

# Physicochemical Characterization of Sludge Originating from Vegetable Oil–Based Cutting Fluids

A. J. B. Sutton<sup>1</sup> and D. J. Sapsford<sup>2</sup>

**Abstract:** Vegetable oil–based cutting fluids are a relatively recent development in large-scale metal machining. A metal machining factory in Wales that switched from mineral oil-based to vegetable oil-based cutting fluids has experienced the occurrence of a problematic floating sludge within the settling and holding tanks at the on-site effluent treatment plant. Physicochemical analyses have found that the sludge is composed of on average 33% water, 20% oleic acid, and 18% palmitic acid, originating from the vegetable oil–based cutting fluids used at the factory. A solvent separation step was devised and used successfully to separate water inherent within the sludge so as to study the division of the inorganic elements within the water and organic phases of the sludge. It was found that only a minor constituent of the sludge can be accounted for by Ca-bonded fatty acids. Formation of the sludge is suspected to be due to the biologically induced hydrolysis and oxidation of the oils from esters to the free fatty acids and subsequent creaming, forming a layer of stable floating sludge on the surface of the effluent storage tanks. DOI: 10.1061/(ASCE)EE.1943-7870.0001014. This work is made available under the terms of the Creative Commons Attribution 4.0 International license, <http://creativecommons.org/licenses/by/4.0/>.

**Author keywords:** Fat, oil, and grease (FOG); Sludge; Esters; Rapeseed; Oleic acid; Palmitic acid; Tribology.

## Introduction

This study focuses on the occurrence of a problematic floating sludge that accumulated within the holding tanks of an on-site effluent treatment plant (ETP) at a metal-machining plant. The sludge occurrence began after the introduction of vegetable oil–based cutting fluid (VOCF) in the plant to replace the use of mineral oil–based cutting fluid (MOCF). The sludge occurrence was not limited to a single on-site treatment plant, but has been reported to be occurring at many other plants that have likewise switched from MOCFs to VOCFs for their machining processes.

The use of vegetable oils as a replacement for mineral oils in lubrication applications (such as VOCFs) becoming much more widespread (Bartz 1998; Erhan and Asadauskas 2000) has been brought about by the need for environmentally friendly and biodegradable products. In common with other lubricants, MOCFs and VOCFs are known within the tribology field to degrade (e.g., Rasberger 1997; Schneider 2006) and form sludge, and specific tests exist to measure the likelihood of oil to oxidize or hydrolyze and form sludge [e.g., ASTM 2015; Coordinating European Council (CEC) L-103-12 (CEC 2014); Wooton 2007]. Sensitivity to hydrolysis, low resistance to oxidative degradation, and poor low-temperature properties are recognized as major issues for vegetable oils (Erhan and Asadauskas 2000; Schneider 2006). However due to the recent (circa 2000) introduction of VOCFs to the metal-machining industry and limited introduction at manufacturing plants, the large-scale sludge accumulation problem in ETPs reported in this paper has hitherto not been systematically

recorded or studied and is thus of interest to environmental engineers.

A similar sludge was found after spillage of VOCFs during shipping at sea (ITOPF 2010); aside from this there is currently no literature available on VOCF sludge and its composition. A related phenomenon, fat, oil, and grease (FOG) formation in sewers, has been more extensively studied (e.g., Nitayapat and Chitprasert 2014; He et al. 2011; Williams et al. 2012; Keener et al. 2008) and results in sludge with similar physiochemical characteristics to that observed in the ETP. FOG is partially composed of metallic salts of fatty acids and free fatty acids (FFAs) (He et al. 2011; Williams et al. 2012), with a water content of 15-95% (Williams et al. 2012). It has similar semisolid, adherent, and buoyant physical properties as the sludge found at the metal-machining factories. The main source of FOG in sewers is from cooking oils, with one of the most widely used being rapeseed oil (USDA 2009).

The aims of this study are to present a methodology for the physicochemical characterization of the VOCF sludge, determine whether soap constitutes a significant fraction of the sludge (as has been found in studies of FOG), and suggest a plausible mechanism to the route of formation of the VOCF sludge.

## Vegetable Oil–Based Cutting Fluids

Cutting fluids are used in the machining and forming of metals to lubricate and cool the processes. Several kinds of cutting fluid exist including neat oils, oil in water emulsions using petroleum distillates (MOCFs) or vegetable oils (VOCFs), pastes, aerosols, and gases. The use of VOCFs has increased since its introduction in circa 2000 because of their demonstrably reduced environmental impacts and toxicity compared to MOCFs (Lawal 2012; Clarens 2008; McManus 2003). Commonly used vegetable oils used include soybean, sunflower, rapeseed, and palm oil (Shashidhara and Jayaram 2010). All vegetable oils comprise numerous components such as monoglycerides, diglycerides, and FFAs in varying concentrations; however their main constituent is triglycerides, with three fatty acid chains linked by a glucose molecule

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(Ștefănescu et al. 2002), e.g., trimethylolpropane trioleate. The physical properties of the oils are influenced by which FFAs are bonded to the glucose (or alternative) molecule, which may not all be the same fatty acid (Shashidhara and Jayaram 2010). For example, the triglycerides in rapeseed oil are composed of oleic acid (60%), palmitic acid (4%), linoleic acid (20%), and alpha-linoleic acid (10%); the values in parentheses indicate the average percentage composition of the ester by the named free fatty acid (Gunstone 2009).

## Site Description

A floating sludge of unknown composition had accumulated within the settling and holding tanks at an on-site ETP in a metal-machining factory in Wales. Prior to 2006, the factory had been using MOCFs; however, following a drive to reduce the environmental impacts of its cutting processes, it changed the bulk of its systems to use VOCFs and vegetable oil-based hydraulic fluids (lubricants). Within 6 months a floating sludge had started to form in the on-site effluent settling tanks. Other sites with similar sludge occurrence had also recently changed from MOCFs to VOCFs.

The VOCFs used as cutting fluid, slideway oils, and hydraulic fluids at the plant are refined rapeseed oil and synthetically produced oil using oleic acid as the FFA. Triethanolamine is the surfactant used. Cutting fluid is continuously circulated around the metal-machining terminals, with each circuit being topped up with water (lost to evaporation), cutting oil, and surfactant. Biocides and acticides are also added to increase the longevity of the circulating VOCF. Along with these chemicals the systems use trace amounts of antifoam, pH adjusters, and corrosion inhibitors. When the VOCF quality is compromised the circuit is completely drained to the ETP holding tanks. Other inputs to the ETP include surfactant-water mixtures used in cleaning the components.

Approximately 350 m<sup>3</sup> of VOCF was used annually at the factory, with the bulk of this being treated at the on-site ETP. The ETP uses ceramic ultrafiltration modules, which produce water with a chemical-oxygen demand averaging 5,000 mg/L that is disposed of into the sewer. The waste oil produced is approximately 50% purity and is transported by vacuum tanker off-site for acid splitting or incineration. The ETP treats approximately 24,000 m<sup>3</sup> of wastewater annually. The effluent is stored in 500-m<sup>3</sup> settling tanks for up to a month before being processed through the ultrafiltration modules. It was in these

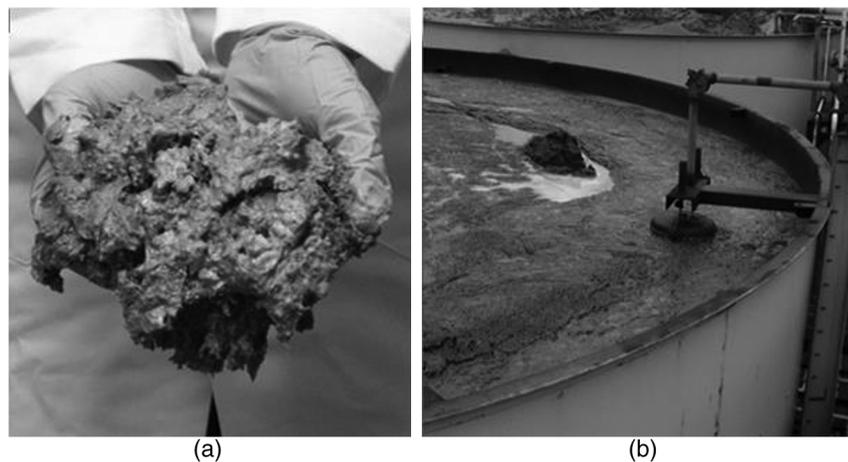
settling and holding tanks that the floating sludge was occurring. Over a period of 6 years there has been an estimated 1,000 m<sup>3</sup> of sludge formed between the five 500-m<sup>3</sup> effluent settling tanks. Two types of sludge were observed (Fig. 1). Sludge 1 is firmer, higher viscosity, and more claylike in appearance, while Sludge 2 is comparatively lower in viscosity, but still semisolid.

## Methods and Materials

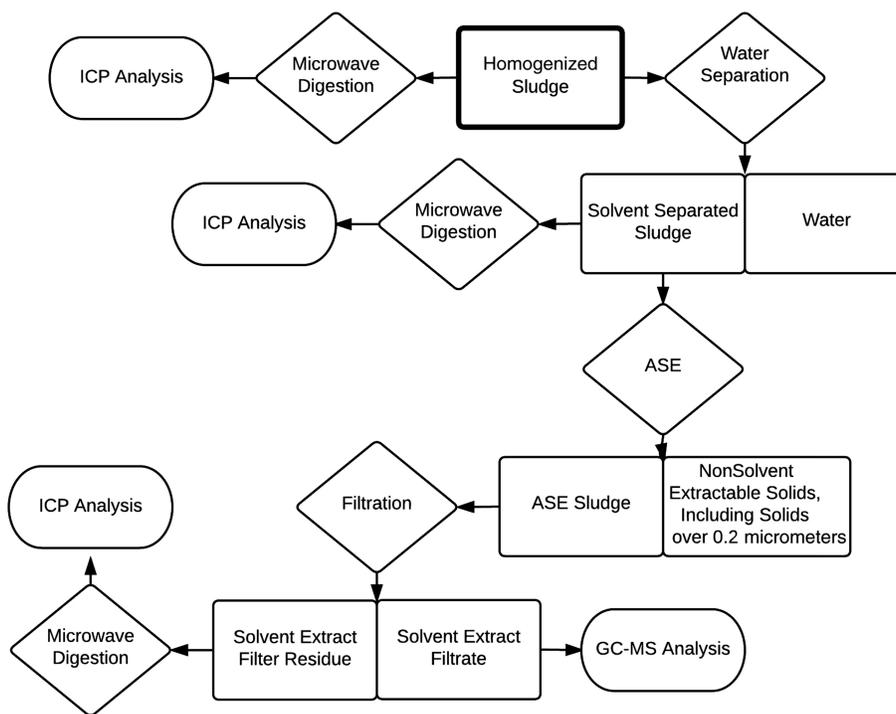
Samples were extracted from the holding and settling tanks and were taken at a depth of 0.1–0.3 m below the surface in multiple locations. The sludge was mixed by hand to homogenize it and subjected to a range of physicochemical analyses to determine organic and inorganic composition, including microscopic examination, gas chromatography–mass spectrometry (GC-MS), inductively coupled plasma–optical emission spectrometry (ICP-OES), total inorganic-organic carbon determinations, Fourier transform infrared spectroscopy (FTIR), and melting point determination. A technique for the separation of the water and organics was devised to differentiate aqueous inorganic elements in the sludge water from inorganic elements associated with the sludge organic fraction. The methods detailed subsequently are summarized in the flow diagram in Fig. 2, which shows the processes that are undertaken on the sludge prior to each analysis, with each process starting with homogenizing the sludge. For example, sludge that has been analyzed by GC-MS was initially homogenized, followed by water separation, then accelerated solvent extraction (ASE), filtration, and finally analysis by GC-MS. Inorganic analytes in the water and solvent extract filtrate were calculated from ICP-OES measurements on other parts of the sludge. FTIR analysis was conducted on the unadulterated sludge.

## Optical Microscopy

A fresh (same day sampled) homogenized sample of sludge was used for analysis for all of these tests. A sample was placed on a microscope slide and carefully compressed using another slide. Magnifications between 10× and 200× were used to observe the sample, using dark field, light field, and phase contrast microscopy. Alongside this a dip slide was used to calculate the number of living bacteria within the sample. Both sides of the dip slide were wiped across the surface of the homogenized sludge and then incubated at 37°C for 48 h.



**Fig. 1.** (a) Consistency of Sludge 1 held in an analyst's hands; (b) Sludge 2 in one of the 500-m<sup>3</sup> settling tanks at the on-site ETP in Wales (images by A. J. B. Sutton)



**Fig. 2.** Flow diagram detailing the separations undertaken and the analysis conducted on the sludge

### **Total Carbon, Total Organic Carbon, and Total Inorganic Carbon**

Vacuum-dehydrated sludge was used for carbon content analysis. Total carbon (TC) and total inorganic carbon (TIC) analysis was conducted using a Shimadzu SSM-5000 A solid sample module and Shimadzu TNM-1 detector; total organic carbon (TOC) was calculated by the difference between the two. TC in triplicate was measured using 0.5 g of dehydrated sludge. A calibration check was run and showed accuracy to be  $\pm 5\%$  against a glycerol standard for TC and against calcium carbonate standard for TIC prior to analysis of the sludge. Three repetitions of each analysis were undertaken, with the results showing the average of the three, giving Sludge 1 a standard deviation of  $\pm 0.6\%$  and Sludge 2  $\pm 1.5\%$ .

### **Fourier Transform Infrared Spectroscopy**

A Varian 3100 FTIR was used along with a Varian 600 UMA FTIR microscope to analyze the unadulterated sludge, which was placed directly on the crystal. Scans at a resolution of 4 cm, wave number of 4,000–650  $\text{cm}^{-1}$ , and 100 cycles were conducted.

### **Melting Point**

Melting point tests have been used in analyses of FOG samples (e.g., Williams et al. 2012; Nitayapat and Chitprasert 2014). The melting point test in this case was conducted to aid in differentiation between metal-bound fatty acids and FFAs. Using a syringe, 10 g of sludge was injected into the bottom of a test tube and placed into a water bath, which was heated at a rate of  $5^\circ\text{C}/\text{min}$  from ambient. Once the sludge started to melt the bath was allowed to cool by  $10^\circ\text{C}$  and the test tube replaced with fresh sludge. The heating rate was altered to  $1^\circ\text{C}/\text{min}$  increase, where the initial and full melting points were measured to determine the melting range. This was repeated three times for each sample.

### **Water Separation**

Separation and removal of the water is required for organics analyses by GC-MS and has been achieved using various methods in the literature applied to FOG samples and oily wastes and soils: (1) melting the lipid followed by water-fat separation by centrifugation or use of anhydrous sodium sulphate to absorb water, or by drying at  $103^\circ\text{C}$  (Hamilton and Rossell 1986) or  $105^\circ\text{C}$  (Nitayapat and Chitprasert 2014), (2) entrainment distillation using the Dean and Stark method (Hamilton and Rossell 1986), (3) direct oven drying at temperatures between 101 and  $105^\circ\text{C}$  (e.g., Hamilton and Rossell 1986; Williams et al. 2012; He et al. 2011; Keener et al. 2008), (4) freeze drying, (5) microwave drying [ASTM D4643-08 (ASTM 2008)], and (6) vacuum dehydration using a vacuum desiccator with silica gel crystals. Water determination in oil sludge, but not water separation can be achieved using nuclear magnetic resonance (Zheng et al. 2013) or Karl-Fischer titration.

The properties of fats can be affected by excessive heat, chemical addition, and oxidation. In particular, heating can cause oxidation of fatty acids. Although drying is the most popular method, in this separation the aqueous inorganic elements remain within the dried sludge. Thus in this study liquid-liquid separation was the preferred method to allow determination of the deportment of inorganic elements between organic and water portions of the sludge.

Water separation was conducted for GC-MS and ICP-OES analysis using the following technique. Into a separating funnel 25 g of homogenized sludge and 50 mL of dichloromethane (DCM) were added and shaken vigorously, then left to settle for 15 min to develop a boundary layer. The lower layer with DCM and dissolved organics was drained. This was repeated five times, at which point the DCM was clear, indicating that minimal solvent-soluble organics remained within the separating funnel. The solvent was evaporated from the solution, leaving the resultant oily residue to be weighed and subject to further analyses; this residue is

referred to as solvent-separated sludge (SSS). Three repetitions were undertaken, with the results showing the average of the three.

### Organics Extraction and GC-MS

Water-insoluble organics are typically extracted from environmental solids, such as soils, clays, sediments, and sludge using Soxhlet extraction [e.g., Furniss et al. 1989; U.S. EPA method 3545 (U.S. EPA 2007)]. In the present study the extractor used was a Dionex accelerated solvent extractor (ASE100). A polar (hexane) and nonpolar (acetone) solvent mix, of 1:1 ratio was used as the extractant. The following ASE operating conditions were used: 175°C oven temperature, 10,300–13,800 kPa (1,500–2,000 psi) pressure, 5–10 min static time, 60–75% of cell volume for flush, 60 s nitrogen purge at 1,030 kPa (150 psi), and one cycle for extraction. (U.S. EPA 2007), repeated once to ensure complete extraction. Non-solvent-extractable (NSE) solids and solids  $>0.2 \mu\text{m}$  were filtered out during the extraction, leaving the ASE sludge for further processing. After extraction the solvent extract was cooled to room temperature, where solids were seen to have formed and were filtered using a 0.2- $\mu\text{m}$  filter. Solids filtered out at this point are hereafter referred to as solvent extract filter residue (SEFR), while the liquid to be analyzed by GC-MS is known as the solvent extract filtrate.

The solvent extract filtrate was qualitatively and quantitatively analyzed using a Perkin Elmer Clarus 500 GC-MS using an Elite 5MS column of 30 m length, 0.25 mm inner diameter, and film thickness of 0.25  $\mu\text{m}$ , with the following settings: system pressure 72 kPa ( $\sim 10.5$  psi), 1 mL/min helium carrier, injection temperature of 250°C, and temperature program comprising 100°C initial temperature, hold for 2 min, increasing at 4°C/min until 310°C, hold for 4 min. The column was cleaned between analysis runs using blank DCM samples. Qualitative analysis was performed using the *NIST MS Search 2.0* database. Qualitative analyses indicated that palmitic and oleic acid were the dominant chemicals, with quantitative analyses being performed using a three-point calibration using standards made up from analytical grade palmitic acid and oleic acid in DCM. Triglycerides with more than 58 carbon bonds in their structure were suspected to be in the sludge, however due to their high molecular mass and boiling point (e.g., 851°C for trimethylolpropane trioleate) they would not elute from the columns. Samples of 99.5% purity of palmitic and oleic acid were run using the same operating conditions to confirm that the NIST database was correctly identifying the compounds.

### Microwave Acid Digestions and ICP-OES

Due to the organic content of the sludge (approximately 99% excluding water), digestion was required. Typical digestions in the literature include the following examples used for FOG-type samples: (1) refluxing with 50%  $\text{HNO}_3$  at 95°C (Williams et al. 2012), (2) digestion using concentrated nitric acid at 95°C followed by addition of hydrogen peroxide (Keener et al. 2008; U.S. EPA 1994), (3) microwave-assisted acid digestion using  $\text{HNO}_3$  and of HF (or other appropriate acid),  $\text{KMnO}_4$  or  $\text{H}_2\text{O}_2$  used as oxidants (U.S. EPA 1996), and (4) ashing at 500°C followed by acid ( $\text{HCl}/\text{HNO}_3$ ) digestion (He et al. 2011).

Ashing was trialed but found to be problematic, therefore microwave digestion was used: To 0.5 g of sludge 9 mL of  $\text{HNO}_3$ , 3 mL of  $\text{HCl}$ , and 2 mL of  $\text{H}_2\text{O}_2$  were added. The sample was heated to 180°C in 5.5 min and maintained at that temperature until the total heating time reached 10 min. The digested sample was diluted to 50 mL using deionized water and subjected to ICP-OES analyses (Perkin Elmer Optima 2100DV) using a multielement certified standard.

Ten repetitions of the full sludge extraction, microwave digestion, and ICP-OES analysis were conducted.

## Results and Discussion

### Optical Microscopy

Microscopic examination of wet sludge spread onto a glass slide revealed that the sludge samples predominantly consisted of an emulsion of spherical liquid droplets, typical in appearance to an oil emulsion. A very small amount of microbial biomass, namely, some fungal fragments, were also present. Dip-slide testing (data not included) of the sludge revealed only moderate microbial growth. Fig. 3 shows spherical droplets of a liquid with another liquid. This is likely to be a water-in-oil emulsion (inverted emulsion) due to the low water content of the sludge. Also visible are minor fragments of swarf from the machining processes.

### Total Carbon, Total Inorganic Carbon, and Total Organic Carbon

The TC, TIC, and TOC analyses sludge showed that none of the TC present was present as TIC, ruling out the presence of dissolved or solid phase carbonates in the sludge and that all the TC = TOC for the sludge. The values of TC for the vacuum dehydrated sludge were 79.84% ( $\pm 0.6\%$ ) and 75.47% ( $\pm 1.5\%$ ) for Sludges 1 and 2, respectively. TC corrected to the wet sludge was 55.60 and 48.64% for Sludges 1 and 2, respectively.

### Compounds Identified by GC-MS

A number of organic compounds were detected (Table 1) in the solvent-separated sludge using the NIST library. Of these compounds palmitic acid and oleic acid had by far the largest peak areas, therefore these were subsequently analyzed quantitatively. No vegetable triglycerides were detected, although their presence is suspected due to their existence in the virgin VOFC, but the GC-MS settings did not allow elution of triglycerides.

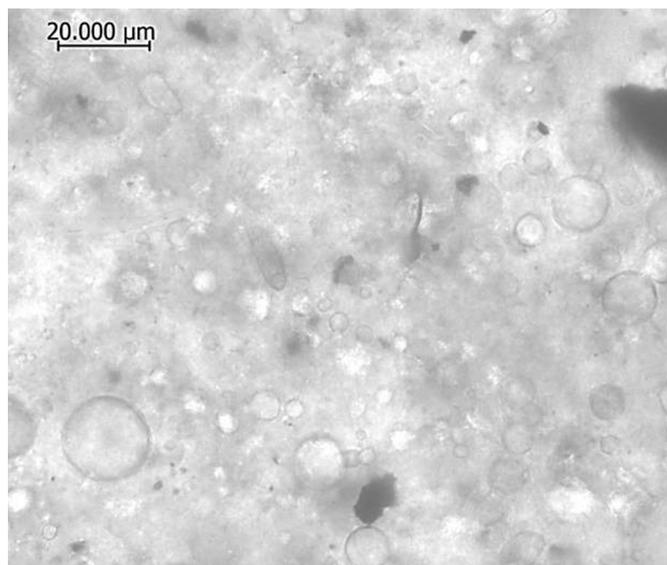


Fig. 3. Optical microscope image of Sludge 2 using transmitted light from underneath at a zoom of 100 $\times$

**Table 1.** Organic Compounds Detected during Qualitative Analysis of the Solvent Extracted Sludge by GC-MS Using an Elite 5-MS Column and the NIST Library

Compound	Sludge 1	Sludge 2	Melting point (°C)
Dicyclohexylamine	Yes	Yes	-2
Palmitic acid	Yes	Yes	63
Oleic acid	Yes	Yes	14
Stearic acid	Yes	Yes	69
Palmitic anhydride	Yes	No	61–64
Pentadecane	No	Yes	8–10
Pentadecane, 7-methyl-	No	Yes	Unknown
Hexadecane	No	Yes	18
Myristic acid	No	Yes	52–54
Octadecane	No	Yes	28–30
Hexadecanoic acid, 2-methylpropyl ester	No	Yes	Unknown
Decyl oleate	No	Yes	Unknown

Note: Melting point also shown to reference against melting test data.

The quantitative analysis of the sludge revealed that palmitic acid formed 23.95 and 11.78% of total sludge mass and oleic acid content was 17.18 and 23.13% of Sludge 1 and Sludge 2, respectively. These are within the range of the 10–70% oleic acid content found in FOG (Nitayapat and Chitprasert 2014). Oleic acid and palmitic acid were found in many FOG samples (Nitayapat and Chitprasert 2014; Keener et al. 2008; Williams et al. 2012) in varying concentrations and ratios.

Non-solvent-extractable solids account for 2.29 and 1.50% of Sludge 1 and Sludge 2. The solvent extract filter residue comprised 0.49% of Sludge 1 and 0.71% of Sludge 2 by mass. These solids are suspected to be calcium soaps, i.e., calcium palmitate, oleate, and stearate, which while not soluble in organic solvents at room temperature and pressure (Harrison 1924) may have been solubilized under the elevated pressure and temperature of the ASE extraction to later precipitate as the solvent cooled.

### Elemental Analyses

The results of the 28-element ICP-OES analysis are detailed in Table 2. The relative concentrations are  $\text{Ca} > \text{Na} > \text{Al} > \text{Fe} > \text{Mg} > \text{Li} > \text{Zn}$ , with these seven elements comprising 94% of the elements found within the sludge. Relatively high concentrations of the main elements present remain within the water after solvent separation, showing that significant amounts of the calcium, sodium, and lithium are not bound to the solvent soluble organic fraction. This is important because studies on FOG by authors such as Nitayapat and Chitprasert (2014), He et al. (2011), Williams et al. (2012), and Keener et al. (2008) have not separated the water from the organics in this way and have assumed that all of the inorganic elements detected are inherent within the organic phase, which is not the case for this sludge.

Calcium concentrations within the organic portion of the sludge were 135.5 and 1,303 mg/kg for Sludge 1 and Sludge 2, respectively. Total concentrations in the wet sludge are 932.3 mg/kg ( $\pm 3.6\%$ ) for Sludge 1 and 1,973 mg/kg ( $\pm 3.6\%$ ) for Sludge 2. These concentrations are only 10–20% of the total concentrations found by Williams et al. (2012), although those results are based on dried sludge, so could be up to 20 times lower if water content of up to 95% was included in the concentration calculation. FOG studied by Keener et al. (2008) had a calcium content of two to four times greater than that of the sludge under study and a sodium concentration within the range found in Sludge 1 and Sludge 2.

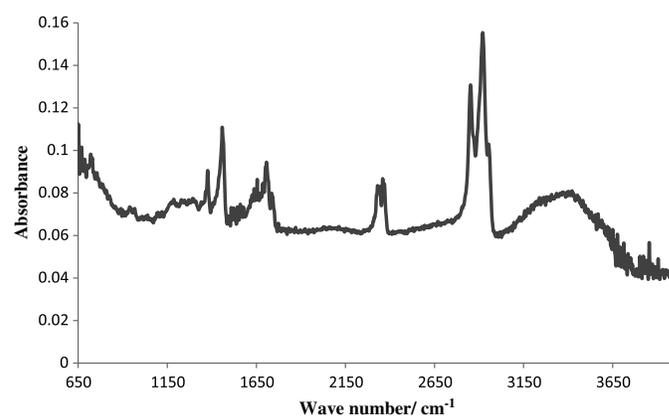
**Table 2.** Results of the 28-Element ICP-OES Analysis of the Microwave-Digested Sludge

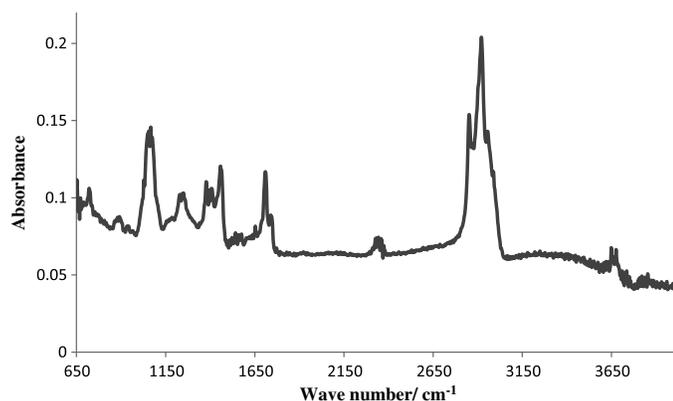
Analyte	Sludge 1			Sludge 2		
	Total (mg/kg)	Solvent separated (mg/kg)	Water (mg/kg)	Total (mg/kg)	Solvent separated (mg/kg)	Water (mg/kg)
Ca	932.3	135.5	797.9	1,973	1,302	670.4
Na	303.6	96.85	206.7	77.74	33.97	43.77
Mg	26.15	9.38	16.76	84.61	39.43	45.18
K	13.76	4.67	9.09	25.35	11.11	14.24
Al	131.63	76.91	54.71	775.5	439.57	335.96
Fe	124.09	47.59	76.50	1,258	854.7	403.1
Mn	1.36	0.27	1.09	22.38	13.63	8.75
Ag	0.13	0.08	0.04	0.11	0.14	-0.03
As	0.47	0.47	0.00	0.12	0.36	-0.23
Be	4.77	1.42	3.34	6.33	1.83	4.50
Ba	16.35	9.09	7.26	32.01	17.53	14.48
Bi	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
Cd	3.99	2.08	1.91	3.88	2.07	1.81
Co	0.60	0.34	0.25	0.71	0.43	0.28
Cr	0.28	0.13	0.15	0.65	0.39	0.27
Cu	2.01	1.03	0.97	6.32	3.80	2.52
Li	24.46	13.40	11.06	66.98	36.92	30.06
Mo	0.69	0.32	0.37	0.73	0.40	0.33
Ni	4.69	2.80	1.89	7.34	4.84	2.49
Pb	3.24	1.56	1.68	8.44	4.54	3.90
Sb	11.58	5.82	5.76	29.09	19.23	9.85
Se	2.47	1.34	1.12	2.57	1.54	1.03
Si	6.07	3.51	2.56	5.92	3.85	2.07
Sr	4.75	1.53	3.22	4.27	2.47	1.80
Ti	1.34	0.71	0.63	4.48	2.29	2.19
Tl	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
V	0.22	0.10	0.12	0.64	0.38	0.26
Zn	18.56	11.35	7.21	108.04	69.75	38.29

Note: Units are mg/kg of wet sludge; b.d. = below detection.

### Fourier Transform Infrared Spectroscopy

The FTIR spectra are almost identical for Sludge 1 (Fig. 4) and Sludge 2 (Fig. 5), which show intense, sharp peaks at 2,800–3,000  $\text{cm}^{-1}$ , which correspond to the C–H bond. Smaller but still sharp peaks are seen at 1,600–1,800  $\text{cm}^{-1}$ , representing C=O bonds; more precisely, the peak is between 1,650 and 1,750  $\text{cm}^{-1}$ , which relates to acids and esters. Another C–O bond is detected at 1,200–1,300  $\text{cm}^{-1}$ . Overall there are C–O bonds, C–H bonds, and C=O bonds, along with acids and ester bonds.

**Fig. 4.** FTIR spectra of unadulterated Sludge 1 in the range 4,000–650  $\text{cm}^{-1}$



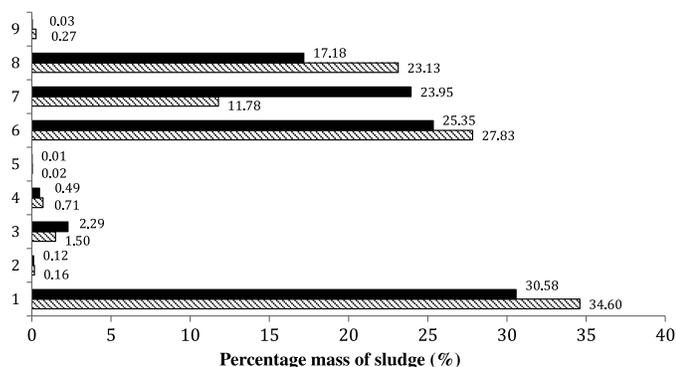
**Fig. 5.** FTIR spectra of unadulterated Sludge 2 in the range 4,000–650  $\text{cm}^{-1}$

All of these bonds are present within palmitic and oleic acid, however the most common bond in these chemicals was the C–H bond, which relates to the intense peak seen at 2,800–3,000  $\text{cm}^{-1}$ . The detection of esters confirms that not all of the oil had been degraded into free fatty acids.

Direct comparisons with calcium palmitate, palmitic acid, oleic acid, calcium stearate, stearic acid, and the mineral oil used in the metal machining factory showed that no one chemical alone matched the sludge spectra, but each had their similarities on different peaks, except the mineral oil. Therefore it is likely that the sludge is formed of a mix of these chemicals, along with others chemicals that were not analyzed.

### Total Sludge Composition

The results from water separation, GC-MS, and ICP-OES analyses were combined to form an overall composition for the sludge, shown in Fig. 6. The sludge has been shown to be an organically based inverted emulsion, composed mostly of water, oleic acid, palmitic acid, and unidentified organics, with little or no mineral oil present. These unidentified organics are suspected to be triglycerides (rapeseed oil or trimethylolpropane trioleate) found in the virgin VOFC and other organic compounds that have been qualitatively identified (Table 1).



**Fig. 6.** Chemical breakdown of Sludge 1 (black) and Sludge 2 (hatched), where 1 = water, 2 = inorganics in water, 3 = non-solvent-extractable solids including solids over 0.2  $\mu\text{m}$ , 4 = solvent-extract filter residue, 5 = inorganics in solvent extract filter residue, 6 = unquantified organics, 7 = palmitic acid, 8 = oleic acid, and 9 = inorganics in ASE sludge

The composition of the sludge can be described as similar to that of FOG because water, palmitic acid, oleic acid, and calcium are present in similar concentrations. Water (moisture) content of the sludge is on average 32.6%, compared with 54.7% (Williams et al. 2012) and 53.9% (Keener et al. 2008), although the range of moisture content in the studies by Williams et al. (2012), Keener et al. (2008), and Nitayapat and Chitprasert (2014) have a wide variation of 0–95%.

### Metallic Salts of Fatty Acids: Soap

Soap is defined as a salt of a fatty acid, saturated or unsaturated, containing at least eight carbon atoms or a mixture of such salts (IUPAC 2014). Soaps have been identified as a principal component of FOG (e.g., Keener et al. 2008), in addition saponification has been identified as a suspected causal mechanism in the formation of FOG deposits (He et al. 2011; Williams et al. 2014). Thus it is important to establish whether soaps, particularly calcium palmitate and calcium oleate, contribute significantly to the composition of the VOFC sludge or whether the FFAs dominate.

The mass requirements of calcium bonds to two fatty acids to form soap (Ca:FFA) from stoichiometry are 1:12.8, 1:14.1, and 1:14.2 for palmitic acid, oleic acid, and stearic acid respectively. The mass requirement of sodium bonds to one fatty acid to form soap (Na:FFA) from stoichiometry are 1:11.1, 1:12.3, and 1:12.3 for palmitic acid, oleic acid, and stearic acid respectively. Assuming that all of the calcium, sodium, and lithium are bonded to oleic acid and palmitic acid in a 1:1 ratio, the soap content of Sludge 1 would be 0.35%, and it would be 1.85% for sludge 2. Soap is a minor contributor to the chemical makeup of the sludge compared to water and the FFAs, oleic acid, and palmitic acid. While it is feasible that the soap may act as a surfactant in the inverse water in oil emulsion, it is unlikely that soap is important in the formation and accumulation of the VOFC ETP sludge.

Furthermore, the level of Ca present as calcium palmitate is lower than this because calcium palmitate and calcium oleate are insoluble in water (Harrison 1924), and the water contains 86% of the Ca in the sludge (Table 2). This highlights the benefit of using solvent extraction to separate water from the sludge compared to drying, which causes aqueous constituents to remain within the dried sludge and appear as part of an undifferentiated total sludge assay.

Ca is present in high concentrations, which is also observed by Williams et al. (2014) in FOG deposits. They suggested that bio-calcification may be an important mechanism in this Ca accumulation (and in FOG formation), however in the case of the VOFC sludge the TC, TIC, and TOC analyses show that inorganic carbonate such as calcite is not present in significant concentrations within the sludge.

The presence of FFA rather than soaps is further supported by the melting point analysis (see comparative data in Tables 1 and 3). Calcium palmitate, calcium oleate, and calcium stearate have no definite melting point, rather they are observed to conglutinate at 110°C and 115–120°C, respectively, and decompose at temperatures 140–160°C (Harrison 1924). The melting point of palmitic acid and oleic acid, principal components of the sludge, are

**Table 3.** Mean Initial and Full Melting Points of Sludge Samples: Three Repetitions

Sample	Initial melting point (°C)	Full melting point (°C)
Sludge 1	40.3 ( $\pm 1.2^\circ\text{C}$ )	46.0 ( $\pm 0.0^\circ\text{C}$ )
Sludge 2	59.7 ( $\pm 0.5^\circ\text{C}$ )	65.0 ( $\pm 0.8^\circ\text{C}$ )

reported to be 63 and 14°C, respectively, which ties in with the melting point analysis for palmitic acid and also explains the anecdotally operator-reported thickening of the sludge in winter months, which on consideration of the compositional data was probably due to solidification of the oleic acid fraction of the sludge.

Ca is known to accumulate in cutting fluid circuits because it is a closed loop where water is topped up to replace water lost to evaporation, which naturally leads to concentration of Ca and other ions. Ruling out Ca soaps as a major component of the VOFC sludge precludes control of Ca concentrations in the effluent, which was one of the early proposed strategies considered in preventing the VOFC sludge formation.

### Routes of Formation

Understanding the routes of formation is an important step in being able to halt the formation of the floating cutting fluid-based sludge. The two main oils used at the metal-machining factory are trimethylolpropane trioleate and rapeseed oil. Trimethylolpropane trioleate is a triglyceride containing three oleic acids and trimethylolpropane as the base. The fatty acids in rapeseed oil vary, but on average are composed of 60% oleic acid, 4% palmitic acid, 20% linoleic acid, and 10% alpha-linoleic acid (Gunstone 2009). It is suspected that the trimethylolpropane trioleate and rapeseed oil are being microbiologically degraded to free-floating oleic acid and palmitic acid. This route is mostly biologically achieved, however low and high pH can also lead to the formation of free fatty acids. Conditions within the factory VOFC coolant circuits are constantly monitored, with the pH being kept around 9 and the emulsion dosed with biocide to slow biodegradation of the cutting fluids. However, during prolonged storage in the ETP storage tanks the biocide itself will degrade or deplete, thus allowing the microorganisms to become active and biodegrade the oils.

The first stage in the degradation is bacterial lipase-promoted hydrolysis of the triglyceride (microbial rancidity) (VIU 2010). Evidence for this mechanism occurring is the qualitative detection of palmitic acid esters and decyl oleate within Sludge 2, which were not detected in the virgin VOFCs. During the triglyceride degradation mechanism other biodegradation processes can take place, including that of the degradation of the surfactant stabilizing the emulsion, triethanolamine (West and Gonsior 1996; Speranza et al. 2006). This degradation causes a decrease in the concentration of surfactant in the solution and decrease in pH. Degradation of surfactant and lowering of pH reduces the stability of micelles, thus allowing the oil and its components to separate from the solution. Because the free fatty acids densities are less than that of water, they float where they agglomerate into the mass of sludge seen in the ETP storage tanks, a phenomenon known as creaming. The glycerol or trimethylolpropane is miscible in water and remains dissolved and is processed through the ETP, which is why it is not detected within the holding tank sludge. The final stage of the sludge formation is via the generation of palmitic acid through breakdown of the oleic, linoleic, and alpha-linoleic acids. It was determined that the concentration of palmitic acid found within the sludge could not solely come from the fatty acid separation of the rapeseed ester, which contains on average only 4% palmitic acid (Gunstone 2009), therefore it must come from the degradation of the unsaturated fatty acids. The first stage in the process of fatty acid degradation starts by the breaking of double bonds, which may be why there is no linoleic or alpha-linoleic acid found within the sludge (although alpha-linoleic, linoleic, and oleic acid have almost identical retention times on the GC-MS columns). Once all of the

double bonds have been (bio)hydrogenated, then no further biohydrogenation can occur, which leaves stearic acid. Stearic acid, also known as octadecanoic acid, is then broken down to palmitic acid. Myristic acid, which is the next breakdown product of palmitic acid, was detected during the qualitative analyses of the sludge.

The buildup of the floating sludge on the surface of the water and the subsequent exclusion of water from its physical structure results in stabilization of the sludge because the microbial lipases can no longer interact with the fatty acids and degrade them further (Gurr et al. 2002); this has important implications because in the sludge state rapid biodegradation dramatically slows, which is counter to the intended full biodegradability of the VOFC products. Limitation of biodegradation due to sludge flotation was also noted by Hwu et al. (1998); other factors that may be important in preventing rapid breakdown of the sludge include lack of nutrients and high oleic acid concentrations (Pereira et al. 2002).

### Conclusions

This study has examined in detail a floating sludge at an ETP of a metal-machining factory that has switched from MOCFs to VOFCs, from which the following conclusions are drawn.

Methods have been developed and presented for the physico-chemical characterization of VOFC sludge from a metal-machining plant effluent. The sludge under study has been shown to be composed of water, oleic acid, and palmitic acid, which together form more than 70% of the mass of the sludge. Using a liquid-liquid separation using DCM provides a useful way to separate water content which preserves the identity of waterborne constituents. Not only have the data contributed to the understanding of VOFC sludge, but they may also prove useful in analysis and interpretation of similar FOG deposits.

A notable difference from FOG in the literature is that based on the analyses only a minor constituent of the sludge can be accounted for by Ca bonded fatty acids (soaps).

The route of formation of the sludge is thought to be through the creaming of existing FFA in the quiescent conditions of the holding tanks after attenuation of surfactant and biologically induced hydrolysis and oxidation of other FFAs to palmitic acid.

These findings have significant implications for the metal-machining industry (and other lubricant-using industries) because globally the switch from MOCFs to VOFCs continues. With this change in oils comes (1) the risk of formation of the sludge in ETPs with the consequent risk of closure due to reduction in capacity to store and treat effluent, high sludge disposal costs, storage risks, and increased costs associated with cleaning and maintenance, and (2) the risk to the environment posed by a stabilized floating sludge that is resistant to biodegradation.

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