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Determining Organic Pollutants in Automotive Industry Sludge

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Abstract In Brazil, the policy for disposing industrial sludge is changing from an emphasis on using controlled landfills to other treatment or co-processing methods; however, the monitoring of organic pollutants is not mandatory. The present study evaluated two general screening methods for organic pollutants in sludge generated in an automotive industrial complex in southern Brazil. The screening was performed using Soxhlet and sonication extractions and Gas Chromatograph coupled with Quadrupole Mass Spectrometry (GC/qMS). It was concluded that both techniques were effective and that most of the compounds identified were alkanes, phenols and esters. Important pollutants were detected in the sludge, which confirms the necessity of monitoring this type of residue.

Keywords Automotive sludge · Co-processing

The purification of water used in industrial processes through effluent treatment generates sludge with a high concentration of residual compounds, including ink waste, lubricants, and others (Amana et al. 2008). Moreover, sludge also contains a variety of potentially harmful substances, such as organic contaminants and metals (Laturnus et al. 2007). It is important to identify the presence of organic pollutants from different sources that might reside in industrial sludge. These pollutants include polycyclic aromatic hydrocarbons (PAHs), phthalate esters, polychlorinated biphenyls (PCBs), and other organic compounds and are especially problematic when the destination of this sludge is a co-processing facility (Laturnus et al. 2007; Laturnus and Grøn 2007; Eisentraeger et al. 2008). These substances can be toxic to animal and plant life (Eisentraeger et al. 2008). The US Environmental Protection Agency has listed as priority pollutants those that are thought to be carcinogenic or have been associated with estrogenic effects (USEPA 2012). Specific legislation regarding permissible concentrations of these organic pollutants in solid residues for Brazil and several other developing countries could not be found, even though the use of these residues for agriculture is permitted, leading to great concerns about food safety and environmental protection. This gap is evident in the legislation establishing the national policy, which contains general guidelines and establishes control of this issue, even from a qualitative point of view. One of the reasons for this gap is the limited number of laboratories that perform such analyses due to the high cost associated with standards and the high cost of each analysis.

Analysis of organic compounds with potentially toxic properties has been investigated in different types of solid waste using several techniques that are generally applied to sludge from water-treatment plants. Several studies have focused on the determination of polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) due to their known high toxicity, persistence in the environment and tendency towards bioaccumulation (Littarru and Vargiu 2003). Various extraction techniques were applied to the determination of these compounds, including Soxhlet extraction, dynamic or pressurized liquid extraction (PLE), and supercritical fluid extraction (SFE) (Korenková et al. 2006). Khadhar et al. (2010) carried out a study to determine 16 EPA-priority PAHs in samples from nine Tunisian waste water treatment plants. The authors tested two techniques

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(sonication and Soxhlet) and different organic solvent combinations for Soxhlet extraction. The best results were obtained with Soxhlet and toluene as extractor solvents for liquid–liquid separation. The quantification was conducted with gas chromatography coupled with quadrupole mass spectrometry (GC/qMS) operating with select ion monitoring, which is important in quantifying particular compounds but not useful for screening. Work related to the screening of organic pollutants in sludge produced by the automotive industry could not be found in the literature—even work using standardized methods for qualitative screening, such as EPA 3540C and 3550C, which use Soxhlet and sonication extractions, respectively (USEPA 1996, 2007), for subsequent GC/qMS analysis. These methods could be applied to sludge screening in developing countries because the quantitative evaluation of all possible organic pollutants in industrial sludge on a regular basis is not economically viable at present.

The present study is intended to characterize volatile and semi-volatile organic compounds in industrial sludge produced in an automotive industrial complex. The production capacity of this complex is more than 230,000 vehicles per year, and it occupies 140,000 square feet of building space. The production process follows the basic pattern of automotive production.

This industrial complex generates approximately 25,000 tons of solid waste per year, of which 95.1 % is Class II recyclable, 2.7 % Class I recyclable, 1.3 % Class II non-recyclable, and 0.9 % Class I non-recyclable (ABNT 2004). The plant also annually generates more than 550 tons of Class I and Class II non-recyclable solid waste that is disposed of at industrial landfills but that has the potential for reuse (Wonghon et al. 2011). Liquid effluent from all industries in this complex is treated in one place. The effluents are divided into oil, ELPO (containing emulsions of electrophoretic ink from the painting process), industrial effluents, and sanitary waste. The process operates with a grating in each line to remove solids; there are also equalization tanks for the oil line and for the ELPO. In the oil line, the equalization tank is used to remove excess oil using hydrophobic strings. Next, the oil, ELPO, and industrial effluents are mixed in a neutralization tank to adjust their pH and to precipitate and remove solids using dissolved air flotation, followed by decantation. Subsequently, sanitary effluent is combined with this effluent to perform a biological treatment using aerobic degradation. A polishing pond is also used, and all of the sludge generated from the primary and secondary treatment is combined in a sludge filler, followed by a press filter. The organic pollutants present in this sludge are the focus of the present study.

To extract the analytes, two extraction techniques based on EPA methods 3540C and 3550C were used (USEPA 1996, 2007). Compounds were separated by gas chromatography and identified by quadrupole mass spectrometry, using mass spectra similarity comparison and retention index as identification tools. Both extraction techniques applied were statistically compared by means of a significance test using the *F* test.

Materials and Methods

The solvents used in the experiment were acetone (99.8 %) and *n*-hexane (96.0 %), both from Merck KGaA (Darmstadt, Germany), which were previously distilled for further purification. Anhydrous sodium sulfate (Merck, Darmstadt, Germany) was used to remove humidity from the sample. Cartridges from Filtrak, 33 × 80 mm (Main, Germany), were used for Soxhlet extractions after a purification process with the same solvent used for sample extraction. The automotive industry sludge was collected in amber bottles and stored at below 0.8°C.

For Soxhlet extraction, 10 g of anhydrous sodium sulfate was added to 10 g of solid sample, and the mixture was homogenized and transferred to the extraction cartridge. The cartridge was placed in an extraction thimble. Approximately 300 mL of the extraction solvent acetone/*n*-hexane 1:1 (v/v) was placed in a round-bottom flask containing three clean boiling chips. The sample was extracted for 16 h after attaching the flask to the extractor and a refrigerated condenser (USEPA 1996). The extracts were concentrated to approximately 10 mL in a rotator evaporator (Quimis, Brazil) and passed through an anhydrous sodium sulfate column, along with a small portion of the extraction solvent mix, into a 10 mL volumetric flask. The final volume was corrected with the same solvent mix. In sonication extraction, approximately 30 g of the solid sample was weighed out into a beaker and homogenized with 60 g of anhydrous sodium sulfate. To this mixture was added 100 mL of an acetone/*n*-hexane 1:1 (v/v) mixture. The sample was extracted ultrasonically for 3 min and decanted. After that, it was passed through filter paper in a Buchner funnel attached to a clean filtration flask. The extraction was repeated twice with 100 mL of clean solvent each time, and the solvent was decanted after each sonication period. Next, the final extract was poured with the entire sample into a Buchner funnel, a vacuum was applied to the filtration flask, and the solvent extract was collected. The filtration was continued until all visible solvent was removed from the funnel (USEPA 2007). The extracts were concentrated to 5 mL using the procedure described for the Soxhlet extraction.

Analyses were carried out with a QP5050A GC/qMS (Shimadzu, Japan), using helium as a carrier gas. The GC column used was a DB-1 column (30 m × 0.25 mm × 0.25 μm), with injector and interface temperatures of 250 and 280°C, respectively. Then, 2 μL of sample was injected using a 1:50 split with an oven temperature program of 35°C for 5 min, raised at 10°C/min to 150°C, 5°C/min up to 180°C (held for 2 min), and then 5°C up to 210°C, followed by a final increase of 20°C/min to 300°C (held for 20 min). Mass spectra were obtained at a mass-to-charge (*m/z*) ratio scan ranging from 30 to 450 μ, with a 70 eV electronic impact. Compounds were identified using the NISTMS (Version 2.0, NIST/EPA/NIH, USA) and ADAMS libraries. A 25 mg L^{-1} n-alkane standard solution (C_8–C_{40}) was injected to improve compound identification by calculating the retention index of each compound (Mühlen and Marriott 2011).

The most commonly used retention indexes are known as the Kovats Index and the Linear Temperature Programmed Retention Index (LTPRI). LTPRI, as the name suggests, is used when a chromatographic run is performed with the linear temperature programmed, and it was first discussed by van den Dool and Kratz in 1963. For that reason, it is also known as the van den Dool and Kratz Index (see Eq. 1) (Kovats 1958; van den Dool and Kratz 1963).

$$LPTRI = 100n + 100\frac{TR(i) - TR(n)}{TR(n+1) - TR(n)} \qquad (1)$$

where *i* analyte, *n* number of carbon atoms of the adjacent standard that is less retained, and n + 1 is the number of adjacent carbon atoms more retained.

The obtained retention index was used as an additional identification tool and summarized for the library search using the reverse function in AMDIS (Version 2.1, DTRA/NIST, 2002) software.

To statistically compare the results obtained by the two extraction techniques, a significance test was performed using the *F* test, according to Eq. 2 (Miller and Miller 1993):

$$F = s_1^2/s_2^2 \qquad (2)$$

where s_1 is the higher standard deviation and s_2 is the lower standard deviation.

Results and Discussion

The methods described by the USEPA do not relate exactly which compounds can be extracted by each technique, only that both the Soxhlet extraction (3540C) and sonication extraction (3550C) can be used for nonvolatile and semivolatile organic compound extraction in sludge. Based on that information, the selectivity of each extraction procedure can be responsible for the misidentification of priority pollutants in the sample. Both methodologies use a large volume of organic solvent, but the Soxhlet method has a longer extraction time (approximately 16 h) compared with sonication extraction, which takes only a few minutes. Although the amount of sample used in sonication is two times higher than in the Soxhlet extraction, this difference is not an important issue for sludge samples because it is easy to collect a significant amount of sample. Typical chromatograms obtained from both techniques are illustrated in Fig. 1. Identified peaks are listed in Table 1.

It was possible to tentatively identify 68 compounds in the sludge sample; 44 compounds were detected in both extracts, whereas 13 compounds were only detected using Soxhlet extraction and 11 compounds were only detected using sonication extraction. The marked peaks in Fig. 1 that are not described in the table are branched alkanes and

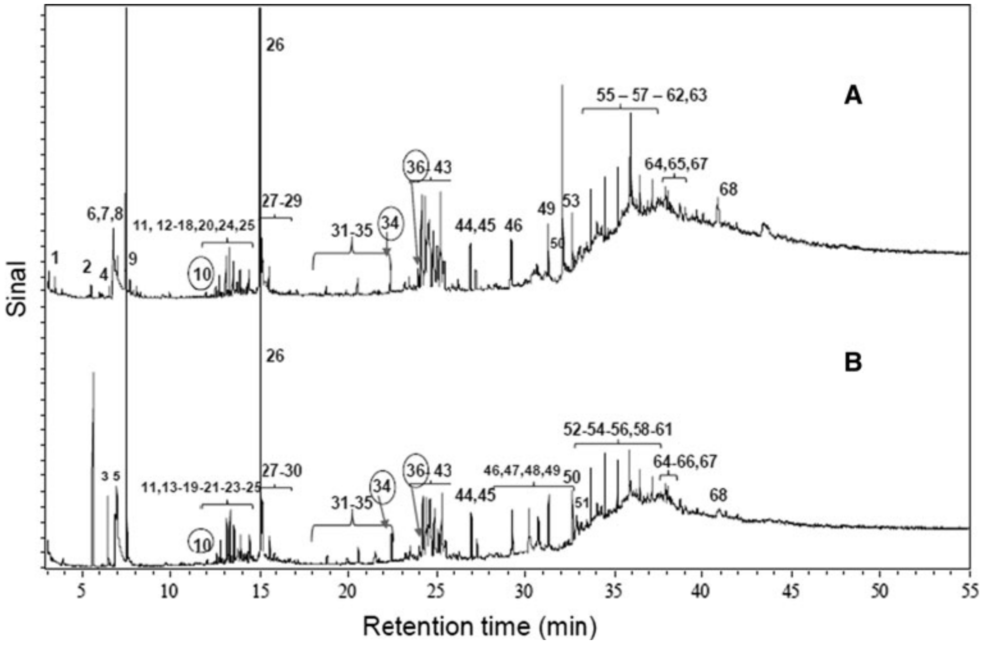

Fig. 1 Chromatograms of extracts obtained by the Soxhlet (*b*) and sonication (*a*) techniques

Table 1 Compounds identified in Soxhlet and sonication extracts

Number	Compound	Sonication			Soxhlet		
		Ret. time	Similarity	LPTRI	Ret. time	Similarity	LPTRI
1	1,3,6-trioxocane	3,867	94				
3	4-methyl-3-penten-2-one				6,456	95	
5	2-propoxy-ethanol				6,892	94	
6	Acetic acid, 2-methylpropyl ester	7,040	92				
10	Decane*	11,975	89	1000	12,042	92	1003
20	Undecane*	13,883	93	1100	13,942	92	1104
26	2-(2-butoxyethoxy)-ethanol	14,989	95	1165	15,035	96	1168
29	Dodecane*	15,578	94	1200	15,627	95	1203
31	Tridecane*	17,158	90	1300	17,200	86	1303
32	Tetradecane*	18,787	95	1399	18,841	92	1403
33	Pentadecane*	20,535	93	1500	20,587	95	1505
34	Heptadecane*	22,388	96	1699	22,439	97	1702
36	1-(4-propoxyphenyl)-ethanone	23,939	76	1772	24,006	76	1775
37	4-(1,1,3,3-tetramethyl-butyl)-phenol	24,139	90	1781	24,205	89	1784
38	4-nonylphenol	24,332	90	1790	24,395	89	1793
39	Dodecyl-phenol	24,536	83	1799	24,602	81	1819
40	Nonadecane*	24,787	78	1892	24,857	85	1902
41	1,3-cyclohexadiene-1-carboxylic acid, 2,6,6-trimethyl-, ethyl ester	24,994	76	1909	25,062	76	1912
42	(1,1,3,3-tetramethyl-butyl)-phenol	25,199	89	1918	25,267	91	1922
43	Nonylphenol	25,396	79	1928	25,469	79	1931
44	Eicosane*	26,926	98	1999	26,988	97	2014
45	Heneicosane*	27,236	95	2093	27,302	95	2102
46	Docosane*	29,236	97	2199	29,293	97	2202
47	n-Hexadecanoic acid				30,229	92	2247
48	Cyclic octaatomic sulfur				30,737	87	2272
49	Tricosane*	31,300	92	2299	31,327	93	2301
50	Tetracosane*	32,658	96	2399	32,668	97	2400
51	Oleic acid				32,917	90	2424
52	Octadecanoic acid				33,153	86	2448
53	Pentacosane*	33,677	95	2499	33,676	96	2499
56	Hexacosane*	34,495	93	2598	34,491	95	2598
58	Heptacosane*	35,190	94	2698	35,182	95	2697
59	Octacosane*	35,848	91	2797	35,843	88	2796
61	Nonacosane*	36,503	94	2896	36,499	93	2897
64	Triacontane*	37,184	94	2997	37,184	93	2997
65	Hentriacontane*	37,926	85	3097	37,928	83	3097
67	Dotriacontane*	38,751	91	3195	38,765	91	3197
68	Cholestanol	40,866	84		40,908	74	

*These compounds were identified by comparing them with a standard alkane solution (25 mg L^{-1})

are not specified. It is important to note that the concentrations of sonication extracts are 5 times higher than those of Soxhlet extracts because sonication uses 30 g of sample to achieve a final extract volume of 5 mL, whereas the Soxhlet procedure uses 10 g of sample to achieve a 10 mL final extract, according to standard procedures.

It was possible to observe different chemical groups with the Soxhlet extraction, such as esters, carboxylic acids, ketones and alkanes. The majority of compounds were identified as alkanes and phenols by both extraction methodologies. It is important to emphasize the possibility of toxicological effects that can be caused by exposure to these compounds for short or long periods (Khadhar et al. 2010). As described in the literature, low concentrations of alkanes are not responsible for toxicological effects. Only high concentrations of these compounds cause anesthetic and narcotic effects, although the hydrocarbons with a lower molecular weight cause especially potent effects, mainly due to their high solubility and consequent bioavailability (Hau et al. 1999).

For example, 4-(1,1,3,3-tetramethylbutyl)-phenol, a phenol identified in both methods, is classified as a toxicant as it causes damage to aquatic organisms over time. This compound is also responsible for moving 17-β-estradiol receptors in a competitive manner, which can promote cell proliferation in estrogen-dependent cells. Beyond skin irritation, if orally ingested, this compound may cause damage after a long exposure period, and it may stimulate vitellogenin secretion (IPCS 1994). Vitellogenin is a protein that can cause serious problems for fish reproduction. This protein is naturally found only in females, but it can develop in male fish, resulting in the development of female characteristics and the progressive loss of male characteristics over time (Auriol et al. 2006; WHO 2012). Nonylphenol has also attracted attention because of its potential to mimic the action of natural hormones in vertebrates. The presence of this compound is most likely due to the incomplete biodegradation of nonylphenol polyethoxylates, which have been widely used as non-ionic surfactants in industrial processes (Birkett and Lester 2003; Chang et al. 2009).

Compounds found in either one or the other extraction procedure are not described as hazardous compounds in the literature, especially in comparison to those described above. Those compounds are branched alkanes or organic acids, such as oleic acid, octadecanoic acid, and n-hexadecanoic acid. The source of these organic acids may be food and/or human endogenous metabolism (Legrand 2007), as industrial sewage is treated in the same place.

The number of pollutants detected in both extracts is already sufficient to justify the monitoring of organic pollutants in this type of sludge, especially if its intended use is for agriculture. Recovery studies were not presented in this study as such studies might direct the reader to only one extraction method based on results obtained with a specific class of compounds. The objective was to perform a general screening, based on the capabilities of GC/qMS and the use of Retention Index, and to evaluate the results for their consistency when using two different extraction methods.

For the statistical comparison of both extraction techniques, a two-tailed test was used, for which the critical value of F is 39.00 ($p = 0.05$). A significant difference was observed only among the areas of peaks 10, 34 and 36, which were tentatively identified as decane, hexadecane, and 1-(4-propoxyphenyl)-ethanone, respectively. This result means that, for the 41 other compounds detected by both techniques, meaningful differences regarding detectability efficiencies were not observed, although the amounts of samples extracted and final extraction volumes were significantly different. However, these three compounds are not regarded as pollutants due to their low toxicity in comparison with the other pollutants detected.

From the comparative results presented in this study, it is possible to conclude that the toxic compounds tentatively identified can be extracted with both the Soxhlet and sonication techniques, providing similar analytical information. With regard to time and reagent consumption, sonication extraction is the more efficient choice.

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