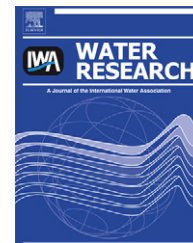


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Fat, oil and grease deposits in sewers: Characterisation of deposits and formation mechanisms

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ABSTRACT

Fat, oil and grease deposits (FOG) in sewers are a major problem and can cause sewer overflows, resulting in environmental damage and health risks. Often simplistically portrayed as cooling of fats, recent research has suggested that saponification may be involved in FOG formation. However there are still questions about the mechanisms effecting transformations in sewers and the role and source of metal cations involved in saponification. This study characterises FOG deposits from pumping stations, sewers and sewage works from different water hardness zones across the UK. The sites all had previous problems with FOG and most catchments contained catering and food preparation establishments.

The FOG deposits were highly variable with moisture content ranging from 15 to 95% and oil content from 0 to 548 mg/g. Generally the pumping stations had lower moisture content and higher fat content, followed by the sewers then the sewage works. The water in contact with the FOG had high levels of oil (mean of about 800 mg/L) and this may indicate poor kitchen FOG management practices. FOG fatty acid profiles showed a transformation from unsaturated to saturated forms compared to typical cooking oils. This seems to relate to ageing in the sewer network or the mechanism of formation, as samples from pumping stations had higher proportions of C18:1 compared to C16. This may be due to microbial transformations by bacteria such as *Clostridium* sp. in a similar process to adipocere formation. There was an association between water hardness and increased Ca levels in FOG along with harder deposits and higher melting points. A link between FOG properties and water hardness has not been previously reported for field samples. This may also be due to microbial processes, such as biocalcification.

By developing the understanding of these mechanisms it may be possible to more effectively control FOG deposits, especially when combined with promotion of behavioural change.

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1. Introduction

Fat, oil and grease (collectively termed FOG) deposits in sewers are a major problem for large cities in developed regions. Per

capita FOG consumption in many developed countries is over 50 kg/a compared to less than 20 kg/a in most less developed countries. However as urbanisation and affluence increase, people tend move to western diets increasing FOG

Abbreviations: FOG, fat, oil and grease; N, number of samples; SEM, standard error of the mean; SEW, sewer; STW, sewage treatment works; PS, pumping station; MC, moisture content; MP, melting point; VS, volatile solids.

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consumption (Popkin, 1999) and as a consequence global per capita consumption rose from 26 kg/a in 1999 to 30 kg/a in 2007 (FAO, 2010). FOG deposits are therefore becoming a global challenge for sanitation development schemes.

FOG deposits impact on health and the environment. They reduce sewer diameters and can completely block pipes (Ashley et al., 2000) causing flooding or sewer overflows, especially in combined systems. In the UK over 25,000 flooding events per annum are due to sewer blockages (Scott et al., 2008). FOG is thought to contribute to over 50% of such incidents (Keener et al., 2008). The subsequent release of sewage increases water pollution and exposure to pathogens (Bridges, 2003). FOG also attracts vermin, such as rats, and sloughed deposits can affect the operation of pumping stations and sewage treatment works. One unsavoury health risk is illegally recycled “gutter oil” in China where 10% of meals are estimated to be cooked with FOG from sewers (Jinfu and Gaoming, 2011; Moore, 2010).

Despite public information campaigns, significant quantities of FOG enter sewers from kitchen practices or poorly maintained oil interceptors. As a consequence, UK water companies spend an estimated £15 m to £50 m per annum controlling FOG (CIEH, 2007), often by jetting or manual removal. Although the discharge of “any matter likely to injure the sewer or drain, (or) to interfere with the free flow of its contents” is against UK law (UK Govt., 1991) it is difficult to identify sources of FOG and prosecute offenders. There is much speculation in the water industry about the causes and perpetrators of FOG. Studies indicate the worst problems are associated with fast food establishments (Chu and Hsu, 1999) or industrial food production (Cammarota and Freire, 2006).

Oils and fats are mainly composed of triglycerides, which are esters of glycerol (a trihydric alcohol) and fatty acids. Solid fat sales have declined significantly over the last decade and over 95% of cooking oil sold in the UK is in liquid form, predominantly vegetable, sunflower and olive oil (Mintel, 2011). The percentage fatty acid profiles by mass of common cooking fats and oils are shown in Table 1.

The FOG problem is simplistically portrayed as the cooling and solidification of FOG poured down sinks and drains. However the majority of fat released is a liquid or emulsion so the mechanisms are likely to be more complex. FOG has been the subject of several national conferences in the UK and recent research in the USA has provided insights into formation mechanisms. Keener et al. (2008) reported on the

screening of physical and chemical properties of FOG samples sent from 23 locations, mainly in the South East USA. The deposits were highly variable but no link between water chemistry and FOG properties was found. Calcium was found to be the most abundant metal and saponification in the sewers was suggested as a formation mechanism, possibly mediated by alkali kitchen products reacting with free fatty acids. This hypothesis was supported by a follow on study which observed similar Fourier Transform Infrared (FTIR) spectra for FOG (both field and synthetic) and pure soaps (He et al., 2011).

Although the understanding of the nature and formation of FOG deposits has developed, there are issues concerning the formation mechanisms of FOG that need resolving. These include the source and effect of calcium availability on deposits and the transformations seen in sewers. This study offers some insights into these factors through systematic sampling of FOG from different parts of the UK and from different parts of the sewerage network over time to allow the variability and ageing factors to be investigated.

2. Materials and methods

The experimental design used water hardness and location in the network (sewer, pumping station and sewage treatment works) as independent variables and a multivariate sampling strategy was established to investigate the composition and variability of FOG. A range of techniques were adapted to characterise FOG properties but as this study commenced before the 2008 (Keener et al.) paper was published some methods are not directly comparable.

2.1. Site selection

UK water companies were asked to identify and offer sites for monitoring of FOG characteristics. Nine locations across England, with a history of FOG problems, were selected for monitoring over a 14 month period to February 2008. However difficulties in sampling and access meant that the data set is based on 7 groups. Table 2 shows the sampling locations, the water hardness class according to the UK Drinking Water Inspectorate definition (with the “Hard” class split between high and low) (DWI, 2009) and number of samples taken at each location.

Table 1 – % Mass Fatty Acid profiles of cooking fats and oils (Beare-Rogers et al., 2001; Ma and Hanna, 1999).

Common name (cis)	Lipid no.	Melting point, °C	% Composition by fatty acid					
			Sunflower	Corn	Olive	Rape	Tallow	Lard
Myristic	C14	55	0	0	0	0	3	2
Palmitic	C16	63	6	12	13	3	23	24
Stearic	C18	69	3	2	3	1	19	14
Oleic	C18:1	13	17	25	71	64	42	44
Linoleic	C18:2	–15	74	60	10	22	3	11
α -Linolenic	C18:3	–11	0	1	0	8	1	0
Arachidic	C20	76	0	0	0	0	0	0

Table 2 – FOG sampling site characteristics.

Network location	Location code	Hardness	Hardness class	Hardness code	Number of samples
Sewer	SEW	300	Hard (high)	HH	11
Pumping Station	PS	300	Hard (high)	HH	10
Sewer	SEW	220	Hard (low)	HL	9 ^a
Pumping Station	PS	220	Hard (low)	HL	8
Sewage Works	STW	220	Hard (low)	HL	7
Sewer	SEW	140	Slightly Hard	SH	10
Sewage Works	STW	140	Slightly Hard	SH	10

a 7 from one site and 2 from a replacement site.

2.2. Sample collection

Sewage and FOG samples were taken using telescopic rods lowered into manholes to avoid risks associated with sewer entry. FOG samples were scraped or cored from deposits in sewers or sewage works, or collected as “fat balls” from the water surface in pumping stations. Apart from the pumping stations where sewage levels were constantly changing, FOG deposits tended to occur at the sewage/water interface and samples were taken from there. Often, as sampling visits were made during the middle of the day, the sewers had low flow conditions and the FOG was exposed, conversely under high flow conditions FOG in combined sewers would be submerged, although for access and safety reasons sampling was not undertaken during storm events. Sewage was collected in a beaker from the immediate vicinity of the deposits and immediately tested for general water quality parameters. pH was measured using a portable Hanna HI8014 m calibrated with buffers of pH 4.0 and pH 9.0 and water hardness was measured using the Palintest™ tablet count system (ELE International). All samples were stored in a refrigerated cool box and then refrigerated at 4 °C for further analyses within 5 days.

At the laboratory the cone penetrometer test (Section 2.3.3.) was performed on the intact FOG samples. Samples were then homogenised in a food blender (30 s at the highest setting and a 1 min at low) and split into three sub-samples for the remaining tests.

2.3. Physical and chemical testing

The sub-samples were analysed for i) general physical and gravimetric based properties, ii) elemental analysis and iii) fatty acid profiling.

2.3.1. FOG dry solids and volatile solids

Moisture content and volatile solids were measured gravimetrically by sequentially drying and then incineration. A ceramic dish was dried in an oven at 105 °C, and cooled in a desiccator to room temperature and weighed to four decimal places. A 1 g sample of FOG was placed on the ceramic dish and put into an oven at 105 °C for 18 h. The sample was cooled in a dessiccator until it reached room temperature and it was then reweighed. Moisture content was calculated as the % weight loss.

The sample on the ceramic dish left over from the moisture content test was placed into a muffle oven at 550 °C for 30 min. The sample was then removed and placed into a desiccator until it reached room temperature. The weight loss during incineration was taken as the volatile solids as mg/g of dry solids.

2.3.2. Oil content of FOG and sewage

The oil content of FOG and sewage was measured gravimetrically according to APHA 5520B (2005): after extraction with n-Hexane (80%) and methyl-tert-butyl ether (20%). Samples (1.0 g FOG or 30 ml of sewage) were acidified to pH 2.0 with HCl, 20 ml of solvent was added and samples shaken vigorously for 2 min. The solvent was then either decanted from a conical flask (FOG) or separating funnel (sewage) before repeating the extraction. Residual solids from both sample types were washed using a further 10 ml of solvent.

Solvent extracts were passed through a filter paper (Whatman 540) containing 10 g of NaSO₄ into a dried and weighed distilling flask. The flask was placed in a water bath at 90 °C for 60 min with solvent recovery. Once solvent recovery was complete, the residue was dried in a desiccator for 15 min. The flasks were then reweighed with the difference in weight giving the mass of extractable oil.

2.3.3. FOG hardness index

Hardness was measured using the cone penetrometer test (BSI, 1990). FOG was placed into 40 mm Ø × 30 mm deep containers to give a smooth surface and no voids. The samples were then cooled to 4 °C. A cone (3.5 cm long, 80 g mass and 30° angle) on a rod was lowered to make contact with the centre of the sample. The cone was released and the penetration depth after 5 s measured with a micrometer (increments of 0.1 mm with a maximum of 40 mm). The mean of 10 replicates was taken.

2.3.4. FOG melting point

The melting point of extracted oils was measured using the Thiele tube method (Brittain and Bruce, 2006). A sample of extracted fat was placed into a capillary tube with no air between the base of the tube and the sample. The tube was then placed into heat transfer oil in a Thiele tube next to a thermometer. The arm of the Thiele tube was gently heated to raise the temperature by about 10 °C per minute to the melting point to give an approximate value. This was then

repeated over the 10 °C range with a 2 °C per minute rise to give a more accurate value.

2.3.5. Metals in FOG

1 g of homogenised FOG was mixed with 10 ml of 50% HNO₃ and refluxed at 95 °C for 15 min. After cooling a further 5 ml HNO₃ was added followed by 30 min under reflux. If brown fumes were produced a further 5 ml of HNO₃ was added and refluxed for a further 30 min, this cycle was repeated until no oxidation was apparent. The sample was then heated to 95 °C for 2 h to reduce the volume to 5 ml. The samples were then diluted using distilled water to give 2% HNO₃ content (APHA: 3120 B, 2005).

Samples were analysed using an Agilent 7500ce Inductively Coupled Plasma - Mass Spectrometer with octopole reaction cell using the semi-quantitative method in He mode. Samples were introduced using an integrated auto-sampler and calibration was by a tuning solution of 10 ppb of 6 elements across the mass range.

2.3.6. FOG fatty acid profiles

Twenty grams of homogenised FOG were frozen and sent to GC Laboratories™, Hitchin, UK. A portion of the sample was weighed into a glass flask and an internal standard solution in toluene was added, followed by 10 ml of 1% H₂SO₄ in methanol (methylating reagent). The mixture was refluxed for 2 h to hydrolyse the triglycerides and methylate the fatty acids to their methyl esters. The mix was allowed to cool and saturated NaCl solution added. The upper toluene layer was removed and transferred to a glass tube containing a small amount of anhydrous NaSO₄. Aliquots of the toluene layer were then analysed by a Varian CP-3800 GC under the following conditions:

Injection Volume: 0.6 µL

Injection Temperature: 200 °C

Column: 30 m × 0.25 mm Solgel WAX, 0.25 µm film

Column Temperature: 50 °C for 1 min, 10 °C/min to 270 °C, held at 270 °C for 10 min. Carrier Gas: O₂-free N₂ at 2.0 mL/min Split Ratio: 50:1

Detector: Flame Ionisation at 275 °C

The sample peak areas, relative to the internal standard, were compared to fatty acid methyl esters standards run under the same conditions (every 3 samples) to give concentrations of each fatty acid. Commonly used oils and fats were also tested before and after cooking to test the method and investigate the transformations during use. The fatty acid profiles obtained for beef tallow and vegetable oil are shown Fig. 1.

2.4. Data analysis

Data analysis was carried out using Minitab15™. Variables were tested for normality, where distributions were significantly different a Log₁₀ transformation was applied and the distribution re-tested for normality, the most appropriate distribution was then used for subsequent analysis with parametric statistics. Relationships between variables tested using linear regression and analysis of variance (ANOVA).

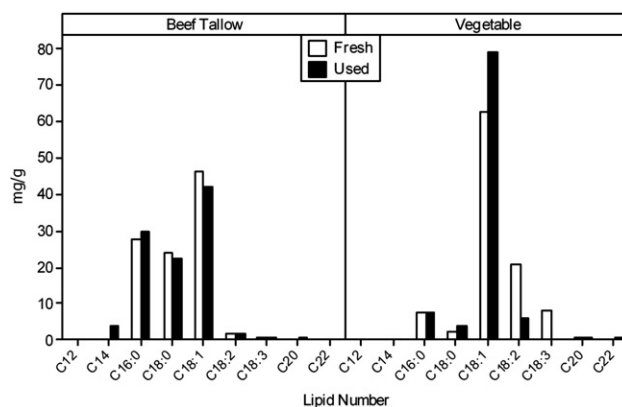


Fig. 1 – Changes in the fatty acid profile of vegetable oil and beef tallow during domestic cooking.

Some box plots (e.g. Fig. 6) show some sub-sets in some classifications were not normally distributed, however non-parametric tests showed the same significant differences and associations and therefore these have not been presented to avoid repetition.

3. Results

The FOG samples were either soft/waxy or the consistency of soft chalk with a distinctive ammoniacal odour. Colours ranged from a light brown to white, but colour did not provide a good indication of fat content (Clarkson, 2011).

3.1. Physical characteristics

The characteristics of FOG deposits and sewage are shown in Table 3. The composition of FOG was highly variable. Over 94% of the solids were volatile and the extractable oils made up 15% of this fraction (as means). However the range of all these values was large with 9 samples having less than 5 mg/g oil content and 2 samples less than 0.1 mg/g.

The oil concentration in sewage was also highly variable, although the geometric mean was about 800 mg/L, values ranged from 0 to 15,000 mg/L. There was no association between the oil content of the FOG deposits and oil content of the sewage (Fig. 2).

There was no significant difference for the oil content of the sewage or temperature between the 3 network locations. However SS was significantly different with mean values falling from over 970 mg/L in the pumping stations to about 330 mg/L in the sewage works inlets (ANOVA, $p = 0.001$) and pH was also significantly different with the pumping stations having the lowest mean value of 6.4 (ANOVA, $p = 0.004$).

Network location did not significantly affect the hardness or melting point of the FOG deposits but did affect the moisture content with the sewage works samples being significantly higher than the other sites (ANOVA, $p = 0.000$). There was also a significant difference in the proportions of oil in the FOG, with pumping stations having a mean of about 18%, sewers 9% and sewage works 1.2% (ANOVA, $p = 0.000$).

Table 3 – Characteristics of FOG and sewage by network location.

Sample	Variable		Overall	PS	SEW	STW
FOG	MC (%)	Mean (range)	54.7	44.6 (31.0–71.4)	51.7 (21.5–87.1)	70.7 (14.9–94.7)
	VS (mg/g)	Mean (range)	432	541 (277–673)	459 (64.2–768)	270 (42.1–777)
	Oil (mg/g)	Mean ^a (range)	63.5	181 (2.80–560)	87.7 (0–548)	12.0 (0–456)
	Penetration (mm)	Mean ^a (range)	11.6	9.56 (0.37–40)	11.4 (0.20–40)	14.8 (2.60–40)
Water	MP (°C)	Mean (range)	31.1	33.3 (27–38)	30.7 (15–52)	33.6 (22–52)
	Oil (mg/L)	Mean ^a (range)	801	881 (50–8210)	972 (0–15670)	520 (16–5466)
	SS (mg/L)	Mean ^a (range)	684	971 (120–7520)	836 (100–5100)	329 (120–840)
	pH	Mean (range)	6.7	6.4 (5.4–7.8)	6.8 (5.8–8.0)	6.9 (6.3–7.9)
	Temp (°C)	Mean (range)	13.4	13.6 (12.2–14.8)	13.4 (12.0–14.8)	13.4 (12.4–14.6)

a The geometric mean is shown for variables with a lognormal distribution.

3.2. Metals in FOG

Concentrations of common metals and those of most toxicological concern are presented in Table 4 as mg per kg dry weight of FOG. Ca was the most common metal in the deposits, followed by Na, Fe, Al and Mg.

There was shared variation between metals, with significant positive linear relationships for most associations; mercury was the exception with only a weak association with Al ($r = 0.27$, $p = 0.035$). Some of the associations between metals were very strong having an r -value above 0.9 e.g. Mg and Fe (0.94), Mg and Al (0.93) and Mg and Pb (0.90).

3.3. FOG fatty acid profiles

The mean concentrations of fatty acids (mg/g) in the FOG are shown in Fig. 3. Similar profiles were seen at all locations with palmitic (C16), oleic (C18:1), stearic (C18), and linoleic (C18:2) making up the majority of the deposits, although there were several samples where oleic was most common.

The two most common acids, palmitic (C16) and oleic (C18:1), are plotted in Fig. 4 as their proportions of the oil content (i.e. their concentration divided by the total amount of oil in FOG) to standardise for moisture and solids content. There was a strong inverse relationship between the two acids ($r = -0.912$, $p = 0.000$). The proportions of the two most

common fatty acids were significantly different in the three locations; the pumping stations had the lowest proportion of oleic (C16) acid and the highest proportion of palmitic acid (C16) while the inverse was observed for sewage works samples (Fig. 5).

3.4. Water hardness

Fig. 6 shows the properties of FOG in the water hardness classes (Table 2). There were significant increases in the Ca content and proportion of oil as water hardness increased (ANOVA, $p = 0.012$ and 0.050 respectively). Although the difference in volatile solids across the classes was not significant (ANOVA, $p = 0.191$) there was a difference between the slightly hard (SH) water samples and the others, having a mean volatile proportion of 90% compared to 98% at higher classes. No differences were seen in the overall fatty acid profiles or proportions of main fatty acids (e.g. C16 vs C18). Significant changes were also seen in the physical properties of FOG with moisture content decreasing (ANOVA, $p = 0.000$) and melting point increasing (ANOVA, $p = 0.000$) with water hardness. Although there was a progressive decrease in cone penetration from a geometric mean of 16.5 mm–7.5 mm as water hardness increased, there was slightly outside the significance level to establish a statistical difference between the hardness classes (ANOVA, $p = 0.068$).

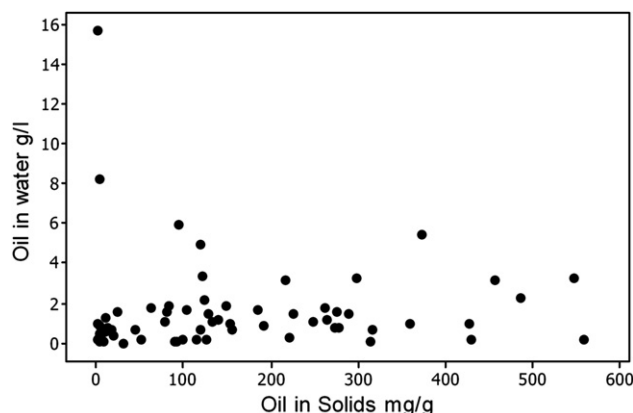


Fig. 2 – Relationship between the oil content of sewage and FOG.

4. Discussion

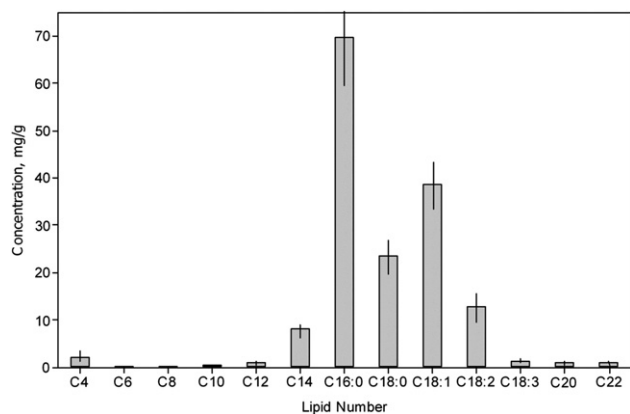
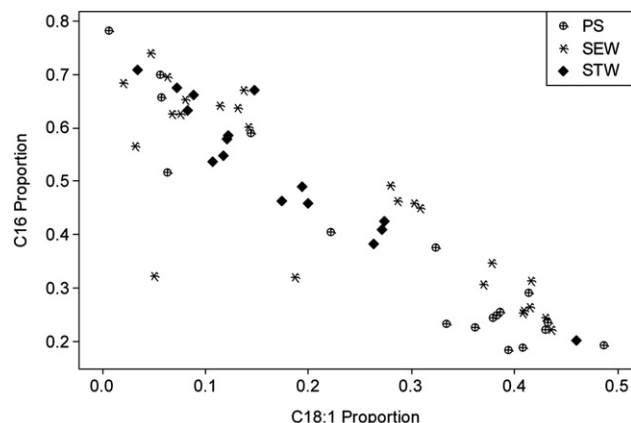
The repeated sampling at each location in this study allowed the variability of FOG deposits to be reviewed and for differences between sites to be examined. The sampling sites were identified as problem locations by water companies and the water quality results show they were very different from the typical sewage received at treatment works. The pumping station and sewer samples had very high levels of suspended matter and oil. These sites were mainly close to catering establishments and therefore the water was a mixture of commercial effluent with varying quantities of sewage. A link between catering establishments and FOG deposits has been suggested for over 60 years (Cohn, 1944), and this is particularly a concern in the UK where many city centres have high density “take away alleys” with multiple curry houses,

Table 4 – Metal concentrations in FOG ($n = 60$).

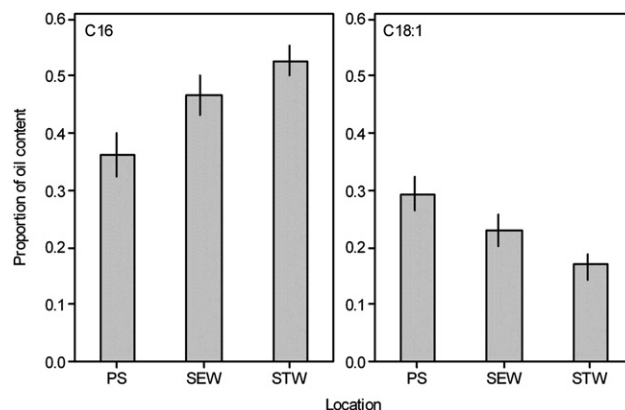
Metal	Mean Concentration, mg/kg DW	SEM
Ca	10,940	1190
Na	1952	141
Fe	1845	357
Al	1082	161
Mg	910	198
Zn	378	57.3
Cu	124	11.1
Pb	63.2	13.8
Ni	15.0	2.42
Cd	0.434	0.046

Chinese and kebab food shops. Since 2000 the UK Building Regulations (UK Govt., 2000) have required all new and converted premises to have grease management systems: catering premises established before 2000 generally only have grease interceptors or other FOG management systems if they have been identified as problematic. Even when grease interceptors are installed maintenance is often poor, leading to releases of poorly treated kitchen wastewater (Drinkwater, 2012).

The water quality in the sewerage systems was generally worse than the loading criteria of 1000 mg/L BOD recommended by British Water for the design of package sewage treatment plants serving fast food establishments (2005). A study in Texas concluded that restaurant loadings were highly variable and although lower than the values seen in this study, they were higher than local design guidance (Lesikar et al., 2006). The UK also has lower per capita water use than the USA (146 compared to 376 L/d.capita), so there will be generally less dilution of pollutants entering UK sewers (EA, 2008; Kenny et al., 2009). Moreover pumping stations and old sewers with slack gradients (such as at several sampling sites) can accumulate solids and possibly also FOG, so this could also contribute to the level of pollutants in the water. In-sewer processes are also reported to give up to 40% reduction in chemical oxygen demand during passage of water (Almeida et al., 2000) so this may be another

**Fig. 3 – Mean concentrations of fatty acids in the FOG deposits, with the error bars showing the SEM.****Fig. 4 – Relationship between the proportions of palmitic (C16) and oleic (C18:1) acid in FOG deposits (PS = Pumping Station, SEW = Sewer, STW = Sewage Treatment Works).**

factor influencing the high water quality measurements in initial sections of the sewer systems. However, similar levels of FOG and organic matter to this study have been reported in untreated wastewater from restaurants in South Korea, Hong Kong and mainland China (Nisola et al., 2009; Chan, 2010; Kang et al., 2011). Chen et al. (2000) also found significant differences in the wastewaters from different types of restaurant, with high levels of FOG seen in “Western” food and a student canteen, there has been no similar systematic study of the wastewater from different take-away outlets in the UK. Another study in the USA showed that even when grease interceptors are installed, effluent FOG concentrations can peak at well over 1000 mg/L (Ducoste et al., 2008). The suspended solids in the sewage works inlets were more typical of raw sewage in the UK, but high levels of oil were still seen in these samples reflecting that these too had FOG problems. So although the sites selected for this study are atypical of the sewer network they may be representative of sites with a severe FOG issue.

**Fig. 5 – Proportions of palmitic (C16) and oleic (C18:1) acid at the sewerage network sampling sites, with the error bars showing the SEM (PS = Pumping Station, SEW = Sewer, STW = Sewage Treatment Works).**

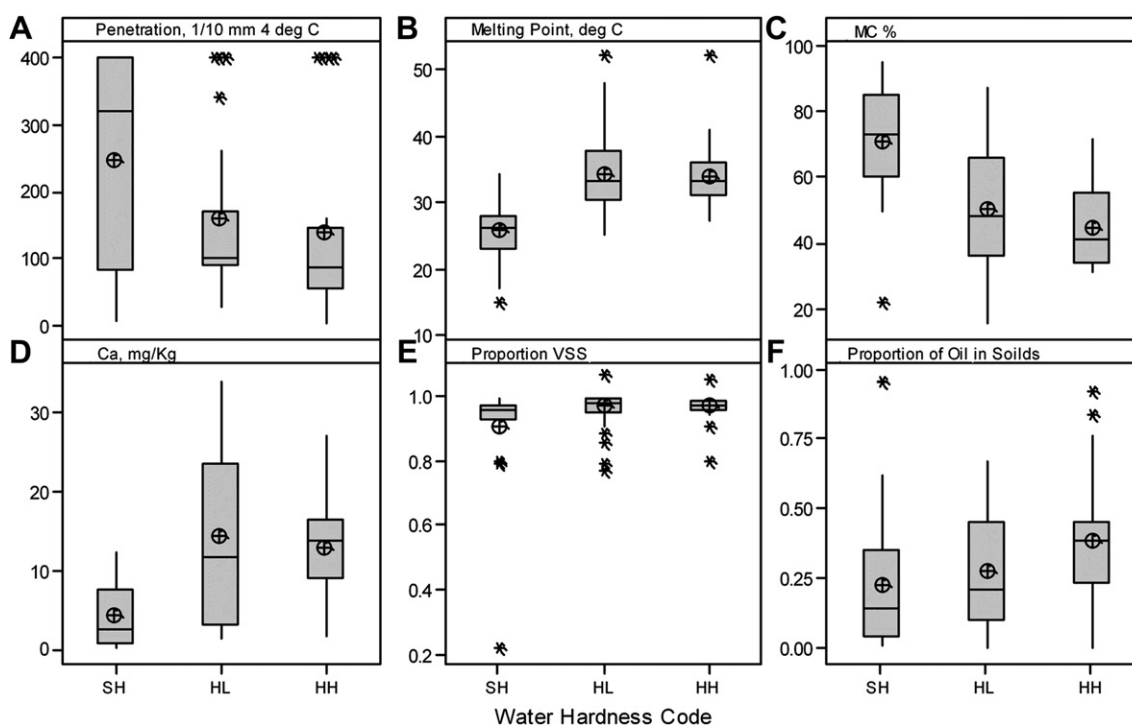


Fig. 6 – Variation of FOG characteristics with water hardness classification (SH = Slightly Hard, HL = Hard (Low), HH = Hard (High)). The solid bars show the inter-quartile ranges, the cross bars the median, the lines the 95% confidence intervals, circular symbols the mean and stars the outliers.

4.1. Physical characteristics

The solid FOG samples were very different to the emulsified liquid form released from kitchens, which supports the hypothesis that saponification occurs in the sewerage system. The deposits had a mean moisture content of 55% (Table 3), but this was highly variable ranging from 15 to 95%. Highly variable moisture content (between 6 and 86%) was also noted in the USA (Keener et al., 2008) but this was not thought to be a significant factor in formation. There were significant differences in moisture content between the network locations, with FOG from sewage works having generally higher moisture content than that in the pumping stations. This may reflect the different environments and sewage characteristics, and possibly the maturation of the FOG in the network. The majority of the solids were volatile (93%) but there was no significant difference in the proportion between the network locations. However there was a significant difference in the proportion of extractable oils, with the highest in the pumping stations. The “fat balls” in the pumping stations may be formed by a different accumulation mechanism to that for attached deposits and also be less aged.

Levels of oil in sewage were not significantly different between the network locations and there was no association between the oil content of FOG and water (Fig. 2). Although the sewage samples were spot samples, this does suggest that deposition or sorption processes related to water concentration were not the predominant effectors of oil in FOG. However, the high oil content measured in sewage may affect the accumulation rate of FOG and this may be why the sites

were identified by Water Companies for inclusion in this study. The deposits were generally softer than common solid fats (lard and butter were tested giving 7.7 and 11.5 mm penetration at 4 °C respectively) but had similar melting points. There was no significant difference between the material properties of the deposits between locations, which is surprising considering the differences in moisture content. Ca was the most abundant metal, this was also seen in the USA (Keener et al., 2008) but the concentrations reported there were about 2.5 times lower (Table 4). As most of the USA samples were from the South-East where water supplies are very soft (Briggs and Ficke, 1977) this may reflect the water chemistry. This may also explain the higher levels of Mg, Al and Fe encountered in the UK samples since there was a high degree of correlation between metals in FOG. The levels of Na and Pb seen in this study are approximately an order of magnitude higher when compared to the USA. However, there were 3 individual sites from the North of the England where Pb was 1 or 2 orders of magnitude higher than the other sites, so industrial or geochemical factors may be the cause. The explanation for Na is more complex as although there are differences between sampling sites, these are not of the orders of magnitude required to account for this finding. Road de-icing salts are a possible source, but there does not appear to be a seasonal trend to these concentrations.

The concentrations of potentially toxic metals (Zn, Ni, Cu, Cd, and Pb in Table 4) were generally below the EU limits for sewage sludge applied to agricultural land, although some EU countries have individually set limits for some metals below the values seen in FOG (Salado, 2008). The UK Environment

Agency has also published Soil Guideline Values for several toxic metals and all the levels in FOG were well below these values (EA, 2009). Therefore FOG would not appear to pose a toxic metal hazard and this should not affect disposal options.

4.2. Fatty acid profiles

The fatty acid profiles for the FOG deposits (Fig. 3) show that the majority were between C14 and C18, with palmitic acid (C16) being the most abundant followed by oleic (C18:1). In most liquid oils the unsaturated oleic and linoleic (C18:2) acids predominate (Table 1), therefore the FOG accumulations do not reflect the composition of the most commonly used fats. An increase in saturated fats was also observed in the USA (Keener et al., 2008) and FTIR analysis indicated that this was not due to preferential accumulation of animal fats (He et al., 2011). Sample processing or cooking did not appear to be responsible for the effect as this only gave a small reduction in the levels of poly-unsaturated C18 acids and no increase in C16:0 for beef tallow and vegetable oil (Fig. 1). This corresponds with patterns observed in other studies (Knothe and Steidley, 2009; Chung et al., 2008). However cooking transformations appear to have an important role as He et al. (2011) found that FOG was not synthesised in jar tests with unused rapeseed oil. This suggests that free fatty acids, which can account for up to 40% of fatty acids in used oils, are required to initiate FOG formation (Chung et al., 2008).

The strong negative association between the proportions of palmitic and oleic acid in FOG (Fig. 4) does suggest that in-sewer transformation process were occurring. The proportions are significantly different between network locations, with the highest oleic to palmitic ratio in the pumping station and the lowest in the sewage treatment works inlets. It is possible that the pumping station samples may be the closest to discharges and “freshest” while those for sewage works may represent the most aged samples. This suggests that processes are occurring in the sewer to transform oleic acid into palmitic acid. Beta oxidation was suggested as a mechanism for this in-sewer transformation by Keener et al. (2008) but this does not account for the hydrogenation. Work on anaerobic sewage treatment has shown that anaerobic reactors fed with C18:1 generate “encapsulated” layers of C16 in the sludge (Pereira et al., 2005; Matsui et al., 2005). As part of our study (not reported here), waste vegetable oil in water was circulated through 6 m long microcosms with various amendments (e.g. starch, detergent) to investigate factors effecting accumulations. Some deposits were generated but the fatty acid profiles were unchanged from the used oil, suggesting that sewer microbial assemblages and conditions are required for the hydrolysis and hydrogenation of C18:1 to C16 (Clarkson, 2011). The formation of adipocere (or “grave wax”) around corpses is well documented. It occurs in damp anaerobic environments and has the same patterns of change in physical characteristics and fatty profiles as FOG. Chalky white deposits form around bodies from the saponification of liquid fatty acids released from bodies with alkaline metals from soil (Ubelaker and Zarenko, 2011). Unsaturated fatty acids are converted to saturated forms (palmitic) changing the fatty acid profiles of the deposits from the original body fat.

These saturated fats move to the surface of the water phase and form solid deposits due to their higher melting point (Fründ and Schoenen, 2009). Enzymes released by anaerobic *Clostridium perfringens* are thought to have a major role in the hydrolysis and hydrogenation of C18:1 (Mohan Kumar et al., 2009). The nature of deposits, conditions and microbes associated with FOG and adipocere formation are similar and it is possible that similar mechanisms may be involved in the formation of both deposits.

The transformation from oleic to palmitic acid would be expected to influence physical properties as palmitic acid has a significantly higher melting point (over 50 °C higher, Table 1). However physical properties were not significantly affected by proportions of different fatty acids. However the results do not distinguish between the free, bound or saponified components and since palmitic acid was highest in almost every FOG sample, any effect of this transformation may not be seen in the deposits.

Water Industry sources have suggested that the fatty acid composition of FOG deposits in sewers could be a way of “fingerprinting” deposits to trace the source, which could then be used as evidence to make polluters pay for clearing deposits (Drinkwater, 2012). The in-sewer transformations mean that this is not possible. However companies producing microbial amendment sewer cleaning products have shown interest in these findings and are ensuring that bacteria degrading palmitic acid predominate in FOG remedy cultures.

4.3. Effect of water hardness

Comparison between the water hardness groups suggested that FOG properties were affected by water geochemistry, for example the melting point and hardness tended to increase with water hardness (ANOVA, $p > 0.05$ for both) (Fig. 6). This is the first report of a potential link between water hardness and the properties of FOG in the field and is contrary to the findings of Keener et al. (2008) who did not find any difference in FOG properties with water hardness. However that study did not undertake repeated sampling from the same locations so was not able to make comparisons.

Ca concentrations in FOG tended to increase with water hardness (Fig. 6), possibly indicating a concentration dependent exchange between the sewage and the FOG. Jar tests in the USA (He et al., 2011) did note that increased CaCl_2 concentrations (50, 400–750 mg/L) increased the mass and Ca content of synthesised FOG and they suggested that the elevated Ca levels in field FOG could be due to free fatty acids drawing Ca from sewage or concrete pipes for saponification. Our studies indicate that there was also an increase in the proportion of oil in solids as water hardness increases (Fig. 6), possibly indicating that more free fatty acids are being saponified, although the association between Ca and oil content was not significant, suggesting that other process are affecting Ca levels. Stoichiometrically, the molar ratio for saponification should be 2:1 between the free fatty acid and a divalent metal. However, the mean composition of FOG shows a large excess of Ca, with approximately 0.27 mol Ca/g FOG (10.94 g Ca/g FOG divided by 1 mol of Ca being 40.078 g) compared to about 0.000614 mol FA/g FOG (165 mg total FA/g FOG divided by 268.5 g as the weighted average molecular

weight of fatty acids in FOG). Biofilms in other environments, without excess fatty acids, have also been shown to enrich Ca (and other cations) by over 10,000 times bulk water concentrations (Kröpfel et al., 2003), this suggests that saponification may not be the only driver for the high levels of Ca in FOG. The precipitation of CaCO_3 is known to occur as a result of microbial (bacterial) intervention (Zamarreno et al., 2009). A wide range of bacterial species can form CaCO_3 when the environment is rich in Ca ions and the cells become the nucleus of the precipitation. Biofilm material, common in sewerage systems, can also help to cause the aggregation of calcite crystals. Thus a Ca rich environment that also encourages biofilm formation could also promote FOG formation.

The changes in the physical characteristics (hardness and melting point) may be due to Ca consolidating the deposits through inter-molecular forces or physical deposition of calcite or other minerals within the FOG deposits. A study in Lebanon which examined the “biofilms” in sewers, which looked similar to FOG deposits, showed that Ca concentration increased cohesion (Mahfoud et al., 2009), which suggests Ca has a significant role in determining FOG structure.

5. Conclusions

Sewer processes are complex and it is suggested that two mechanisms may affect the properties of FOG causing the transformation from cooking oils released from kitchens into sewer FOG deposits.

One is the biodegradation of the oil content associated with a transformation of fatty acid profiles from unsaturated to saturated forms. This may relate to ageing in the sewer network or the mechanism of formation, as the pumping station samples had the highest oil content associated with higher proportions of C18:1 compared to C16. This may be due to microbial transformations by bacteria such as *Clostridium* sp. in a similar process to adipocere formation. Understanding these mechanisms may allow more accurate targeting of bioaugmentation strategies to manage FOG deposits. Companies could either ensure cultures effectively degrade the predominant fatty acid, palmitic, or perhaps create conditions in sewers to promote degradation of palmitic soaps, as degradation of saturated compounds has been shown to be more effective than unsaturated in anaerobic reactors (Prats et al., 1999).

The second process appears to be linked to water hardness and affected the physical characteristics of FOG; a possible link between FOG properties and water hardness has not been previously reported for field samples. Increasing water hardness was associated with increased Ca levels in FOG. This may be due to physico-chemical processes or microbial activity, such as biocalcification. The deposits in harder water areas tended to be harder and have higher melting points, and possibly had more cohesion. These findings may allow physical interventions, such as jetting, to be adjusted for different types of FOG deposits, possibly allowing more effective removal and energy saving.

By developing the understanding of these mechanisms it may be possible to more effectively control FOG deposits,

especially when combined with promotion of behavioural change, and reduce the environmental and health impacts of sewer overflows.

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