

# Evidence for Fat, Oil, and Grease (FOG) Deposit Formation Mechanisms in Sewer Lines

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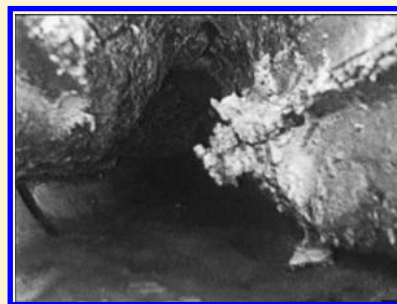
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 Supporting Information

**ABSTRACT:** The presence of hardened and insoluble fats, oil, and grease (FOG) deposits in sewer lines is a major cause of line blockages leading to sanitary sewer overflows (SSOs). Despite the central role that FOG deposits play in SSOs, little is known about the mechanisms of FOG deposit formation in sanitary sewers. In this study, FOG deposits were formed under laboratory conditions from the reaction between free fatty acids and calcium chloride. The calcium and fatty acid profile analysis showed that the laboratory-produced FOG deposit displayed similar characteristics to FOG deposits collected from sanitary sewer lines. Results of FTIR analysis showed that the FOG deposits are metallic salts of fatty acid as revealed by comparisons with FOG deposits collected from sewer lines and pure calcium soaps. Based on the data, we propose that the formation of FOG deposits occurs from the aggregation of excess calcium compressing the double layer of free fatty acid micelles and a saponification reaction between aggregated calcium and free fatty acids.



## INTRODUCTION

As the numbers and density of commercial food preparation and serving facilities increase, so do the amounts of fats, oils, and grease (FOG) that are routinely discharged into sewer collection systems. Of the estimated tens of thousands of sanitary sewer overflows (SSOs) that occur each year in the United States, approximately 48% are due to line blockages, of which 47% are related to FOG deposits that constrict the cross-sectional access of pipes.<sup>1</sup> Despite the central role that FOG deposits play in SSOs, very little is known about the mechanisms of FOG deposit formation in sanitary sewers. Examination of the physical properties and chemistry of FOG deposit samples from 23 cities around the United States<sup>2</sup> showed that FOG deposits display an adhesive character, have a grainy, sandstone-like texture and high yield strength. In addition, 16 of 19 FOG deposit samples (84%) contained greater than 50% lipid content, with the primary lipid being palmitic, a saturated fat and 85% of FOG deposit samples contained calcium as the primary metal, with average concentrations of 4255 mg/L.<sup>2</sup> The preferential accumulation of fats and calcium further suggests that FOG deposits may be metallic salts of fatty acids, and chemical saponification may be responsible for their formation.<sup>2</sup> Calcium ions are naturally present in domestic and industrial wastewater, and high levels of free fatty acids have been found in wastewater due to processes such as food frying.<sup>3</sup> Additionally, calcium may be released from biologically induced concrete corrosion.<sup>4–6</sup> While the saponification process may be a plausible explanation for the formation of these deposits due to

their chemical constituents and physical structure, proof for this mechanism requires additional data, including the actual formation of FOG deposits under saponification conditions. The objective of this study is to verify the hypothesis that FOG deposit formation is the result of a saponification reaction between free fatty acids and metal ions such as calcium.

## MATERIALS AND METHODS

**Formation of FOG Deposits under Laboratory Conditions.** Grease interceptor (GI) effluent from a steakhouse in Cary, NC was collected and used as the source of free fatty acids. The GI effluent characteristics were as follows: COD of 1136 ± 368 mg/L, alkalinity of 237 ± 17 mg CaCO<sub>3</sub>/L, pH of 6.9 ± 0.25, and average Ca, Mg, Fe, and K concentrations of 9.1, 3.1, 0.4, and 7.2 mg/L, respectively. The reaction was performed using a jar-test apparatus (Phipps & Bird JarTester). In each beaker, 1 L of GI effluent was added and mixed with calcium chloride salt (CaCl<sub>2</sub>·2H<sub>2</sub>O) at varying concentrations. The mixing speed was set at 20 rpm and operated continuously at 20 °C for 10 days. On day 10 of the reaction process, the solution in each beaker was filtered through a wet-strengthened qualitative filter

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paper ( $>25\ \mu\text{m}$ ) using a vacuum pump to collect formed FOG deposits. The filter paper with the FOG deposits was then dried at  $105\ ^\circ\text{C}$  overnight, and the concentration of FOG deposit was determined as total suspended solids.<sup>7</sup> Vegetable oil (canola) mixed with the same amount of calcium chloride and exposed to the same conditions as the GI effluent samples was used as control. FOG deposits were not expected to form in the control samples since no free fatty acids would be produced by hydrolysis to react with calcium salt under laboratory conditions.

**Sampling of FOG Deposits in Full Scale Field Sewer Lines.** Three FOG deposit samples from sanitary sewer lines in Cary, NC were obtained to compare their chemical makeup with the FOG deposit formed in the lab. One FOG deposit sample was from an apartment area (apartment), one sample was from a food service establishment (shopping center 1), and one sample was from a commercial, food service, and retail area of a shopping center (shopping center 2). Sites were chosen with input from utility personnel, based on past experience with sewer lines that form FOG deposits. The wastewater at all the sampling sites represented a mixture of wastewater from food service and bathroom activities. Samples were placed on ice and stored in the lab at  $4\ ^\circ\text{C}$ .

**Fatty Acid Profile.** Samples of the deposits were directly saponified and converted to fatty acid methyl esters according to AOCS Ce 2-66<sup>8</sup> and analyzed using gas chromatography (GC). In brief, 0.5 to 1.0 g of sample were weighed in triplicate into glass screw topped tubes. Each tube was spiked with 0.5 mg of tridecanoin (C13:0) in ethanol to serve as an internal standard. One mL of 0.5 N NaOH in methanol was added to each, and the tubes were heated for 10 min at  $85\ ^\circ\text{C}$  in a water bath. After cooling, 1 mL of 14% boron trifluoride in methanol was added to each tube. The tubes were recapped, vortexed, and returned to the water bath for 10 min. After cooling, 1 mL of water followed by 1 mL of hexane was added to each tube. The tubes were vortexed at top speed for 30 s and then allowed to stand to form layers. The top (organic) layer containing the fatty acid methyl esters was removed and dried over sodium sulfate. The fatty acid methyl esters were analyzed with a Perkin-Elmer Autosystem XL GC (Sheldon, CT) fitted with a capillary BPX-070 column (SGE Inc., Austin, TX) using a flame ionization detector (FID). The temperature gradient was  $60\ ^\circ\text{C}$  with a 2 min hold time, increased at  $4\ ^\circ\text{C}$  per min to  $180\ ^\circ\text{C}$ , and then increased at  $10\ ^\circ\text{C}$  to a final temperature of  $235\ ^\circ\text{C}$ . The run time was 27.7 min. The carrier gas used was helium. The injection was split at 150 mL/min. The results were reported as percent of the total fatty acids based on peak areas as per the official method (AOCS Ce 1f-96),<sup>8</sup> and the total fatty acids were calculated based on the ratio of internal standard to the fatty acid peaks present when compared to a standard mixture (Kel Fir Fame 5 Standard Mix, Matreya, Pleasant Gap, PA). The standard mixture of fatty acid methyl esters was run with each sample set to determine retention times and recoveries.

**Calcium Analysis.** Calcium concentration was determined using a Perkin-Elmer 2000 inductively coupled plasma optical emission spectrometer (ICP-OES). A solid sample was placed on an acid-washed crucible and then put in a muffle furnace, ramping up the temperature  $100\ ^\circ\text{C}$  every hour until  $500\ ^\circ\text{C}$  was reached. The sample was maintained at  $500\ ^\circ\text{C}$  for 16 h. After cooling the sample, 2 mL of deionized water was used to rinse residue toward the center of the crucible. Four mL of 6 N HCl was then added, and the sample was heated on a hot plate at  $95\ ^\circ\text{C}$  for 45 min until completely dry. The sample was cooled,

and another 4 mL of 6 N HCl was added, with subsequent warming on the hot plate for 15 min. After cooling, the acid solution was filtered through a Whatman filter paper into a 25 mL glass volumetric flask and brought to volume with deionized water. The sample was then analyzed by ICP-OES for calcium. Since the FOG deposit formed in the lab was attached to the filter paper, both the filter paper and FOG deposit were simultaneously digested. The calcium concentration in the FOG deposit was determined by subtracting the calcium concentration of filter paper (0.034 mg). The liquid sample was diluted 10-fold with 1% HCl and 1%  $\text{HNO}_3$ . After dilution, the liquid sample was analyzed by ICP-OES.

**Formation of Calcium Soap.** An alkali hydrolysis of the vegetable (or animal) fats similar to the method used by Poulenat et al.<sup>9</sup> was performed to produce calcium soap at room temperature since the average temperature range in sanitary sewer collection systems was observed to be 5 to  $25\ ^\circ\text{C}$ .<sup>10</sup> Calcium chloride (9.8 wt %) was added to a solution of sodium hydroxide (0.6 wt %) and deionized water (14.9 wt %). The solution was allowed to cool to room temperature ( $22\ ^\circ\text{C}$ ). The oil fat (Pure Wesson Canola Oil, ConAgra Foods, Omaha, 74.7 wt %) at room temperature was gradually added and mixed to the solution. The mixture was stirred at 450 rpm using a Stir-Pak Laboratory Mix Impeller (Cole Parmer, 23–2300 rpm). The calcium soap sample for FTIR analysis from the batch reactor was collected after four hours of mixing.

**Fourier Transform Infrared (FTIR) Spectrometer Analysis.** FTIR analysis was performed for the FOG deposit sample created in the lab, a calcium soap developed from calcium chloride and canola oil, three FOG deposit samples from the sewer collection systems, pure lard, and three pure fatty acids (palmitic acid, oleic acid, and linoleic acid). Infrared absorption spectra of these samples were determined with a Digilab FTS-6000 Fourier Transform Infrared (FTIR) spectrometer using a mounted crystalline Zinc Selenide attenuated total internal reflection (ATR) sampling attachment (Pike Technologies Inc., MIRacle Single Reflection ATR). The infrared light is focused onto the photodiode of a liquid nitrogen-cooled, wide band mercury-cadmium-telluride (MCT) detector with a linearized normal spectral response of  $450$  to  $7000\ \text{cm}^{-1}$ . The spectra were converted into absorbance units by taking the negative of the log ratio of a sample spectrum to that of an air spectrum. The data were then computed with a data processing program (Microcal Origin, v7.0, Microcal Software Inc., Northampton, MA.).

## RESULTS AND DISCUSSION

**FOG Deposit Formation under Laboratory Conditions.** FOG deposits formed under laboratory conditions are shown in Figure 1. The white pinpoint particles started to form on day 2, with the size of the particles increasing until the maximum observed sizes were achieved on day 7. To our knowledge, this is the first reported formation of FOG deposits from GI effluent under laboratory conditions. No solids were formed in the control beaker, which contained calcium and the vegetable oil. The vegetable oil was observed on the surface at all times within the control beaker. These results are consistent with the hypothesis that in the absence of free fatty acid, calcium salt will not react to form a FOG deposit.

Similar fatty acid profiles (Table 1) were found in FOG deposit samples (R1, R2, R3) formed in the lab and FOG deposit

samples taken from sewer lines (apartment, shopping center 1, and shopping center 2). Saturated fat was the major component, and palmitic was the primary saturated fatty acid in all FOG deposit samples, consistent with the results of Keener et al.<sup>2</sup> Monounsaturated fat was the second major component in all FOG deposit samples. Although the percentages of monounsaturated fat in FOG deposit samples from sewer lines were higher than those of the deposits formed in the lab, low percentages (around 10%) of monounsaturated fat in FOG deposits were observed in 12 FOG deposits from sewer lines.<sup>2</sup> Oleic was the primary monounsaturated fat in the FOG deposits formed in the lab and in those collected in the apartment area and shopping center 1. In addition, linoleic was the primary polyunsaturated fat in all FOG deposit samples, similar to the results of Keener et al.<sup>2</sup>

Three reactions (R1, R2, and R3) of GI effluent and calcium chloride were assessed at calcium concentrations of 50, 400, and 750 mg/L, respectively. Increasing concentrations of calcium were explored to determine any impact on the amount of FOG deposit formed. As mentioned earlier, biological reactions that induce corrosion of concrete pipes<sup>4–6</sup> may release excess calcium beyond that found in typical wastewaters. As the calcium concentration was increased from 50 mg/L to 750 mg/L, the resulting FOG deposit weight also increased (Table 2). From R1 to R3, increasing levels of calcium led to higher calcium levels measured in the FOG deposits.

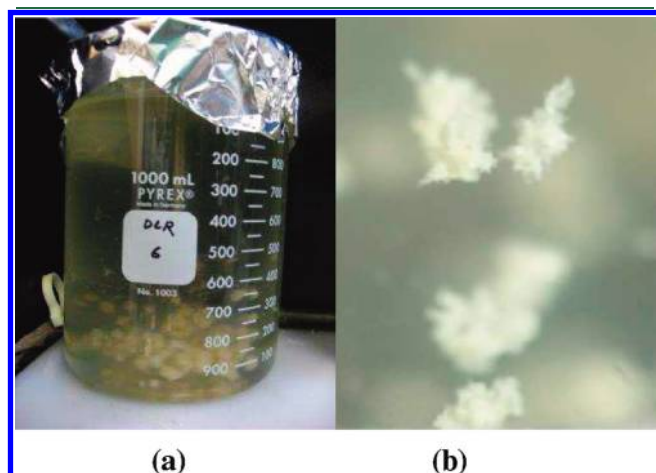
Total fat in the FOG deposit increased from R1 to R2, indicating that additional calcium reacted with surplus free fatty acids in

R2. Total fat, however, remained constant at 23 mg from R2 to R3, suggesting that although more calcium was added, no more free fatty acids were available to react with calcium.

The total fat to calcium ratios are higher in FOG deposit samples collected from shopping centers than in those formed under laboratory conditions, which may have been caused by different reaction conditions such as the finite amount of available free fatty acids to react with excess calcium under lab batch conditions. The FOG deposits from the shopping centers were likely the result of long-term reactions with higher concentrations of available free fatty acids that were continuously discharged from food service establishments. However, with the same fatty acid substrate (GI effluent), in R2 and R3, the total fat concentration remained at 23 mg, but the total fat to calcium ratio decreased from 5.16 in R2 to 3.67 in R3. The decreased ratio suggests that there may be other processes aside from saponification that led to accumulation of calcium within these deposits.

The results in Table 2 suggest that there may be two processes involved in FOG deposit formation. In the first process, calcium tends to accumulate around fatty acid micelles due to a DLVO type process<sup>11</sup> (i.e., compression of charged double layer) due to the slightly negative carboxylic end of the free fatty acids. In the second process, free fatty acids react with calcium to form calcium based fatty acid salts through a saponification reaction. The slightly negative carboxylic ends of unreacted free fatty acids continue to attract positive calcium ions, since the saponification reaction may be slow compared to the transport of calcium ions toward the solid deposit (i.e., a reaction limited process).<sup>9</sup> Due to the slower saponification reaction, it is hypothesized that more calcium than the stoichiometric amount needed for saponification would accumulate in the deposit. Research is needed, however, to confirm the involvement of a double layer compression process along with a saponification reaction to create solid FOG deposits in sewer lines.

**FTIR Analysis.** FTIR is a simple and powerful technique that is widely applied to determine oil and grease in water,<sup>12–15</sup> oily materials in different chemical processes,<sup>16–19</sup> trans fat in food,<sup>20,21</sup> and fatty acids and fatty acid salts.<sup>9,22–24</sup> If the saponification hypothesis is correct, then the calcium soap should be detected in the FOG deposit. In the infrared spectra, when free fatty acids react with calcium salt and the “hard” metallic salts of fatty acids (soaps) is formed, the carbonyl group stretching vibration at  $1745\text{ cm}^{-1}$  of triacylglycerols (TAG) disappears, and three characteristic calcium soap bands appear: (i) the carboxylate ion symmetric stretching vibration,  $\nu_1$  at  $1422\text{ cm}^{-1}$ ; (ii) the carboxylate ion asymmetric stretching vibration,  $\nu_2$  at  $1577\text{ cm}^{-1}$ ; and (iii) the metal–oxygen bond vibration at  $665\text{ cm}^{-1}$ .<sup>9,25</sup> Poulenat et al.<sup>9</sup> identified four regions that can be attributed to



**Figure 1.** FOG deposits formed under laboratory conditions. (a) Photo was taken at day 10 when free fatty acids reacted with calcium salt in 1 L beaker; (b) Close-up of FOG deposit particles.

**Table 1. Fatty Acid Composition of FOG Deposits**

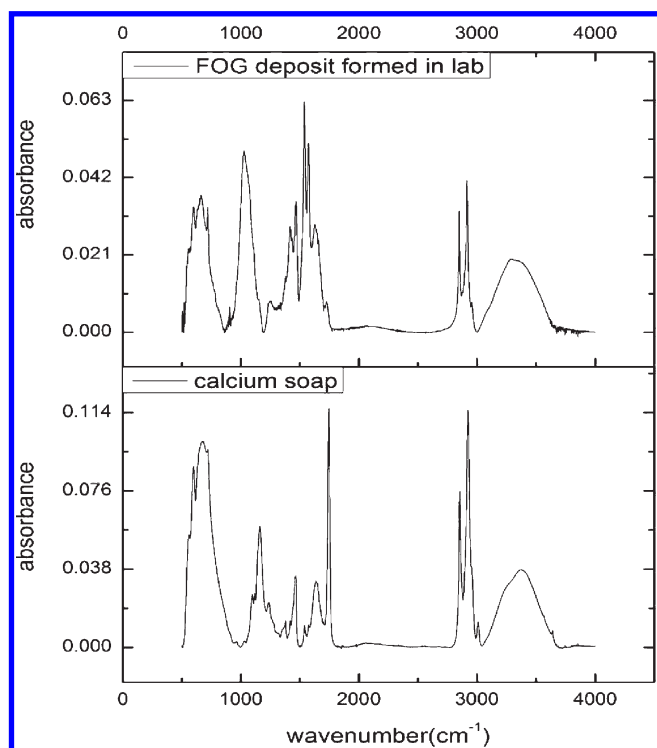
sample	total fat <sup>a</sup> (g/g)	saturated fat <sup>b</sup> (%)	primary saturated fat	mono unsaturated fat <sup>c</sup> (%)	primary mono unsaturated fat	poly unsaturated fat <sup>d</sup> (%)	primary poly unsaturated fat
R1	0.344	78.8	palmitic	9.8	oleic	0.8	linoleic
R2	0.255	57.5	palmitic	9.0	oleic	0.6	linoleic
R3	0.18	70.6	palmitic	14.0	oleic	0.7	linoleic
apartment	0.261	56.5	palmitic	38.3	oleic and palmitoleic	1.0	linoleic
shopping center 1	0.393	38.7	palmitic	37.2	oleic	15.3	linoleic
shopping center 2	0.489	64.7	palmitic	31.7	palmitoleic	0.6	linoleic

<sup>a</sup> Total fat content was calculated from a 1 g FOG deposit sample. <sup>b</sup> Saturated fat is shown as a percentage of the total fat. <sup>c</sup> Monounsaturated fat is shown as a percentage of total fat. <sup>d</sup> Polyunsaturated fat is shown as a percentage of total fat.



Table 2. Calcium and Total Fat Amounts in FOG Deposits

sample	FOG deposit weight (mg)	calcium in FOG deposit (mg)	total fat in FOG deposit (mg)	total fat/calcium (mg/mg)	calcium/FOG deposit (mg/mg)
R1	52.6	2.15	18.07	8.40	0.0409
R2	93.5	4.61	23.81	5.16	0.0493
R3	123.5	6.06	22.23	3.67	0.0491
apartment	415.2	21.35	108.16	5.07	0.0514
shopping center 1	145.5	0.13	57.22	438.42	0.0009
shopping center 2	143.5	1.78	70.10	39.41	0.0124



**Figure 2.** Baseline corrected infrared spectra of FOG deposit formed in the lab and calcium soap.

the formation of calcium soaps: region 1: 4000–3000  $\text{cm}^{-1}$ ; region 2: 1800–1350  $\text{cm}^{-1}$ ; region 3: 1350–1180  $\text{cm}^{-1}$  and additional sideband near 720  $\text{cm}^{-1}$ ; region 4: near 670  $\text{cm}^{-1}$ .

**Infrared Spectrum of FOG Deposit Formed in the Lab.** The infrared spectra of the FOG deposit formed in the lab, and calcium soap made from canola oil and calcium chloride are shown in Figure 2. The lab FOG deposit infrared spectra appear quite similar to the pure calcium soap infrared spectra. Comparisons were made between these two samples based on the four characteristic regions of calcium soap discussed in Poulenat et al.<sup>9</sup>

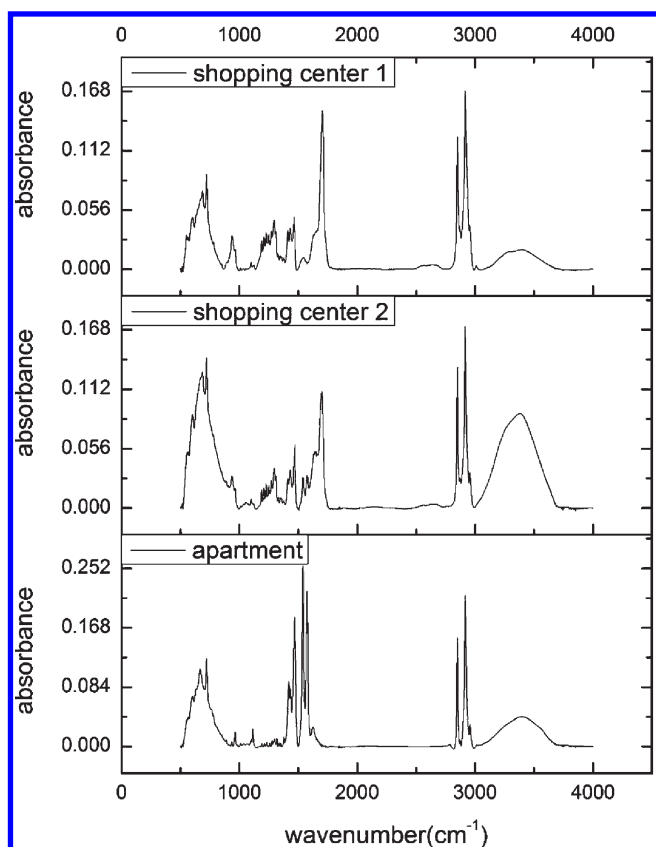
In region 1 between 4000 and 3000  $\text{cm}^{-1}$ , the band has been associated with the O–H stretching vibration of hydrated water.<sup>9</sup> Soaps have a broad absorption around 3400  $\text{cm}^{-1}$ , which is characteristic of hydrogen bonding and the polar head groups of the soap molecule.<sup>25,24</sup> This strong absorption band at 3400  $\text{cm}^{-1}$  is observed in both the FOG deposit and calcium soap as shown in Figure 2. Both the lab-scale FOG deposit and the pure calcium soap spectra display the presence of water (liquid) (located within the broad peak and between 3500 and 3700  $\text{cm}^{-1}$ ).<sup>26</sup> The presence of water is not surprising since both

fatty acid salts contained water during the saponification process. Four bands, located at 3004, 2955, 2922, and 2851  $\text{cm}^{-1}$ , represent the frequencies of the aliphatic chains of the soap.<sup>9</sup> These bands display no significant modifications as a result of saponification.

In region 2, the total disappearance of the stretching vibration at 1745  $\text{cm}^{-1}$ , attributed to the frequency of the ester bond in triglycerides (TAG), should be observed for calcium soap formation.<sup>9</sup> Two modes of vibration, attributed to the carboxylate group of the fatty acid metallic salt, were expected: the symmetric stretching vibration,  $\nu_1$ ; and the asymmetric vibration,  $\nu_2$ . The appearance of two absorption bands  $\nu_1$  and  $\nu_2$ , of the carboxylate group instead of a single band at 1745  $\text{cm}^{-1}$ , shows that calcium soaps possess an ionized structure and that calcium–oxygen bonds in the soaps have an ionic character.<sup>27</sup> In calcium soaps, these two stretching vibrations were split into two or three bands:  $\nu_2$  was split into 1577 and 1541  $\text{cm}^{-1}$ , and  $\nu_1$  was split into 1468, 1435, and 1422  $\text{cm}^{-1}$ .<sup>9</sup> All five bands were observed in the infrared spectra of the FOG deposit and calcium soap made in the lab as shown in Figure 2. The disappearance of the band at 1745  $\text{cm}^{-1}$  was also observed in the FOG deposit. The existence of the band at 1745  $\text{cm}^{-1}$  in the calcium soap sample (Figure 2), however, may be due to excessive canola oil that was used to react with calcium (data not shown). Unreacted canola oil was visually present when the calcium soap was analyzed.

In region 3, the spectral region of the aliphatic chains is sensitive to the crystallization of soap.<sup>9</sup> Many absorption bands in this region are approximately equally spaced and with weak intensities. Poulenat et al. (2003) observed a 722  $\text{cm}^{-1}$  singlet for their calcium soap spectrum. This band near 720  $\text{cm}^{-1}$  is likely due to the rocking vibration of successive methylene groups, ( $\text{CH}_2$ ) found in calcium<sup>9</sup> and other metallic soaps.<sup>28</sup> The two characteristic bands (1350–1180  $\text{cm}^{-1}$  and an additional sideband near 720  $\text{cm}^{-1}$ ) are found in both the lab-scale FOG deposit and calcium soap as shown in Figure 2. In region 4, the calcium–oxygen bond absorption band is at 665  $\text{cm}^{-1}$ .<sup>9</sup> This band was present in the infrared spectra of both samples. An unknown cluster of spectral peaks was found around 1000–1300  $\text{cm}^{-1}$  in both the lab-scale FOG deposit and the pure calcium soap spectra that was not present in any other FTIR spectra analyzed in this study. These additional peaks may be due to organic constituents within the FOG source (unknown for the lab-scale FOG deposit and canola oil for the pure calcium soap) containing possible unsaturated trans double bonds that display peaks near this region.<sup>26</sup>

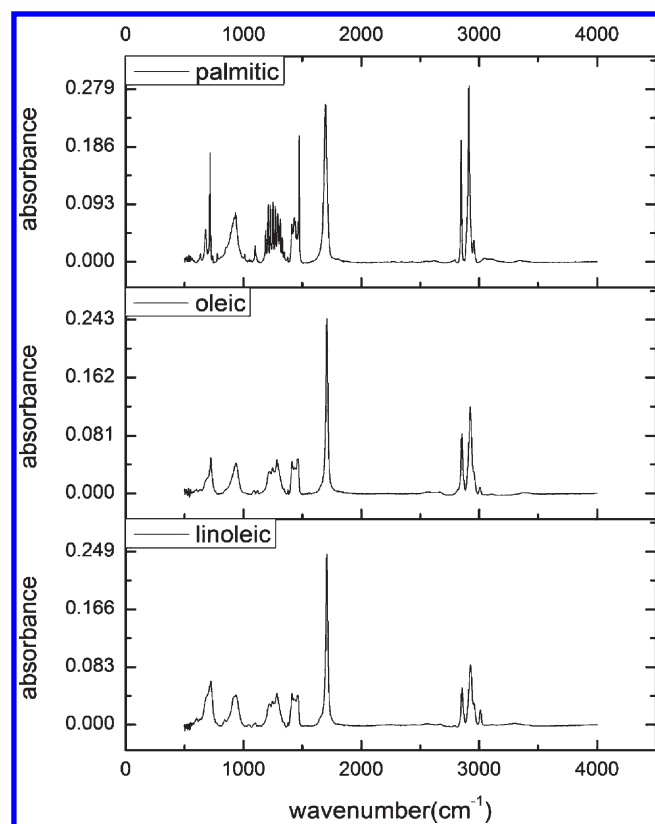
Overall, the strong similarity between FOG deposit and calcium soap infrared spectra, particularly the four absorption bands of Poulenat et al.,<sup>9</sup> suggest that FOG deposits are likely



**Figure 3.** Baseline corrected infrared spectra of three FOG deposit samples from sewer lines.

metallic salts of fatty acid made of calcium and formed as a result of saponification. The question then is whether FOG deposits from actual sewer lines have similar spectral profiles as with the pure calcium soap and the lab-scale FOG deposits, and in addition, if these spectral signatures differ in pure fatty acids or lipid samples.

**Infrared Spectra of FOG Deposits from Sewer Lines.** The infrared spectra of three FOG deposit samples are shown in Figure 3. The FOG deposit sample from the apartment area has a strong infrared spectral similarity to the FOG deposits formed in the lab. The absorption bands in four characteristic parts of the calcium soap were present in the FOG deposit sample from the apartment area, including the broad band at around  $3400\text{ cm}^{-1}$  (region 1), the disappearance of absorption band at  $1745\text{ cm}^{-1}$  and appearance of two absorption bands of  $\nu_1$  and three absorption bands of  $\nu_2$  (region 2), the singlet at  $722\text{ cm}^{-1}$  (region 3), and the calcium–oxygen band at  $665\text{ cm}^{-1}$  (region 4). The FOG deposits from shopping centers 1 and 2 display some similarity but differ from the lab FOG deposit and apartment area samples. All samples displayed the absorption bands from characteristic regions 1, 3, and 4 in their infrared spectra. Significant differences, however, were noted in region 2 ( $1800\text{--}1350\text{ cm}^{-1}$ ). In this region, although the absorption band at  $1745\text{ cm}^{-1}$  was not present, two strong intensity absorption bands appeared at around  $1700\text{ cm}^{-1}$ . Absorption bands at  $1577\text{ cm}^{-1}$  and  $1541\text{ cm}^{-1}$  were observed in  $\nu_2$  from shopping center 2, but only  $1541\text{ cm}^{-1}$  was observed in  $\nu_2$  from shopping center 1. Three other bands at  $1462$ ,  $1430$ , and  $1411\text{ cm}^{-1}$  appeared in both shopping center samples.



**Figure 4.** Baseline corrected infrared spectra of palmitic, oleic, and linoleic acids.

The differences noted in region 2 could be attributed to other materials accumulating in the FOG deposit, which led to the overlap of other absorption bands. In particular, the calcium–oxygen bond was present in region 4, but unlike the lab-scale and apartment area FOG deposit samples, the peak of the broad band was not at  $665\text{ cm}^{-1}$  but at  $680\text{ cm}^{-1}$ . It is likely that other materials accumulating in the FOG deposit affected the appearance of absorption bands. As discussed earlier, a large amount of fatty acids accumulated in shopping center FOG deposits. It is likely that the accumulation of fatty acids or unsaturated oil such as canola affected the appearance of absorption bands since a number of different food service establishments that potentially discharge a wide variety of lipid contents are present in the shopping center.

**Infrared Spectra of Pure Fatty Acids and Fat.** Three dominant fatty acids measured in the FOG deposits (palmitic, oleic, and linoleic) were subjected to FTIR analysis (Figure 4). In the region of  $1800\text{--}1350\text{ cm}^{-1}$  (region 2), for palmitic acid, a single strong intensity band was found at  $1690\text{ cm}^{-1}$ . Three other bands also appeared in the palmitic acid spectrum at  $1470$ ,  $1430$ , and  $1411\text{ cm}^{-1}$ . For oleic acid, a single strong intensity band was located at  $1704\text{ cm}^{-1}$  with three other bands located at  $1464$ ,  $1430$ , and  $1411\text{ cm}^{-1}$ . The linoleic acid spectrum also displayed a single strong intensity band at  $1704\text{ cm}^{-1}$  with three other bands observed at  $1460$ ,  $1430$ , and  $1411\text{ cm}^{-1}$ .

The three strong intensity bands at  $1690\text{ cm}^{-1}$ ,  $1704\text{ cm}^{-1}$ ,  $1704\text{ cm}^{-1}$ , from palmitic, oleic, and linoleic, respectively, may account for the two strong intensity bands observed near  $1700\text{ cm}^{-1}$  in shopping center FOG deposit samples. The three bands located at  $1464$ ,  $1430$ , and  $1411\text{ cm}^{-1}$  in the shopping

center FOG deposits are very similar in position to the three bands observed in the oil standards. There were no bands located at 1577 and 1541  $\text{cm}^{-1}$ . However, the weak intensity bands at 1577 and 1541  $\text{cm}^{-1}$  were observed in the FOG deposits. The results of the fatty acid spectra appear to support the hypothesis that five characteristic bands of calcium soap are present but with weak intensities and are masked by the bands attributed to the accumulation of fatty acids. In the region at around 670  $\text{cm}^{-1}$ , palmitic had an absorption band at 680  $\text{cm}^{-1}$ , while oleic and linoleic had shoulders at 680  $\text{cm}^{-1}$ . These differences in peaks for the fatty acids investigated could explain why the spectral peak of FOG deposits from shopping centers was at 680  $\text{cm}^{-1}$  instead of 665  $\text{cm}^{-1}$  as suggested by Poulenat et al.<sup>9</sup>

Lard or an equivalent saturated fat is another possible candidate accumulating in the FOG deposit as it solidifies at room temperature. The infrared spectrum of lard is shown in Figure S1 in the Supporting Information (SI). In the region of 1800–1350  $\text{cm}^{-1}$ , a strong intensity absorption band was located at 1731  $\text{cm}^{-1}$  instead of near 1700  $\text{cm}^{-1}$ . No absorption band was observed at or near 670  $\text{cm}^{-1}$ . Consequently, lard was not likely one of the materials that accumulated in the shopping center FOG deposits.

Therefore, the FOG deposit from the apartment area is likely the product of a saponification reaction as is the lab-scale FOG deposit. However, the FOG deposits from the shopping centers are not only the products of the reaction between free fatty acids and calcium but also contained unreacted fatty acids such as palmitic, oleic, and linoleic acids. These unreacted free fatty acids may likely draw calcium and other cations toward the solid FOG deposit matrix based on the effects of van der Waals attraction and electrostatic repulsion (DLVO theory).<sup>11</sup> However, more research needs to be performed to prove this additional mechanism of drawing calcium toward the FOG deposit.

FTIR analysis demonstrated a strong similarity between the lab-scale FOG deposit and calcium soap as shown in their infrared spectra, particularly in the absorption bands of four characteristic regions previously identified for calcium soap. Analysis of these four infrared spectral band regions indicated that FOG deposits are likely metallic salts of fatty acid made of calcium and formed as a result of saponification. However, the difference among FOG deposit samples, such as different total fat to calcium ratios and appearance of additional bands due to the unreacted fatty acids (e.g., palmitic, oleic and linoleic), indicated that some FOG deposits are not only formed by the reaction between free fatty acids and a metal but are also aggregates made of excess calcium or fatty acids based on DLVO theory. Although the spectral peak positions of the different samples analyzed in this study are not significantly shifted, peak intensities were different. It is possible that the different FOG sources may have gone through oxidative changes (i.e., become more oxygenated), causing the fatty acid salt to contain more polar groups that lead to band shifts as well as changes in intensity. In addition, changes in intensity could be the result of different FOG source concentrations. Nonetheless, the results of this study shed light on the formation mechanisms of FOG deposits and will ultimately lead to an improved understanding of possible measures to prevent FOG deposit from forming and blocking sewer lines.

## ■ ASSOCIATED CONTENT

● **Supporting Information.** Figure S1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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