the 3.5-day stripping period starting on day 315. These results allow comparison of stripping performance for initial TAN concentrations of 2.5 and 1.5 g N L^{-1}, and for duplicate columns C2 and C4 used to strip digestate from T4 under the same conditions. As expected, TAN removal was non-linear with most removal occurring on the first day. The results also showed, however, that there were slight differences in performance between different columns even when operated under conditions as similar as experimentally possible. This can be seen in C1 and C4 which both achieved a final removal rate of over 75% but showed a difference in kinetics, with C4 reaching a plateau sooner. Small differences were also visible between C1 and C3, with the poorer performance of C1 possibly associated with fouling of the diffuser as noted above. The final concentration at the end of the stripping period appeared to depend on the initial concentration. In all cases the final pH was 9 or below, and it would be interesting to see whether sequential lime addition could enable further removal in C1 and C3 which had the higher initial and final TAN concentrations. The small number of data points made reliable estimation of time constants for ammonia removal difficult, but values appeared to be at the lower end of those reported by Serna-Maza et al. (2015) for fresh FW digestates, indicating stripping was relatively easy. C2 and C4 (2.5 kg stripped) had stripped ~70% of TAN by the second day, while C3 (2.1 kg) had removed 61%.

Fig. 4d shows TKN and organic N (i.e. TKN minus TAN) in the digesters. There is a clear reduction in TKN while the organic N is relatively unaffected, indicating that removal was almost entirely in the form of TAN. No evidence of additional breakdown of organic material in the stripper was seen in the current experiment, as organic N in the digester remained almost constant throughout the experiment. This differs from the results of Serna-Maza et al. (2015) who saw conversion of organic nitrogen to TAN in the stripping process for ammonia removal from mesophilic food waste digestates, and speculated that thermophilic digestion could give a slight improvement in overall biogas yield through improved degradation. The current result may indicate that the thermophilic conditions already have the capacity for additional hydrolysis of organic N, leaving little scope for further physico-chemical degradation in the stripping column. As there was no mesophilic control digester it was not possible to identify or quantify any differences in specific gas production at different operating temperatures.

Overall TKN removal rates for T2 were calculated from the feedstock TKN value (6.67 g N kg^{-1} WW) and the digestate TKN, taking into account the reduction in digestate volume associated with VS destruction. The digestate TKN concentration without stripping was estimated as 8.3 g N kg^{-1} WW on a mass balance basis based on VS

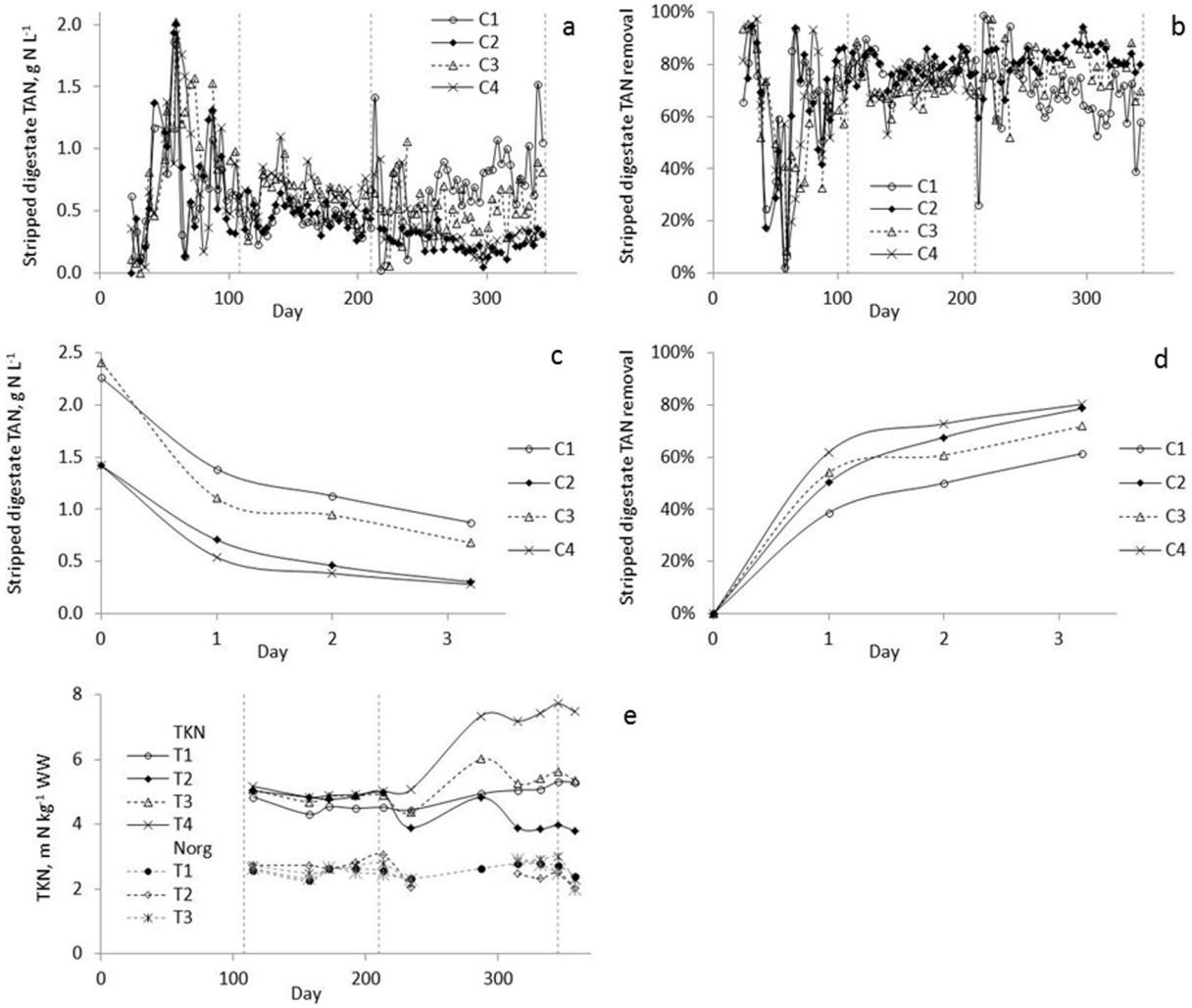

Fig. 6. Stripping parameters: (a) TAN concentrations in stripped digestate, (b) TAN removal rates in stripper during experimental period, (c) TAN concentration and (d) % TAN removal over the 3-day stripping period starting on day 315, (e) TKN and organic N in digesters during experimental period. Vertical dotted lines indicate ends of stages.

measurements, or 8.5 g N kg^{-1} WW based on weight of dry biogas produced. The measured TKN in T2 at the end of stage 3 was around 3.9 g N kg^{-1} WW, corresponding to a removal rate of 53% or 54% respectively for these two methods of estimating VS destruction. Serna-Maza et al. (2014) noted that for mesophilic digestion with stripping at high temperature (≥70 °C) and pH ~10, 48% of the TAN was removed over a 138-day period without any detrimental effects on digester performance. The removal in the current study equates to a potential recovery of around 3.6 kg of N per tonne of feedstock treated.

An earlier study (Serna-Maza et al., 2014) showed how ammonia could be removed from a mesophilic digester using a side-stream stripping process: this indicated the critical parameters for time/temperature/pH that were used in the design of these experiments. The major differences here were that the digestion was under thermophilic conditions, and TAN was controlled at the desired values by preventing its accumulation rather than by stripping from a high initial concentration. The current work confirmed the process conditions for ammonia stripping, and adjusted the stripping rate to achieve target TAN concentrations in the digesters. The maximum quantity of digestate stripped from one digester was 10 kg per week, to which 140 g of lime had been added. The average daily proportion of the digester stripped was therefore 4.1%, corresponding to an equivalent retention time of 24.5 days for stripped material. This is a considerably lower fraction than the 21% of digester contents treated 3 or 5 times per week in the air stripping system used by Pedezzi et al. (2017), although the latter required no chemical addition. In the current work the material was held in the stripping column at an initial pH ≥10 for a period of around 84 h before being returned to the digester, without any apparent detrimental effect. Such treatment, however, is likely to disrupt microbial activity in the treated portion and may cause thermal hydrolysis. The process will therefore increase the overall growth rate of the system, as the dead biomass can be regarded as being 'washed out' in terms of its activity, even though the residues were returned to the digester. Evidence for any effect from the alkaline thermal hydrolysis is largely speculative, as it is not possible to run a parallel thermophilic system without ammonia stripping due to the issue of toxicity; but the SMP of ~0.47–48 L CH_4 g^{-1} VS of the food waste was slightly higher than when the same batches of FW were digested mesophilically with typical SMP values between 0.45 and 0.46 L CH_4 g^{-1} VS (Yirong et al., 2013). Further evidence can be seen in the solids data in stage 3 where the rates of stripping varied between the digesters. As expected the total solids in T2 increased with the higher lime dose. The VS content in this digester was lower than in the other digesters, however, suggesting a greater breakdown of solids than in T1 and T3 although these digesters appeared to perform equally well in terms of methane production. The experimental results presented do not allow a firm conclusion to be reached, and a comparative study of specific methane yields between stable mesophilic digestion and a lime stripped thermophilic system would be required to quantify any differences. The organic loading used in the study was also comparatively low in relation to those now used in

commercial digestion systems, which are usually in the region of 4 kg VS m^3 day^{-1} in mesophilic conditions: a more marked effect may have been seen if a higher loading had been used. This would also have affected the stripping rate required to maintain the target digestate TAN concentration. There is ample capacity in the system to achieve this, however, as demonstrated by the low TAN concentrations that were achieved in T4. While the current trial successfully demonstrated stable digestion for periods of > 3 HRT for the main digester, and > 5.5 cycles in terms of the stripping column, there is considerable scope for optimisation of the stripping conditions.

4. Conclusions

Thermophilic food waste digestion was possible using a sidestream stripping process at 70 °C with initial pH > 10. Ammonia inhibition thresholds were established for this substrate, and the process could control TAN below these without detrimental effects. Stripping achieved 54% TKN removal, potentially allowing recovery of 3.5 g N kg^{-1} substrate. Stripping kinetics indicated removal could be achieved within 1 day, but there is still scope for process optimisation. The pattern of VFA accumulation without stripping suggested that the acetate oxidation pathway failed as TAN approached 5 g N L^{-1}, although progressive instability was noted at > 2.5 g N L^{-1}.

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Thermophilic Digestion of Food Waste by Dilution: Ammonia Limit Values and Energy Considerations

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ABSTRACT: Source segregated domestic food waste (FW) collected by Veolia Environmental Services was used as a test substrate for thermophilic anaerobic digestion in a laboratory-scale trial with semicontinuous feeding at an organic loading rate of 3 g of volatile solids (VS) L^{-1} day^{-1}, reached after an acclimatization period of 60 days. The FW had a total Kjeldahl nitrogen content of 0.73% on a wet weight basis which, without dilution, gave a digestate total ammonia nitrogen (TAN) concentration of >5.0 g of N L^{-1}. This led to the accumulation of propionic and other longer-chain volatile fatty acids (VFA), followed by a sharp increase in acetic acid, which was sufficient to overcome the ammonia buffering capacity, causing the pH to fall and gas production to cease. In digesters run in parallel, TAN concentrations were regulated by diluting the FW with water. This allowed the determination of critical threshold concentrations for TAN, and for free ammonia nitrogen (FAN) by calculation, and monitoring of the pattern of VFA production. Below 2.5 g of N L^{-1} of TAN, there was no evidence of digestion instability. Between 2.5 and 3.5 g of N L^{-1} of TAN, transient peaks in VFA could be seen, but without long-term accumulation; above 3.5 g of N L^{-1} of TAN, continuous accumulation of VFA occurred, which eventually led to failure. Stable digestion could be maintained by a dilution of 0.5:1 water to FW. The energy implications of using a dilution strategy were evaluated using the ADAT modeling tool for a range of scenarios at dilution ratios of 0.5−3:1, ambient temperatures of 5−35 °C, and different plant sizes. As expected, dilution had the largest effect on the net energy demand, but at the lowest dilution required to overcome toxicity, this only equated to a 2−6% loss of the raw energy potential of the biogas produced from the FW when compared to mesophilic digestion with pasteurization.

1. INTRODUCTION

Anaerobic digestion (AD) of food waste has grown in popularity as the energy value of this digestion substrate is more widely recognized[1] and the use of these materials into animal feeds becomes increasingly regulated in many parts of the world due to concerns over disease transmission. The potential for nutrient recovery and the benefits of using digestion to close the loop between urban food waste generation and the fertilizer requirements of agriculture are also important drivers for the promotion and adoption of AD.[2]

Food residues of many different types arise in the food production chain from land or sea to the market place, each having specific characteristics that may or may not make them suitable substrates for AD. In the U.S., food waste is estimated to make up 15% or more of the municipal waste stream,[3] while in European countries this figure is typically 20−25%, and in China the proportion may be as high as 50%:[4] this material is therefore available in substantial quantities. While postconsumer food waste from different countries differs in appearance, from the perspective of its biochemical composition, it has some similarities, as human dietary inputs tend to be balanced in terms of their protein, carbohydrate, and fat contents, particularly in the developed regions of the world.[1,5]

In the U.K., the first demonstration-scale digester treating source segregated food waste from domestic and commercial properties was built in 2006[6] and formed the basis of an industry that processed 1.6 million tonnes of waste per year in 400 plants generating 480 MW of energy in 2016 in the UK alone.[7] The path of commercialization was not without difficulty, however, and one of the major problems was high ammonia concentrations in the digester that could lead to inhibition and ultimately failure of the process.

The issue of ammonia toxicity has been recognized for many years, as detailed in two recent review papers.[8,9] It is now generally accepted that in mesophilic digestion, the acetoclastic methanogens are more sensitive to ammonia than the hydrogenotrophs.[10−13] There have been numerous reports in the literature of acclimatization of digesters to ammonia.[8,14] It is likely, however, that under mesophilic conditions, this is adaptive acclimatization resulting from community structure changes in which the balance between acetoclastic methanogens and hydrogenotrophic methanogens coupled to acetate oxidizers shifts in favor of the latter.[15−18] In food waste digestion, this switch in population was seen to be stimulated by the addition of selenium, which unlocked the acetate oxidation route and prevented propionic acid accumulation.[16] Digestion at high ammonia concentrations is associated with the predominance of a hydrogenotrophic population, and in particular *Methanomicrobiales*:[19] this was also found to be the dominant group in an analysis of full-scale digesters operating at total ammonia nitrogen (TAN) concentrations above 2.8 g^{-1} of N L^{-1} or 0.44 g^{-1} of N L^{-1} of free ammonia nitrogen (FAN).[20]

In operational terms, tolerance to ammonia has been variously reported in the literature with a wide range of values quoted.[8,9] This is not surprising when TAN (NH_3 plus NH_4^+)

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concentrations are reported, as the toxicity is due to free ammonia nitrogen (FAN, NH_3) with the equilibrium concentration depending at least upon pH and temperature. Under mesophilic conditions, threshold FAN values of around 1.0 g of N L^{-1} have been reported in well-controlled experiments where ammonia concentrations have been raised using an external nitrogen source such as urea.[19] In a typical mesophilic digester treating source segregated food waste from households or from the retail sector, the TAN concentration will equilibrate at between 5 and 6 g of N L^{-1}[16] equivalent to a FAN of ∼0.75 g of N L^{-1}, and below the mesophilic inhibition threshold, provided that adequate trace element supplementation is supplied.[16] The same food waste added to a thermophilic digester at 55 °C may cause severe inhibition as the FAN will rise above 1 g of N L^{-1}, in excess of threshold inhibitory values.[21]

Yet the thermophilic digestion of food waste may offer some advantages if the limitation of ammonia toxicity could be overcome. These may include achieving higher rates of digestion, greater conversion of waste organics to gas, improved solid liquid separation, and minimization of bacterial and viral pathogen accumulation.[8] Acclimatization to increasing ammonia concentrations appears not to be possible for this substrate under thermophilic conditions, despite long-term exposure.[22,23] The alternative is to reduce the ammonia concentration, and the two main approaches are based either on stripping ammonia from the liquor[24−26] or more commonly on dilution to below the toxicity threshold.[27] The latter approach, however, results in an increase in the volume of material to be treated, which in turn can make the process economically unattractive[28] and energetically less favorable. As an alternative to water addition, codigestion with a low nitrogen material also serves to "dilute" the TAN: this strategy was also demonstrated by Nielson and Angelidaki[29] as a means of recovery from ammonia inhibition in the thermophilic digestion of cattle manure. Codigestion has the benefit of gaining further energy from the added carbon and is therefore likely to be preferable in terms of the overall energy balance. In the EU, the additional energy inputs required for thermophilic digestion of diluted food waste materials may be partially offset by the potential for omitting the 70 °C pasteurization stage, which is required for compliance with Animal Byproducts Regulations (EC 1069/2009) when operating under mesophilic conditions. Thermophilic digestion of a more dilute mixture may also offer improvements in mixing behavior and solids separation and increase the potential for heat recovery from the effluent. Both of these gains, however, are only compensatory, and further consideration of energy balances is needed to elucidate the value of this approach.

The current study had two main aims: first, to test the threshold inhibition concentration for TAN in food waste digestion at 55 °C using diluted municipally collected source segregated food waste and to assess the performance of the digestion process under these conditions and, second, to make a preliminary assessment of the energy implications of adopting this type of strategy.

2. MATERIALS AND METHODS

2.1. Feedstock. The feedstock was source segregated domestic food waste (FW) collected from households in Eastleigh, Hampshire, U.K. by Veolia Environmental Services (UK) Ltd. A sample of around 300 kg was removed from the biodegradable bags in which it was collected. Any obvious nonfood contamination was removed along with any large bones and seeds. The sample was then ground (S52/010 Waste Disposer, IMC Limited, UK) to a homogeneous pulp, mixed thoroughly, and frozen at −18 °C in ∼3 kg portions. When needed, the feedstock was thawed and stored at 4 °C and used within a period of a few days. This source of feedstock has been used in a number of trials,[21] and the key characteristics of the current batch are shown in Table 1.

Table 1. Food Waste Characteristics

parameter	unit	value
total solids (TS)	% wet weight (WW)	23.9
volatile solids (VS)	% WW	22.4
VS/TS	%	93.7
total Kjeldahl nitrogen (TKN)	% WW	0.73

2.2. Digester Construction, Startup, and Operation. Three pairs of 4-L working volume anaerobic digesters were used, of a continuously stirred tank reactor (CSTR) design. These were constructed of PVC tube with gastight top and bottom plates. The top plate was fitted with a gas outlet, a feed port sealed with a rubber bung, and a draft tube liquid seal through which an asymmetric bar stirrer was inserted with a 40 rpm motor mounted directly on the top plate. Digester temperature was maintained at 55 ± 1 °C by circulating water from a thermostatically controlled bath through heating coils around the digesters. Biogas was measured using tipping-bucket gas counters with continuous data logging. Gas counter calibration was checked regularly by collecting the gas produced over a one-day period in a gas-impermeable bag and measuring its volume in a weight-type gasometer.[30] All gas volumes reported are corrected to a standard temperature and pressure (STP) of 0 °C and 101.325 kPa.

The digesters were initially filled with inoculum from a mesophilic digester treating municipal wastewater biosolids (Millbrook, Southampton, U.K.). The inoculum was supplemented with trace elements to give an added concentration of 0.8 mg L^{-1} of selenium and 4 mg L^{-1} of cobalt; these values are higher than typically used in mesophilic digestion as it has been suggested that thermophilic systems have higher TE requirements.[31] These concentrations were maintained throughout the run by weekly addition of trace element solutions in proportion to the total volume of daily feed (i.e., including water). The temperature was adjusted to 55 °C in a single step, and the digesters were left for 5 days without feeding. The organic loading rate (OLR) was then raised gradually from 0.5 g of VS L^{-1} day^{-1} to the target of 3 g of VS L^{-1} day^{-1} over a period of 51 days, using FW diluted with tap water at a ratio of 2:1 (water/FW) on a wet weight (WW) basis. In all cases, feed was added once per day and 7 days per week.

After day 62, the feeding regime was modified so that in one pair of digesters (T1 and T2), the feed was added without water (dilution 0:1); in one pair (T3 and T4), the dilution was reduced to 0.5:1; and in one pair (T5 and T6), the dilution remained at 2:1 as before. On day 164 after T5 and T6 had completed more than 4 HRT (hydraulic retention time) at a 2:1 dilution, the dilution in these digesters was reduced to 1:1 to provide a further set of operating conditions for assessment. The experiment ran for a total of 238 days, and the OLR and HRT in each set of digesters during this period are shown in Figure 1.

2.3. Analytical Methods. Total and volatile solids (TS and VS) were measured according to Standard Method 2540 G[32] using a Heraeus Function Line Series oven and a 201/301 Carbolite muffle furnace. pH was determined using a Jenway 3010 m (Bibby Scientific Ltd., UK) with a combination glass electrode calibrated in buffers at pH 4, 7, and 9.2 (Fisher Scientific, UK). Alkalinity was measured by titration with 0.25N H_2SO_4 to end points of pH 5.75 and 4.3 using an automatic digital titration buret system (SCHOTT titroline easy), to allow calculation of total (TA), partial (PA), and intermediate alkalinity (IA).[33] Total ammonia nitrogen (TAN) was measured using a BÜCHI Distillation Unit K-350 with NaOH addition, followed by collection of the distillate in a boric acid indicator and titration with 0.25 N H_2SO_4. VFA concentrations were determined by gas chromatography (Shimadzu GC-2010), with a flame ionization

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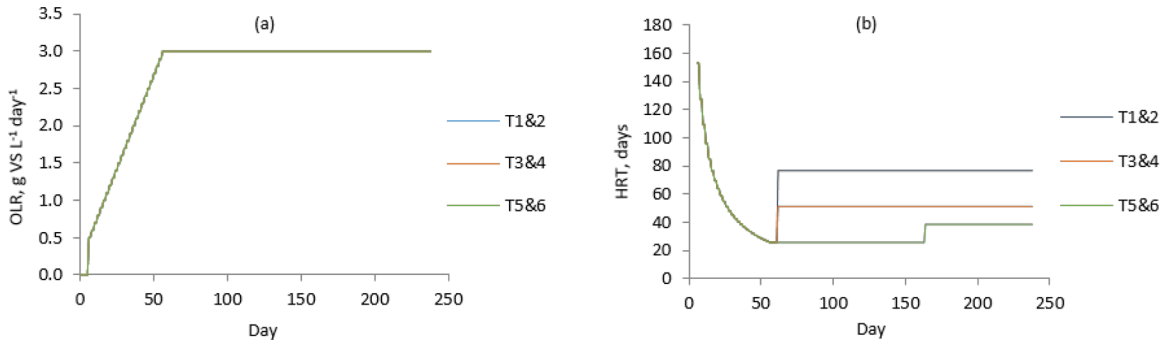

Figure 1. Operating conditions for FW digesters with and without dilution. (a) OLR, (b) HRT.

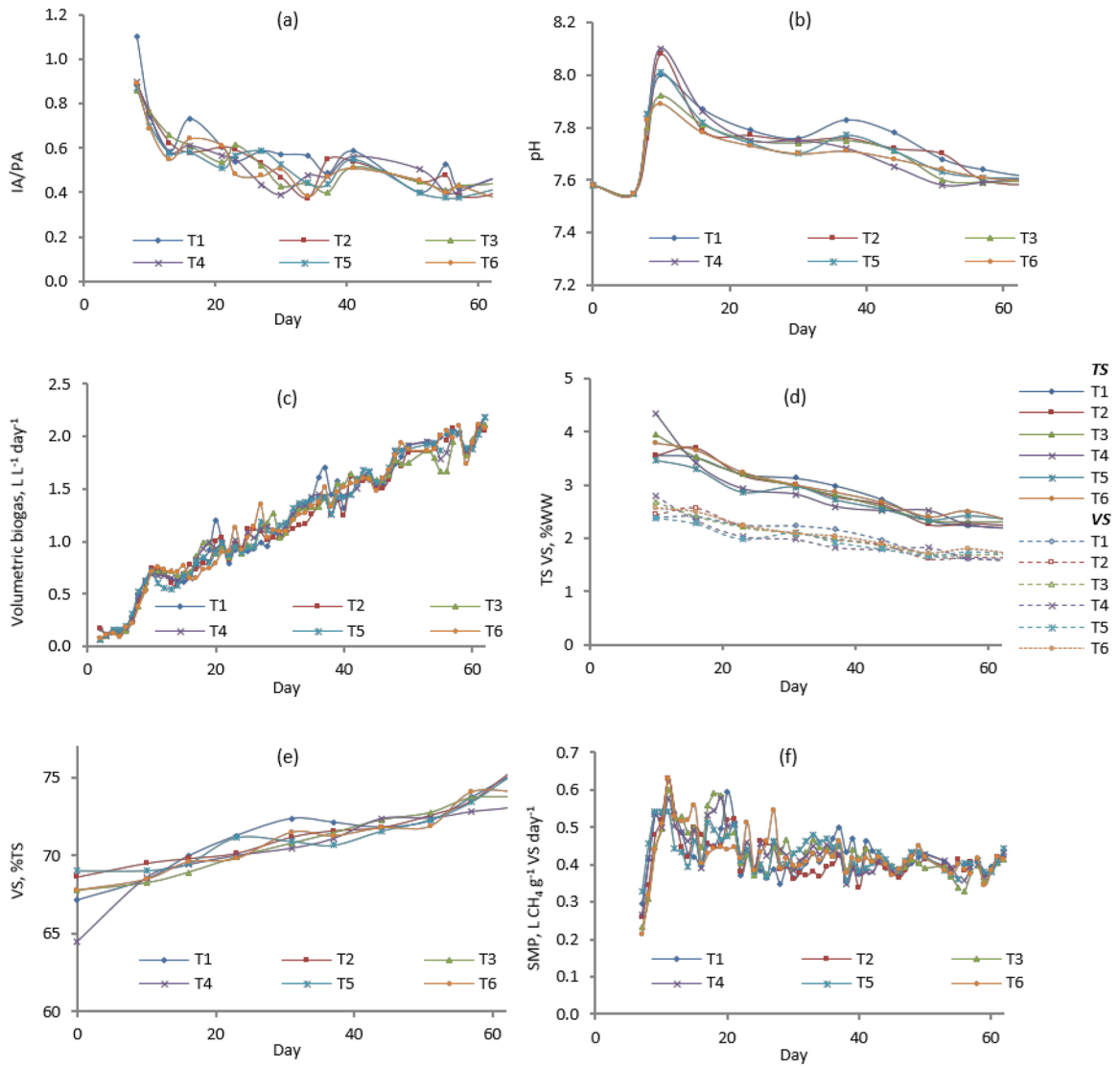

Figure 2. Selected monitoring parameters during acclimatization (days 0−62). (a) IA/PA ratio, (b) pH, (c) volumetric biogas production (VBP), (d) TS VS as % of wet weight (WW), (e) VS as %TS, (f) SMP.

detector and a capillary column (SGE BP-21) and helium as a carrier gas. Samples were acidified to 10% using formic acid and measured against mixed standards of 50, 250, and 500 mg L^{-1} of acetic, propionic, iso-butyric, n-butyric, iso-valeric, valeric, hexanoic, and heptanoic acids. Biogas composition (CH_4 and CO_2) was determined using a Varian star 3400 CX Gas Chromatograph fitted with a packed stainless steel SUPELCO 80/100 mesh porapack-Q column and a TCD detector. The GC was calibrated with a standard gas containing 65% CH_4 and 35% CO_2 (v/v) (BOC, UK).

2.4. Modeling. Dilution scenarios were modeled using ADAT, a mass and energy balance modeling tool that was developed with support from various sources including the FP6 CROPGEN project (SES6-CT-2004-502824), RCUK RELU (RES-229-25-0022), FP7 VALORGAS (241334), BBSRC ADNet (BB/L013835/1), and IEA Task 37 (UK) and which is freely available for download from www.

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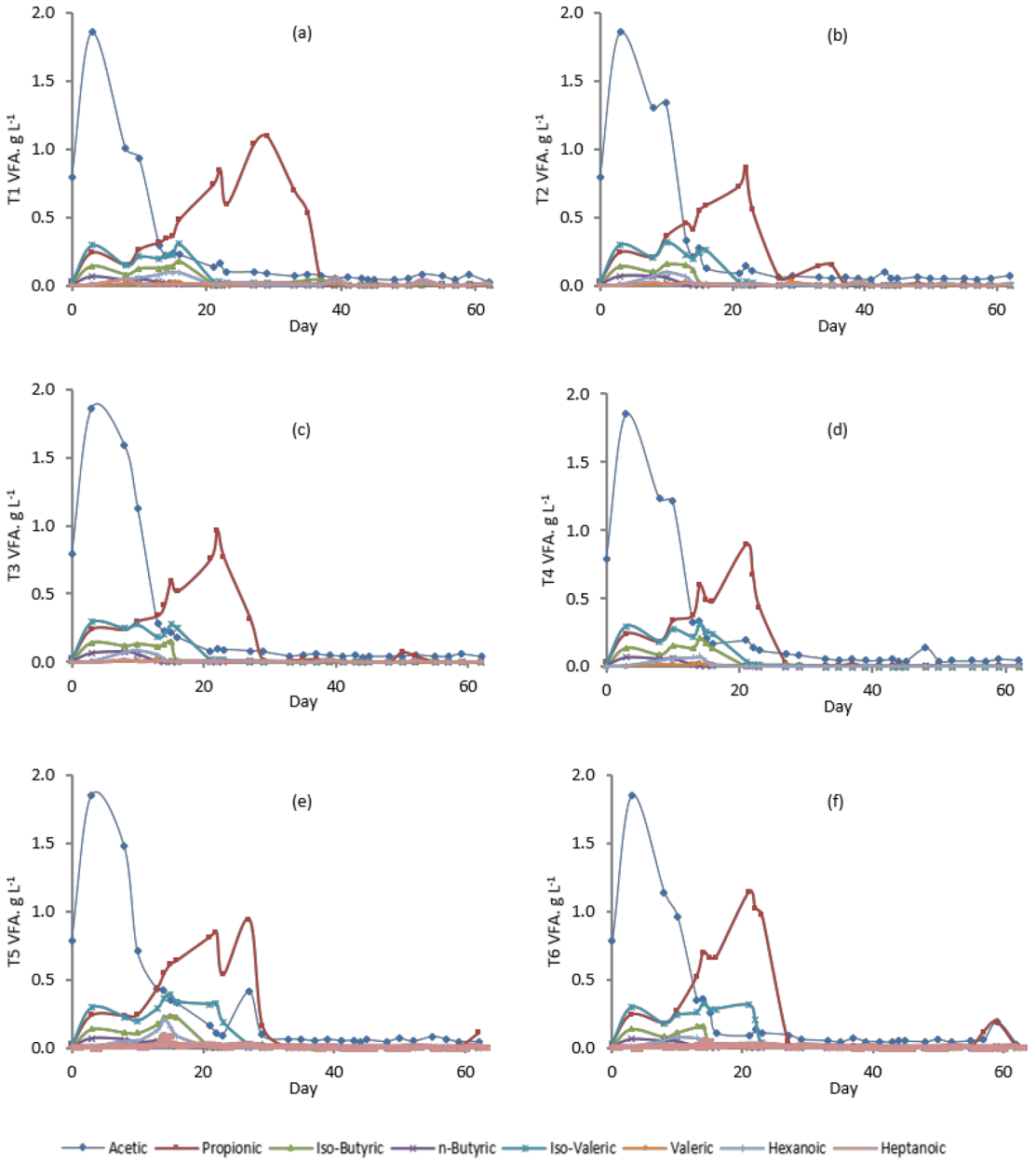

Figure 3. VFA profiles in all digesters during acclimatization (days 0−62).

bioenergy.soton.ac.uk/resources.htm. The modeling tool takes account of energy requirements for feedstock heating, pre- or postpasteurization, and heat losses through the floor, walls, and roof of the digester. It includes the estimated parasitic energy demand for mixing and pumping, and from fugitive methane losses in the process. It also takes into account the efficiency of the CHP plant or boiler, and/or the energy use in upgrading and compressing biogas (as appropriate). The modeling tool can also include energy requirements for transport and pre- and postprocessing of feedstock and digestate fractions, energy offset savings from fertilizer substitution, and embodied energy in the major plant components, but these were not included in the current work unless noted in the text. The model is written in C# and compiled with a user interface allowing input values to be modified. Unless noted, the default values in the modeling tool were used.

Modeling was carried out for a user-defined feedstock with a specific methane production (SMP) of 0.45 L of CH_4 g^{-1} of VS added, 60% CH_4 in the biogas, TS 23.9%, VS 90.5% of TS, nutrient values 31 g of N kg^{-1} of TS, 4 g of P kg^{-1} of TS, 13 g of K kg^{-1} of TS, and 10 kWh $tonne^{-1}$ parasitic energy for feedstock (not including dilution). These properties were based on the current feedstock but are closely similar to default values for source segregated domestic food waste in the ADAT modeling tool. The SMP value used for modeling mesophilic digestion was the same as that for thermophilic, as previously reported for this FW feedstock.[23] Digester design was based on an OLR of 3 g of VS L^{-1} day^{-1}, now regarded as fairly moderate for food waste digestion. The digester was assumed to be a steel tank with 50 mm of high performance insulation (typical U value of 0.0245 W m^{-1} K^{-1}, giving a composite heat transfer coefficient of 0.49 W m^{-2} K^{-1}), and a double membrane roof with a composite heat transfer coefficient of 1 W m^{-2} K^{-1}.[34] Digester temperature was set at 55 °C for thermophilic operation and 37 °C for mesophilic. Modeling was carried out for default conditions in Southampton, UK (annual average air and soil temperatures 10.6 °C), and also at annual average temperatures from 5 to 35 °C. Unless noted, it was assumed there was no separate pasteurization step, as at 55 °C compliance with the Animal Byproduct Regulations (EC 1069/2009) may be achieved by providing a guaranteed HRT, e.g., through intermittent feeding and discharge. It was assumed that the biogas produced was used on site in a combined heat and power (CHP) plant.

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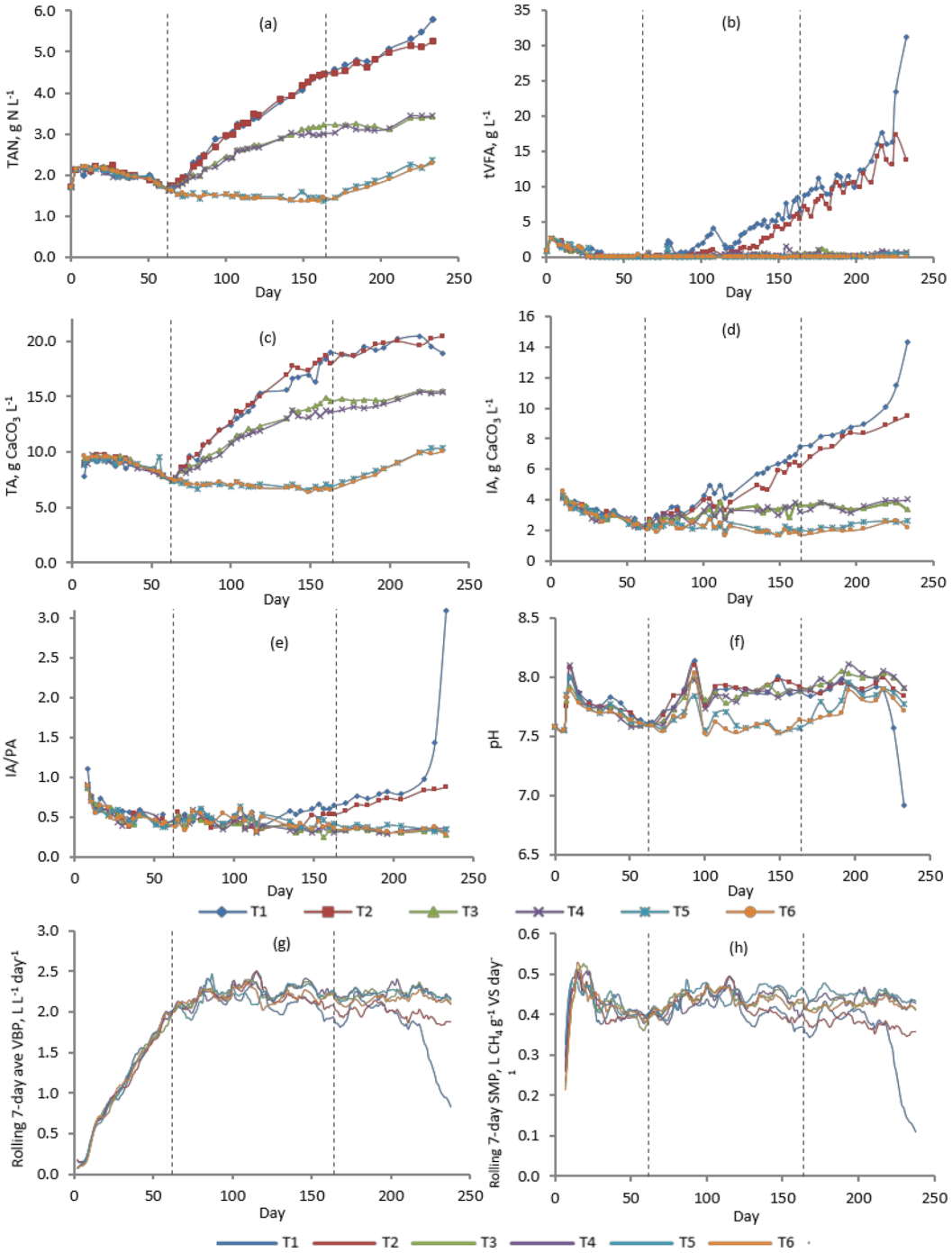

Figure 4. Selected monitoring parameters during experimental period (days 0–238). (a) TAN, (b) TVFA, (c) TA, (d) IA. (e) IA/PA ratio, (f) pH, and rolling 7-day averages of (g) VBP and (h) SMP. Vertical dotted lines indicate change in feed dilution.

3. RESULTS AND DISCUSSION

3.1. Startup and Acclimatization (Days 0–62). Following the single-step increase in operating temperature, there were some signs of process disturbance. Total VFA concentrations in all digesters rose to a peak of around 2.6 g L^{-1} by day 3. This was accompanied by IA/PA ratios of between 0.9 and 1.1 (Figure 2a), although pH remained unaffected at around 7.5 (Figure 2b). When feeding began on day 6, the pH and TAN concentrations rose to between 7.9 and 8.1 and 2.1–2.2 g of N L^{-1}, respectively, indicating that effective hydrolysis of the feedstock was occurring. Biogas production began, and volumes increased in line with the increasing OLR (Figure 2c). Over the following 6 weeks, TAN gradually declined to around 1.6 g of N L^{-1}, probably as a result of uptake by microbial biomass in response to the increasing OLR and reducing HRT. TA, PA, and IA fell slightly in all digesters, reaching values of around 7.4, 5.2, and 2.2 g of $CaCO_3$ L^{-1} respectively by the end of the acclimatization period, with the IA/PA ratio dropping to around 0.4. The nature of the digestate solids also changed in this period, with a slight fall in TS and VS concentrations (Figure 2d) and an increase in VS/TS ratio (Figure 2e), reflecting the change from the previous wastewater biosolids feed to a dilute feedstock with a high VS content.

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VFA profiles in this period showed an interesting transition, which was almost identical in all digesters (Figure 3) and probably reflected changes in the microbial community structure as the slower-growing methanogens came into balance with the acidogenic and acetogenic populations. There was an initial peak in acetic acid of around 1.9 g L^{-1}, suggesting that the temperature shock had disturbed the acetoclastic methanogenic population. This fell to less than 0.1 g L^{-1} by days 22−27, indicating that acetate consumption rates, either through the acetoclastic route or via acetate oxidation, had recovered to match the rate of production. Propionic acid concentrations increased to around 1 g L^{-1} up to day 27, indicating, first, that the capacity of the syntrophic hydrogenotrophic methanogenic community was overloaded at this point and, second, that the accumulation of longer chain VFA seen between days 0 and 15 (Figure 3a−f) was beginning to reduce through conversion to propionate. Concentrations of all VFA had reached very low values by days 30−35, indicating that populations had stabilized in all digesters. A similar initial response was seen in previous work on acclimatization of inoculum from the same source to thermophilic digestion of a similar but undiluted food waste feedstock,[21] but in that case, after 40 days, ammonia concentrations had reached inhibitory values, causing a second increase in propionic acid which eventually led to digester failure.

By day 62 at the end of the acclimatization period and after the OLR had reached its target value, the process was operating stably with a pH of around 7.6, TAN = 1.6 g of N L^{-1}, and VFA around 0.1 g L^{-1}. The biogas methane content was steady at around 60%, and SMP had reached 0.400 L of CH_4 g^{-1} of VS added (Figure 2f), similar to the start-up value reported for this feedstock in other work[21] and within 10% of the long-term steady-state value. During the start-up period, values for all monitoring parameters showed very similar behavior in all six digesters, and by day 62, all digesters were considered to be successfully acclimated to the new feedstock and thermophilic conditions.

3.2. Digester Performance and Operational Stability (Days 63−238). On day 62, the dilution regime was changed with the aim of allowing TAN concentrations in one pair of reactors (T1 and T2) to increase to the point of failure. The feedstock to another pair of reactors (T3 and T4) was diluted to a level at which some instability was expected, while one pair (T5 and T6) was maintained at the previous "safe" dilution until day 164.

In T1 and T2 (dilution 0:1), TAN rose steadily and exceeded 5.0 g of N L^{-1} by day 215 (Figure 4a), equivalent to 2 HRT in this operating mode. In T3 and T4 (dilution 0.5:1), TAN concentrations began to stabilize by day 160 and remained steady at around 3.1 g of N L^{-1} until the digesters reached 3 HRT on day 215. T5 and T6, which remained at dilution 2:1, reached 3 HRT at day 130 with TAN concentrations stabilizing at around 1.5 g of N L^{-1}. On day 164, the dilution in these digesters was changed to 1:1, and the TAN concentration rose, reaching 2.3 g of N L^{-1} by day 238 after 2 HRT in this operating mode.

Total VFA (TVFA) showed a clear response to the changes in TAN concentrations (Figure 4b). In T1 and T2, minor fluctuations in TVFA appeared from day 80 onward, when the TAN reached 2.2 g of N L^{-1}; from day 120 when TAN reached 3.5 g of N L^{-1}, there was a steady rise until the end of the experiment. In T3 and T4 during the period between days 160 and 215, TVFA increased from its previous baseline value to around 0.5 g L^{-1}, with short-term fluctuations up to 1.6 g L^{-1}. Between days 75 and 164, the average TVFA concentration in T5 and T6 was <0.15 g L^{-1}. The TVFA profiles indicated that T3 and T4 were showing signs of stress at TAN concentrations of 3.1 g of N L^{-1}, but without VFA accumulation; whereas there were clear signs of metabolic inhibition in T1 and T2 once the TAN concentration exceeded 3.5 g of N L^{-1}.

Alkalinity parameters confirmed the above observations. As expected the TA concentration closely mirrored the TAN (Figure 4c). IA remained relatively stable in digesters T5 and T6 and T3 and T4 throughout the experimental period (Figure 4d), reflecting the absence of VFA accumulation, while in T1 and T2 there was a rapid increase in IA clearly related to the rise in VFA. The IA/PA ratio was below 0.4 for T3 and T4 and T5 and T6 (Figure 4e), a typical value for stable operation of food waste digesters, whereas in T1 and T2 this ratio showed a rising trend, with a very rapid increase where VFA accumulation finally broke the buffering capacity of the digester. This led to a rapid drop in pH (Figure 4f) and PA (not shown). The available alkalinity was also reflected in the pH values, which were lower in T5 and T6 than in T1 and T2 or T3 and T4 until the dilution in T5 and T6 was reduced and the TAN and PA increased.

After day 100, volumetric biogas production (VBP) in T3 and T4 and T5 and T6 fluctuated around 2.2 L L^{-1} day^{-1} (Figure 4g) with an SMP of around 0.44 L of CH_4 g^{-1} of VS (Figure 4h). Although T1 and T2 continued to produce biogas, the VBP gradually decreased to around 2.0 L L^{-1} day^{-1} in both digesters by day 150, and SMP fell to 0.39 L g^{-1} VS. After day 220, biogas production in T1 fell rapidly, corresponding to the period when the pH dropped from 7.9 to 6.8 and the IA/PA ratio rose from 0.98 to 3.1. By day 233, the biogas methane content for T1 had fallen below 50%. These results demonstrated that an anaerobic digester can appear to be operating normally even at a relatively high TAN concentration under thermophilic conditions, as long as there is sufficient alkalinity to buffer pH changes. Examination of the data, however, clearly shows metabolic instability as indicated by VFA accumulation. The higher threshold of inhibition for the process can thus be taken as the point at which there is an irreversible increase in VFA concentration. In this particular study, this occurred at a TAN concentration of around 3.4 g of N L^{-1}, yet signs of instability were obvious at 3.1 g of N L^{-1}. These values are reported as TAN concentrations, as this was the parameter measured, but correspond to a calculated FAN of 0.82 and 0.57 based on the measured operating temperature and pH.[35]

At the end of the acclimatization period, the digestate TS content was 2.3% of wet weight (WW), and this continued to fall in T5 and T6, reaching around 1.8% WW by the end of 3 HRT. TS concentrations in these digesters began to rise again after the feedstock dilution was decreased to 1:1, reaching a final value of 2.0%. The TS content rose in T3 and T4 and in the period between days 160 and 215 stabilized at 3.0%WW. T1 and T2 showed a rising trend in TS content, reaching 5.9% by the end of the experiment without achieving a steady state. This corresponded to the period of falling gas production and indicates that the degree of solids destruction was also declining. VS content in T1 and T2 followed similar trends to TS, and the VS/TS ratio was slightly higher than in T3 and T4 and T5 and T6, again indicating less efficient conversion of VS.

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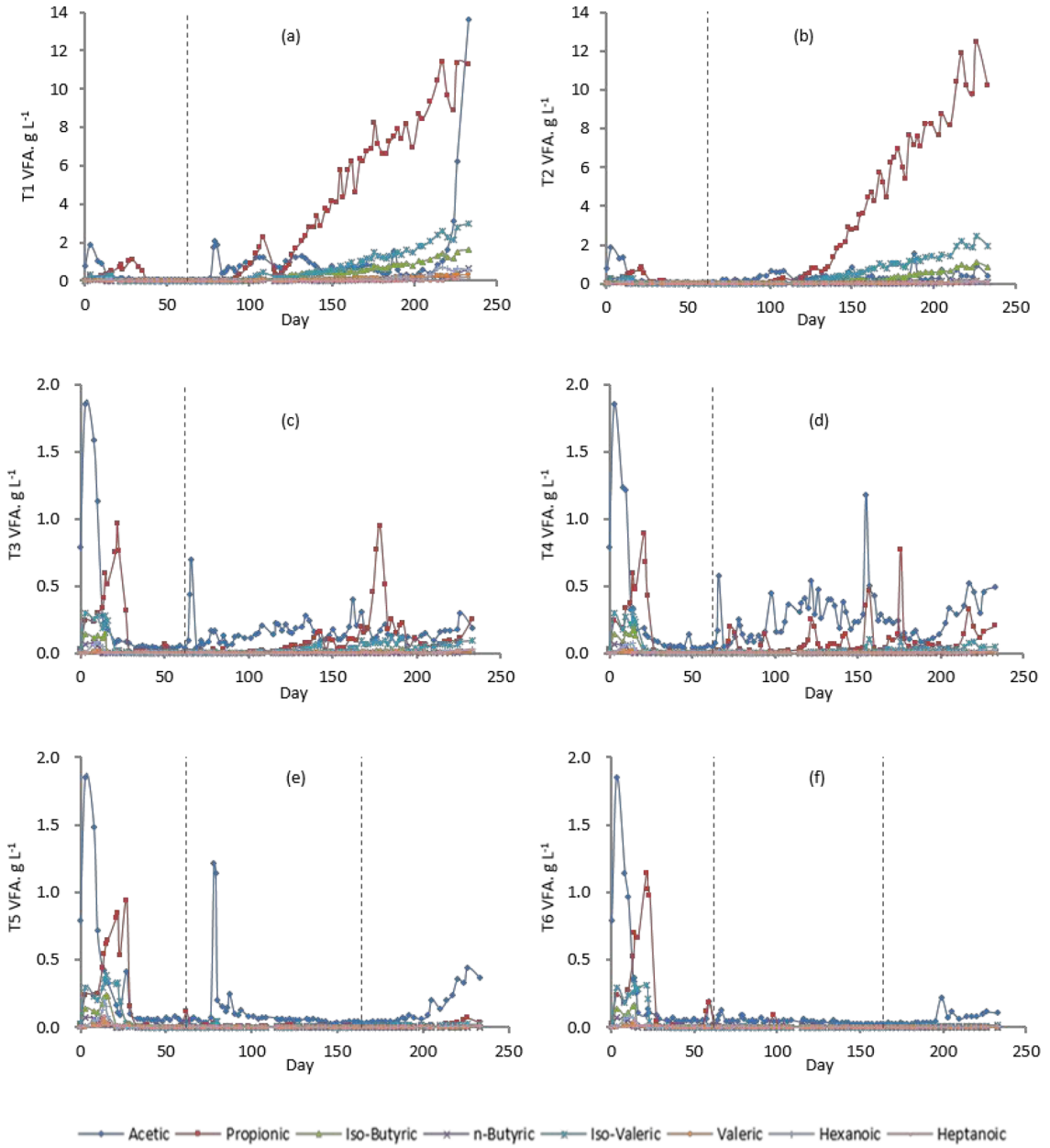

Figure 5. VFA profiles in all digesters during the experimental period. Vertical dotted lines indicate a change in feed dilution. Note the difference in *y*-axis scale for T1 and T2 compared to T3 and T4 and T5 and T6.

VFA profiles for T1 and T2 (Figure 5a and b) showed that the increase in TVFA concentration from day 120 onward was due mainly to accumulation of propionic acid, which reached around 12 g L^{-1} by the end of the experiment; although iso-butyric and iso-valeric concentrations also rose to between 1 and 2 g L^{-1}. At the beginning of this period, acetic acid concentrations showed no consistent upward trend in T1 or T2. After day 215, however, the acetic acid concentration in T1 rose very sharply, reaching 14 g L^{-1} by day 233. VFA concentrations in T2 lagged slightly behind T1 throughout the preceding period (Figure 4d) but by the end of the experiment also showed signs of an increase in acetic acid. The appearance of acetic acid clearly indicates severe disruption of the conversion to methane by either the acetoclastic route or through acetate oxidation. The sequence of VFA accumulation suggests that the syntrophy between acetogens and methanogens had become imbalanced. The mechanism for this was not further investigated, but it is likely that under high TAN concentrations methane formation was primarily through acetate oxidation, and any increase in hydrogen concentrations may lead to feedback inhibition of the acetogenic propionate-degrading bacteria as the thermodynamics of the reaction become less favorable. VFA profiles in T3 and T4 showed no accumulation of individual VFA (Figure 5c and d), but there were elevated levels of acetic acid with occasional transient peaks of propionic and a small increase in iso-valeric concentrations, all indicating mild instability. Although analysis of the dynamic community structure was not carried out, this could provide a useful insight into whether this instability is related to the transition between acetoclastic and hydrogenotrophic pathways, as has been noted under mesophilic conditions at the point where ammonia becomes toxic, or to the onset of inhibition of acetate oxidation, as recent evidence suggests some syntrophic acetate oxidizers may be more

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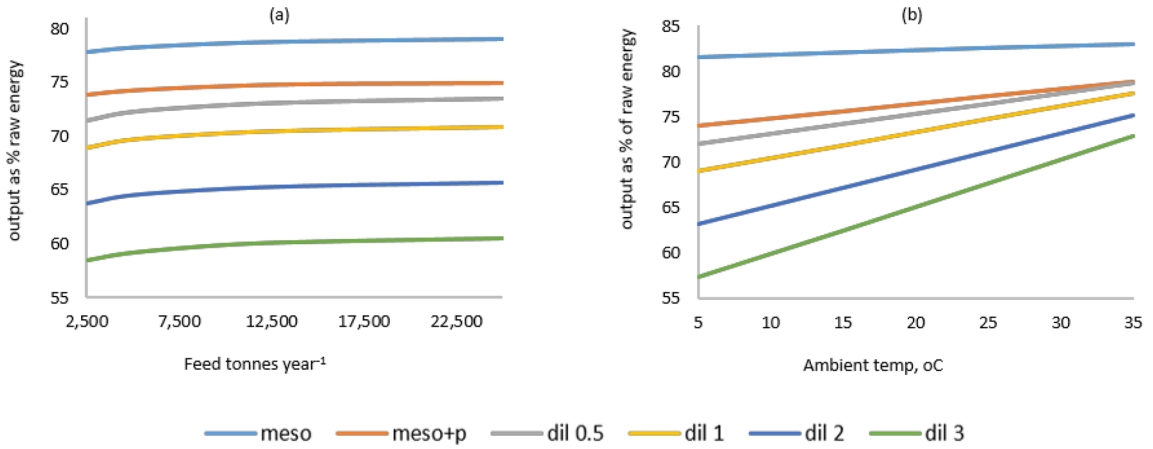

Figure 6. Modeling results for final energy output with variations in (a) digester feed input (ambient temperatures Southampton, UK) and (b) average ambient temperature, under thermophilic conditions in a range of dilutions (0.5:1. 1:1. 2:1, 3:1 water/FW) and under mesophilic conditions with no dilution with and without prepasteurization. Final energy output (electricity + heat) is expressed as % of energy in raw biogas produced.

sensitive than hydrogenotrophic methanogens to high TAN concentrations.[36] After the initial acclimatization period, T5 and T6 showed consistently low concentrations of all VFA species up to day 164 (Figure 5e and f) apart from a transient spike in acetic acid on day 78, the reason for which is unknown. When the dilution in this pair of digesters was reduced to 1:1, the acetic acid concentration rose slightly from day 200, indicating the onset of mild instability at a TAN concentration corresponding to 1.8−1.9 g of N L^{-1} (FAN 0.5 g of N L^{-1})

The results indicated that digester operation could be carried out without VFA accumulation at TAN concentrations below 3.1 g of N L^{-1}, as achieved by a 0.5:1 (water/FW) dilution. At this TAN concentration, some signs of incipient instability were observed, indicated by a slight rise in baseline VFA concentrations with transient VFA peaks. It can be argued that this makes a digester more vulnerable to minor shocks in operation, such as short-term temperature shifts or changes in feed composition: a more cautious approach in terms of process stability would therefore involve increasing the dilution to give a TAN concentration below the lower threshold for onset of instability, corresponding in this study to a FAN of around 0.5−0.6 g of N L^{-1}. The experimental data showed that at the OLR used, dilution of the input FW did not affect the specific methane production, despite a reduction in the retention time from 75 days using undiluted material to 25 days at a dilution of 2:1. The dilution strategy adopted would therefore not change the required digester volume or surface area and is thus unlikely to have a major effect on heat losses (as confirmed with the assumptions used in the modeling work) or on the capital cost associated with the digester, although the required capacity of ancillary equipment such as heat exchangers, pumps, and CHP systems may be affected.

3.3. Modeling. Rajagopal et al.[9] commented that, in anaerobic digestion, dilution is commonly considered as a solution to ammonia toxicity, but this strategy has resource and energy implications that may be economically unfavorable. The actual impact, however, is very dependent on the energy value of the substrate, the availability of water, the potential for recycling of effluent after nutrient removal, and the final markets for the energy products. The most important consideration is the net energy yield, and where the energy potential of the substrate is low, the energy requirement to raise the temperature of dilute materials may be greater than that embodied in the substrate. The energy potential in food waste is high, however, and the proportion that is required for digester heating is thus relatively small.

A number of scenarios were modeled to quantify the energy balance for food waste digestion. The first step was to simply assess the impact of dilution itself, and a thermophilic AD plant treating 2500−25 000 tonnes $year^{-1}$ was modeled using 0.5:1 to 3:1 dilutions of the input material. This was compared to a mesophilic plant with the same tonnage feed range but without dilution, and with or without a prepasteurization stage at 70 °C for 1 h. The final output energy (combined electricity and heat for export, after deduction of parasitic energy requirements) in all cases was expressed as a percentage of the energy available in the raw biogas produced. It can be seen (Figure 6a) that, while operation in thermophilic conditions with dilution does reduce the final energy output, the difference between thermophilic at 0.5:1 dilution and mesophilic digestion with a prepasteurization phase for ambient temperatures in Southampton, UK is only about 2% of the energy in the raw biogas. At a 3:1 dilution, this difference would increase to around 15%, all of which is a demand for heat energy. Where pasteurization is not needed, the difference in energy demand rises to around 6% and 19% at the smaller and larger dilution, respectively, but in the EU, the pasteurization step would be required as a condition of the Animal Byproducts Regulations (EC 1069/2009).

The heat loss from the plant is affected by the size of the digester as its surface area to volume ratio changes. The size of the digester in this case was determined by the feedstock tonnage as a uniform loading rate was applied. For the range of tonnages considered, digester volumes from 665 to 6647 m^3 would be required. Above this size range, it is common practice to use multiple units rather than a single digester, and smaller digesters may have a higher specification for insulation. The results showed that although the heat loss from the smallest plant was higher, this was in fact a relatively minor impact (Figure 6a).

The parasitic heat demands taking into account heat loss and feedstock and diluent heating were compared to heat availability from a CHP unit. Under UK climatic conditions a mesophilic digester with prepasteurization processing 15 000 tonnes $year^{-1}$ (mid size-range) would consume 16.7% of the available heat output from the CHP unit. The equivalent thermophilic digester with a 0.5:1 dilution and no pasteurizer

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would consume 20.0%, a relatively small increase in comparison with mesophilic operation. At a 3:1 dilution, the heat demand would increase to 46.4% of the CHP output, while for the worst case scenario (highest dilution of 3:1 and smallest plant at 2500 tonnes year^{-1}) the heat demand rises to 49.9% of CHP output, still well within the heat generation capacity of the plant.

Different climatic conditions will also affect the final energy output. Figure 6b shows the effect of annual average ambient temperatures (air and soil) from 5 to 35 °C on a digester processing 15 000 tonnes year^{-1} under mesophilic or thermophilic conditions, with the results expressed as a percentage of energy in the raw biogas. Again, there is an increased energy cost for thermophilic operation compared to the mesophilic/pasteurization combination, which is only between 0.2 and 2% of the energy at dilution 0.5:1 but rises to between 6 and 17% for 3:1 dilution.

When the energy output of the digester is electrical power from a CHP plant, there is often no economic use for the heat produced, and if this is the case, then thermophilic operation with dilution is a feasible alternative as no additional energy inputs are required. Even where CHP heat is used, for example in district central heating systems, the extra heat demand of thermophilic digestion at the lowest dilution is small. There are also other potential advantages of this mode of operation which may offset the additional energy requirement. There is some evidence that thermophilic digestion can improve the solids handling and dewatering properties of digestate,[37−39] and dilution itself may also improve dewaterability. This in turn will influence the types of equipment used for mixing and pre- and postprocessing and could affect the ancillary parasitic power demand, but little comparative data is available. Some of the additional energy demand for thermophilic operation could be compensated for by more efficient heat recovery, for example from the digestate discharge, as a result of the higher temperature gradients. The use of surplus heat from CHP may therefore be economically acceptable, although it should not be regarded as providing an environmental benefit in terms of fossil fuel replacement or avoided greenhouse gas emissions. Where the energy output is not as electrical power but through upgrading the biogas to biomethane as a fuel or for gas grid injection, there is no surplus heat, and the parasitic heat requirements of the digester have to be found by importing fuel or burning a proportion of the biogas in a boiler. The modeling tool allows gas upgrading as an alternative to CHP, but the final combined energy balance is the same as that reported here as the parasitic heat demands of the digester remain the same.

A number of other factors affect the overall energy balance and could also be taken into consideration in modeling. The modeling tool estimates the embodied energy in the plant, but in the current study the required digester volume is the same for any given input tonnage of FW, since the OLR was kept constant and the HRT allowed to alter at different dilutions. For feed inputs of 2500 to 25 000 tonnes year^{-1}, the embodied energy was equivalent to 0.9 to 0.4%, respectively, of the total energy in the raw biogas produced over the assumed working life of the plant (taken as 30 years for the digester and 15 years for gas utilization equipment). Digestate transport costs were not included in the overall energy balance analysis, as these are highly site-specific, but it is recognized that transport of unseparated digestate would have some impact on the final energy balance. For example, if a travel distance of 15 km in a rigid 17-tonne vehicle is assumed for a 3:1 diluted digestate, transportation would account for 4.3% of the raw biogas energy. In practice, however, at higher dilutions, it is likely that the digestate would be separated and treated to recover water or allow disposal on site or to the sewer. Energy gains from fossil fuel displacement through N and P recovery are calculated by the modeling tool and for the current FW could represent a contribution of 10.3% of the energy in the raw biogas. This figure was also not included in the final balance, as there are also associated energy costs that will differ considerably depending on whether recovery is by direct application of unseparated digestate onto land, or through on-site treatment of separated liquor and solids. The modeling tool allows input of an energy demand for post-treatment of separated liquors, but this option was not used in the present work.

The idea that using dilution to solve the problems of ammonia toxicity is unattractive does not appear to be well founded. There are clearly cases where the energy value of the waste and the final target energy market of the plant will allow thermophilic operation and still produce waste heat, even with small plant, high dilution, and unfavorable climatic conditions. The difference in energy output between mesophilic and thermophilic digestion is in fact surprisingly small for food waste. The main reason for this is the requirement under mesophilic conditions to include a pasteurization step which requires heating of the material to 70 °C. FW is a special case, however, and for other high N wastes where a pasteurization step is not required the difference would be larger: for example, the energy differentials reported above of 0.2−2% at a 0.5:1 dilution and 6−17% for 3:1 dilution would rise to 4−10% and 10−24%, respectively, when thermophilic digestion is compared to mesophilic digestion without pasteurization. In the end, it may not be energy alone that is the arbiter between thermophilic and mesophilic operation. Equal importance is now being placed on sustainability of resources, and nutrient capture and recycling is a high priority. Replacing the direct spreading of digestate with methods that allow recovery of nutrients as higher value-added products may be more feasible either as part of, or following, thermophilic digestion. Stripping and recovery of ammonia in the gaseous phase requires high temperatures,[24] and process integration would favor thermophilic operation. Where recovery using membranes has been proposed[40,41] this could be facilitated by working with more dilute material. Thermophilic operation is also well suited to the vacuum thermal stripping-acid absorption process described by Ukwuani and Tao,[42] or simply to a direct aeration strategy.[43] Work on electrochemical systems for ammonia removal[44,45] is new and innovative, but there are, as yet, no indications as to the temperature regime to which these techniques might be best suited. Nutrient recovery where the bioderived product is competitive in its application and usage to the wide range of synthetic fertilizers on the market could, however, have resource and economic benefits that could outweigh any energy penalty.

As a final note, it is worth mentioning that in practice a cost benefit analysis determines the degree of digester insulation used, and in all of the modeling scenarios used the amount of insulation on the mesophilic and thermophilic digesters was equal. It could, however, be improved to the point where the degree of heat loss from both thermophilic and mesophilic systems was the same, and at this point the energy balance for the thermophilic digester will be better than for a mesophilic digester with pasteurizer.

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The suitability of dilution as a technique to solve ammonia toxicity problems is thus dependent on a number of factors that include the source and type of input material, the availability of surplus heat, the availability of a dilution medium, the energy market, and markets for recoverable products, and every case should be considered against these criteria.

4. CONCLUSIONS

The thermophilic digestion of a typical source segregated food waste as collected in the UK in single pass mixed digesters with intermittent daily feeding leads to an increase in digester TAN concentrations to a point where the digestion fails. Diluting the feedstock proved a reliable method for establishing the critical TAN concentration at which instability was first observed (2.5 g of N L^{-1}) and also the point where incremental accumulation of propionic and other longer chain VFA began (3.5 g of N L^{-1}). Methane production continued until the digestion finally failed as a result of the pH falling to a critical level when the buffering capacity of the digester was overcome. This happened at a TAN concentration of ~5 g of N L^{-1}. Stable digestion without loss of specific or volumetric biogas production could be maintained at a 0.5:1 water/FW dilution. Energy modeling compared the net energy yields of thermophilic digestion to those of mesophilic digestion with and without a pasteurization stage at different dilutions, digester sizes, and environmental conditions. The results indicated that the impacts of dilution were relatively small for this energy-rich substrate where mesophilic digestion requires pasteurization and can easily be met from the energy available from use of the biogas in a CHP plant even at the highest dilutions, assuming there is no other economic use for the heat. Considering the other potential advantages of thermophilic systems in terms of improved rheology and dewaterability and the enhanced potential for advanced forms of nutrient recovery, dilution may be an acceptable operating strategy.

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Notes

The authors declare no competing financial interest.

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Degradation of some EN13432 compliant plastics in simulated mesophilic anaerobic digestion of food waste

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ABSTRACT

The research looked at the anaerobic biodegradation of 9 different bioplastics, all of which were commercially available and certified in Europe as compostable packaging material compliant with the biodegradation and other requirements of the EN13432 standard. A combination of testing strategies was used to assess the degree of degradation both under batch conditions, and in a simulation in which the plastics and food waste were fed daily to a digester for a period of 147 days. Two non-biodegradable plastics were used as controls, and verified the robustness of the sampling regime and the recovery of the plastic film, with errors of < 1% in the final balance. The simulation allowed quantification of the weight loss of the plastics and determination of a decay coefficient for the different materials, which was then used to estimate long-term degradation. Use of a biochemical methane potential (BMP) batch test allowed estimation of the conversion of carbon into gaseous products. There was no evidence that any of the plastic films inhibited the anaerobic digestion process when continuously fed to digesters, although some inhibition occurred when the most readily degradable materials were tested at higher concentrations in batch mode. There were some interesting differences between results from the various measures of plastic degradation in the batch and simulation experiments, with batch testing in most cases suggesting a higher degree of degradation than was achieved in a semi-continuous system at a solids retention time of 50 days. The exceptions to this were two plastics that appeared to show rapid weight loss in the simulation experiment. BMP test results confirmed this was not through biological conversion of the bioplastic to gaseous carbon products, and was therefore probably due to physical disintegration. It was concluded that, of the 9 bioplastics tested, only 4 showed substantial biodegradability under anaerobic conditions. Further evidence to support the mechanism of biodegradation was obtained by microscopy, and photomicrographs using different techniques are included to illustrate the process. Even the most degradable materials would not break down sufficiently to meet the physical contaminant criteria of the UK PAS110 specification for anaerobically digested material, if fed to a digester at 2.0% of the input load on a volatile solids basis.

1. Introduction

Plastic films are commonly used in food packaging as a means of protecting the food from contamination, both airborne and from manual handling; whilst at the same time allowing customers to see the contents of the package. These films may also have specific properties related to their permeability to moisture and gases, with the goal of improving the product's shelf life and its physical appearance. Other modifications include physical attributes that determine how the film can be applied and sealed. Although plastic films used in consumer-targeted food wrapping only represent a small proportion of the total plastic waste load, this fraction causes significant problems: it is particularly difficult to recover due to its non-uniform size and composition, to its presence in multi-material packaging, and to problems associated with mechanical separation in sorting plants. As a result, this material is not normally targeted by household waste segregation schemes, and is likely to be discarded in the general waste, or as a contaminant in source-segregated food waste streams. Similarly, supermarket products which are past the sell-by date are often disposed of with their packaging. It is the commercial food retailing and catering sectors that have therefore driven growth in the development and use of biodegradable biopolymers [28] as companies seek to meet sustainability goals.

The difficulty in recycling plastic films is compounded by the fact that they often consist of several layers of different compositions; when used in food packaging they are frequently contaminated with residual food; and they are commonly found as small-format items in heterogeneous recycling streams [42]. To overcome these challenges there has

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been considerable interest in developing biodegradable films designed for disposal via composting or anaerobic digestion. These plastics, generally referred to as 'bioplastics', can be produced from conventional petrochemicals or from renewable biological resources; in the latter case they are termed bio-based plastics. Bio-based plastics can be synthesised from bio-based chemical building blocks, e.g. lactic or succinic acids; through modification of natural polymers, such as starch, cellulose or chitin; or through fermentation to produce microbial polymers such as polyhydroxyalkanoates.

Anaerobic digestion is becoming increasingly popular as a means of processing food waste for energy and fertiliser recovery. The inclusion of biodegradable catering films, food wraps and card packaging in the feedstock stream would simplify collection and processing, and eliminate the need for a depackaging stage when the input materials include supermarket wastes and other packaged food materials. It is now recognised that the biodegradability of plastic films is dependent on process conditions, with significant differences reported between aerobic and anaerobic systems [13,22,27,29]. There are also disparities between methods for assessing biodegradability, leading to questions as to whether batch testing methods can adequately predict what will happen under real operating conditions in a full-scale bioprocessing plant [10].

Biodegradation of packaging materials via composting is covered by European standard EN13432 [16] which stipulates the requirements for packaging recoverable through composting and biodegradation: the standard requires testing in accordance with [17] for carbon conversion to CO_2, and in accordance with [18] to show visual disappearance. The US ASTM standard D5338-15 [6] covers the aerobic biodegradation of plastic materials under controlled composting conditions at thermophilic temperatures, and is based on carbon conversion to CO_2. Oxidative degradation is defined by CEN/TR1535 [12] as degradation resulting from oxidative and cell-mediated phenomena, either simultaneously or successively. It applies to conventional plastics that contain additives to speed up oxidative degradation. Oxo-degradable materials do not conform to the EN13432 and [6] standards, and are not considered compatible with composting processes. Anaerobic biodegradability of plastic materials is covered by Ref. [7] and by Refs. [23–25]. All of these consider conversion of carbon in the sample to a gaseous form in batch tests, and thus do not necessarily represent degradation behaviour in continuous systems over extended periods where accumulation, leaching and/or acclimatisation may occur. These tests have a number of other limitations related to the types of inoculum used, the mixing conditions and the operational temperature and do not allow consideration of interaction with any co-substrates.

The aim of the research was to assess the extent to which selected bioplastic films were broken down under anaerobic conditions in a mesophilic digester treating food waste. In addition to the bioplastics, card packaging was added as part of the digester feedstock, to simulate the case where a biodegradable composite packaging is co-digested with food residues in a bio-treatment process. The feedstock in the trial was formulated to contain food waste, card packaging and bioplastic at volatile solids (VS) ratios of 80:18:2 based on a likely composition for segregated waste streams arising either from homes, or from supermarkets if biodegradable packaging is included at source. The nine bioplastics used in the study had all been certified as compliant with the composting standard EN13432, and were therefore recognised as biodegradable in bio-based waste treatment processes in the EU. Their anaerobic biodegradability, biogas production potential and whether the resulting digestate would meet relevant quality standards for use in agriculture had not previously been tested. A simulation trial was chosen in preference to batch testing, as this allows acclimatisation of the inoculum; it also offers less stringent conditions, since co-digestion provides the primary carbon source as well as potentially increasing the supply of 'metabolic' co-factors that may be important in stimulating and promoting biodegradation. The drawback of this type of simulation is that it is difficult to quantify carbon conversion from the polymer alone into a gaseous form: this is recognised as the definitive means of assessing ultimate biodegradation, as opposed to primary biodegradation where the material is no longer detectable by the original analytical approach but may not have been fully mineralised. Testing of ultimate biodegradability is therefore typically carried out in batch assays although, as with aerobic testing, care is required to ensure comparability of results from different methods [10]. To complement the results from a continuous co-digestion trial, where degradation was assessed by gravimetric methods, a batch degradation study was therefore carried out in which production of biogas and biomethane from the polymer was quantified in a biochemical methane potential (BMP) test, and compared with the theoretical value based on substrate elemental composition. A number of variants of the BMP test are available to simulate different conditions [20]: the technique has frequently been used for assessment of degradation, and forms the basis for the now-numerous batch testing strategies that have been proposed specifically for assessing the anaerobic degradation of plastic polymers. The results of the study were intended to provide comparative information on the degradation of selected biopolymers under anaerobic conditions, and to inform stakeholders on whether anaerobic digestion (AD) is a suitable treatment method for a waste stream containing packaged food material that includes carton and renewable plastic film. Although previous studies have considered the biodegradation of plastic polymers under anaerobic conditions in landfill [1,2,8], and numerous batch digestion tests have been carried out [14,19,32,37], this is the first reported study on degradation kinetics in a co-digestion study with feed addition and removal designed to simulate practice in a commercial AD plant.

2. Materials and methods

2.1. Feedstock components

2.1.1. Bioplastics

These were provided by the manufacturers, and had been certified as EN13432 compliant by an independent body after testing in an accredited laboratory, issued with packaging product certification numbers and awarded the right to carry the scheme's certification logo. They were tested alongside non-biodegradable controls of an uncoated polypropylene (PP) film and a plain low density polyethylene (LDPE) film. All of the bioplastics were in sheet form, with the exception of a Polylactic Acid Blend (PLAB) in pelleted form. Each sheet material was measured and weighed and then accurately cut into 1 × 1 cm squares ('tokens'), the average weight of which is shown in Table 1. PLAB was used as supplied, with the average dimensions and weight of each pellet as shown in Table 1.

2.1.2. Food waste

To be certain of avoiding contamination with non-targeted plastic films, the trial used a synthetic food waste (SFW), formulated as described in the Data in Brief article, using food materials purchased in a supermarket. All packaging was removed and the materials were roughly chopped and fed through a macerating grinder (S52/010 Waste Disposer, Imperial Machine Company (IMC) Limited), then packed in 4-L containers and stored at −20 °C. When required the SFW was allowed to thaw, stored in a refrigerator and used within 7 days.

2.1.3. Card packaging

To avoid any potential contamination from plastic films, unprinted card (GK unlined grey machine board 70–100% recycled fibre with bulk 1.4 $cm^3\ g^{-1}$) was obtained from A Stevens & Co Ltd Yeovil, Somerset and shredded in an office-type cross-cut paper shredder to a particle size of ~2 cm^2. The card packaging (CP) was then macerated with water, frozen and stored until use as above.

Table 1
Plastic materials used in trial.

	Abbreviation	Average weight (mg)	No. of tokens in daily feed[a]
		10 × 10 mm square	
Polypropylene film	PP	2.61	61
Low density polyethylene film	LDPE	5.14	31
Cellulose-based metallised film	CBM	3.42	54
Cellulose-based heat-sealable film	CBHS	4.28	43
Cellulose-based high barrier heat-sealable film	CBHB	6.68	27
Cellulose-based non heat-sealable film	CBnHS	6.24	30
Cellulose diacetate film	CDF	6.50	26
Starch-based film blend 1	SBF1	2.17	76
Starch-based film blend 2	SBF2	4.29	38
Polylactic Acid Film	PLAF	3.71	43
		Pellet	
Polylactic Acid Blend	PLAB	24.7	7

[a] No. Of tokens fed to each digester in semi-continuous trial (duplicate digesters used for LDPE).

2.2. Anaerobic digestion trials

2.2.1. Anaerobic digesters

12 digesters were used, each with a working volume of 4 L. The digesters were constructed of PVC tube with gas-tight top and bottom plates. The top plate was fitted with a gas outlet, a feed port sealed with a rubber bung, and a draught tube liquid seal through which an asymmetric bar stirrer was inserted with a 40 rpm motor mounted directly on the top plate. Temperature was controlled at 37 °C by circulating water from a thermostatically-controlled bath through a heating coil around the digesters. Semi-continuous operation was achieved by daily removal of digestate through an outlet in the base of each digester, followed by substrate addition via the feed port. Biogas production was measured using tipping-bucket gas counters with continuous data logging. Counter calibration was checked twice weekly by collecting the gas produced over a 24-h period in a gas-impermeable sampling bag (SKC Ltd, Dorset, UK). Gas volumes were determined using a weight-type water displacement gasometer, and corrected to standard temperature and pressure of 101.325 kPa and 0 °C in accordance with [36].

2.2.2. Inoculation and pre-acclimatisation

The inoculum used was from a 75-L digester which had previously been fed for more than 300 days at an organic loading rate (OLR) of 2 kg VS m^{-3} day^{-1} on a mixture of source segregated post-consumer domestic food waste and card packaging at a ratio of 80:20% on a fresh weight basis [41]. The 75-L digester was then maintained at 37 °C without feed addition for one month to allow any undigested feed to be consumed. The resulting digestate was sieved through a 1 mm mesh to remove any plastic film, then 4 L was added to each digester. The digesters were then pre-acclimatised by feeding them for 30 days on SFW + CP.

2.2.3. Digester operation

After pre-acclimatisation, each digester was fed at an OLR of 2 kg VS m^{-3} day^{-1} for 147 days on a feedstock made up of 80% SFW, 18% CP and 2% of a specified bioplastic on a VS basis. This was prepared by weighing out 23.0 g of SFW and 6.2 g of CP, and adding the appropriate number of bioplastic tokens (Table 1). The solids retention time (SRT) in the digester was maintained at 50 days by removing 560 g of digestate once per week via the bottom sampling tube, while continuing to mix the vessel. Solid and liquid fractions were separated by passing the digestate through a 1 mm stainless steel mesh sieve. The solids were retained for examination, and the amount of the liquid fraction needed to restore a working volume of 4 L after feeding was returned to the digester. Feeding with the specified plastic began on the first day after acclimatisation (day 0), apart from PLAB and the control LDPE where plastic addition started on days 7 and 27 respectively: in each case the expected number of tokens taking into account daily additions and theoretical weekly losses was added to these two digesters to compensate for the delayed start.

2.3. Sampling

Plastic tokens were recovered from the digestate using a modified version of [11]. The stage of drying followed by dry sieving was omitted, as oven drying caused some deformation of the tokens. In the modified procedure the fraction retained on the sieve was washed with tap water and tokens were recovered by hand. These were then air dried for 3–4 days, counted and weighed. Tokens were noted as being approximately full sized, half or quarter size.

During the first 7 weeks of operation it became clear that the expected quantities of tokens were not being found in the digestate in all cases, probably due to certain tokens either floating or sinking depending on their density. To overcome this, the sampling method was modified from day 42 onwards and involved emptying the entire contents of the digester into a wide-mouthed receptacle, and removing the 560 g subsample while agitating thoroughly to ensure that all materials were in suspension. Immediately after removal of this sub-sample the remaining digestate was returned to the digester, and separated liquor added as before to maintain the working volume.

At the end of the trial each digester was emptied and its entire contents were passed through a 1 mm stainless steel mesh sieve. The solids fraction was washed and the tokens retrieved by hand sorting, then air dried, counted and weighed as previously described.

2.4. Biochemical methane potential

The biochemical methane potential (BMP) of the feedstocks was measured using 1.5-L working volume digesters continuously stirred at 40 rpm, and maintained in a thermostatic water bath at a temperature of 37 °C. Inoculum was taken from a mesophilic digester treating municipal wastewater biosolids at Millbrook Wastewater Treatment Plant, Southampton, UK. Tests were run in triplicate at an inoculum-to-substrate VS ratio of 4:1, against triplicate blanks containing inoculum only, and triplicate positive controls of alpha cellulose (Sigma Ltd, UK). Biogas was collected in calibrated glass cylinders by displacement of a 75% saturated sodium chloride solution acidified to pH 2. The height of the solution in the collection cylinder was recorded manually, with continuous data logging by a headspace pressure sensor as back-up. Gas compositions were measured each time the cylinder was refilled, and gas volumes were corrected to STP as above.

2.5. Analysis

Total solids (TS) and volatile solids (VS) were measured according to Standard Method 2540 G [3]. Digestate pH was measured using a combination glass electrode and meter calibrated in buffers at pH 4, 7 and 9. Alkalinity was measured by titration with 0.25 N H_2SO_4 to endpoints of pH 5.75 and 4.3, to allow calculation of total (TA), partial (PA) and intermediate alkalinity (IA) [30]. Total Kjeldahl Nitrogen (TKN) and total ammonia nitrogen (TAN) were determined using a Kjeltech digestion block and steam distillation unit, according to the manufacturer's instructions (Foss Ltd, Warrington, UK). VFA were

quantified in a Shimazdu GC-2010 gas chromatograph (GC) with a flame ionisation detector and a capillary column type SGE BP-21. Calorific values (CV) were measured using a bomb calorimeter (CAL2k-ECO, South Africa). Elemental composition (C, H, N) was determined using a FlashEA 1112 Elemental Analyser (Thermo Finnigan, Italy), following the manufacturer's standard procedures. Biogas composition was measured using a Varian CP 3800 GC fitted with a Hayesep C column and a molecular sieve 13 x (80–100 mesh), and calibrated using a standard gas of 65% CH_4 and 35% CO_2 (v/v). Feedstock carbohydrate content was determined using the method of [15]. Lipids were measured in accordance with [35]; and fibre analysis was by the Fibercap method [26].

Examination of samples by light microscopy was kindly performed by Prof Francisco Torrella of the University of Murcia, with confocal microscopy carried out at the University of Southampton's Imaging and Microscopy Centre (www.southampton.ac.uk/microscopy).

2.6. Assessment of the mass balance of plastic materials

As the number of tokens and the weight of plastic added daily to the digester was accurately known, the expected number and weight of tokens in the 560 g of digestate removed weekly could be estimated based on simple wash-out principles. This was done assuming either no degradation, or a first-order relationship where degradation is proportional to the weight of tokens present. The theoretical results were then compared to the actual number and weight of tokens recovered. The ratio of post-digestion weight to initial weight (the 'weight ratio') based on the number of tokens recovered was also determined. This ratio is closely related to solids destruction, but is based on the air-dried weight of the material rather than its VS content, and provides some additional information on the mode of degradation.

Recovery, counting and weighing of all of the tokens remaining at the end of the experiment enabled a mass balance to be conducted for each type of plastic over the duration of the trial. The final weight values were then used to obtain the empirical first-order decay constant for each plastic and an estimate of solids disappearance or destruction.

3. Results

3.1. Materials characteristics

Characteristics of the plastic materials are shown in Table 2. The theoretical elemental composition of both PP and LDPE is C 85.7%, H 14.3%, N 0% with a calculated calorific value of 43.86 MJ kg^{-1} TS, indicating good agreement between measured and theoretical results.

Table 3 shows the characteristics of the SFW and CP. The results for SFW were compared to typical values for three UK post-consumer source segregated domestic food waste streams [40] and found to be very similar. The SFW contained slightly more carbohydrate and less fibre (average values for typical domestic food wastes 430 and 173 g kg^{-1} VS, respectively). The TS and VS of the SFW were slightly higher (typical domestic food waste values 24.4 and 23.3%). These small differences reflect the fact that the SFW was formulated from fresh materials, and thus contains a higher proportion of the edible components normally consumed by the customer, and proportionately less of the fractions that are typically rejected into the domestic waste stream. The properties of the CP were closely similar to those of post-consumer card packaging used in previous work [41].

Table 2
Characteristics of the plastic materials.

	TS	VS	Calorific value	C	H	N
	%WW[a]	%WW	MJ kg^{-1} TS	%VS	%VS	%VS
PP	99.7	99.7	46.61	85.46	14.92	0.00
LDPE	100.0	99.8	46.56	84.78	15.22	0.00
CBM	87.5	86.7	17.85	47.09	5.49	2.54
CBHS	87.4	87.1	17.83	47.60	5.70	0.00
CBHB	90.1	89.8	17.18	44.56	6.22	2.12
CBnHS	85.9	85.6	18.15	47.03	5.56	1.34
CDF	95.3	95.0	20.14	52.32	5.31	0.00
SBF1	97.6	97.6	22.16	60.01	6.59	0.00
SBF2	97.0	97.0	24.20	60.74	6.97	0.00
PLAF	99.6	99.5	18.35	51.21	5.49	0.00
PLAB	99.7	94.6	22.87	57.44	6.30	0.00

[a] WW = wet weight.

Table 3
Characteristics of SFW and CP.

	Units	SFW	CP
pH		4.78	–
Total solids (TS)	%WW	29.8	29.1
Volatile solids (VS)	%WW	27.9	23.2
VS as %TS	%TS	95.5	79.8
Total Kjeldahl nitrogen (TKN)	g kg^{-1} VS	28.6	1.46
Calorific value (CV)	MJ kg^{-1} TS	21.57	14.34
Crude proteins	g kg^{-1} VS	179	–
Lipids	g kg^{-1} VS	143	–
Carbohydrates	g kg^{-1} VS	631	–
Hemicellulose	g kg^{-1} VS	86	–
Cellulose	g kg^{-1} VS	7.4	–
Lignin	g kg^{-1} VS	20	–
Elemental C	%VS	54.09	43.64
Elemental H	%VS	7.19	5.70
Elemental N	%VS	2.84	0.0

3.2. Digestion performance and stability indicators

A notable feature of the trial was that all of the digesters behaved in a similar manner, with only small differences in values for each monitoring parameter (Fig. 1). pH in all digesters stabilised between 7.7 and 7.9. TAN concentrations gradually increased, but remained < 3.5 g N L^{-1} at the end of the trial (Fig. 1a), below the concentration at which ammonia is considered toxic to a mesophilic methanogenic population [31]. Total alkalinity increased with increasing TAN (Fig. 1b) and around day 100 equilibrated at 25 g L^{-1} $CaCO_3$, indicating a well-buffered system; the IA/PA ratio stabilised at an average of 0.38 in all digesters. VFA concentrations were low throughout, with values in the later part of the trial around 100 mg L^{-1} (Fig. 1c). These results indicated that, as expected, none of the plastics tested showed adverse effects on the acid-base balance or the operational stability of the digesters.

Volumetric biogas production (VBP) was consistent from around day 50 (Fig. 1d) at around 1.4 L L^{-1} day^{-1}, typical for this OLR and feedstock type. The biogas methane content stabilised at around 56% in all digesters from day 105 onwards. Specific methane production was around 0.400 m^3 CH_4 kg VS added (Fig. 2e), again a typical value for the feed material used [41].

The TS and VS of the whole digestate and of the solids fraction could not be measured on a weekly basis, due to the need to recover the plastic tokens. The digestate liquor VS remained constant at around 3.8 %WW (Fig. 1f), however, while the wet weight of digestate solids removed each week fluctuated slightly, averaging around 13 %WW (Fig. 1g). These parameters indicate that stable operation was achieved, and that the separation technique used was able to produce consistent values.

It can be concluded that the digesters showed stable performance throughout the experimental period, with a high level of conversion of feedstock VS to methane. The semi-continuous experiment was not designed to quantify additional gas production from biodegradation of the bioplastics, as at the low loadings applied the expected yield was of the same order as natural variation in overall biogas production.

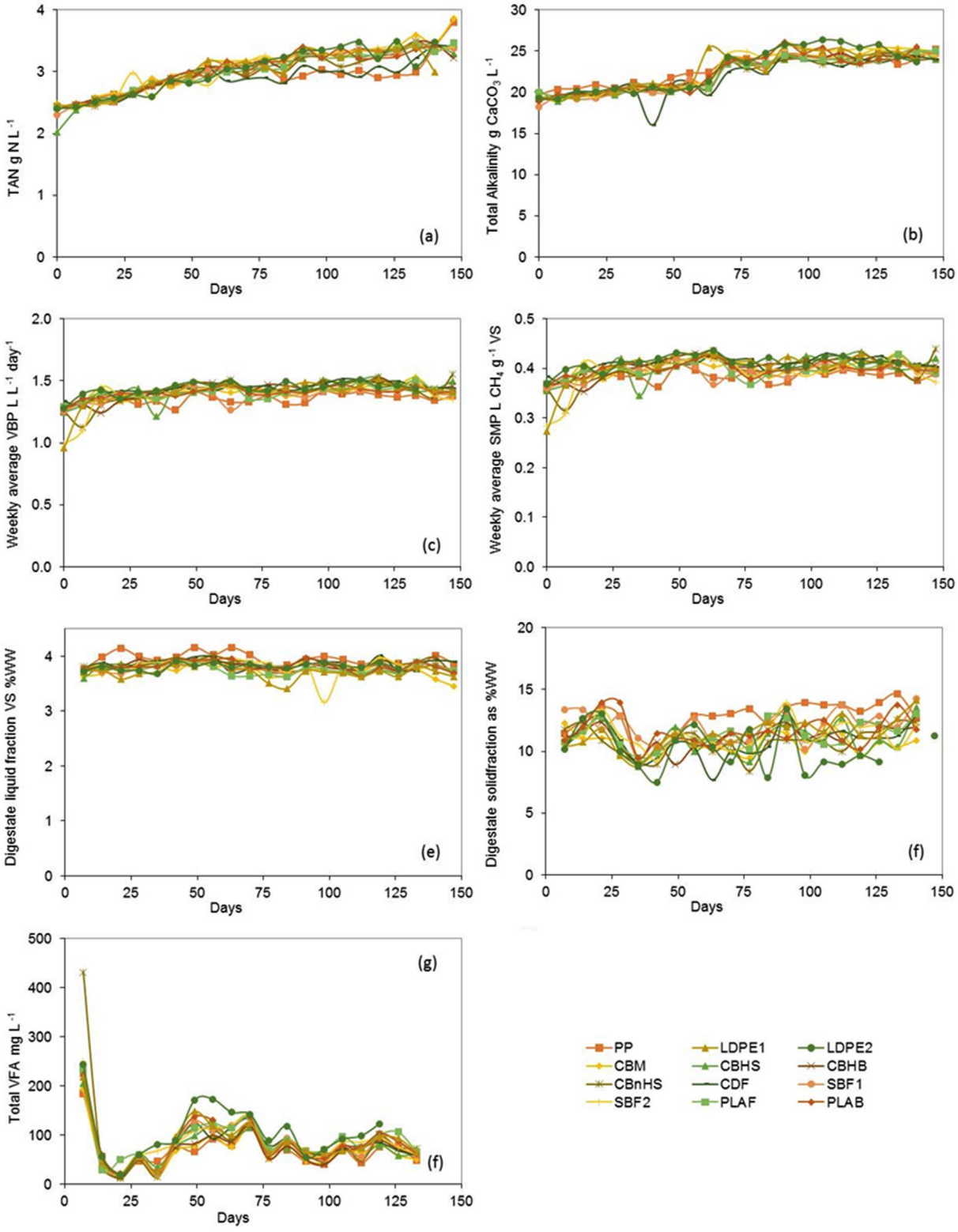

Fig. 1. Digester monitoring parameters during the experimental period: (a) TAN, (b) Total Alkalinity, (c) total VFA, (d) volumetric biogas production, (e) specific methane production, (f) digestate VS and (g) wet weight of digestate solids.

3.3. Assessment of plastics destruction in co-digestion trial

3.3.1. Evidence from recovery of tokens

Fig. 2 shows the number of tokens recovered each week compared to the predicted number assuming no decay. For plastics showing evidence of degradation, the number predicted using the empirically-derived first-order decay constant is also shown.

During the first 7 weeks of operation it became clear that in some cases there were discrepancies between the actual and expected number of tokens found in the digestate, probably due to tokens of certain materials either floating or sinking depending on their density. This was particularly noticeable for PP, LDPE, SBF1, CDF and PLAB. The revised

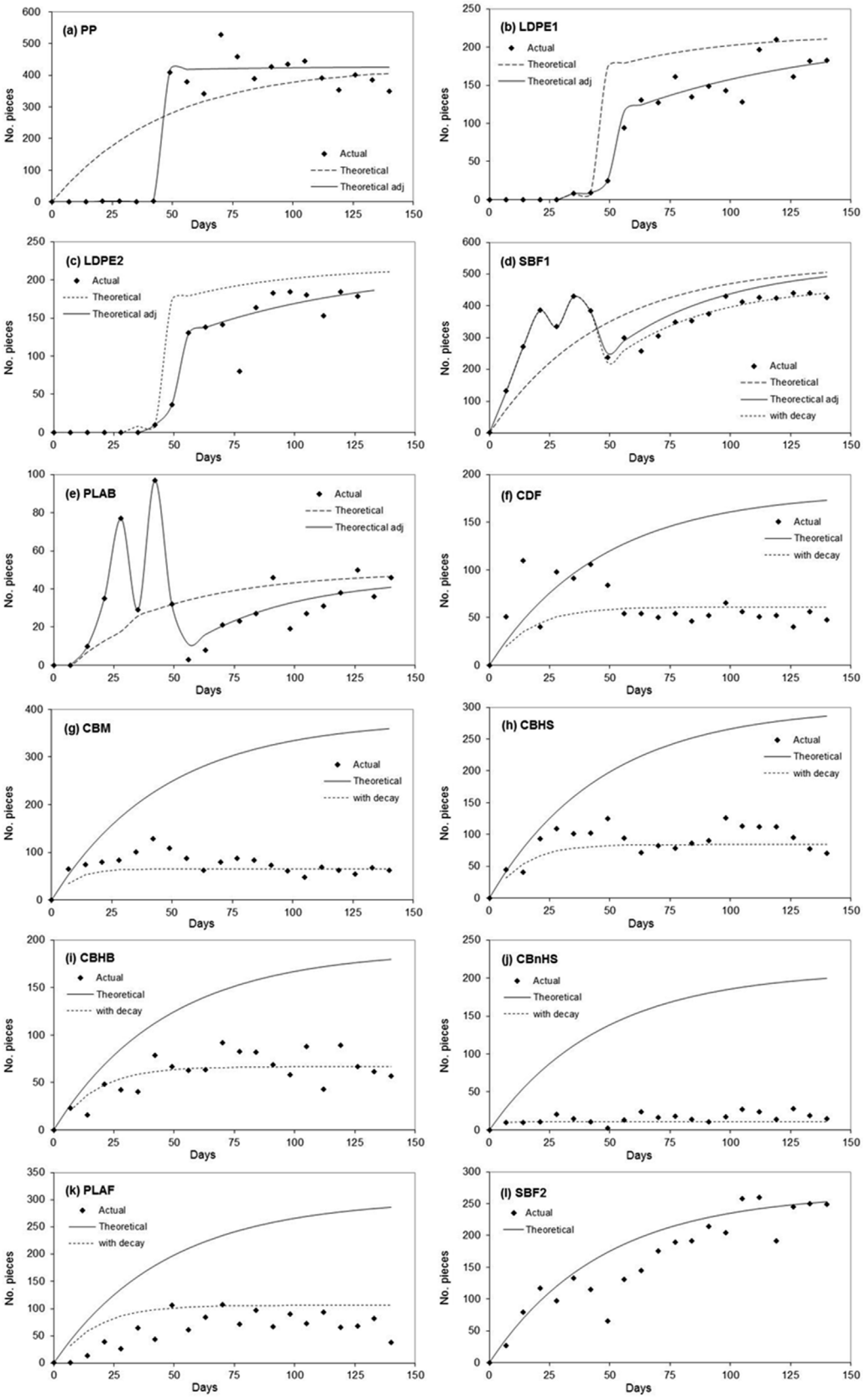

Fig. 2. No. Of plastic tokens recovered from digestate sample, predicted no. assuming no destruction, and predicted no. modelled using an empirical first-order decay coefficient for (a) PP, (b) LDPE1, (c) LDPE2, (d) SBF1, (e) PLAB, (f) CDF, (g) CBM, (h) CBHS, (i) CBHB, (j) CBnHS, (k) PLAF and (l) SBF2.

sampling technique was able to prevent or reduce these irregularities, and where appropriate the actual number and weight of tokens remaining in the digester was used in modelling up to day 42.

For the PP control the subsequent recovery matched the modified theoretical prediction (Fig. 2a), but in the case of LDPE the fit of observed and theoretical values was less good. The reason for this was that, even when the digester contents were drained completely, a proportion of the LDPE tokens remained attached to the digester walls and

stirrer; these were eventually accounted for in the final mass balance. The model for LDPE was therefore adjusted to reduce the number of tokens leaving the digester in the weekly digestate sample to 65% of the expected value, with the rest remaining in the digester. This empirical adjustment showed good agreement with the actual partitioning of tokens in both LDPE digesters (Fig. 2b and c).

For plastics denser than the digestate liquor, until the sampling regime was changed there was a tendency to recover more tokens than predicted: this was the case for SBF1, PLAB and CDF, as can be seen in Fig. 2d, e and f. For SBF1 and PLAB this was successfully addressed by modifying the sampling regime, and using the actual number of tokens recovered until the change was introduced. In the case of apparently degradable plastics such as CDF, however, no correction could be made, as part of the difference in token numbers could also be attributed to the breakdown of the material. The results of the mass balance at the end were therefore required to confirm whether the losses were due to degradation, as discussed below.

The results shown in Fig. 2g–j indicated that all four of the cellulose-based films (CBM, CBHS, CBHB and CBnHS) were degraded, but to different degrees, with almost complete disappearance of the CBnHSF film. PLAF and CDF also showed a lower number of tokens than predicted (Fig. 2k and l). After correcting for the sampling error up to day 42, however, the plastics SBF2, SBF1, and PLAB appeared to show little or no destruction in the AD process.

3.3.2. Evidence from weight of recovered plastic tokens and the weight ratio

Fig. 3 shows the weight of tokens recovered from each digestate sample, the predicted weight based on actual number of tokens recovered and using the empirically-derived first order decay constant, and the ratio between these. As the weight ratio considers both the number and the weight of tokens displaced from the digester, it provides a useful insight into the mechanism of degradation of the plastic tokens.

After adjustment for the change in sampling methodology, there was good agreement between the calculated weights assuming no degradation and the actual weight of tokens recovered for both of the LDPE controls (Fig. 3a and b) and the PP control (Fig. 3c). The weight ratio for these two materials was above 1.0, indicating that these plastics may be absorbing small amounts of some component in the digestate. The two starch-based plastics SBF1 and SBF2 also showed little or no evidence of degradation based on weight loss and weight ratio (Fig. 3d and e): for SBF1 the ratio stabilised at 0.94 and for SBF2 at 1.0. The PLAF and PLAB plastics (Fig. 3f and g) had very similar weight ratios, close to 1.0; but the high weight ratio and low number of tokens recovered for the PLAF suggested that the material was breaking up quite rapidly in the digester.

The most readily degraded plastic was CBnHS (Fig. 3h), which showed a weight ratio of around 0.3–0.4. For CBHB (Fig. 3i) the ratio was between 0.6 and 0.7, while the other two cellulose-based film products CBM and CBHS (Fig. 3j and k) the ratio was between 0.7 and 0.8. These results indicate that individual tokens of cellulose film materials lose weight before disappearance or removal from the system. The CDF had a weight ratio of around 0.78, similar to that of the less degradable cellulose-based plastics.

3.3.3. Final balances and parameters from modelling

Table 4 shows the results of the final balance based on the number and weight of tokens added, removed, and present in each digester at the end of the trial. The balance between number of tokens input and finally accounted was −64 (0.7%) and +6 (0.1%) respectively for the PP and LDPE controls, confirming the accuracy of the method used.

The value of the empirical first-order decay constant for each of the bioplastics was taken as that giving the best match to the actual total weight recovered in each case. This value was then used to predict the weight of tokens removed during the run and remaining in the digester at the end. The recovery values shown in Table 4 are calculated from the weight of tokens actually removed or remaining in the digester at the end of the run, divided by the predicted weight and expressed as a percentage. The percentage recovery indicates whether the tokens were evenly distributed throughout the digestate when samples were removed. It can be seen that PP, CBM and PLAB were relatively evenly distributed (predicted recovery during run and end is 100 ± 10% of actual); whereas the uneven partitioning seen with LDPE (recovery 80% during run, 137.7% at end) also affected CBHS (89.1% and 128.5%), CBHB (74.3% and 164.9%), CBnHS (62% and 206.1%) and PLAF (67.3% and 182.6%), and to a lesser extent CDF, SBF1 and SBF2 (predicted recovery = 100 ± 20% of actual).

The empirical first-order decay constant was also used to predict the total number of tokens recovered. The values for the control plastics, SBF1, SBF2, PLAF and PLAB show good agreement whereas for CBM, CBHS, CBHB, CBnHS and CDF the actual number recovered is considerably higher than the predicted number. This reflects the fact that the tokens lose weight as they degrade, but still remain as visible components, posing a potential problem with regard to acceptability of the digestate as a commercial product.

The weight of each material destroyed provides a basis for estimating the plastics destruction during the experiment. A further estimate of destruction was obtained by modelling the system beyond the experimental period, using first-order decay kinetics, to allow steady state conditions to be established: the difference between the input weight and predicted weight of tokens removed each week can then be used as an estimate of solids destruction potential. Table 4 shows that there was reasonable agreement between values obtained using these two methods. Differences can be attributed to several factors, one being that the simple first-order decay model assumed may not be fully adequate to describe the degradation, especially for complex multi-layer materials. The results suggested that SBF2 is not breaking down; PLAB may show slight degradation, but it is at the limit of detectability by this method; while SBF1 has a small but definite weight loss. The slight weight gain of the control plastics is also confirmed.

3.3.4. Physical status of the plastics

The recovered tokens were visually inspected. The two control plastics showed only small changes. PP showed no sign of decay or damage but tended to curl into small cylinders (Fig. 4a) making counting difficult; the plastic also took on a yellowish colour, indicating absorption of some component from the digestate, which may also have accounted for the slight weight gain. LDPE showed relatively little change in shape or colour. The PLAB pellets also showed little sign of change apart from a very slight darkening in colour. Colour changes to degradable plastics have previously been reported in samples placed in landfill sites under anaerobic conditions, even though no other physical changes were noted [2].

The four cellulose-based film plastics showed different responses. CBM tokens gradually lost their metal layer and the remaining fragments appeared to become progressively smaller and more fragile, ending as a clear colourless thin film (Fig. 4b). CBHS took up colour from the digestate evenly throughout the material. In CBHB the surface of the plastic showed clear signs of progressive attack at specific points, indicated by discoloured areas on the surface and around the cut edges (Fig. 4c). The small number of tokens of CBnHS recovered showed little sign of damage, but changed from a clear plastic with a shiny surface to a slightly milky semi-translucent appearance. These degradation modes reflected the material structure and components: CBnHS consists of a simple uni-layer cellulose film that is highly permeable to water vapour. CBHS has a heat-sealable layer on each surface, providing a moisture barrier; while CBM also has a metallised layer on one surface, giving improved moisture resistance. CBHB has the highest specification of moisture barrier and heat seal on both sides, making it resistant to attack until this coating is penetrated.

SBF1 and SBF2 both showed slight changes in colour, with some deformation of SBF1 tokens (Fig. 4d). Signs of damage could be seen on

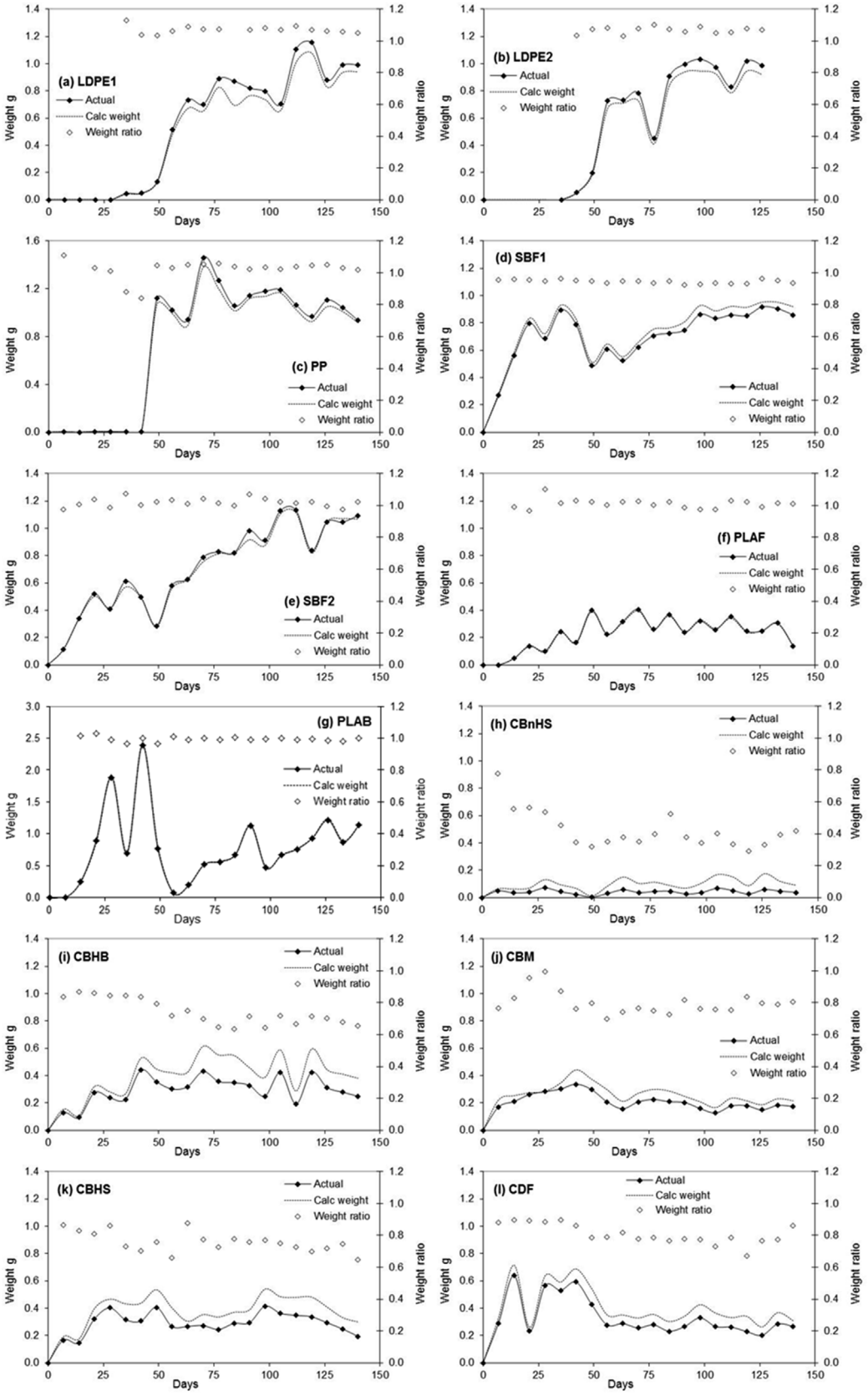

Fig. 3. Weight of plastic tokens recovered from each digestate sample, predicted weight based on actual number of tokens recovered, and ratio between these values, for (a) LDPE1, (b) LDPE2, (c) PP, (d) SBF1, (e) SBF2, (f) PLAF, (g) PLAB, (h) CBnHS, (i) CBHB, (j) CBM, (k) CBHS and (l) CDF.

individual tokens of both plastics, corresponding to either biodegradation or mechanical damage. PLAF and to a lesser extent CDF showed little change in appearance, remaining shiny and regular in shape, but small numbers of fragments and part-tokens were observed. When this observation is considered in conjunction with the weight data and with microscopic observations and the BMP test results, it appears likely that any tokens of PLAF and CDF found in the digestate may have been in the digester for relatively short periods; and that

Table 4
Final balance results based on no. and weight of tokens and experimentally determined values for degradation constants.

	PP	LDPE	CBM	CBHS	CBHB	CBnHS	CDF	SBF1	SBF2	PLAF	PLAB
No. Of tokens added	8906	4293	7884	6278	3942	4380	3796	11096	5548	6278	999
Actual no. Of tokens in digester at end	3137	2256	565	918	1038	286	671	3638	1992	1327	320
Actual no. Of tokens removed in run	5705	2043	1540	1826	1230	320	1261	7082	3337	1274	655
Predicted total no. Of tokens recovered [a]	8906	4293	1721	2141	1679	289	1556	10227	5436	2670	969
Actual total no. Of tokens recovered	8842	4299	2104	2743	2268	606	1932	10720	5329	2601	975
Balance (no. at end + no. Out – no. in)	−64	6	−5780	−3535	−1675	−3774	−1864	−376	−219	−3678	−24
No. Of tokens destroyed	0.7%	−0.1%	73.3%	56.3%	42.5%	86.2%	49.1%	3.4%	3.9%	58.6%	2.4%
Weight added (g)	23.29	22.06	26.97	26.89	26.34	27.32	24.68	24.05	23.78	23.31	24.69
Predicted weight in digester at end (g) [a]	7.93	7.88	1.59	2.55	3.18	0.47	2.86	6.90	7.60	2.81	7.36
Actual weight in digester at end (g)	8.56	10.85	1.67	3.28	5.25	0.98	3.40	7.64	8.69	5.13	7.86
Recovery at end	107.9%	137.7%	104.7%	128.5%	164.9%	206.1%	119.0%	110.8%	114.3%	182.6%	106.8%
Predicted weight removed in run (g) [a]	15.35	14.19	4.29	6.62	8.04	1.33	7.26	15.24	15.70	7.10	16.58
Actual weight removed in run (g)	15.51	11.38	4.22	5.90	5.97	0.82	6.71	14.50	14.60	4.78	16.08
Recovery in run	101.0%	80.2%	98.3%	89.1%	74.3%	62.0%	92.5%	95.2%	93.0%	67.3%	97.0%
Actual total weight recovered (g) [b]	24.08	22.23	5.89	9.17	11.22	1.80	10.12	22.14	23.29	9.91	23.93
Balance (end + out – in)	0.79	0.16	−21.09	−17.72	−15.12	−25.52	−14.57	−1.91	−0.49	−13.40	−0.76
Weight destroyed	−3.4%	−0.7%	78.2%	65.9%	57.4%	93.4%	59.0%	7.9%	2.1%	57.5%	3.1%
1st-order degradation k	0.00	0.00	0.10	0.06	0.04	0.39	0.04	0.00	0.00	0.04	0.00
VS destruction potential [c]	0.0%	0.0%	82.7%	72.3%	64.7%	94.9%	66.2%	12.4%	2.9%	64.8%	6.2%

[a] Based on 1st-order degradation coefficient.
[b] Actual total weight recovered = Actual weight in digester at end + Actual weight removed in run.
[c] Based on value from longer-term modelling with 1st-order degradation coefficient.

these materials were not biodegraded to single-carbon gaseous products, but showed rapid physical disintegration in the digester. This behaviour of PLA film materials has been previously reported under anaerobic conditions [8] and in composting [5], and these films can be manufactured in such a way as to accelerate or retard this disintegration [4].

Images of all of the plastics materials removed from the digesters on day 98 are shown in the Data in Brief article (Figure S2).

3.3.5. Microscopic examination

Four of the plastics were selected for preliminary microscopic examination based on their apparent degradation characteristics. Samples were taken from the washed and air-dried material removed from the digestate, with no special measures taken to preserve microbial films. The tokens were examined using a stereoscopic microscope with surface illumination and a high power oil immersion lens with phase contrast and transmitted light. The surface of CBnHS was found to be extensively pitted and perforated in places, accounting for its loss of shine (Fig. 5a). Under high power oil immersion there was evidence of bacterial colony growth at the bottom of each pit. CBHS had much more dispersed surface pitting, with pits of a larger diameter. In this case there were clear signs of the growth of rod-shaped bacteria around the immediate edge of the pit and extending into it (Fig. 5b). CBM was only observed with surface illumination, as its opacity made it unsuitable for the use of oil immersion and transmitted light; but the metal layer could be seen to be leaching away (Fig. 5c). On examination of PLAF, sharp fracture lines were noted around the edges of smaller tokens, and the entire surface showed signs of crazing which was not evident in undigested material. In the sample examined no evidence of surface pitting or bacterial colonisation was seen under oil immersion and transmitted light. The CBHS was also briefly examined using fluorescent confocal microscopy: again it was possible to identify colonies of

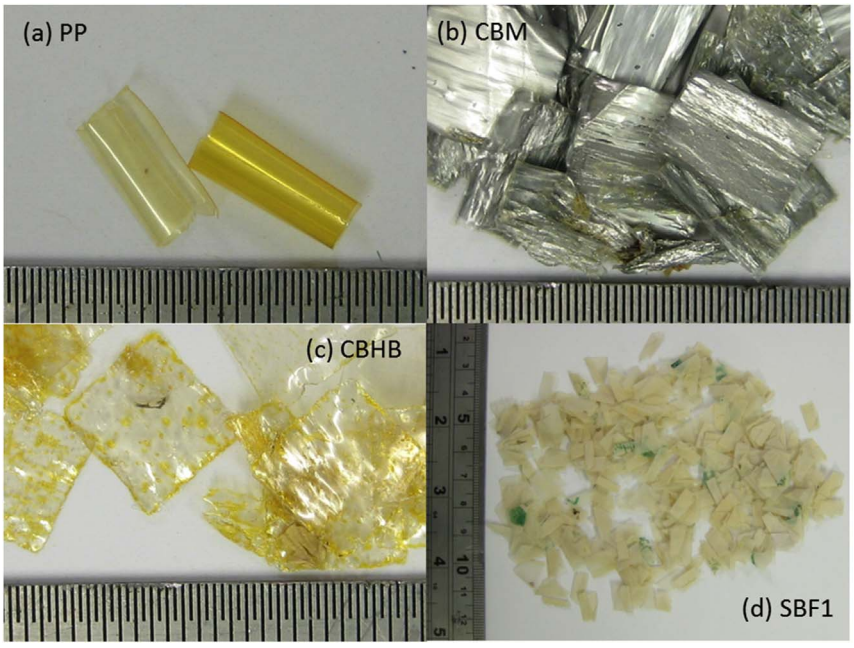

Fig. 4. Photographic images of selected examples of plastics removed in digestate on day 98: (a) PP, (b) CBM, (c) CBHB, (d) SBF1.

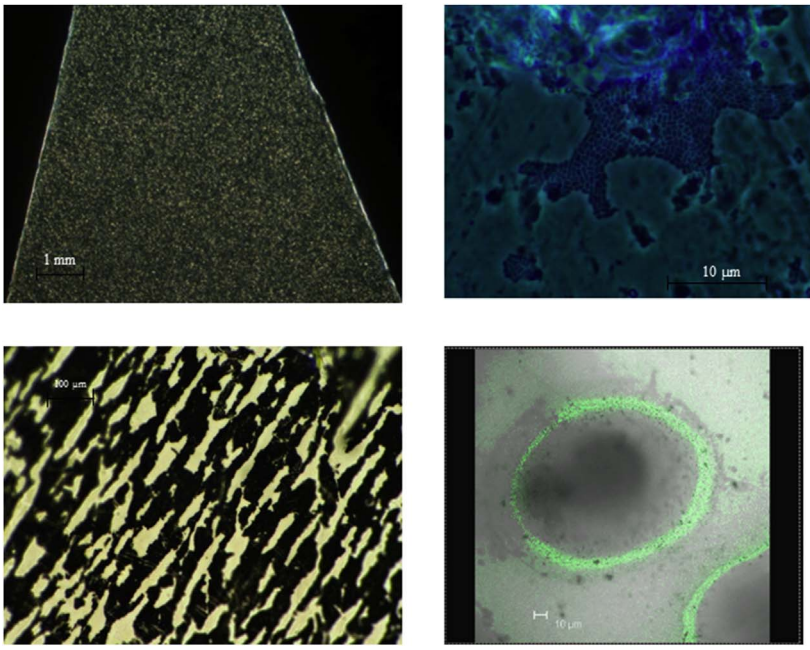

Fig. 5. Microscopy images (a) Dark field image of CBnHS showing heavily pitted surface; (b) bright field image of stained CBHS showing microbial colony at edge of pit; (c) bright field image of CBM showing loss of metallic layer; (d) CBHS Combined fluorescent and differential interference contrast images showing microbial presence around pit, using a Leica TCS SP2 confocal laser scanning microscope. Images (a), (b) and (c) courtesy of Prof Francisco Torrella, University of Murcia. Image (d) courtesy of Dr Yue Zhang, University of Southampton.

bacteria within the pitted areas, and to observe that these were within the interior cellulose layer (Fig. 5d). These preliminary investigations suggest confocal microscopy is a promising technique that could help to elucidate the mechanisms and constraints on the degradation process. (See also Data in Brief article for additional images).

3.3.6. Energy balances

The BMP test is the most commonly used method for assessing the bioconversion of a substrate to methane. Methane and carbon dioxide production in the test can be compared to the theoretical methane potential calculated using the Buswell equation [33], and the carbon conversion in the test material can therefore be accounted. This batch test provides favourable conditions with a guaranteed retention time which eliminates any of the 'short circuiting' that may occur in continuous systems; and also uses a high inoculum-to-substrate ratio to maximize the degradation of the sample and its conversion into gaseous end products, while reducing the potential for accumulation of inhibitory intermediate compounds. Even under these conditions the BMP value is generally lower than the theoretical methane potential, as a proportion of the carbon is converted into new biomass. The batch test hence gives a measure of the potential methane yield of the test substrate under anaerobic conditions: this value, however, is often higher than can be obtained in a fully-mixed, continuously-fed digester. The batch BMP test format is the basis for the various anaerobic biodegradability tests that have evolved to take into account different operating temperatures, types of inoculum and duration of exposure (e.g. [23,24,25]). In this work BMP testing took place over a period of 65 days (Table 5 – see Data in Brief article for more detailed results), at which time the rate of methane production in most samples had slowed to that of the inoculum-only control. Elemental composition data (Table 2) was used in the Buswell and Du Long equations [21] to predict the calorific value (CV). The CV of dried material was also measured and used to supplement the BMP test results to confirm degradation through carbon conversion to methane. The results of these analyses were compared using a mass balance approach (Table 5).

Measured and calculated calorific values were in reasonably good agreement, giving support to the accuracy of the elemental composition analysis. The recovery of energy in the form of methane from the four cellulose-based films (CBM, CBHS, CBHB and CBnHS) ranged from 75 to 86% of the energy potential based on the measured higher heat values, confirming the excellent degradation of these materials under the wet mesophilic test conditions used. The theoretical VS destruction during the 65-day BMP test was calculated from the actual methane yield, the carbon content of the substrate, and the methane and carbon dioxide concentrations predicted by the Buswell equation (Table 5). For the cellulose-based film plastics, the calculated solids destructions were slightly higher than expected based on the values from the semi-continuous trial (Table 3), suggesting that the measured carbon content may have been slightly low. The actual specific methane yields for CBHS, CBHB and CBnHS, however, showed very good agreement with the Buswell predictions of 0.438, 0.410 and 0.423 m^3 CH_4 kg^{-1} VS respectively, and indicated a high degree of biodegradability.

The energy recovery from PLAB (2.6%) was very close to the values for the two control plastics PP and LDPE (1.9 and 1.4% respectively), again indicating that PLAB pellets show little or no degradation in these conditions. The four remaining plastics CDF, SBF1, SBF2 and PLAF showed energy recovery values ranging from 8.9 to 18.8%, suggesting only partial degradation. The BMP tests for PLAB, CDF, SBF1, SBF2 and PLAF were left running until day 103. With the exception of PLAF there was little or no change in the final methane yield. PLAF continued to produce methane at a higher rate than in the first 50 days, possibly indicating that some acclimatisation to the substrate had occurred. By day 103 it had produced a further 0.119 m^3 CH_4 kg^{-1} VS added, giving a total of 0.216 m^3 CH_4 kg^{-1} VS, with good agreement between replicates. Yagi et al. [39] also noted a long slow increase in biodegradability assessed in terms of methane yield during mesophilic batch testing of PLA powder over 277 days.

Based on the specific methane yields shown in Table 5, the bioplastic component might produce a maximum of 2% of the total specific methane production from a mixed feedstock of food waste, card packaging and bioplastic at 80:18:2 %VS as used in the current trial. This estimate is based on CBHS, the bioplastic with the highest BMP value, with the other bioplastics giving correspondingly lower contributions. The contribution of a given bioplastic to the total specific methane production is likely to be even lower if the solids retention time in the digester is less than that required for full degradation of the bioplastic.

3.4. Factors affecting digestate standard compliance

Worldwide there are a number of standards for the use of bioprocessed waste materials in agriculture and horticulture, but the UK has

Table 5
Energy balance value of materials.

	Empirical formula				Theoretical CH_4 content of biogas (Buswell)	Calculated CV	Measured CV	Actual CH_4 yield in 65-day BMP test	Recovery as CH_4 in 65-day BMP test	% Recovery of measured CV	Calculated solids destruction
	C mole	H mole	O mole	N mole	%	MJ kg^{-1} VS	MJ kg^{-1} VS	m^3 CH_4 kg^{-1} VS	MJ kg^{-1} VS	%	%
PP	7.12	14.80	−0.02	0.00	76.1	44.40	46.68	0.025	0.89	1.9	2.0
LDPE	7.06	15.10	0.00	0.00	76.7	44.43	46.58	0.018	0.64	1.4	1.5
CBM	3.92	5.44	2.81	0.18	47.7	17.39	18.03	0.374	13.40	74.3	88.9
CBHS	3.96	5.65	2.92	0.00	49.4	17.44	17.90	0.433	15.50	86.6	98.3
CBHB	3.71	6.17	2.94	0.15	49.4	17.04	17.23	0.404	14.48	84.0	98.0
CBnHS	3.92	5.52	2.88	0.10	48.3	17.26	18.28	0.410	14.69	80.4	96.4
CDF	4.36	5.26	2.65	0.00	49.9	19.08	20.20	0.050	1.80	8.9	10.3
SBF1	5.00	6.53	2.09	0.00	55.9	23.89	22.20	0.113	4.05	18.3	18.0
SBF2	5.06	6.91	2.02	0.00	57.1	24.64	24.22	0.069	2.46	10.2	10.6
PLAF	4.26	5.44	2.71	0.00	50.1	18.80	18.39	0.097	3.47	18.8	20.2
PLAB	4.78	6.25	2.27	0.00	54.5	22.44	24.09	0.017	0.62	2.6	3.0
Card packaging (CP)	3.63	5.65	3.17	0.00	47.7	15.70	14.34	0.274	9.81	68.4	70.3
Foodwaste (SFW)	4.50	7.13	2.24	0.20	55.6	22.42	22.59	0.471	16.89	74.8	83.7

adopted separate specifications for aerobically and anaerobically processed materials. The UK's PAS110 Specification for anaerobic digestates [9] contains criteria for pathogen content, Potentially Toxic Elements (PTE), stability and physical contaminants, and was used as a reference in this work. In a mixed food waste, card packaging and plastic feedstock with the plastics present only in small quantities, these parameters are strongly influenced by the composition of the other components. As the current trial used a synthetic food waste and selected print-free card packaging, the contribution from the plastics was considered only in so far as it might affect the overall results, using a mass balance approach.

A number of other parameters such as pH, total nitrogen (N), total phosphorus (P), total potassium (K), TAN, and TS and VS are also reportable under PAS110 as they may influence digestate application rates, but have no limit values. These again are chiefly determined by the SFW and CP components of the feedstock: relevant values for the digestate pH, TAN and solids in the current trial are as seen in Fig. 1.

PAS110 specifies that physical contaminants must not exceed a given proportion of the wet weight of digestate, with the proportion increasing as the digestate nitrogen concentration increases: the logic behind this is that land spreading is often limited by nitrogen load, and hence the amount of contaminant applied per unit area of land area should be the same at a given load. The plastics destruction estimated from modelling was used in conjunction with the permitted mass of physical contaminants to calculate the maximum allowable amount of each bioplastic in the feedstock. For this calculation the VS destruction of the incoming SFW was taken as 86% (experimental data - not shown), and the expected weight of digestate arising from 1 tonne of input feed was thus between 741 and 746 kg depending on the solids destruction for each of the bioplastics. The results are plotted in Fig. 6. This example is illustrative for the conditions used in this study, as in practice the result will depend on the TS and VS of the specific incoming feed, and its VS destruction. With the 2% bioplastic VS load used in this study and the digestate TKN content of around 9 kg N $tonne^{-1}$ WW, none of the digestates would comply with the physical contaminant criteria of the PAS110 specification. With regard to these criteria, the apparent disappearance of the plastic is of more importance than whether it in fact undergoes ultimate biodegradation to gaseous products, and the approach developed in the current work thus provides an appropriate testing methodology.

Information on the PTE criterion is provided in the Data in Brief article: at the bioplastics loading required to comply with the physical contaminants specification, calculation showed that the bioplastic materials could not cause the digestate to exceed the specified limit values for PTE. The results of digestate stability testing are also provided in the Data in Brief article.

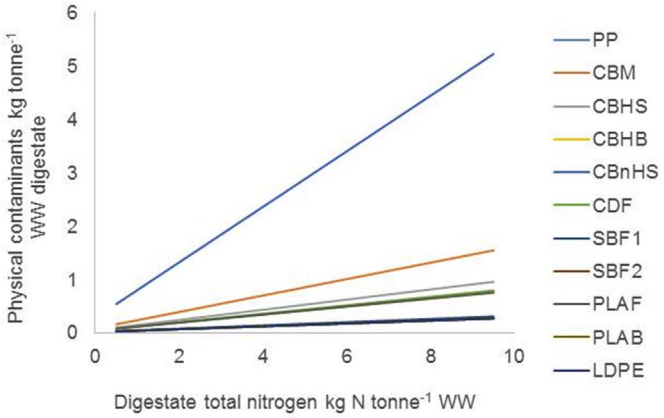

Fig. 6. Permissible plastic load for a given nitrogen content in the digester based on modelled bioplastic destruction rates in Table 4.

4. Discussion

The results clearly demonstrated differences in biodegradability under aerobic and anaerobic conditions: all of the bioplastics tested had been certified under the EN13432 composting standard, yet four of them converted less than 20% of their carbon into biomethane. As expected, it was not possible to quantify additional biomethane production as a result of bioplastic addition in the semi-continuous digestion trial, even where a high degree of degradation was observed, as the relative proportion of gas production from the bioplastics is low in comparison to that from the SFW + CP mixture: this is inevitable unless a much higher plastics loading is used than is likely to occur in a real mixed foodwaste stream. All of the digesters performed well during the semi-continuous trial, showing stable operation based on typical process assessment criteria, with biomethane production in the expected range for this type of substrate. It was therefore clear that none of the bioplastics caused any inhibition of the process at the loading rates used.

The extent of degradation was assessed using a number of criteria, and a summary comparison of these is given in Table 6. While these are not like-with-like comparisons, they do offer some useful insights.

Table 6
Comparison between different measures of plastics degradation from semi-continuous, BMP and analytical tests.

% destruction or recovery values based on:	Semi-continuous		65-day BMP	
	Measured mass balance at end of run[a]	Long-term modelled value[b]	Carbon balance[b]	Calorific recovery[b]
PP	−3.4	0.0	2.0	1.9
LDPE	−0.7	0.0	1.5	1.4
CBM	78.2	82.8	88.9	74.3
CBHS	65.9	72.1	98.3	86.6
CBHB	57.4	64.7	98.0	84.0
CBnHS	93.4	94.9	96.4	80.4
CDF	59.0	66.4	10.3	8.9
SBF1	7.9	12.4	18.0	18.3
SBF2	2.1	2.7	10.6	10.2
PLAF	57.5	64.7	20.2	18.8
PLAB	3.1	6.2	3.0	2.6

[a] See Table 4.
[b] See Table 5.

CBnHS and CBM showed consistently high values for all four measures applied, although the calorific recovery for CBnHS was slightly lower than the other values. CBHB and CBHS showed lower degradation in the semi-continuous test. Unfortunately the BMP tests for these materials showed some initial inhibition, possibly as a result of rapid acid production from readily degradable components, making it difficult to assess and compare degradation kinetics; but the degradation rates in the batch BMP tests appeared lower for these materials. These results are also reflected in the modelled degradation constants for each plastic (Table 4), where CBnHS has the highest value or 0.39 followed by CBM, CBHS and CBHB at 0.10, 0.06 and 0.04, respectively. There are now a number of ISO standards that use carbon conversion as a basis for assessing the ultimate biodegradation of plastic polymers under anaerobic conditions. These are each tailored to specific conditions that reflect different operating modes and types of digester, and are therefore not necessarily interchangeable. The results from the BMP tests in the current study confirmed whether carbon conversion had occurred, and thus indicated which of the test samples were anaerobically biodegradable. In some cases, however, the rates of degradation were lower than those observed in the semi-continuous trial. This difference provides an indication of the potential limitations of batch tests, which may be subject to partial inhibition due to inappropriate inoculum-to-substrate ratios, and may be too short to benefit from adaptive acclimatisation. They are therefore suitable for assessing whether a material is readily biodegradable, but do not necessarily reveal any long-term changes in the system biology that may affect its capability and capacity for ultimate degradation.

The results for CDF, SBF1, SBF2 and PLA provided an interesting contrast to the cellulose-based film plastics. CDF and PLA both showed significant weight loss in the semi-continuous trial (59.0 and 57.5% respectively), but relatively low methane production in the 65-day BMP test (respectively 8.9 and 18.8% calorific recovery as CH_4). The results strongly suggest that the polymeric structure of the PLA and CDF is rapidly destroyed under anaerobic conditions, to an extent where the physical form is no longer recognizable; but this transformation is initially without biodegradation of any macro-molecular subunits. This view was also supported by preliminary microscopic examination of PLA. It is therefore possible to have a relatively high proportion of these materials present in a feedstock without failing the PAS110 physical contaminants criterion, but with little or no energy recovery or ultimate degradation occurring in the system. The nature and long-term stability of the macromolecular components needs further assessment in light of the current concerns over the so-called oxo-degradables, which break down into microplastics and may be highly damaging if they find their way into the environment [34]. Although the PLA did slowly degrade under anaerobic conditions in the BMP test, the CDF showed only a very small apparent conversion into gaseous products; the nature of its disintegration products was not investigated in the current work. Both of the starch-based polymers SBF1 and SBF2 showed low physical breakdown in the simulation experiment (7.9 and 2.1% respectively), despite a proportionately higher gas yield in the 65-day BMP test (18.8 and 10.2% calorific recovery as CH_4). The performance of PLAB on all four parameters in Table 6 was consistent and very close to that of the controls, confirming that for practical purposes no degradation is occurring under wet mesophilic anaerobic conditions. This probably reflects the fact that PLAB is a PLA-based material with a fairly low rate of breakdown, and unlike the other plastics it was in pellet form. The specific surface areas for PLAF and PLAB were calculated as ~54 and ~1.5 $mm^2\ g^{-1}$ respectively, indicating the much lower potential for microbial attack on PLAB. Yagi et al. [38,39] reported relatively high degradation rates in batch tests with PLA powder (125–250 μm), especially in thermophilic conditions.

The results obtained have interesting implications for the choice of digester operating mode. The semi-continuous trial was run at a 50-day SRT, with the liquid separated and returned to the digester. This is a fairly common operating mode at commercial scale, but does not favour plastics that require a long retention time for degradation. A system operating at the very long 'natural' retention times that are possible for food waste digestion without liquid recycle might show better breakdown of plastics such as CBHB, PLAF and SBF1, by keeping them in the digester for longer and thus allowing them to achieve a higher degree of degradation. The higher methane yield achieved in the 103-day BMP test for PLAF supports this view. For the SFW used in this trial, for example, the 'natural' retention time based on feedstock addition without digestate separation and solids removal at an OLR of 2 g VS L^{-1} day^{-1} would be 139 days; the addition of dry card packaging would increase this considerably, due to its high solids content.

The results for partitioning of plastic tokens between the digestate sample and the digester are unlikely to scale up directly, but are of interest as similar behaviour will occur in an industrial plant. This means the location of the outlet and the mode of digester mixing may have a considerable effect on plastic retention: for less dense plastics, digesters with a low-level outlet may have a longer retention time while those regulated by a high-level weir may lose material more rapidly, and vice versa for denser plastics.

The advantage of the semi-continuous methodology used is that it replicates some aspects of behaviour in full-scale operational digesters which are not seen in batch tests, and provides information on the degradation behaviour with respect to standards for visual contaminants. It does not provide robust values for the specific methane yield and ultimate biodegradability of a given bioplastic, and batch tests are preferable for this purpose.

5. Conclusions

The method developed to assess the extent of degradation of bioplastic film material under anaerobic conditions with daily feed additions and digestate removal was successful in quantifying the rates and allowing estimation of decay coefficients, which were further used to model the likely long-term destruction. Of the nine bioplastics tested only the four cellulose-based materials showed extensive biodegradation in the static BMP assay. This verified that both polylactic acid film (PLAF) and cellulose diacetate film (CDF), which were shown to be removed in the simulation trials, were initially disrupted but not degraded; it was likely that only the PLAF showed biodegradation over a longer period. None of the bioplastics inhibited or destabilised the digestion process, which ran for 177 days in total and provided some useful insights into issues relating to the physical properties of the plastic materials that are likely to affect the behaviour of full-scale systems. Although the digestion trial was run with a solids retention

time of 50 days, the degree of breakdown of even the most biodegradable of the polymers tested was unlikely to meet more stringent environmental requirements for the exclusion of physical contaminants, such as those specified in the UK PAS110 for digestate utilisation. Observation of the films using light and confocal microscopy clearly showed the mechanisms of attack, and these could be related to the properties and degradation behaviour of each of the materials tested.

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Data Article

Data related to anaerobic digestion of bioplastics: Images and properties of digested bioplastics and digestate, synthetic food waste recipe and packaging information

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ABSTRACT

The data presented in this article are related to the research article entitled 'Degradation of some EN13432 compliant plastics in simulated mesophilic anaerobic digestion of food waste' (W. Zhang, S. Heaven, C. Banks, 2018). Zhang et al., 2018. They include quantification of residual materials from preparation of a synthetic food waste feedstock; photographic images of the physical appearance of the test plastics after prolonged exposure to microbial degradation in a continuously-operated anaerobic digestion trial; microscopic images of selected plastics after anaerobic biodegradation; test data and results for a Biochemical Methane Potential assay for the plastics; analytical data for potentially toxic elements in the plastics; and values for residual biogas potential of the digestate. Additional data on experimental methods is given, including a recipe for a synthetic food waste specifically designed for use in anaerobic digestion simulation studies; and details on adjustment of calculations after amendment of the digestate sampling methodology used in the main study.

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Specifications table

Subject area	*Engineering*
More specific subject area	*Anaerobic digestion of bioplastics*
Type of data	*Tables, images (photographic and microscopic), graphs*
How data was acquired	*Laboratory experimental (in-house anaerobic digestion equipment), laboratory analytical (gas composition by gas chromatography using a Varian CP* 3800 GC*) and microscopy (Olympus BX53 with phase contrast system and digital camera DP72; Leica TCS SP2 confocal laser scanning microscope).*
Data format	*Analyzed*
Experimental factors	*Methylene blue staining for some microscopic samples*
Experimental features	*Batch biochemical methane potential tests and semi-continuous trials in mesophilic continuously-stirred tank reactors as described in [1]*
Data source location	*Faculty of Engineering and the Environment, University of Southampton, Southampton SO17* 1BJ, *UK*
Data accessibility	*Data is with this article*
Related research article	*Zhang, W., Heaven, S. and Banks, C., 2018. Degradation of some EN13432 compliant plastics in simulated mesophilic anaerobic digestion of food waste. Polymer Degradation and Stability. 147, 76–88,* https://doi.org/10.1016/j.polymdegradstab.2017.11.005. *[1]*

Value of the data

- Visual data on physical appearance of plastics after digestion may be used in comparative evaluation of degradation performance and in assessment of mechanisms
- Microscopy images may offer researchers supporting evidence for theories on degradation and attack mechanisms
- Biochemical methane potential (BMP) values, Potentially toxic element (PTE) content and residual biogas potential provide comparative data for alternative methods and other research
- Synthetic food waste recipe can be used in other investigations
- Data on reject materials from the synthetic food waste can be used in research on food-related packaging waste generation rates.

1. Data

The data presented in this document are related to a work on degradation of some EN13432 compliant plastics in simulated mesophilic anaerobic digestion of food waste [1].

1.1. Residual materials from synthetic food waste recipe

During preparation of the synthetic food waste (SFW) used in the trial, the packaging material in which it came was separated (Fig. 1) and weighed. The total unsorted weight of material including all food items and packaging was 101.836 kg, of which the rejected packaging stream made up 4.604 kg. Plastic film made up 774 g or 0.76% of the total unsorted weight, while solid plastics (trays, pots and bottles) made up a further 880 g or 0.86%, giving a plastics total of 1.62% on a wet weight basis (Table 1). Further details of the mixed SFW and card packaging (CP) feedstock used in the trial are given in section 2.1.

1.2. Physical appearance, weight and numbers of plastic tokens after digestion

Table 2 lists the types of plastic used in the trial in [1]. Fig. 2 shows the plastic tokens removed from the digestate sampled on day 98 of the trial, with the left-hand images showing the total amount recovered in each case. Numbers and weights of tokens during and at the end of the trial are shown in Table 9 and Fig. 11 in Section 2.

Fig. 1. Items rejected during SFW preparation: (a) Packaging materials, (b) Materials not put through macerator.

Table 1
Food and packaging streams from SFW materials.

Item	Weight (g)	% of total unsorted weight (including food items)
Plastic bottles	140	0.14%
Plastic trays	446	0.44%
Plastic containers/pots	294	0.29%
Subtotal solid plastic	880	0.86%
Plastic film	774	0.76%
Total plastic (not including Tetra pak components)	1654	1.62%
Tetra pak - mixed materials	88	0.09%
Aluminium trays	59	0.06%
Metal cans	141	0.14%
Card packaging	1207	1.19%
Glass bottles and jars inc tops	1455	1.43%
Total packaging	4604	4.52%
Unmacerated food - eggshell, pepper top, onionskin	541	0.53%
Total reject stream	5145	5.05%
Food materials - macerated to form SFW	96691	94.95%
Total weight of material	101836	100.00%

Table 2
Plastic materials used in trial.

	Abbreviation	Average token weight (mg) 10 × 10 mm square
Polypropylene film	PP	2.61
Low density polyethylene film	LDPE	5.14
Cellulose-based metallised film	CBM	3.42
Cellulose-based heat-sealable film	CBHS	4.28
Cellulose-based high barrier heat-sealable film	CBHB	6.68
Cellulose-based non heat-sealable film	CBnHS	6.24
Cellulose diacetate film	CDF	6.50
Starch-based film blend 1	SBF1	2.17
Starch-based film blend 2	SBF2	4.29
Polylactic Acid Film	PLAF	3.71
		Pellet
Polylactic Acid Blend	PLAB	24.7

1.3. Images from microscopy

Fig. 3–7 present micrographs of selected plastic pieces recovered from the digestate samples taken on day 98. No special measures were taken to preserve these pieces at the time of sampling. Figs. 3–6 were taken with light and dark field microscopy and Fig. 7 with confocal microscopy.

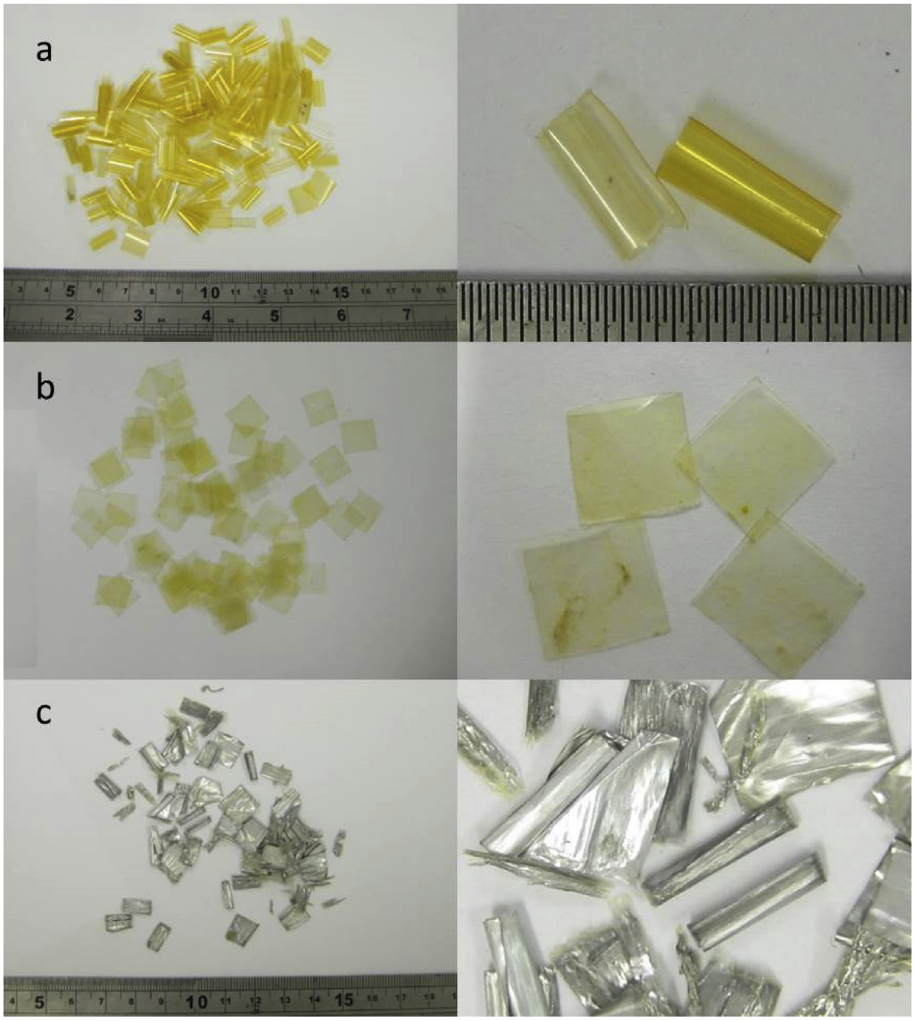
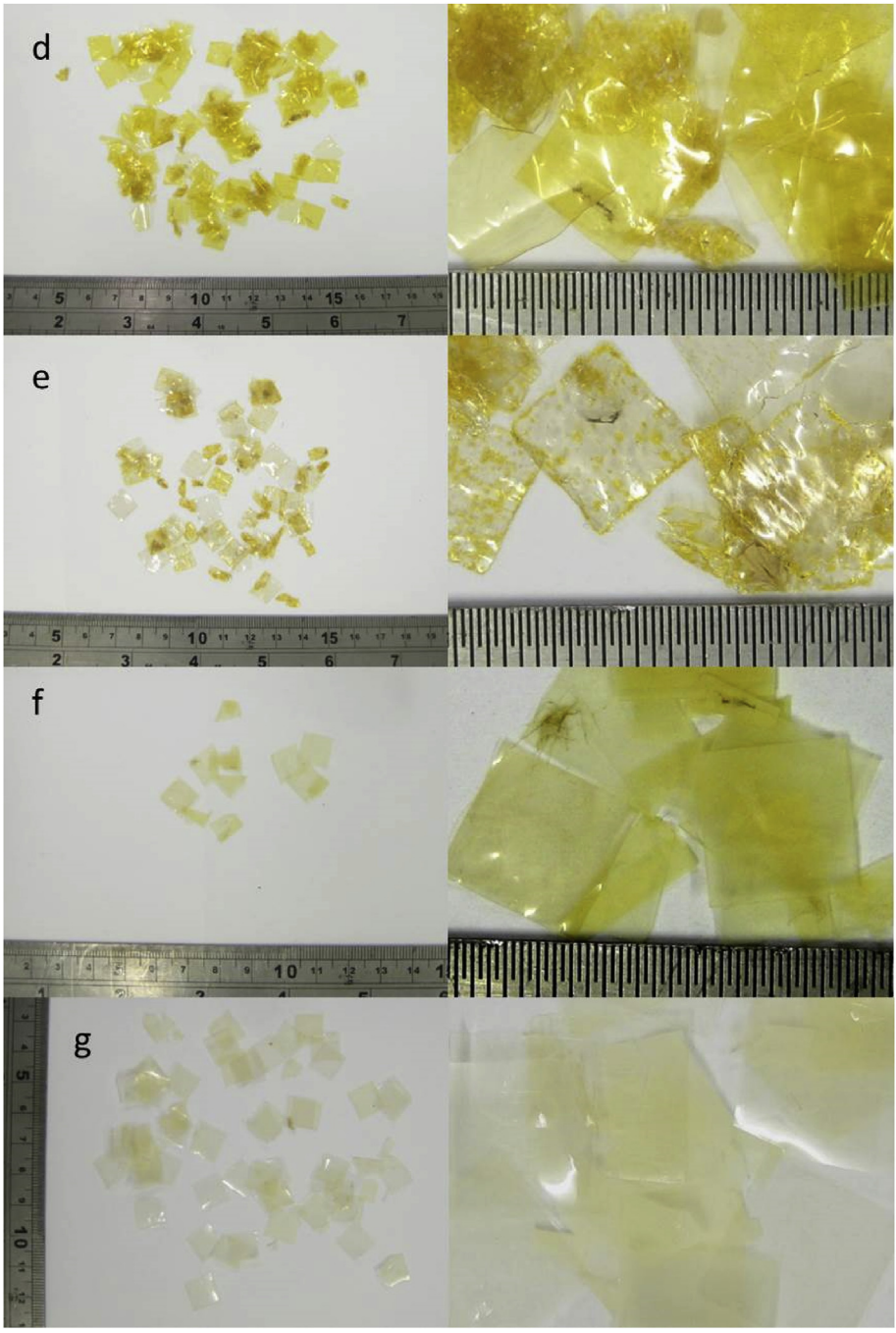


Fig. 2. Plastic tokens recovered from digestate samples on day 98 of the digestion trial: (a) PP, (b) LDPE, (c) CBM. (Left-hand image shows total amount recovered in each case). Fig. 2 continued Plastic tokens recovered from digestate samples on day 98 of the digestion trial: (d) CBHS, (e) CBHB, (f) CBnHS, (g) CDF. (Left-hand image shows total amount recovered in each case). Fig. 2 continued Plastic tokens recovered from digestate samples on day 98: (h) SBF1, (i) SBF2, (j) PLAF, (k) PLAB. (Left-hand image shows total amount recovered in each case).

1.4. Biodegradability of plastics as assessed by the BMP assay

Data from Biochemical Methane Potential (BMP) assays on the feedstock materials (SFW, CP and plastics) used in the trial are shown in Fig. 8 and Table 3. During the BMP assays one replicate for CP and one for PLAB suffered a small loss of digester contents. These replicates were omitted from the BMP calculation and graphical data are presented only up to the point before this loss occurred. Results from another test carried out in accordance with DIN 38414 Teil 8 (high-rate dry fermentation at 50 °C) [2] were made available by the funders of the trial, and are included in Table 3 for comparison.

Degradation of the cellulose based plastics appeared to show inhibition in the first two days of the BMP assay. Table 4 gives the time of onset of inhibition in each case.



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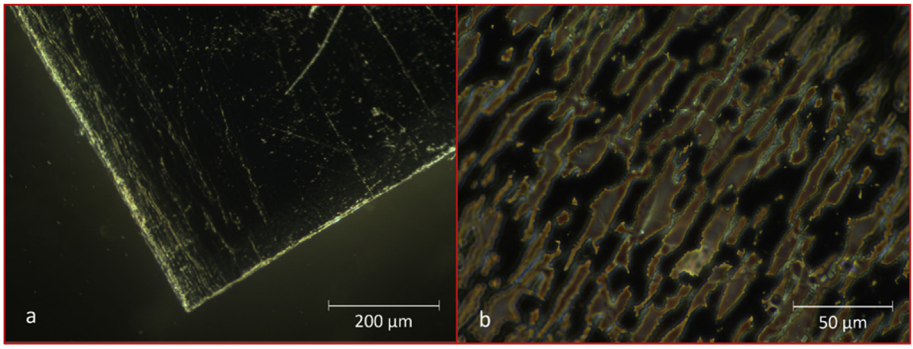


Fig. 3. CBM. (a) Low magnification dark field image of CBM film showing areas where the metallic layer has ruptured and is detaching from the surface. (b) Image taken at a higher magnification using phase contrast, showing fractured surface where the metal coating has broken away. Images by Prof Francisco Torrella, University of Murcia.

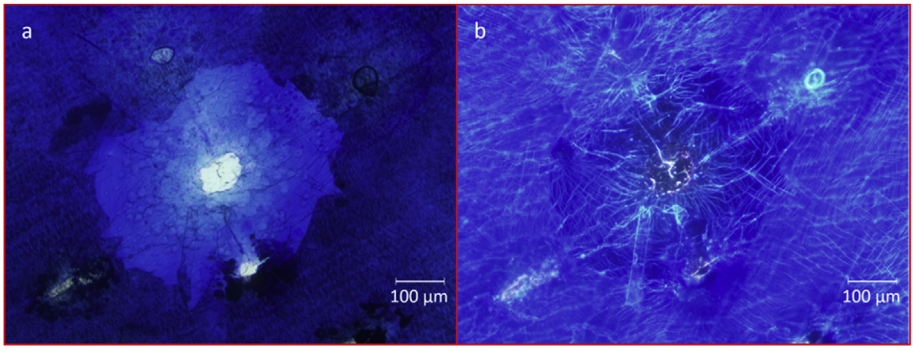


Fig. 4. CBM film stained with aqueous methylene blue (MB), showing cellulose beneath the fractured film degrading through the formation of crater-like erosion pits. Bright field image (a) shows darker portions corresponding to areas where metal film is still attached. The reflection of the light in the dark field image (b) of the same area shows details of the material still present at the bottom of the erosion pit, unseen under bright field, with cracks on the film surface as seen from above. Images by Prof Francisco Torrella, University of Murcia.

The BMP tests for CDF, SBF1, SBF2, PLAF and PLAB (at both I/S ratios) were left running until day 103. All but PLAF showed little or no change in methane production rate or final yield. PLAF continued to produce methane at a higher rate than in the first 50 days. After 103 days it had produced a further 0.119 m^3 CH_4 kg^{-1} VS added, giving a total of 0.216 m^3 CH_4 kg^{-1} VS with good agreement between replicates.

1.5. Potentially toxic elements

Table 5 shows the concentration of Potentially Toxic Elements (PTE) in the feedstock materials. The method for comparing these with the limit value in the UK's PAS110 standard [3] is outlined in section 2.4.

1.6. Residual biogas potential of digestate

The Residual Biogas Potential of the digestate from the trial in Ref. [1] was 0.084 L biogas kg^{-1} VS (0.070 L CH_4 kg^{-1} VS) at day 28. The digestate sample continued to produce gas after the 28-day

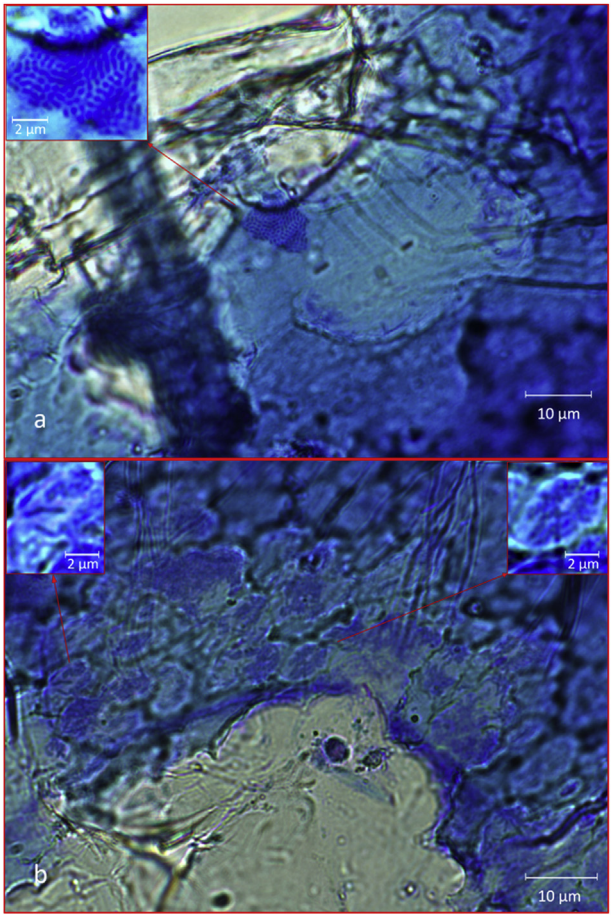


Fig. 5. CBM film under bright field (oil immersion 100× objective). (a) Edge of an erosion pit showing bacteria on the pit sides spreading out as a biofilm over a component of the remaining cellulose film. The pinkish-red metachromasy surrounding the clear eroded area in the top left corner is evidence of bacterial growths at the periphery. The depth of focus (approx 0.5 µm) only shows a few bacteria on the borders of the eroded area but visual examination shows bacterial growth extending down into the pit. (b) Image showing bottom of pit and areas of bacterial attack around the edges. Images by Prof Francisco Torrella, University of Murcia.

standard test duration: Fig. 9 shows the data for the cumulative net specific methane production up to day 45. The kinetic constants obtained using two modelling approaches described in Section 2.5 are given in Table 6.

2. Experimental design, materials and methods

2.1. Synthetic food waste and card packaging

A synthetic food waste, based on materials purchased for the purpose from supermarkets, was prepared for the trial in Ref. [1] as described below. This approach was adopted to ensure that the feedstock for the trial was not contaminated with other plastics, which would have been difficult to avoid using either post-supermarket or post-consumer food waste. A study on post-consumer UK food waste [4] with data categorised into the 100 items most commonly thrown away by households (Table 7) was used as the basis for selection of the materials used. These were further grouped by

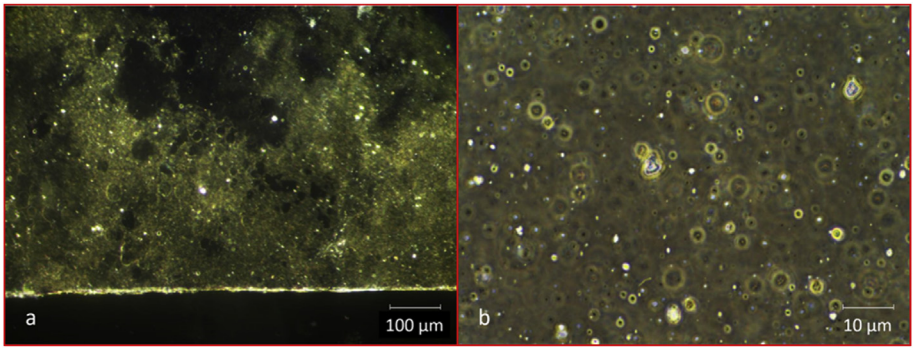


Fig. 6. CBnHS. (a) Dark field low magnification clearly showing perforation of film as bright areas where light penetrates thinner sections. (b) Phase contrast showing extensive surface pitting. Images by Prof Francisco Torrella, University of Murcia.

category according to data provided by a major UK supermarket chain. The selected products were then purchased in appropriate proportions on a fresh weight basis (Table 8), and processed in a macerating grinder (S52/010, IMC Limited, UK) (Fig. 10).

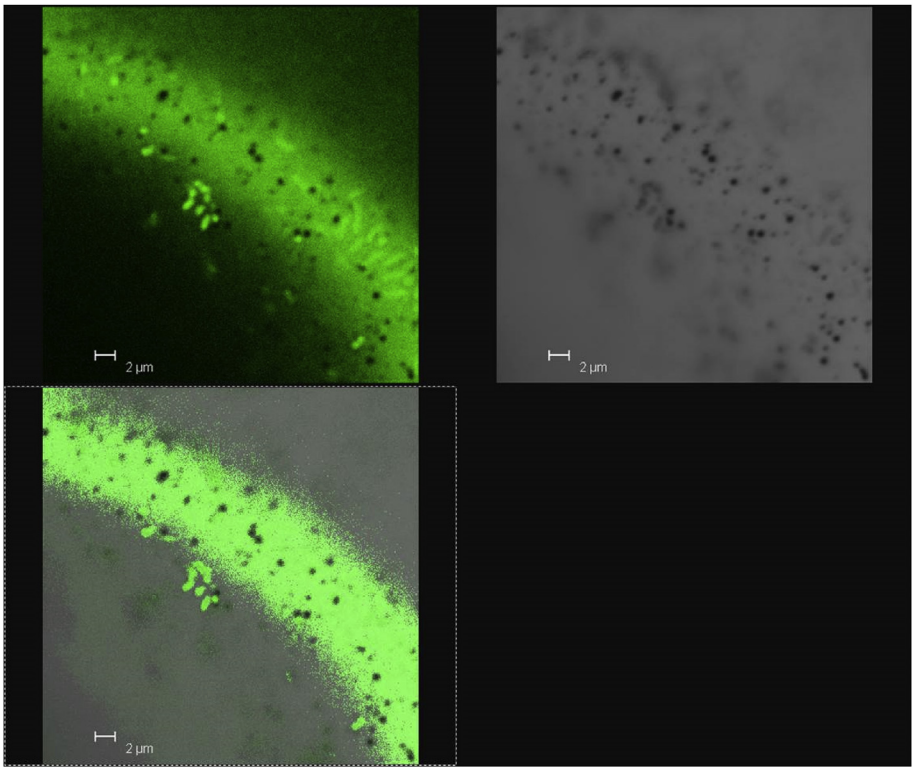


Fig. 7. CBHS. Combined fluorescent and differential interference contrast images for sample CBHS showing pitting and microbial attack. Sample viewed using a Leica TCS SP2 confocal laser scanning microscope. Images courtesy of Dr Yue Zhang, University of Southampton.

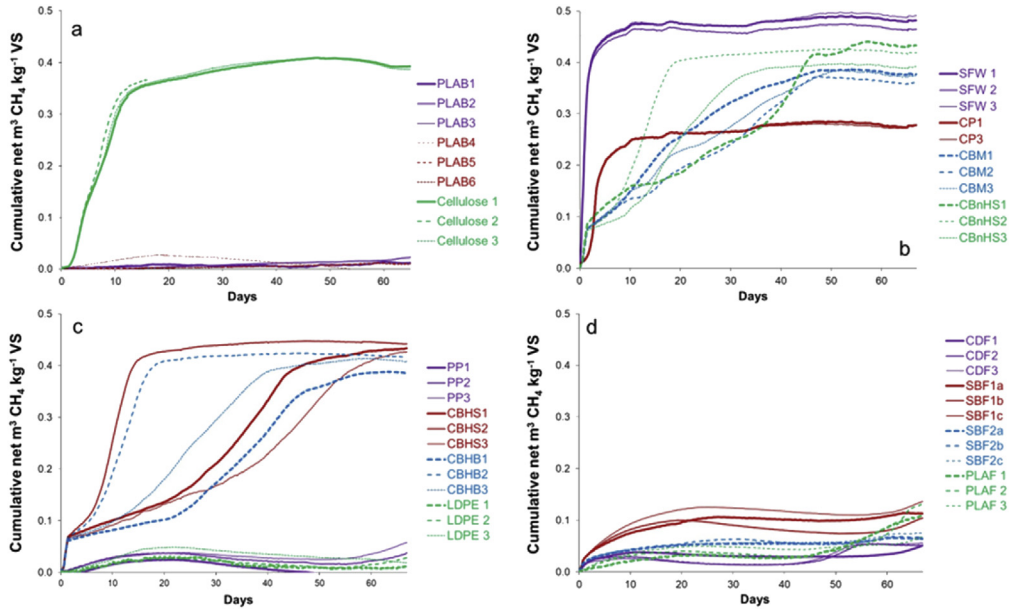


Fig. 8. Data from BMP tests on feedstock components: (a) PLAB (1–3 = I/S ratio 3.8, 4–6 = I/S ratio 1.9), cellulose control; (b) SFW, CP, CBM and CBnHS; (c) PP, CBHS, CBHB, LDPE; (d) CDF, SBF1, SBF2, PLAF. I/S ratio = inoculum to substrate ratio used in the assay.

Table 3
65-day BMP values for plastic samples.

	This work			DIN 8414	DIN 38414	Comments
	m^3 CH_4 kg^{-1} VS			m^3 CH_4 kg^{-1} VS	days	
PP	0.025	±	0.030	–	–	
LDPE	0.018	±	0.007	0.360	28	
CBM	0.374	±	0.009	0.398	28	DIN 38414 - different grade of CBM
CBHS	0.433	±	0.009	0.340	42	DIN 38414 - not finished
CBHB	0.413	±	0.015	0.397	28	DIN 38414 - almost finished
CBnHS	0.410	±	0.021	0.259	28	
CDF	0.050	±	0.005	0.108	64	
SBF1	0.113	±	0.016	0.069	64	DIN 38414 - not finished
SBF2	0.069	±	0.005	0.058	28	This work - not finished?
PLAF	0.097	±	0.032	0.014	28	
PLAB	0.017	±	0.005	–	–	
Card packaging (CP)	0.274	±	0.046	–	–	
Food waste (SFW)	0.471	±	0.013	–	–	
Cellulose control	0.391	±	0.002	–	–	

2.2. Semi-continuous digestion trials: adjustment of calculations after amendment of digestate sampling methodology

Semi-continuous digestion trials designed to simulate full-scale operating modes with the addition of plastic tokens were set up and run as described in Ref. [1].

The number and weight of tokens added to each digester, removed each week during the trial, and remaining in each digester at the end of the trial is shown in Table 9. If the sampling method used is representative and the plastic shows little or no degradation, the expected number of tokens removed in any week is simply equal to the number present in the digester multiplied by the fraction of digestate volume removed, and it is easy to keep a running total. For the first weeks of the trial in Ref. [1] the

Table 4
Onset of inhibition in BMP test for Cellulose-based plastics.

	Onset of inhibition - Days from start of test
CBM	1.49–1.52
CBHS	1.35–1.39
CBHB	1.28–1.30
CBnHS	1.50–1.55

Table 5
Concentration of PTE in feedstock and plastic materials.

	Unit	Mercury (Hg)	Cadmium (Cd)	Chromium (Cr)	Copper (Cu)	Lead (Pb)	Nickel (Ni)	Zinc (Zn)
PAS110 limit value [a]	kg tonne^{-1} WW	0.08	0.12	8	16	16	4	32
Cardboard	mg kg^{-1} TS	BDL	0.37	4.1	46.8	8.8	2.37	42.8
SFW	mg kg^{-1} TS	BDL	0.02	1.4	3.2	0.08	0.619	17.8
PP	mg kg^{-1} TS	BDL	0.080	0.5	0.4	BDL	0.42	3.0
LDPE	mg kg^{-1} TS	BDL	0.19	0.3	5.4	1.3	0.28	4.1
CBM	mg kg^{-1} TS	BDL	0.693	0.1	0.2	0.2	0.44	4.6
CBHS	mg kg^{-1} TS	BDL	0.06	BDL	BDL	0.2	0.26	1.6
CBHB	mg kg^{-1} TS	BDL	0.04	BDL	BDL	BDL	0.876	0.2
CBnHS	mg kg^{-1} TS	BDL	0.079	0.2	BDL	BDL	0.48	0.4
CDF	mg kg^{-1} TS	BDL	0.12	0.2	0.2	0.1	0.12	1.4
SBF1	mg kg^{-1} TS	BDL	0.064	0.5	2.0	0.2	0.41	1.3
SBF2	mg kg^{-1} TS	BDL	0.16	0.1	0.4	0.1	0.18	2.2
PLAF	mg kg^{-1} TS	BDL	0.15	0.3	1.0	0.4	0.21	1.7
PLAB	mg kg^{-1} TS	BDL	0.068	10.0	BDL	BDL	3.49	0.3

BDL = Below Detection Limit of 0.1 mg kg^{-1} TS.
[a] PAS110 limit values in kg tonne^{-1} WW at a digestate total N concentration <1 kg N tonne^{-1} WW [3].

Table 6
Kinetic parameters for specific methane yield from digestate.

	Y_m	P	k_1	k_2	R^2 ave
Model 1	0.085	1	0.10	0.000	0.9796
Model 2	0.085	0.3	0.90	0.060	0.9976

sampling method was not representative, and tended to remove proportionately larger numbers of denser plastic tokens and smaller numbers of less dense tokens. The number of tokens actually removed is still known, however, and if no tokens are lost through degradation the number remaining in the digester at the point when the sampling method was modified can therefore be calculated by simple arithmetic. This value can then be used as the start point for calculating the expected number removed once the sampling method has been adjusted. There are thus two ways to check the assumptions made: firstly, the number of tokens removed or present in the digestate at the end of the run should equal the total number added; and secondly, once the revised sampling method is adopted the number of tokens removed each week should approximately match the expected number.

In the case of the PP control, for example, Table 9 shows that a total of 8906 tokens were added throughout the trial. Of these 8842 were accounted for, either removed with the digestate or present in the digester at the end. Since this material is considered non-degradable, this corresponds to an error of 64 tokens or 0.7% of the total. The equivalent figures for the LDPE control were 4293 tokens with an error of 6 tokens or 0.1%. In Fig. 11 it can also be seen that the expected number of tokens removed showed a reasonably good match to the actual number, once the sampling method had been adjusted and the actual number of tokens present at that point taken into account. This validated the approach used. The same approach could then be applied to plastics such as SBF1 and PLAB, where the number of tokens removed in the first weeks of operation was higher than expected, but the total recovery at the end indicated little or no degradation, as did the other methods of assessment used. In Table 9 it can be

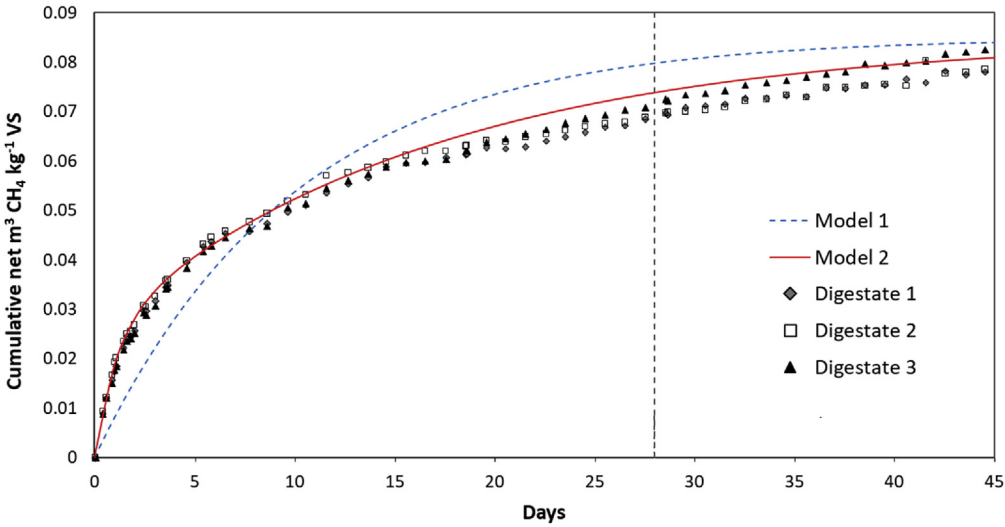


Fig. 9. Cumulative net specific methane production from residual whole digestate. Vertical dashed line indicates 28-day test duration.

seen that the discrepancies in final token numbers for these plastics were 3.4% and 2.4%, only slightly above those for the control plastics; while Fig. 11 again shows good agreement between expected and actual recovery with the adjusted value for tokens once the revised sampling method has been adopted.

This method cannot be reliably applied to more readily degradable plastics without making further assumptions, since the number of tokens recovered is also affected by degradation. The final number and weight of tokens can still be used to estimate the degree of degradation, however. The only readily degradable plastic, which showed clear, signs that a larger than expected number of tokens were being removed during the first few weeks was CDF. In this case no attempt was made to correct the number of tokens present when the sampling method was adjusted (Fig. 11).

2.3. BMP test

The conditions used in the BMP assay are described in Ref. [1]. The BMP for a given test substrate was obtained by calculating the cumulative volume of methane produced from each test digester; subtracting the average cumulative STP methane production from the inoculum-only controls; and dividing the result by the weight of substrate volatile solids added to each test digester. The average value in L CH_4 g^{-1} VS for all test digesters fed on a given substrate was taken as the final BMP value. All gas volumes are reported at STP of 101.325 kPa and 0 °C.

The BMP of the cellulose controls was used to indicate whether the test conditions are satisfactory: the value of 0.391 m^3 CH_4 kg^{-1} VS added in this case was very close to the theoretical value of 0.3415 m^3 CH_4 kg^{-1} VS added. The SFW and CP had BMP values of 0.471 and 0.274 m^3 CH_4 kg^{-1} VS added respectively, both typical of these types of material. The control plastics PP and LDPE showed very low but non-zero values of 0.025 and 0.018 m^3 CH_4 kg^{-1} VS added respectively, corresponding to around 5% of the methane yield of the controls and indicating the probable limit of accuracy of the assay.

The data for the cellulose-based plastics were not ideal for the purposes of determining the BMP and the calculation was thus adapted to accommodate this. All four plastics produced methane at a rapid and consistent rate from the start of the test until between 1.2 and 1.5 days (Fig. 8b and c), when methane production relative to the inoculum-only controls dropped sharply. Inhibition of this type is often due to production of volatile fatty acid (VFA) intermediates at a rate greater than the capacity of the methanogenic population to process the VFA into methane, and this in turn indicates a very readily

Table 7
Most common post-consumer food items for disposal (based on [4]).

No	Item	All (kg)		Short life only (kg)	
1	Potatoes	359000	9.7%	–	0.0%
2	Bread slices	328000	8.9%	328000	11.3%
3	Apples	190000	5.1%	–	0.0%
4	Meat or fish meals	161000	4.4%	161000	5.5%
5	World breads	102000	2.8%	102000	3.5%
6	Veg mixed meals	96000	2.6%	96000	3.3%
7	Pasta mixed meals	87000	2.4%	87000	3.0%
8	Bread rolls/baguettes	86000	2.3%	86000	3.0%
9	Rice mixed meals	85000	2.3%	85000	2.9%
10	Mixed meals	85000	2.3%	85000	2.9%
11	Bananas	84000	2.3%	84000	2.9%
12	Bread loaves	75000	2.0%	75000	2.6%
13	Yoghurts/drinks	67000	1.8%	67000	2.3%
14	Sandwiches	63000	1.7%	63000	2.2%
15	Cakes	62000	1.7%	62000	2.1%
16	Lettuce	61000	1.7%	61000	2.1%
17	Tomatoes	61000	1.7%	61000	2.1%
18	Cabbage	56000	1.5%	56000	1.9%
19	Cooked rice	55000	1.5%	55000	1.9%
20	Mixed veg	53000	1.4%	53000	1.8%
21	Oranges	51000	1.4%	51000	1.8%
22	Carrots	46000	1.2%	46000	1.6%
23	Onions	43000	1.2%	–	0.0%
24	Pears	42000	1.1%	42000	1.4%
25	Sodas	42000	1.1%	–	0.0%
26	Milk	40000	1.1%	40000	1.4%
27	Cheese	40000	1.1%	40000	1.4%
28	Mixed salads	37000	1.0%	37000	1.3%
29	Cooked pasta	36000	1.0%	36000	1.2%
30	Mixed snacks	36000	1.0%	36000	1.2%
31	Melons	35000	0.9%	35000	1.2%
32	Coleslaw	33000	0.9%	33000	1.1%
33	Pizzas	32000	0.9%	32000	1.1%
34	Chicken portions	32000	0.9%	32000	1.1%
35	Cucumbers	32000	0.9%	32000	1.1%
36	Chocolates/sweets	31000	0.8%	31000	1.1%
37	Sweetcorn	30000	0.8%	30000	1.0%
38	Sausages	30000	0.8%	30000	1.0%
39	Pork portions	29000	0.8%	29000	1.0%
40	Biscuits/crackers	27000	0.7%	27000	0.9%
41	Water	27000	0.7%	–	0.0%
42	Beans (not baked)	26000	0.7%	26000	0.9%
43	Grapes	22000	0.6%	22000	0.8%
44	Ham	22000	0.6%	22000	0.8%
45	Plums	20000	0.5%	20000	0.7%
46	Squashes/cordials	20000	0.5%	–	0.0%
47	Breakfast cereals	20000	0.5%	–	0.0%
48	Cook-in sauces	19000	0.5%	–	0.0%
49	Fruit juices	19000	0.5%	19000	0.7%
50	Eggs	19000	0.5%	19000	0.7%
51	Fish	19000	0.5%	19000	0.7%
52	Beef portions	18000	0.5%	18000	0.6%
53	Dough	18000	0.5%	18000	0.6%
54	Celery	17000	0.5%	17000	0.6%
55	Strawberries	16000	0.4%	16000	0.5%
56	Peppers	15000	0.4%	15000	0.5%
57	Chicken drumsticks	15000	0.4%	15000	0.5%
58	Flour	15000	0.4%	15000	0.5%
59	Chicken breasts	15000	0.4%	15000	0.5%
60	Mushrooms	15000	0.4%	15000	0.5%

(*continued on next page*)

Table 7 (*continued*)

No	Item	All (kg)		Short life only (kg)	
61	Broccoli	15000	0.4%	15000	0.5%
62	Sandwich spreads	14000	0.4%	14000	0.5%
63	Baked beans	14000	0.4%	–	0.0%
64	Bacon	14000	0.4%	14000	0.5%
65	Peaches	14000	0.4%	14000	0.5%
66	Milk drinks	13000	0.4%	13000	0.4%
67	Crisps	12000	0.3%	12000	0.4%
68	Lemons	12000	0.3%	12000	0.4%
69	Beetroot	12000	0.3%	12000	0.4%
70	Fruit pies	12000	0.3%	12000	0.4%
71	Jams	11000	0.3%	–	0.0%
72	Pheasants	11000	0.3%	11000	0.4%
73	Dips	10000	0.3%	10000	0.3%
74	Mixed fruits	10000	0.3%	10000	0.3%
75	Butter/margarine	10000	0.3%	10000	0.3%
76	Herbs/spices	10000	0.3%	–	0.0%
77	Dessert cakes/gateaux	9000	0.2%	9000	0.3%
78	Cream	9000	0.2%	9000	0.3%
79	Pineapples	9000	0.2%	9000	0.3%
80	Crumpets	9000	0.2%	9000	0.3%
81	Pastry	9000	0.2%	9000	0.3%
82	Chicken products	9000	0.2%	9000	0.3%
83	Pet food	9000	0.2%	–	0.0%
84	Yorkshire pudding and batters	8000	0.2%	8000	0.3%
85	Cauliflowers	8000	0.2%	8000	0.3%
86	Uncooked pasta	8000	0.2%	–	0.0%
87	Leeks	8000	0.2%	8000	0.3%
88	Milk pudding (custards etc)	8000	0.2%	8000	0.3%
89	Doughnuts	8000	0.2%	8000	0.3%
90	Oils	8000	0.2%	8000	0.3%
91	Mayonnaise/salad cream	7000	0.2%	7000	0.2%
92	Spring onions	6000	0.2%	6000	0.2%
93	Peas	6000	0.2%	6000	0.2%
94	Turnips/swedes	6000	0.2%	6000	0.2%
95	Parsnips	6000	0.2%	6000	0.2%
96	Burgers	6000	0.2%	6000	0.2%
97	Lamb	6000	0.2%	6000	0.2%
98	Pickles	6000	0.2%	–	0.0%
99	Nuts	6000	0.2%	6000	0.2%
100	Mangoes	6000	0.2%	6000	0.2%
	Subtotal	3691000	100.0%	2913000	100.0%
	UK total	4080000	90.5%	–	–

degradable material and an insufficient I/S ratio in the test. To confirm the cause would require sampling an additional replicate to measure system parameters such as pH, alkalinity and VFA concentration, but this was not carried out in the current work. An alternative explanation of some inhibitory component in the heat-sealable and moisture-resistant surface layers of the plastics was ruled out, as the same effect also occurred in CBnHS without these additional layers. The onset of inhibition appeared to be a characteristic of the material, as there was little overlap between the different plastics (Table 4). Unfortunately recovery from this type of inhibition generally shows considerable variation between replicates, and can have some impact on the final BMP value, as seen in Fig. 8b and c. The outlying values for CBM, CBHB and CBnHS were therefore ignored in calculating the average BMP for each material. Despite this issue, the BMP values showed reasonable correspondence with those obtained from the DIN 38414 test (Table 3), especially when the degree of completion of some of the DIN 38414 test runs is taken into account.

Of the remaining plastics, SBF2 showed a very low BMP of 0.069 m^3 CH_4 kg^{-1} VS added, while SBF1 had a slightly higher value of 0.113 m^3 CH_4 kg^{-1} VS added. In both cases the similarity to DIN 38414 test values may be coincidental, as gas production was still continuing at a low but steady rate at the end of

Table 8
Materials used for preparation of SFW - fresh weight including packaging.

Produce	kg	Bakery	kg	Dry goods	kg	Dairy	kg	Meat and Fish	kg	Ready meals	kg
Potatoes	10.000	White sliced bread	5.650	Bottled water - still	1.700	Yoghurt	2.000	Barbecue mix (sausages, burgers, chicken drumsticks	2.600	Cottage pie	2.000
Apples	6.057	Wholemeal flour	1.740	Potatoes for crisps	1.319	Milk	2.000	Chicken breasts frozen	1.100	Beef lasagne	2.000
Tomatoes	2.518	Sliced wholemeal bread	1.512	Chocolate and confectionery	0.640	Cooked rice	1.175	White fish fillet frozen	0.750	Cooked plain pasta	1.775
Lettuce	2.479	White bread flour	1.500	Mixed breakfast cereal	0.547	Fruit juice	1.000	Breaded chicken breasts	0.640	Pizza	0.930
Bananas	2.270	Pitta bread	1.309	Cook-in sauce	0.540	Coleslaw	0.875	Lamb mince	0.454	Ocean pie	0.900
Oranges	2.048	Wholemeal rolls	1.013	Eggs	0.510	Pasta salad (Chicken/tuna)	0.800	Bacon	0.400	Steak pie	0.800
Mixed vegetables frozen	2.000	Christmas pudding	0.850	Bottled water - sparkling	0.450	Sandwich filling (tuna, onion)	0.750	Ham	0.400	Spinach and ricotta cannelloni	0.600
Melon	1.778	Eggs for cake etc	0.690	Baked beans	0.420	Mayonnaise	0.500	Salami	0.343	Pork pies	0.459
Cucumber	1.525	Tortilla	0.500	Tinned pet food	0.400	Margarine	0.500	Sliced beef	0.100	Spaghetti bolognese	0.450
Pineapple	1.089	Rye bread	0.495	Jaffa cakes	0.300	Custard (liquid)	0.475	–	–	Mushroom Tagliatelle	0.450
Onion	1.009	Apple tart	0.450	Fruit cordial	0.300	Cheddar	0.444	–	–	Stir fry frozen vegetables	0.400
Broccoli mix frozen	1.000	White rolls	0.420	Uncooked pasta	0.250	Fruit dessert	0.400	–	–	Cauliflower cheese grills	0.397
Casserole vegetable mix frozen	1.000	Wholemeal finger rolls	0.400	Granulated white sugar	0.240	Edam	0.320	–	–	Chicken curry	0.375
Sweet corn frozen	1.000	Doughnut	0.330	Jam	0.210	Cottage cheese	0.300	–	–	Beef curry	0.375
Pear	0.860	Crumpet	0.280	Herbs and spices (dry)	0.200	Houmous	0.300	–	–	Chicken curry 2	0.375
Carrots	0.629	Naan bread	0.270	Honey	0.200	Double cream	0.284	–	–	Cheese and onion crisp bakes	0.360
Lemons	0.537	Malt bread rolls	0.230	Mixed nuts	0.200	Brie	0.200	–	–	Beef and yorkshire pudding ready meal	0.360
Celery	0.520	Wholemeal loaf	0.220	Chocolate mini rolls	0.120	–	–	–	–	Vegetable grills	0.340

(*continued on next page*)

Table 8 (*continued*)

Produce	kg	Bakery	kg	Dry goods	kg	Dairy	kg	Meat and Fish	kg	Ready meals	kg
Grapes	0.500	Water for bread dough	0.200	Chutney	0.100	–	–	–	–	Vegetable lasagne	0.300
Beetroot	0.500	Breadsticks	0.200	Tartare sauce	0.060	–	–	–	–	Yorkshire pudding	0.290
Plums	0.500	Powdered milk	0.100	–	–	–	–	–	–	Stir fry frozen veg	0.400
Pepper	0.498	Gingerbread	0.050	–	–	–	–	–	–	–	–
Peaches	0.433	Yeast	0.015	–	–	–	–	–	–	–	–
Mushrooms	0.350	–	–	–	–	–	–	–	–	–	–
Spring onion	0.160	–	–	–	–	–	–	–	–	–	–
Subtotal	41.260		18.424		8.706		12.323		6.787		14.336
% of total	40.5%		18.1%		8.5%		12.1%		6.7%		14.1%

Table 9
Data for final balance based on no. and weight of tokens and experimentally determined values for degradation constants.

	PP	LDPE	CBM	CBHS	CBHB	CBnHS	CDF	SBF1	SBF2	PLAF	PLAB
No. of tokens added	8906	4293	7884	6278	3942	4380	3796	11096	5548	6278	999
Actual no. of tokens in digester at end	3137	2256	565	918	1038	286	671	3638	1992	1327	320
Actual no. of tokens removed in run	5705	2043	1540	1826	1230	320	1261	7082	3337	1274	655
Predicted total no, of tokens recovered [a]	3034	1533	466	595	476	76	440	3174	1773	757	297
Actual total no. of tokens recovered	8842	4299	2104	2743	2268	606	1932	10720	5329	2601	975
Balance (no. at end + no. out - no. in)	−64	6	−5780	−3535	−1675	−3774	−1864	−376	−219	−3678	−24
No. of tokens destroyed	0.7%	−0.1%	73.3%	56.3%	42.5%	86.2%	49.1%	3.4%	3.9%	58.6%	2.4%
Weight added (g)	23.29	22.06	26.97	26.89	26.34	27.32	24.68	24.05	23.78	23.31	24.69
Predicted weight in digester at end (g) [a]	7.93	7.88	1.59	2.55	3.18	0.47	2.86	6.90	7.60	2.81	7.36
Actual weight in digester at end (g)	8.56	10.85	1.67	3.28	5.25	0.98	3.40	7.64	8.69	5.13	7.86
Recovery at end	107.9%	137.7%	104.7%	128.5%	164.9%	206.1%	119.0%	110.8%	114.3%	182.6%	106.8%
Predicted weight removed in run (g) [a]	15.35	14.19	4.29	6.62	8.04	1.33	7.26	15.24	15.70	7.10	16.58
Actual weight removed in run (g)	15.51	11.38	4.22	5.90	5.97	0.82	6.71	14.50	14.60	4.78	16.08
Recovery in run	101.0%	80.2%	98.3%	89.1%	74.3%	62.0%	92.5%	95.2%	93.0%	67.3%	97.0%
Actual total weight recovered (g) [b]	24.08	22.23	5.89	9.17	11.22	1.80	10.12	22.14	23.29	9.91	23.93
Actual total weight recovered (%) [b]	103%	101%	100%	100%	100%	100%	100%	100%	100%	100%	100%
Balance (end + out - in) (g)	0.79	0.16	−21.09	−17.72	−15.12	−25.52	−14.57	−1.91	−0.49	−13.40	−0.76
Weight destroyed	−3.4%	−0.7%	78.2%	65.9%	57.4%	93.4%	59.0%	7.9%	2.1%	57.5%	3.1%
1st order degradation *k*	0.00	0.00	0.10	0.06	0.04	0.39	0.04	0.00	0.00	0.04	0.00
VS destruction potential [c]	0.0%	0.0%	82.7%	72.3%	64.7%	94.9%	66.2%	12.4%	2.9%	64.8%	6.2%

[a] Based on 1st-order degradation coefficient.
[b] Actual total weight recovered = Actual weight in digester at end + Actual weight removed in run.
[c] Based on value from longer-term modelling with 1st-order degradation coefficient.

the DIN 38414 test. For CDF film there was a considerable difference between the value of 0.05 m^3 CH_4 kg^{-1} VS added in this work and the DIN 38414 test value of 0.259 m^3 CH_4 kg^{-1} VS added, suggesting that this material may be more amenable to degradation under thermophilic conditions than in a wet mesophilic system. The BMP value in this work of 0.097 m^3 CH_4 kg^{-1} VS added for PLAF was higher than the DIN 38414 test value, but the DIN 38414 test ran for only 28 days and gas production was continuing steadily at the end (Table 3). In the current work there appeared to be a slight increase in methane production from PLAF from day 50 onwards (Fig. 8d). On the basis of this, the BMP tests for CDF, SBF1, SBF2, PLAFand PLAB (at both I/S ratios) were left running until day 103.

2.4. Potentially toxic elements

Potentially Toxic Elements in the plastic samples were measured by NRM Ltd. The limiting factor for plastic addition can be determined by comparison with the permissible loadings under the UK's PAS110 standard [3], in which application rates are based on the total nitrogen content of the digestate. The following simple assumptions were made to assess this. If a digester were fed on 100% plastic and achieved a 95% degradation rate, then only one material (PLAB) would exceed the standard for chromium and nickel, with five others (CBM, CBnHS, CDF, SBF2 and PLAF) slightly exceeding the cadmium standard. In practice however the concentration of plastic in a mixed feedstock is unlikely to exceed 2%, and degradation rates are generally below 95%. At the bioplastics loading required for compliance with the PAS110 physical contaminants specification, for example, the materials could not cause the

Fig. 10. Feedstock materials: (a) Materials purchased for SFW, (b) preparation of SFW by maceration, (c) unprinted card packaging also used in the mixed feed prepared for the trial.

digestate to exceed the specified limit values for PTE. The determining factor for metals concentrations in the digestate will therefore be that in the food waste and card packaging components.

2.5. Methodology for residual biogas potential of digestate

In order to determine whether the mixed whole digestate from the trial in Ref. [1] was likely to meet the requirements of the PAS110 standard [3], one of the duplicate LDPE control reactors was sacrificed on day 126 and the digestate was tested for residual biogas production (RBP). The test was carried out in triplicate in static reactors with a sewage sludge inoculum according to the methodology used in OFW004-005 (2009) [5]. To provide additional information on the stability of the material, the methane content of the biogas was also measured to give a static batch test BMP value.

To determine kinetic constants, the specific methane production was modelled using two sets of assumptions: simple first-order degradation (Model 1), and a pseudo-parallel first-order model (Model 2). For model 1 the methane production is given by

$$Y = Y_m\,(1 - e^{-kt}) \tag{1}$$

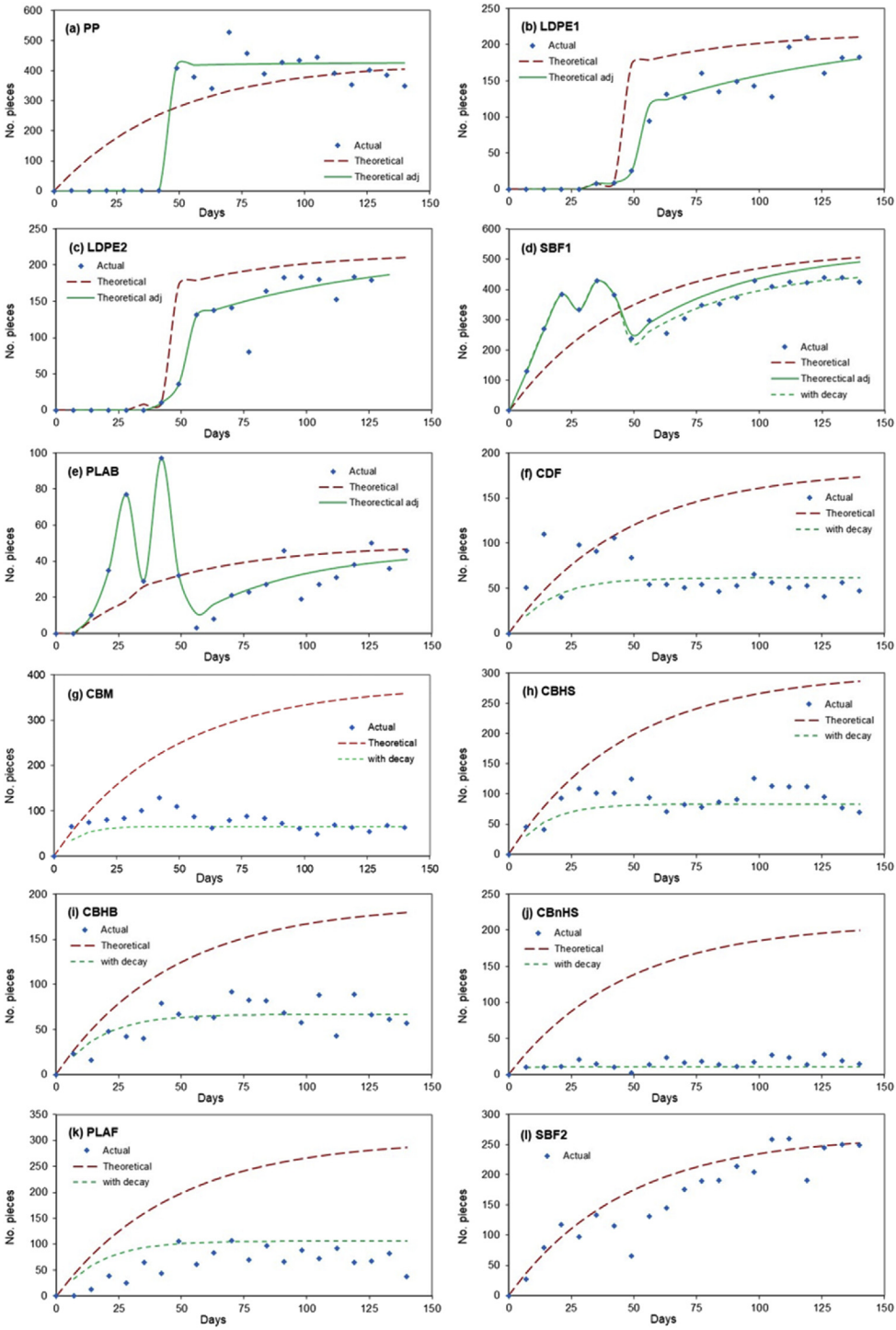
Where.

Y is the cumulative methane yield at time t.

Ym is the ultimate methane yield.

k is the first order rate constant.

Rao (2002) [6] suggests that for certain materials it may be better to consider that the gas production curve corresponds to the rapid breakdown of readily degradable components followed by a


(a) PP
Actual
Theoretical
Theoretical adj
(b) LDPE1
Actual
Theoretical
Theoretical adj
(c) LDPE2
Actual
Theoretical
Theoretical adj
(d) SBF1
Actual
Theoretical
Theorectical adj
with decay
(e) PLAB
Actual
Theoretical
Theorectical adj
(f) CDF
Actual
Theoretical
with decay
(g) CBM
Actual
Theoretical
with decay
(h) CBHS
Actual
Theoretical
with decay
(i) CBHB
Actual
Theoretical
with decay
(j) CBnHS
Actual
Theoretical
with decay
(k) PLAF
Actual
Theoretical
with decay
(l) SBF2
Actual
No. pieces
Days

much slower degradation of the remaining material. The methane production is therefore governed by two rate constants k_1 and k_2 rather than by a single constant:

$$Y = Y_m (1 - Pe^{-kt}_1 - (1-P) e^{-kt}_2) \quad (2)$$

Where:

Y is the cumulative methane yield at time t.

Y_m is the ultimate methane yield.

k_1 is the first order rate constant for the proportion of readily degradable material.

k_2 is the first order rate constant for the proportion of less readily degradable material.

P is the proportion of readily degradable material.

Model 1 gave only a moderately good fit to the data ($R^2 \approx 0.98$). A much better fit was obtained using model 2 ($R^2 \approx 0.998$), especially in the early stages of the digestion period. The data showed that while the material is depleted it still contains a more rapidly-degradable fraction, as expected for a fully-mixed system.

The estimated final BMP value of 0.085 m^3 CH_4 kg^{-1} VS added was compared with limit value of 0.45 L biogas kg^{-1} VS in the UK's PAS110 [3] to confirm that digestate would meet the standard and be suitable for disposal. The 45-day residual methane production of 0.087 m^3 CH_4 kg^{-1} VS from the CSTR trial was compared with the static BMP test and showed good agreement. The 45-day biogas yield of 0.137 m^3 kg^{-1} VS reflects the absence of losses due to CO_2 dissolution using this method, compared to methods involving collection under a barrier solution.

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Fig. 11. No. of plastic tokens recovered from digestate sample, predicted no. assuming no destruction, and predicted no. modelled using an empirical first-order decay coefficient for (a) PP, (b) LDPE1, (c) LDPE2, (d) SBF1, (e) PLAB, (f) CDF, (g) CBM, (h) CBHS, (i) CBHB, (j) CBnHS, (k) PLAF and (l) SBF2.

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Impact of low loading on digestion of the mechanically-separated organic fraction of municipal solid waste

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Energy modelling

ABSTRACT

Changing waste management practice, introduction of new technologies, and population demographics and behaviour will impact on both quantity and composition of future waste streams. Laboratory-scale anaerobic digestion of the mechanically-separated organic fraction of municipal solid waste (ms-OFMSW) was carried out at relatively low organic loading rates (OLR), and results analysed using an energy modelling tool. Thermophilic operation with water addition and liquor recycle was compared to co-digestion with dilution water replaced by sewage sludge digestate (SSD); thermophilic and mesophilic mono-digestion were also tested at low OLR. All thermophilic conditions showed stable operation, with specific methane production (SMP) from 0.203 to 0.296 m^3 CH_4 kg^{-1} volatile solids (VS). SSD addition increased biogas production by ~20% and there was evidence of further hydrolysis and degradation of the SSD. Long-term operation at 1 kg VS m^{-3} day^{-1} had no adverse effect except in mesophilic conditions where SMP was lower at 0.256 m^3 CH_4 kg^{-1} VS and stability was reduced, especially during OLR increases. This was probably due to low total ammonia nitrogen, which stabilised at ~0.2 g N kg^{-1} and limited the buffering capacity. Energy analysis showed thermophilic operation at OLR 2 g VS L^{-1} day^{-1} gave 42% of the theoretical methane potential and 38% of the higher heating value, reducing to 37% and 34% respectively in mesophilic conditions. Scenario modelling indicated that under low ms-OFMSW load even an energy-depleted co-substrate such as SSD could contribute to the energy balance, and would be a better diluent than water due to its nutrient and buffering capacity.

1. Introduction

Anaerobic digestion (AD) of the organic fraction of municipal solid waste (OFMSW) after mechanical separation is a well-established technology, and its performance characteristics and limitations are known both from long-term laboratory and pilot-scale research (Mata-Alvarez, 2002; Hartmann and Ahring, 2006); and from studies of full-scale plant (Montejo et al., 2013; Romero-Güiza et al., 2014; Colón et al., 2017; Barati et al., 2017). By 2014 there were an estimated 244 AD plants in operation or under construction in Europe for which OFMSW made up a significant proportion of the feedstock (De Baere and Mattheeuws, 2012). These plants are of many different types, and have evolved together with technical and engineering developments to accommodate the range of collection and separation systems used in preparation of this waste feedstock. Despite this extensive experience, there are circumstances in which the process may operate under loading conditions that lower than those it was designed for, or otherwise non-optimal. Lower loadings of course occur as a transient state during start-up, and studies have looked at the best strategies to address this (Bolzonella et al., 2003). A more important case is where the plant is oversized and the organic loading rate (OLR) is low due to a shortfall in the anticipated sources of waste: while such information is often commercially

Abbreviations: AD, Anaerobic Digestion; CHP, Combined Heat and Power; COD, Chemical Oxygen Demand; CSTR, Continuous Stirred-Tank Reactor; HHV, Higher Heating Value; HRT, Hydraulic Retention Time; IA, Intermediate Alkalinity; MSW, Municipal Solid Waste; ms-OFMSW, Mechanically-Separated Organic Fraction of Municipal Solid Waste; OFMSW, Organic Fraction of Municipal Solid Waste; OLR, Organic Loading Rate; PA, Partial Alkalinity; SMP, Specific Methane Production; SRT, Solids Retention Time; SSD, Sewage Sludge Digestate; TA, Total Alkalinity; TAN, Total Ammoniacal Nitrogen; TE, Trace Elements; TKN, Total Kjeldahl Nitrogen; TMP, Theoretical Methane Potential; TS, Total Solids; VBP, Volumetric Biogas Porduction; VS, Volatile Solids; WW, Wet Weight.

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confidential, examination of the available data on digester sizes, input waste tonnages and combined heat and power (CHP) generation capacity suggests that not all plants are working at full capacity. This may be due to initial over-sizing, or to successful initiatives to increase recycling, of the type currently being adopted worldwide in a drive towards greater sustainability. While separation of recyclable materials may change the proportion of non-degradable components in the waste, however, there is evidence that it does not greatly alter the suitability of this residual stream as an AD feedstock (Waite, 2013; Fonoll et al, 2016).

A further factor that is likely to have an increasing impact in future is the adoption of alternative technologies for recovery of materials and energy from the general waste stream, which may leave reduced volumes of residual waste for digestion. These include waste-based biorefinery processes to recover selected fractions for conversion into a range of downstream building blocks, including alcohols (Farmanbordar et al., 2018; Mahmoodi et al., 2018), volatile fatty acids (Cavinato et al., 2017; Aguilar et al., 2013), and sugars and high value products (Vaurs et al., 2018; Sadhukhan et al., 2016). Further sources of competition for wastes may include thermal processing technologies for recovery of energy and products through gasification, pyrolysis and hydrothermal carbonisation (Yang et al., 2018a, 2018b; Dong et al., 2018). While many of these processes are still under development, and not all will make the transition to full-scale operation, it is clear there is potential for significant future competition for wastes. AD technologies are likely to retain a place at the core of such biorefineries for post-processing of residues; but, in addition to reduced tonnages, the characteristics of these residues will be significantly different from those of traditional mechanically-separated OFMSW (ms-OFMSW).

In some cases, a shortfall in ms-OFMSW may be addressed by seeking opportunities for co-digestion with complementary feedstocks such as wet wastes. Municipal wastewater biosolids have long been recognised as a promising co-substrate, and have been extensively studied (Hamzawi et al., 1998; Sosnowski et al., 2003; Bolzonella et al., 2006; Silvestre et al., 2015). Few or no studies appear to have looked at co-digestion with sewage sludge digestate (SSD), however, probably because the majority of the readily degradable fraction is already likely to have been converted into biogas. This co-substrate may, however, be useful in complementing the nutrient profile of the original feedstock, which is often cited as a reason for co-digestion (Tyagi et al., 2018).

The current study aimed to consider a number of scenarios where ms-OFMSW digestion is carried out at relatively low OLR. One objective was to provide a baseline for thermophilic digestion of a particular ms-OFMSW feedstock, for comparison with alternative energy recovery options including integrated pyrolysis and anaerobic digestion (Yang et al., 2018b). Another was to simulate the effect of a lower OLR, such as might occur in an existing plant with a long-term shortfall in waste feedstock. The digester operating mode was based upon that used in a number of full-scale UK plants which run at a moderate OLR of around 2 kg volatile solids (VS) m^{-3} day^{-1}. Solids and liquid retention times in these plants are uncoupled by digestate separation and solids wasting, with solids typically retained for around 20–30 days. Input to the digesters normally consists of around 14–15% OFMSW, 35–36% fresh water and 50% recycled digestate on a wet weight basis. This baseline scenario was compared with one where the waste input is reduced to 1 kg VS m^{-3} day^{-1} but the total input tonnage and hydraulic retention time (HRT) is maintained by addition of more water. For the lower OLR, the study also looked at substitution of the added fresh water with SSD to provide additional buffering and input of inoculum, plus some residual biogas potential. The trials were run under thermophilic conditions, but the lower OLR without SSD was also run at a mesophilic temperature to provide comparative data on the energy production potential. The impact of the different scenarios on the energy balance was considered using the ADAT modelling tool (BORRG, N.D). The results provide useful insights for operators of full-scale plant facing current or potential changes in ms-OFMSW feedstock availability, and on benefits that might arise from substrate blending with digestate from municipal wastewater biosolids treatment.

2. Materials and methods

2.1. Feedstock

Mechanically-separated OFMSW was obtained from the Bursom Recycling Centre, Leicester (Biffa Plc, UK). The residual mixed waste entering this plant is processed in a ball mill and then separated by a drum screen into two size fractions of 0–40 mm and 40–80 mm. The 0–40 mm fraction goes through a slotted flip-flop screen to remove excess water and then through a 5 mm grid. The material is then placed in closed containers for transport to the Wanlip AD plant (Biffa Plc, UK). Two batches, each of ~300 kg, of this bulk material were passed through a 10 mm screen to remove any large non-organic contaminants that could damage the smaller-scale digestion equipment. The <10 mm fraction of the processed OFMSW was stored in 2-kg sub-samples at approximately −20 °C, and thawed for 24 h at room temperature before use. Once defrosted, the OFMSW was maintained at 4 °C and used within 5 days.

2.2. Digestion experiments

The trial used four continuous stirred-tank reactor (CSTR) digesters, each with an internal diameter of 0.32 m, a height of 0.55 m and a working volume of 35 L. Each digester was fitted with top and bottom flange plates, and was mixed by a mechanical stirrer connected through a gas-seal draught tube in the top plate connected to a geared motor operating at 35 rpm. Fresh feed was added via a port in the top plate, and digestate removed from the bottom via a drain tube. Digesters were maintained at 36 ± 1 °C (mesophilic) or 55 ± 1 °C (thermophilic) by an internal heating coil. Biogas production from each digester was measured continuously using a tipping-bucket gas flow meter as described in Walker et al. (2009).

Experimental conditions are summarised in Table 1. The experimental period was divided into two stages as described below.

Stage 1. The trial used 2 digesters (T1 and T2) which had previously been operated thermophilically (55 °C) for a period of 345 days treating source segregated domestic food waste with side-stream ammonia removal at an OLR of 2 g VS L^{-1} (Zhang et al., 2017a, 2017b). On day 0 the digestates from T1 and T2 were removed, mixed to ensure homogeneity and replaced in the digesters, then left without feeding for 12 days to allow degradation of residual feedstock. Feeding of T1 and T2 on OFMSW as the sole substrate started on day 13 at an OLR of 0.5 kg VS m^{-3} day^{-1} and was increased to 1 kg VS m^{-3} day^{-1} on day 16. From day 71 onwards the operating mode was changed to include liquid addition, in accordance with typical operational practice at a number of large-scale plants in the UK. To simulate this, each day 1.666 kg of digestate was removed and the liquid and solids fractions were separated using a 1 mm nylon mesh sieve. The separated solids were discarded, giving a digester solids retention time (SRT) of 21 days. The digester received daily a wet weight of fresh OFMSW sufficient to give an OLR of 1 g VS L^{-1} day^{-1}, and 715 g of SSD from a mesophilic AD plant treating municipal wastewater biosolids (Millbrook, Southampton UK). Approximately 833 g of the separated digestate liquor was then returned

Table 1
Experimental conditions.

		Days	OLR kg VS m^{-3} day^{-1}	HRT days	SRT days	Scenario name
Thermophilic	day 0–15	16	Variable	variable	equal to HRT	–
T1 & T2	day 16–70	55	1.0 OFMSW	approx 297	equal to HRT	–
	day 71–235	165	1.0 OFMSW, 0.7 SSD	42	21	TH1 + SSD
	day 236–384	149	1.0 OFMSW	42	21	TH1
	day 385–393	9	Increasing	Falling	21	–
	day 394–525	132	2.0 OFMSW	42	21	TH2
Mesophilic	day 244–384	141	1.0 OFMSW	42	21	ME1
M1 & M2	day 385–478	94	Variable - increasing	42	21	–
	day 479–525	47	1.0 OFMSW	42	21	–

Note: Stage 1 refers to days 0–235, Stage 2 to days 236–525. OLR is shown as value in kg VS m^{-3} day^{-1} followed by feedstock type: with two feedstocks the total OLR is the sum of both values.

to the digester to maintain the working volume, giving a nominal HRT of 42 days. T1 and T2 both received the same feed, and operated at a combined OLR (OFMSW + SSD) of ~1.7 kg VS m^{-3} day^{-1}.

Stage 2. In this part of the work the digesters were operated to simulate low loadings without co-digestion with SSD. On day 236 the addition of SSD to T1 and T2 as part of the feed was discontinued and 715 g of tap water substituted, reducing the OLR to 1 kg VS m^{-3} day^{-1}. From day 385 the OLR was gradually increased over a 10-day period to 2.0 g VS L^{-1} day^{-1}, by increasing the amount of OFMSW added and decreasing the quantity of tap water proportionally. Feeding continued at this loading until the end of the experimental period on day 525.

A second pair of digesters (M1 and M2) was brought into operation on day 243 and inoculated with digestate taken from the Millbrook AD plant. These were operated mesophilically (37 °C) at a HRT of 42 days and SRT of 21 days using the same solids/liquor separation method as for T1 and T2, with the aim of providing comparative data on thermophilic and mesophilic operation with the same feedstock and operating mode. From day 244 onwards M1 and M2 were fed on OFMSW, recycled liquor and tap water at an OLR of 1.0 kg VS m^{-3} day^{-1}. Attempts to increase the OLR after day 385, as in T1 and T2, led to signs of instability. The loading on M1 and M2 thus had to be reduced, then was gradually restored to 1.0 kg VS m^{-3} day^{-1} from day 479 until the end of the experimental period.

Trace element (TE) solutions were added to the digesters on two separate occasions to give the following additional concentrations in the digester (mg L^{-1}): Al 0.1, B 1.0, Co 1.0, Cu 0.1, Fe 5.0, Mn 1.0, Mo 0.2, Ni 1.0, Se 0.2, W 0.2, Zn 0.2 (Banks et al., 2012).

2.3. Analytical methods

Total solids (TS) and VS were measured according to Standard Methods 2540 G (APHA, 2005). pH was determined using a Jenway 3010 m (Bibby Scientific Ltd, UK) calibrated in buffers at pH 4.0, 7.0 and 9.2 (Fisher Scientific, UK). Alkalinity was measured by titration with 0.25 N H_2SO_4 to endpoints of pH 5.75 and 4.3 (Ripley et al., 1986). Total Kjeldahl nitrogen (TKN) and total ammoniacal nitrogen (TAN) were determined using a Kjeltech block digestion and Büchi steam distillation unit according to the manufacturers' instructions (Foss Ltd, Warrington, UK). Crude protein content was calculated by multiplying the difference between TKN and TAN by 6.25 (Hansen et al., 1998). Samples for volatile fatty acid (VFA) analysis were prepared by centrifuging at 13,600*g* for 10 min and acidifying the centrifugate with 10% (v/v) formic acid. VFA in the supernatant was measured by gas chromatography (model GC-2010, Shimazdu, Tokyo, Japan), using a flame ionization detector and an FFAP capillary column (SGE Europe Ltd, UK) with helium as the carrier gas. Biogas composition was analysed using a Varian CP 3800 gas chromatograph with a gas sampling loop, with argon as the carrier gas. The GC was calibrated using a standard gas containing 35% CO_2 and 65% CH_4 (BOC, Guildford, UK). Elemental composition and higher heating values (HHV) were analysed as reported by Yang et al. (2018a, 2018b).

Digestate parameters such as TS, VS, VFA, TAN and alkalinity, as well as biogas composition, were analysed once per week. Gas volumes were measured using a weight-based gasometer and are reported corrected to standard temperature and pressure (STP) of 0 °C, 101.325 kPa as described in Walker et al. (2009).

The theoretical HHV was calculated using the Dulong equation according to IFRF (2017). Theoretical methane potential (TMP) was calculated using the Buswell equation (Symons and Buswell, 1933) and the substrate elemental composition. VS destruction was estimated by assuming the weight of VS destroyed was equal to that of the biogas produced. Total VFA concentrations are expressed in terms of chemical oxygen demand (COD) based on the theoretical COD of individual VFA species measured.

2.4. Modelling

Selected scenarios were modelled using ADAT, a mass and energy balance modelling tool developed with support from various sources including the FP6 CROPGEN project (SES6-CT-2004-502824), RCUK RELU (RES-229-25-0022), FP7 VALORGAS (241334), BBSRC ADNet (BB/L013835/1) and IEA Bioenergy Task 37 (UK), which is freely available for download from http://borrg.soton.ac.uk/resources/adat. The modelling tool calculates the energy requirement for heating of digester inputs, any pre or post-pasteurisation requirements (as specified by the user), and heat losses through the digester floor, walls and roof. It takes into account the efficiency of the CHP, includes estimated parasitic energy demands for mixing and pumping, and allows for fugitive methane losses in the process. It can also include energy requirements for transport and pre and post-processing of feedstock and digestate fractions, energy offset savings from fertiliser substitution and embodied energy in the major plant components, but these were not considered in the current work. The model is written in C# and compiled with a user interface allowing input values to be modified. Default values in the modelling tool were used unless otherwise noted.

3. Results

3.1. Stage 1: Thermophilic co-digestion with SSD

Operating parameters: The applied OLR and HRT over the 235 days of operation during stage 1 are shown in Fig. 1a and b. In general there were no disturbances to the planned operating conditions.

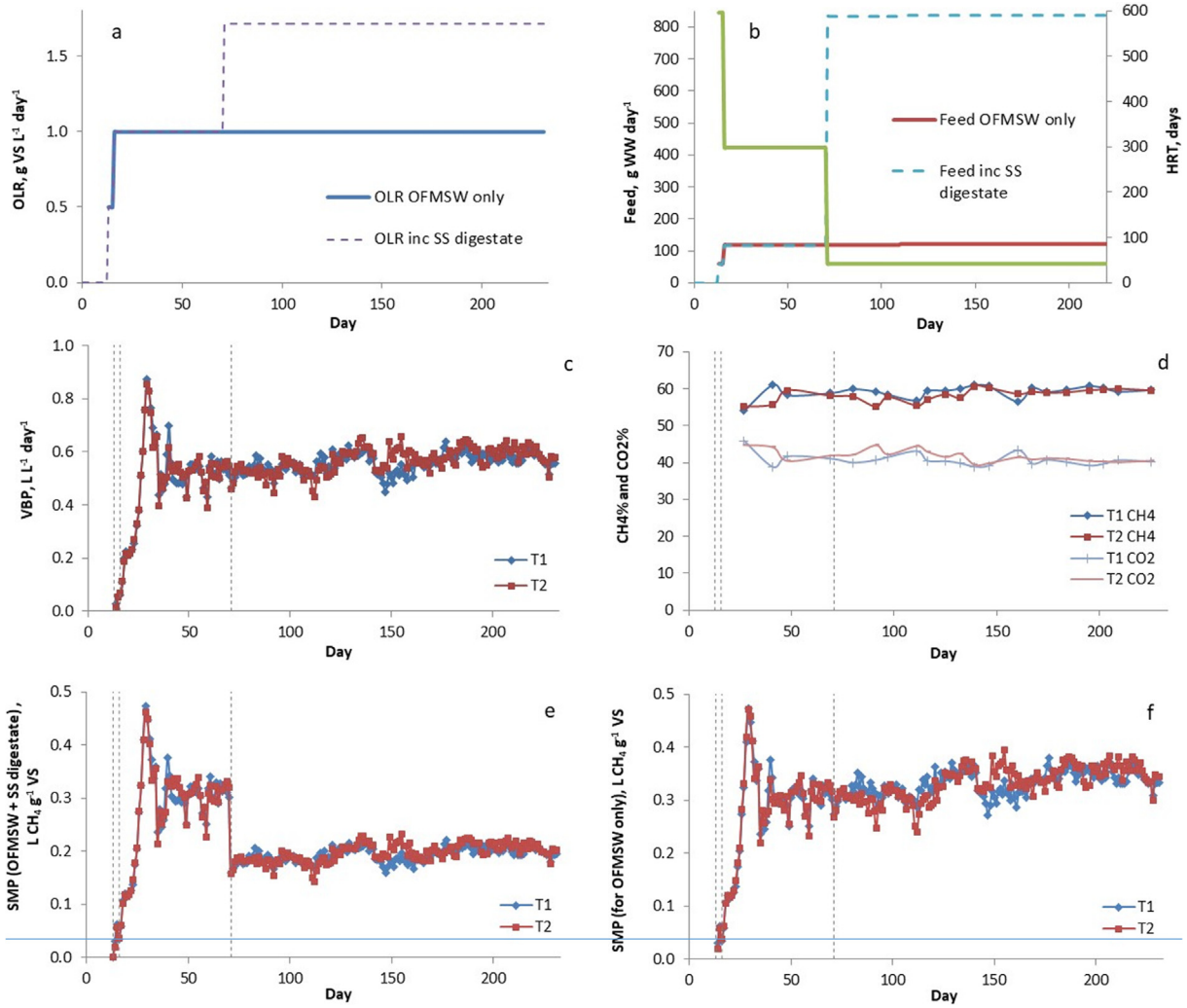

Fig. 1. Organic loading rate (a), daily feed and hydraulic retention time (b), volumetric biogas production (c), biogas composition (d) and specific methane production based on OFMSW and SSD (e) and OFMSW only (f) for T1 and T2 during stage 1. Vertical dotted lines indicate change in OLR on days 13 and 16 and change in operating mode on day 69.

Gas production. Volumetric and specific biogas and methane production and biogas methane content during stage 1 are shown in Fig. 1c–f. Volumetric biogas production (VBP) stabilised at around 0.56 L L^{-1} day^{-1} (Fig. 1c), and gas composition remained steady at around 59% CH_4 (Fig. 1d). Over the first 70 days where there was mono-digestion of OFMSW the specific methane production (SMP) appeared to stabilise at 0.307 m^3 CH_4 kg^{-1} VS. During the period of co-digestion with SSD from day 71 onwards the SMP fell to 0.203 m^3 CH_4 kg^{-1} VS (Fig. 1e), while the total SMP based on the OFMSW input alone (Fig. 1f) showed only a slight increase to 0.345 m^3 CH_4 kg^{-1} VS. This was mainly due to the low SMP of the SSD, although there may also have been some reduction in methane yield due to the shorter SRT and HRT.

Operational stability. pH in digesters T1 and T2 showed a small initial decline as the system acclimated to the change in feedstock followed by the increase in OLR (Fig. 2a). By day 50 the pH had stabilised, however, and remained close to 8.0 for the rest of stage 1, despite the change in operating mode from day 71. TAN concentrations also remained relatively steady at around 2.3 g N kg^{-1} wet weight (WW) (Fig. 2b). This is below the threshold for progressive VFA accumulation in thermophilic conditions, but close to the value where the first signs of mild instability may appear in the form of slightly elevated VFA concentrations (Yirong et al., 2017; Zhang et al., 2017a).

Total alkalinity (TA) in T1 and T2 dropped slightly with the initial change of feedstock, then fell more sharply as a result of the reduction in HRT from day 71 (Fig. 2c). TA and partial alkalinity (PA) decreased to around 13.6 and 9.5 g $CaCO_3$ kg^{-1} WW respectively (Fig. 2d and e): the reduction in intermediate alkalinity (IA) was proportionally less, with the result that the IA/PA ratio in both digesters rose from an initial value of around 0.3 to an average of around 0.4–0.5 (Fig. 2f). The absence of any sudden changes in IA/PA ratio indicates, however, that these were still stable operating conditions for this feedstock (Ripley et al., 1986). Total solids content in T1 and T2 rose after the new feedstock was introduced, then fell from the introduction of solids wasting on day 71, and stabilised at around 6 %WW (Fig. 2g). VS as a proportion of TS rose in the first 70 days (Fig. 2h), reflecting the much lower biodegradability of the OFMSW feedstock compared to the source segregated food waste on which the digesters had previously been fed. By the end of stage 1 VS had stabilised at around 56% of TS, with an estimated overall VS destruction of ~42% based on biogas production.

Fig. 2i and j show the total VFA concentrations in both digesters, and the individual VFA species in digester T2. In both T1 and T2

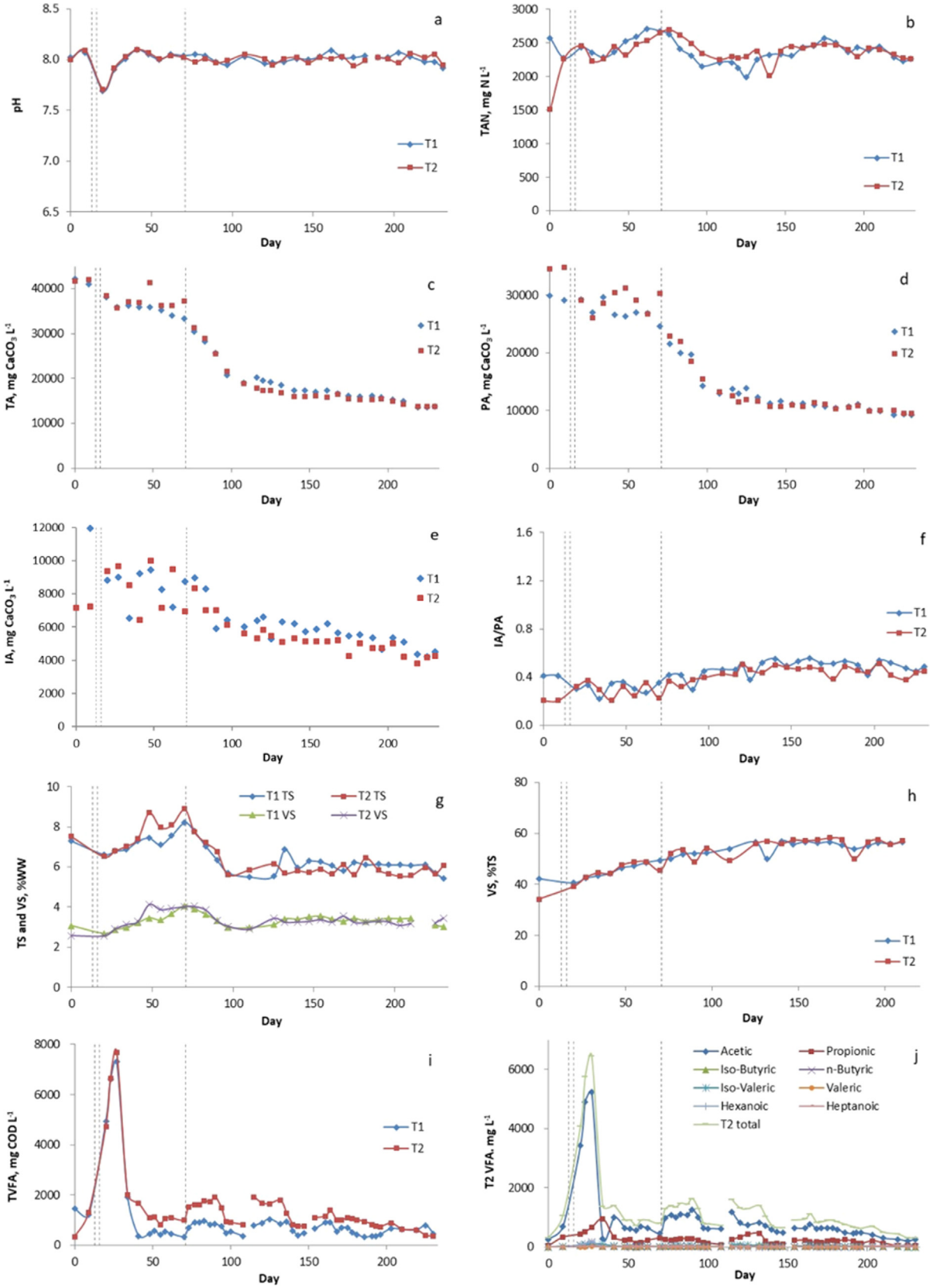

Fig. 2. pH (a), TAN (b), TA (c), PA (d), IA, (e), IA/PA (f), TS and VS (g), VS as %TS (h), total VFA (i) and VFA profile (j) during stage 1. Vertical dotted lines indicate change in OLR on days 13 and 16 and change in operating mode on day 69.

there was a brief peak in VFA associated with the initial change in feedstock, which reached around 6.5 g COD L^{-1} and consisted mainly of acetic acid. This fell rapidly and for the rest of stage 1 VFA in T1 remained below 1 g COD L^{-1}, though with continuing small fluctuations. VFA concentrations in T2 were slightly higher than in T1 and included 0.1–0.2 g L^{-1} of propionic acid. A one-off dose of TE solution was added to both digesters on day 80, but did not appear to have any immediate effect, and minor fluctuations in VFA continued. Total VFA in T2 started to fall from around day 175 and stabilised at below 1 g COD L^{-1} by the end of stage 1 (Fig. 2j). This small difference between the digesters was also reflected in the TAN and TA concentrations and the IA/PA ratio, which were slightly higher in T2 than T1 for most of this period.

Average values for gas production and stability parameters over the last 20 days of stage 1, after 3.9 HRT and 7.8 SRT in the same operating mode, are shown in Table 2 below.

3.2. Stage 2: Thermophilic and mesophilic digestion without SSD addition

Operating parameters: Fig. 3a and b show the OLR and HRT applied during stage 2. For the thermophilic digesters there were no disturbances to the planned conditions, apart from an accidental spill of around 3 kg of digestate from T1 on day 447. Over the next 8 days the daily OFMSW feed to T1 was reduced slightly in order to maintain an approximately constant OLR, and digestate removal was decreased until the digester reached its previous working volume, leading to a small temporary increase in HRT.

Feeding of the mesophilic digesters was adjusted in response to changes in the monitoring parameter values. Feeding of M1 followed the same pattern as in the thermophilic digesters until day 389, shortly after the start of the incremental rise in OLR. Feeding of M1 was stopped for 3 days, then an attempt was made to resume the OLR increase, but this was abandoned on day 398. M1 was left without feeding for 8 days, then the OLR was gradually stepped up between days 407–479 when it reached the previous value of 1 g VS L^{-1} day. M2 showed earlier and more severe signs of stress than M1, and reduced or intermittent feeding began on day 364 after 3 HRT under the new operating conditions. An attempt was made to increase the OLR in parallel with the other digesters between days 385–398, but this was abandoned and M2 was left without feeding for 11 days before the same stepped return to OLR 1 g VS L^{-1} day was applied as in M1. These changes in OLR were reflected in the HRT, which rose to infinity in the periods without feeding (Fig. 3b).

Gas production. VBP, SMP and biogas methane content during stage 2 are shown in Fig. 3c–e. In T1 and T2 following the switch from SSD to water addition the VBP fell, but stabilised after 5 days and reached an average of 0.490 L L^{-1} day^{-1} in the last 20 days before the OLR was increased from 1 to 2 g VS L^{-1} day^{-1}. VBP then increased in parallel with the rise in OLR between day 385–394. There was a small fall in VBP around day 450 for T1 and day 462 for T2: the reason for the former is unknown, while the latter was due to the reduction in feed associated with the digestate spill. Apart from day-to-day fluctuations VBP in T1 and T2 then remained stable, reaching an average of 0.999 L L^{-1} day^{-1} at the end of the experimental period. Gas composition in T1 and T2 remained steady at around 59% CH_4 (Fig. 3d). SMP was closely similar in both digesters and averaged 0.290 L CH_4 g^{-1} VS in the last 20 days before the OLR increase, and 0.296 L CH_4 g^{-1} VS at the end of the run at OLR 2 g VS L^{-1} day^{-1}.

VBP in the mesophilic digesters at OLR 1 g VS L^{-1} day^{-1} was slightly lower than in the thermophilic (Fig. 3c), with an average value of 0.452 L L^{-1} day^{-1} between day 343–362. From day 363 the OLR on M2 was reduced, with a corresponding fall in VBP, while M1 showed a slight downward trend in VBP despite the constant OLR. Subsequent variations in VBP reflected the applied loading rates, with VBP finally recovering to around its previous value once the OLR was restored to 1 g VS L^{-1} day^{-1}. Gas composition was relatively stable apart from a dip in CH_4 content around day 370 for M2 and a peak around day 407 in both M1 and M2 (Fig. 3d). SMP averaged 0.267 L CH_4 g^{-1} VS for the two digesters between day 344–363 and 0.263 L CH_4 g^{-1} VS in the last 20 days of the run.

Operational stability. Fig. 4 presents the values for monitoring parameters during stage 2. TAN concentrations in both sets of digesters initially fell as ammonia from the inoculum in M1 and M2 and from the SSD addition in T1 and T2 was progressively

Table 2
Average steady-state values for digestion monitoring parameters.

	Unit	TH1 + SS[a,b]	TH1[a,c]	TH2[a,d]	ME1[c,e]	ME1[a,d,f]
Temp	°C	55	55	55	37	37
MSW	kg VS m^{-3} day^{-1}	1.0	1.0	2.0	1.0	1.0
SS dig	kg VS m^{-3} day^{-1}	0.7	0.0	0.0	0.0	0.0
VBP	L L^{-1} day^{-1}	0.583 ± 0.005	0.490 ± 0.003	0.999 ± 0.000	0.432	0.457 ± 0.007
CH4	% vol	59.3 ± 0.2	59.3 ± 0.3	59.3 ± 0.0	59.2	59.1 ± 0.1
SMP	L CH_4 g^{-1} VS	0.203 ± 0.002[g]	0.290 ± 0.000	0.296 ± 0.000	0.256	0.263 ± 0.002
pH	–	7.98 ± 0.02	7.44 ± 0.01	7.57 ± 0.01	7.04	6.94 ± 0.00
TA	g $CaCO_3$ L^{-1}	13.9 ± 0.0	3.8 ± 0.0	8.2 ± 0.04	3.6	2.9 ± 0.2
PA	g $CaCO_3$ L^{-1}	9.6 ± 0.2	2.8 ± 0.0	5.1 ± 0.5	2.6	1.5 ± 0.0
IA	g $CaCO_3$ L^{-1}	4.3 ± 0.2	1.0 ± 0.0	3.0 ± 0.1	1.1	1.4 ± 0.2
IA/PA	–	2.8 ± 0.0	0.4 ± 0.0	0.4 ± 0.0	0.4	0.9 ± 0.1
TAN	g N kg^{-1} WW	2.27 ± 0.0	0.42 ± 0.0	0.75 ± 0.0	0.29	0.19 ± 0.0
VFA	mg COD L^{-1}	532 ± 82	20 ± 0.3	21 ± 0.8	92	22 ± 0.3
TS	%WW	5.8 ± 0.1	2.1 ± 0.1	4.3 ± 0.0	2.2	2.2 ± 0.0
VS	%WW	3.2 ± 0.1	1.2 ± 0.1	2.2 ± 0.0	1.3	1.3 ± 0.0
VS	%TS	55.8 ± 0.9	57.9 ± 0.7	52.4 ± 0.6	59.7	57.7 ± 1.9
VS destruction[g]	%VS	42%	60%	61%	53%	56%

[a] Values shown as ± are range of averages for 2 digesters.
[b] Average day 215–234, i.e. end stage 1.
[c] Average day 365–384, i.e. before OLR step.
[d] Average day 505–524, i.e. end stage 2.
[e] Values for M1 only.
[f] Not full steady state, <3 HRT at OLR 1 g VS L^{-1} day^{-1}.
[g] Based on combined organic load.
[h] Based on gas production.

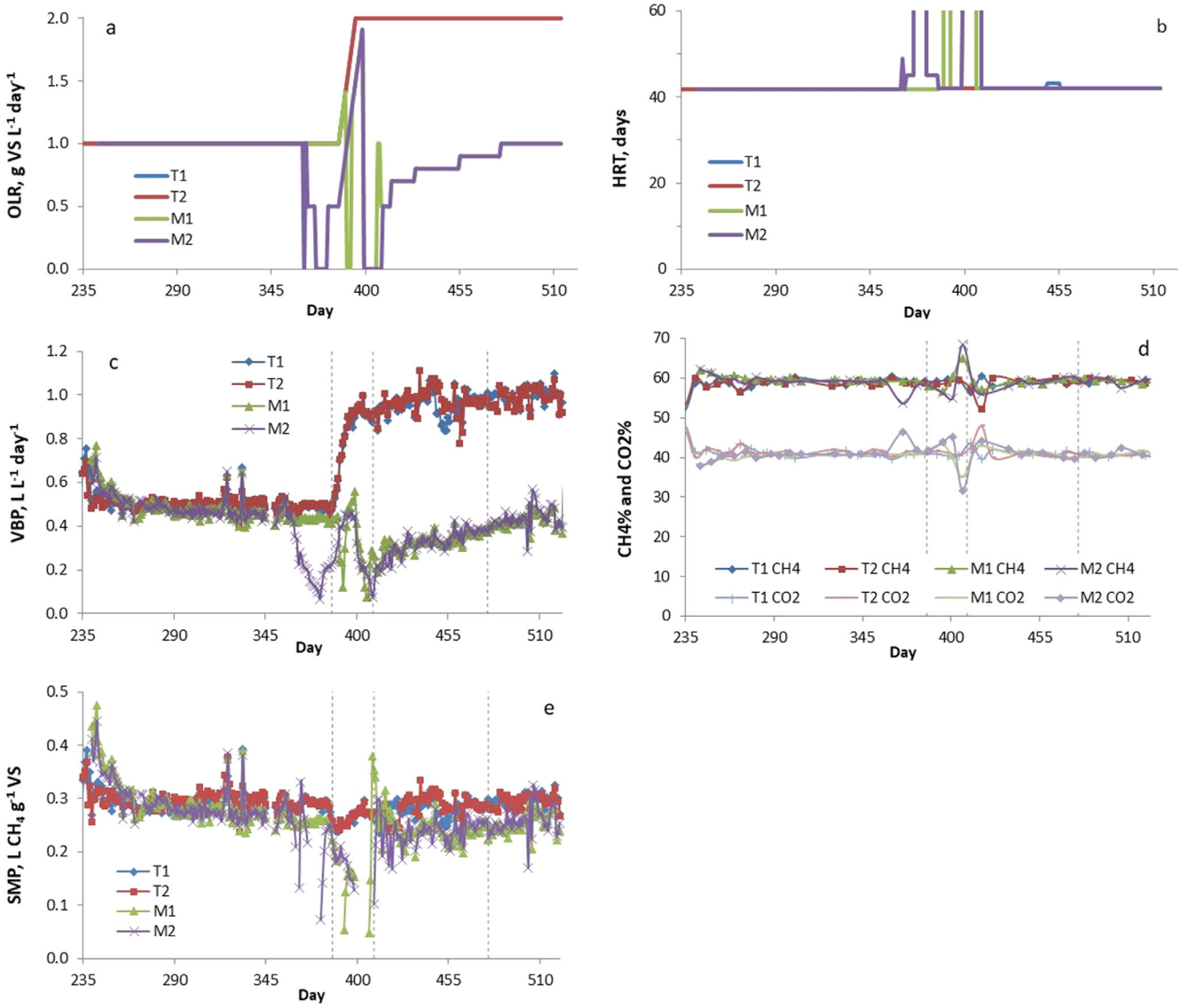

Fig. 3. OLR (a), HRT (b) VBP (c), biogas composition (d) and SMP (e) in stage 2 for all digesters. Vertical dotted lines indicate changes in OLR as shown in Table 1.

washed out (Fig. 4a). After 3 HRT under the new operating conditions, TAN had stabilised and was slightly higher in the thermophilic digesters at an average of 0.42 g N kg^{-1} WW for day 365–384 than in M1 at 0.29 g N kg^{-1} WW. Feeding of M2 had altered after day 363 due to signs of instability, but until then it showed a closely similar trend to M1, while the slight increase in TAN in M2 after day 363 may indicate some associated biomass die-off and lysis.

TA and PA values mirrored the fall in TAN (Fig. 4b–d), with the TA stabilising at around 3.8 and 3.6 and PA at 2.8 and 2.3 g $CaCO_3$ kg^{-1} WW in the thermophilic and mesophilic digesters respectively. After some minor fluctuations the IA/PA ratio settled at around 0.3–0.4 in all digesters (Fig. 4e). The pH in both sets of digesters also gradually fell in response to the changing TAN, but from different start points and to different degrees (Fig. 4f). In T1 and T2 the initial pH was just below 8.0, reflecting the higher initial TAN content of around 2.2 g N kg^{-1} WW. After 3 HRT, this appeared to be stabilising at pH 7.4. The initial pH in M1 and M2 was around 7.4 with a TAN content of 1.8 g N kg^{-1} WW and this stabilised at just above 7.0.

The main difference in digester operational stability parameters was in the VFA concentrations. T1 and T2 showed initial peaks in total VFA of up to 1.3 g COD L^{-1} immediately after the cessation of SSD addition. These declined to <0.1 g COD L^{-1} by day 300 and remained very low throughout the rest of the trial, apart from a brief increase around day 363. These initial peaks were primarily acetic acid but also contained up to 0.5 g COD L^{-1} of propionic acid and small amounts of longer chain VFA. In contrast the mesophilic digesters had total VFA of <0.1 g COD L^{-1} until day 363 when concentrations rose, especially in M2. It was thought this could be caused by washout of essential TE after 3 HRT; and as a precautionary measure on day 368 all four digesters were given a one-off dose of TE solution as described above. Total VFA concentrations in M2 fell to <0.1 g COD L^{-1} by day 377 and values in the other digesters reduced even further. The attempt at raising the OLR in M1 and M2 led to another increase in VFA concentrations, however, reaching 1.5 g COD L^{-1} in M2 and consisting almost entirely of acetic acid. VFA concentrations finally stabilised at very low levels after day 475 once the OLR was returned to 1 g VS L^{-1} day^{-1}. Although the trial continued for a further 3.8 HRT after the one-off TE dosing

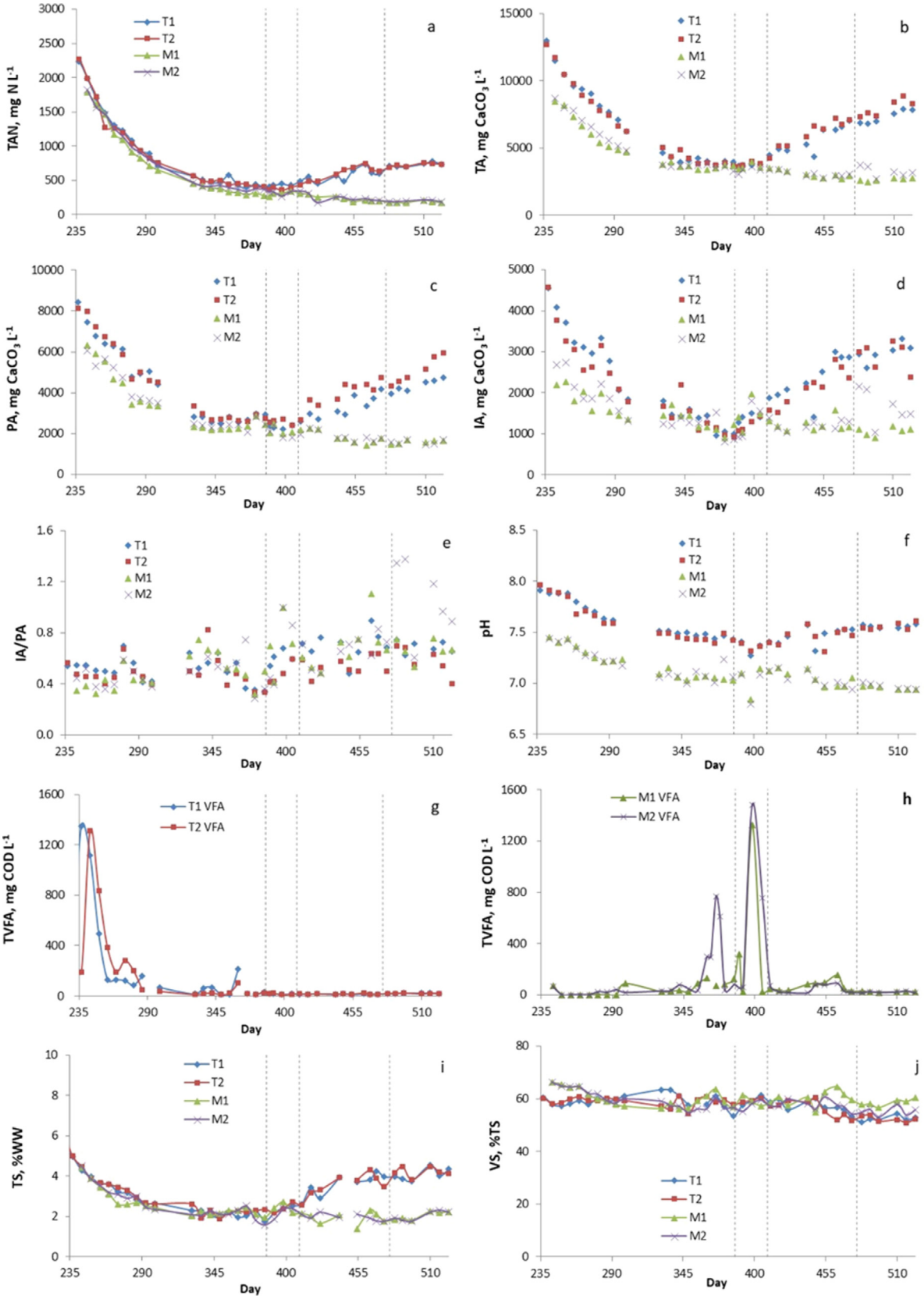

Fig. 4. TAN (a), TA (b), PA (c), IA (d), IA/PA (e), pH (f), VFA (g and h), TS (i) and VS as %TS (j) for all digesters during stage 2. Vertical dotted lines indicate changes in OLR as shown in Table 1.

there were no further TE additions and no sign of reappearance of VFA.

TS in both sets of digesters fell from the start of stage 2 (Fig. 4g), stabilising at around 2.1% in T1 and T2 and 2.2% in M1 and M2 after 3 HRT, with VS/TS ratios of 57.9 and 59.7% respectively. After the increase in OLR in T1 and T2 there was a clear rise in TS content but a decline in VS/TS ratio to around 52%. Estimated VS destructions based on gas production were around 60% for the thermophilic digesters and 53% for mesophilic.

Table 2 shows average values for gas production and operational stability parameters over the last 20 days before the OLR increase from 1 to 2 g VS L^{-1} day^{-1}, and before the end of the experimental period. These periods correspond to 3.5 HRT and 7.0 SRT and to 3.1 HRT and 6.2 SRT respectively in each operating mode.

3.3. Energy and performance considerations

Characteristics for Batch 1 of the feedstock shown in Table 3, with typical values for mechanically-sorted OFMSW from a 'medium complex' plant (Cecchi et al., 2003) and those previously reported for waste from the same source (Zhang et al., 2012). The TS and VS values given in Table 3 are the average from the experimental period, with a relative standard deviation of approximately 5% in each case.

Table 3 also shows the calculated TMP and theoretical and measured HHV values for the OFMSW feedstock based on elemental composition, with values from Zhang et al. (2012) for comparison. Measured and theoretical HHV show good agreement, providing support for the elemental analysis results. The biogas methane content of 60.0% predicted by the Buswell equation is close to the observed average value of around 59.3%. The SMP of 0.290 L CH_4 g^{-1} VS achieved in thermophilic operation at OLR 1 g VS L^{-1} day^{-1} represents conversion of 42% of the TMP and 38% of the measured HHV. Equivalent conversion values for the SMP of 0.256 L CH_4 g^{-1} VS in mesophilic conditions are 37% and 34%. The methane yield of the OFMSW on a wet weight basis was 86 and 77 m^3 CH_4 $tonne^{-1}$ in thermophilic and mesophilic conditions respectively.

Zhang et al. (2012) reported a lower TMP and HHV, a higher mesophilic SMP of 0.304 L CH_4 g^{-1} VS, and thus higher conversion rates of 55% TMP and 55% HHV for material from the same plant. There were no known changes in on-site processing between the two trials; but Zhang et al. (2012) included an additional in-house pre-processing step in which small pieces of plastic and glass were manually picked out before feeding to the digesters. In addition to natural variation between batches and over time, this may account for the lower VS content and VS/TS ratio in the current feedstock (Table 3). Removal of small fragments of plastic will lead to an apparent increase in biogas and methane yield on a VS basis, which may partially account for the slightly higher SMP. On the other hand removal of plastics will reduce the measured and theoretical TMP and HHV, and may account for the lower values of these parameters compared to the current feedstock. Removal of inert materials (glass and metal fragments) will also slightly increase the SMP on a TS basis; while removal of both inerts and plastics may increase or reduce the HHW on a TS basis depending on the relative proportions removed. It is likely that at least part of the difference in conversion is due to the additional pre-processing by Zhang et al. (2012). Specific methane production on a wet weight basis was 20% lower in the current study, suggesting that there may have been some reduction in feedstock VS content and biodegradability between the two trials, perhaps due to increasing popularity of source separated collections for domestic food waste. This is also supported by the differences in measured and predicted biogas methane content in each case. The SRT of 21 days used in the current study was shorter than the 30 days in Zhang et al. (2012), and this may also have accounted for some of the difference. Zhang et al. (2012) measured the BMP of the feedstock at inoculum-to-substrate (i/s) ratios of 2:1 and 4:1 on a VS basis. At i/s 2:1 the methane production at 21 days was only 73% of the value at 28 days and 69% of the final BMP value, but at 4:1 it was respectively 97% and 95%.

Table 3
Physico-chemical characteristics and energy values for ms-OFMSW substrate.

Parameter	Units	This study	Zhang et al. (2012)[a]	Cecchi et al. (2003)[b]
Characteristics				
Total solids (TS)	g TS kg^{-1} wet weight (WW)	536	528	~540
Volatile solids (VS)	g VS kg^{-1} WW	296	336	~270
	% TS	55.1	63.5	47
Total Kjeldahl Nitrogen (TKN)	g N kg^{-1} WW	7.3	7.3	~6
C	%TS	28.8[c]	33.0	–
H	%TS	4.7[c]	3.8	–
N	%TS	1.4[c]	1.3	–
S	%TS	0.2[c]	0.3	–
O	%TS	16.1[c]	24.2	–
Measured HHV	MJ kg^{-1} TS	15.4[c]	13.9	–
Energy values				
TMP[d]	L CH_4 g^{-1} VS	0.684	0.548	–
Calculated biogas composition[d]	%CH_4	60.0	56.6	–
HHV of CH_4 in TMP[d]	MJ kg^{-1} TS	15.7	13.9	–
Theoretical HHV[d]	MJ kg^{-1} TS	15.3	13.9	–
Measured HHV	MJ kg^{-1} TS	15.4	13.9	–
Thermo SMP	L CH_4 g^{-1} VS	0.290	–	–
	% TMP	42%	–	–
	% measured HHV	38%	–	–
	m^3 CH_4 $tonne^{-1}$ WW	86	–	–
Meso SMP	L CH_4 g^{-1} VS	0.256	0.304	–
	% TMP	37%	55%	–
	% measured HHV	34%	55%	–
	m^3 CH_4 $tonne^{-1}$ WW	77	102	–

[a] Zhang et al. (2012).
[b] Cecchi et al. (2003).
[c] Analysed by Yang et al. (2018a, 2018b).
[d] Calculated from elemental composition

In the current trial the SMP in thermophilic conditions was higher than in mesophilic (0.290 and 0.256 L CH_4 g^{-1} VS respectively at OLR 1 g VS L^{-1} day^{-1}). It is often stated that thermophilic digestion can give higher gas production, especially for feedstocks with relatively high lignocellulosic content. In some cases this is simply an assertion without supporting data, while in others insufficient detail is given on how or whether gas volumes have been normalised to STP: measurement at 35 or 55 °C gives a 6% difference in gas volume. In some technical trials where appropriate datasets are provided, significant improvements have been demonstrated (Cecchi et al., 1991; Fernández-Rodríguez et al., 2013). In the current work there is reasonable confidence in the data, as the gas counters used were calibrated approximately weekly against the collected volume of gas at a measured room temperature and pressure. Moisture content can also account for 5–6% of gas volume at 35 °C and 15–16% at 55 °C; but in the method used any associated errors should be small as the gas bags were allowed to equilibrate to room temperature before measurement. It is therefore likely that there was a real difference in SMP at the two temperatures: while the nature of the digested material makes it difficult to obtain very accurate and consistent VS concentrations, a small difference in the VS/TS ratios (Table 2) may also support this. To further reduce small day-to-day differences in gas volume measurement, such as those seen on days 322 and 331, direct correction of gas counter data by continuous logging of ambient temperature and pressure would be beneficial.

The SMP in thermophilic conditions at OLR 2 g VS L^{-1} day^{-1} was closely similar to that at 1 g VS L^{-1} day^{-1}, at 0.296 and 0.290 L CH_4 g^{-1} VS respectively, indicating that the thermophilic digesters operated well at the lower OLR despite the lower TAN and alkalinity (Table 2). In mesophilic conditions, however, there were signs of reduced stability at the lower OLR, with IA/PA ratios of around 1 by the end of the experimental period (Table 2), and the appearance of VFA during periods of moderate loading increase (Fig. 4h). This was probably linked to the low TAN concentration and associated reduction in buffering capacity in the mesophilic digesters (Fig. 4a). The low TAN may possibly indicate a slightly lower degree of hydrolysis in mesophilic conditions. TAN concentrations in the thermophilic digesters rose from 0.42 to 0.75 g N kg^{-1} WW when the OLR was raised from 1 to 2 g VS L^{-1} day^{-1}, with the resultant increases in pH, TA and IA/PA ratio all suggesting improved operational stability. Zhang et al. (2012) reported stable operation at a TAN concentration of 1.4 g N kg^{-1} WW with total VFA concentrations <0.1 g L^{-1} and a pH of 7.5 in mesophilic conditions. The higher TAN concentration is due to the higher OLR of 2 g VS L^{-1} day^{-1} but also to recycling of digestate liquor only, unlike the current trial where a proportion of water was added to simulate the operation of a number of full-scale UK AD plants working on this type of feedstock. Where digester TAN concentrations are low in this mode of operation, for example due to a reduction in OLR, increasing the digestate recycle and reducing water input may offer a simple means of improving stability and performance.

At an OFMSW OLR of 1 g VS L^{-1} day^{-1}, the addition of SSD reduced the SMP but gave a higher VBP (Table 2). If it is assumed that the SMP of the OFMSW fraction at this OLR was constant with or without SSD, the estimated SMP of the SSD is around 0.078 L CH_4 g^{-1} VS. This is slightly higher than the value of 0.04–0.06 L CH_4 g^{-1} VS typically found for this digestate when used as inoculum in long-term mesophilic BMP tests (unpublished data, University of Southampton), indicating that some additional hydrolysis may be occurring at the higher temperature. Alternatively the increased buffering capacity and addition of inoculum and trace elements in the SSD may lead to a slight increase in the OFMSW SMP; in either case, the overall methane productivity of the system is increased. The proportion of SSD added was sufficient to maintain the TAN concentration just below that associated with the onset of instability in thermophilic conditions. SSD addition might also have been beneficial to stability in mesophilic digestion, especially at the lower OLR, but this was not tested in the current work.

3.4. Modelling

The scenarios considered were those tested in the laboratory trials, i.e. thermophilic operation at OLR 1 kg VS m^{-3} day^{-1} with and without SSD addition (TH1 and TH1 + SSD), thermophilic operation at OLR 2 kg VS m^{-3} day^{-1} without SSD addition (TH2), and mesophilic operation at OLR 1 kg VS m^{-3} day^{-1} without SSD addition (ME1). User-defined feedstock properties were based on average properties for the OFMSW used (Table 3) and on steady state gas production and composition data in Table 2. Feedstock parasitic energy demand was taken as 40 and 10 kWh $tonne^{-1}$ for OFMSW and SSD respectively, based on the model's default values for mechanically-recovered biodegradable municipal waste and sewage sludge, respectively.

The working volume of the digester was set at 3439 m^3 to give an OLR of 2 kg VS m^{-3} day^{-1} for an assumed OFMSW input of 8500 tonnes WW $year^{-1}$. Digester construction was taken as a steel tank with 75 mm of high performance insulation (typical U-value 0.0245 W m^{-1} K^{-1}, giving a composite heat transfer coefficient of 0.35 W m^{-2} K^{-1}), with gas stored in a separate gas holder. Digestion temperatures were set at 55 °C for thermophilic operation and 37 °C for mesophilic, with ambient conditions based on Southampton, UK (annual average air and soil temperatures 10.6 °C). In thermophilic conditions no separate pasteurisation step was included, since compliance with the Animal By-product Regulations (EC 1069/2009) may be achieved by providing a guaranteed HRT, e.g. through intermittent feeding and discharge. In mesophilic conditions pre-pasteurisation of the OFMSW at 70 °C for one hour was specified; based on earlier work this was assumed not to affect the methane yield of the OFMSW (Banks and Zhang, 2010). It was assumed that the biogas produced was used on site in a CHP plant with an electrical conversion efficiency of 38% and heat recovery of 47% of input biogas energy. Fugitive emissions were set at 0.5%.

Table 4 shows the output from the modelling. Total biogas and methane production are determined by the experimental SMP values: as expected, total energy output followed the same sequence, being highest for TH2, TH1 + SSD, TH1 then ME1. All scenarios show a positive energy balance, even when waste input is halved in this operating mode.

The heat demand of the AD process is the same for all three thermophilic scenarios, but considerably higher for the ME1 scenario, due to the requirement for pre-pasteurisation. The relative proportions of the raw biogas energy required for heating thus show a wide range, from 3.6% for TH2 to 13.7% for ME1. Very small differences in the AD plant parasitic electricity demand are due to the degree of solids breakdown in each scenario. The model calculates the VS destruction based on biogas production and adjusts the amount of digestate accordingly; since the energy demand for centrifugation is based on the tonnage of digestate, this leads to a small reduction in scenarios with higher biogas yield.

Reducing the OLR from 2 to 1 kg VS m^{-3} day^{-1} halves the required CHP generation capacity, but adding SSD recovers some of this. For larger AD plants with multiple digesters and CHP generators the simplest response to a major fall in feedstock tonnages is to close one or more units down: but where there is a single line this option may not be practicable. The experimental and modelling results both suggest that under thermophilic conditions the plant could still operate with a positive energy balance at a substantially reduced loading; although this may not be economically attractive, particularly if a proportion of the income stream is obtained from gate fees. The results show clearly that the worst option would be to drop the operating temperature of the digester

Table 4
Modelling results.

	Unit	TH2	TH1	TH1 + SSD	ME1
Temperature	oC	55	55	55	37
OFMSW input	tonnes $year^{-1}$	8500	4250	4250	4250
Water input	tonnes $year^{-1}$	21,415	25,665	0	25,665
SSD input	tonnes $year^{-1}$	0	0	25,665	0
Total digester Input	tonnes $year^{-1}$	29,915	29,915	29,915	29,915
OLR	kg m^{-3} day^{-1}	2.0	1.0	1.7	1.0
Methane produced	m^3 $year^{-1}$	728,003	364,002	432,065	330,292
	m^3 $tonne^{-1}$ OFMSW	86	86	102	77
VS destroyed	tonnes $year^{-1}$	1516	758	900	688
Digestate for disposal	tonnes $year^{-1}$	28,399	29,157	29,015	29,227
Required CHP electrical capacity	kW	330	165	196	150
Parasitic heat demand	GJ $year^{-1}$	949	949	949	1629
Parasitic electricity demand	GJ $year^{-1}$	3450	3001	2999	3002
Electricity for export	GJ $year^{-1}$	6410	1929	2852	1471
Heat for export	GJ $year^{-1}$	11,246	5148	6288	3904
Total energy for export	GJ $year^{-1}$	17,655	7077	9141	5375
	GJ $tonne^{-1}$ OFMSW	2.1	1.7	2.2	1.3

as this would reduce the biogas yield, and make the plant more susceptible to pH fluctuations as a result of loss of buffering capacity and a tendency for VFA accumulation in response to load variations. The scenario of mesophilic co-digestion with SSD was not tested experimentally, but could provide a solution for instability resulting from the loss of buffering, although the additional biogas production in mesophilic conditions is likely to be lower. Addition of SSD in thermophilic conditions gives a 48% increase in electricity available for export and a 22% increase in heat compared to the equivalent output for water addition.

The results for the scenarios tested were as expected, confirming the accuracy of the modelling with respect to the growing knowledge base gained from operation of OFMSW digesters over a number of years. The model does, however, provide a flexible tool for testing different scenarios at scale and can be used both to provide baseline values for comparison with alternative process options; and to assess the potential for integration of AD with other emerging waste management options and technologies. An example where further process integration could be applied is in the use of waste heat in drying OFMSW as pyrolysis feedstock. The model cannot, however, predict some of the unforeseen outcomes of such integration: as noted by Yang et al. (2018a, 2018b) the pyrolysis of OFMSW at higher feedstock solids concentrations is associated with greater toxicity of the aqueous fraction when used as an AD feedstock.

One potential benefit of using co-digestates such as SSD is the increased nutrient content and fertiliser value of the resulting digestate. In countries such as the UK, where digestate from municipal solid waste (MSW) can still be applied to industrial crops, the enhanced nitrogen content from the addition of SSD could in theory be beneficial. This route, however, is very likely to be closed off in the near future due to growing environmental concerns over issues such as microplastics, endocrine disrupters and other priority pollutants; in many countries land application of this material is already specifically prohibited. Thermal processing of the digestate is therefore the most likely option for final disposal of residues from MSW digestion in future. Where SSD and residual OFMSW both contain heavy metals and other contaminants making them unsuitable for land application, the case for co-digestion is potentially attractive, as the increase in total energy output from the CHP plant can provide a heat source for pre-drying the centrifugate solids. This would reduce the energy input required for incineration or gasification of digestate from these mixed contaminated sources. The model allows inclusion of a value for post-processing energy per tonne of digestate, and this could be explored further using experimental data from dewatering; but this was not included in the current work.

4. Conclusions

Thermophilic CSTR digesters fed on mechanically-separated OFMSW at a moderate OLR of 2 kg VS m^{-3} day^{-1} and operated to simulate a full-scale plant with combined digestate recycling and water addition showed stable operation with a specific methane production of 0.296 m^3 CH_4 kg^{-1} VS, equivalent to 87 m^3 CH_4 per tonne of waste input. VS destruction was estimated at 82% based on the weight of biogas produced. Operating in the same mode but at a lower OLR of 1 kg VS m^{-3} day^{-1} and constant HRT had no adverse effect on performance, with specific methane production of 0.290 m^3 CH_4 kg^{-1} VS (86 m^3 CH_4 $tonne^{-1}$ OFMSW). Under mesophilic conditions at OLR 1 kg VS m^{-3} day^{-1} with the same operating mode, however, the specific methane yield was lower at 0.256 m^3 CH_4 kg^{-1} VS (77 m^3 CH_4 $tonne^{-1}$ OFMSW); and signs of reduced operational stability were seen especially when at incremental increases in OLR were attempted. This was probably due to the low TAN concentrations, which stabilised at around 0.2 g N kg^{-1} WW and led to limited digester buffering capacity. In practice if the OLR in such a plant is to be reduced steps should be taken to maintain TAN and buffering capacity, e.g. by reducing water addition and allowing an increase in HRT.

When the water was replaced by addition of municipal wastewater biosolids digestate (SSD) at OLR 1 kg VS m^{-3} day^{-1} in thermophilic conditions, volumetric biogas and methane yields increased by around 20%. This may have been due in part to the addition of supplementary inoculum and trace elements, but a more likely explanation is the further hydrolysis and degradation of the mesophilically-digested biosolids. Modelling indicated that addition of SSD in thermophilic conditions gave a 48% increase in electricity available for export (from 0.45 to 0.67 GJ $tonne^{-1}$ OFMSW) and a 22% increase in heat (from 1.21 to 1.48 GJ $tonne^{-1}$ OFMSW) compared to the equivalent output for water addition.

If transport and handling costs permit, addition of SSD may be an alternative to fresh water inputs, but it is important to maintain the digester TAN concentration below the threshold value of around 2.5 g N kg^{-1} WW of digestate to avoid the onset of inhibition and intermittent or progressive VFA accumulation.

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Data accessibility statement

The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

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