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ScienceDirect

Chemosphere 68 (2007) 907–914

CHEMOSPHERE

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Dioxins, metals, and fish toxicity in ash residue from space heaters burning used motor oil

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Received 1 November 2006; received in revised form 24 January 2007; accepted 26 January 2007
Available online 12 March 2007

Abstract

Ash residue, generated from burning used motor oil, is a complex and ubiquitous waste stream. Ash samples were collected from space heaters and analyzed for dioxins ($N = 10$), expressed as toxic equivalents (TEQ), and heavy metals ($N = 9$). TEQ averaged 148–164 ng kg^{-1} (standard deviation [SD] 385–416 ng kg^{-1}), depending on methods used for non-detects (NDs) and toxic equivalency factors (TEFs). It is notable that median TEQ (2.89–3.49 ng kg^{-1}) was about 50 fold lower, reflecting the influence of several high end values on the mean. The proportion of NDs among 17 polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in each sample averaged 38.2% (range 0–94.1%). Total metals averaged 103 000 mg kg^{-1} (SD 26 600 mg kg^{-1}), with Zn, Cu, and Pb contributing 89.3%, 6.4%, and 3.0% of the total, respectively. Rainbow trout bioassays resulted in median mortalities of 3.2% and 42.0% (respective SD 25.3% and 43.2%) at ash concentrations of 10 and 100 mg l^{-1}, respectively. Nominal concentrations of several metals (e.g., Cu, Zn) in the fish bioassay exceeded their reported median lethal concentrations (LC50s) for the test species. Multiple regressions (Bonferroni $P < 0.05$) demonstrated that most of the variance in fish mortality could be accounted for by pH, metals (e.g., As, Cd, Pb), and TEQ. Mean TEQ concentration in used oil ash ranked on the high end of TEQ content in other environmental matrices, including wood ash, cement kiln dust, biosolids, and soils. Overall, these results suggest that suitable disposal methods are needed for ash generated from burning used motor oil.

Keywords: Metal; Dioxin; Toxic equivalent; Fish toxicity; Used oil; Ash

1. Introduction

A large amount of used mineral-based motor oil is generated when oil is removed from the crankcase of internal combustion engines (ATSDR, 1997). This used oil is similar to unused oil except that it contains additional chemicals that are produced or introduced when oil is used as an engine lubricant or during engine repair and cleaning operations. As such, used oil is a highly complex mixture, containing compounds distilled from petroleum (e.g., aliphatic hydrocarbons, aromatic hydrocarbons, polycyclic aromatic hydrocarbons [PAHs]), as well as compounds associated with its engine operations (e.g., metals, water, gasoline, antifreeze, halogenated organic solvents, various additives). The large variation in the composition of used oil relates to its crude oil source, chemical additives, fuel type, and combustion and mechanical properties of the engine.

Due to its chemical composition, global distribution, and potentially toxic effects, used motor oil can be a serious environmental problem (Korte and Boedefeld, 1978; Vazquez-Duhalt, 1989; ATSDR, 1997). The regulatory framework for used oil management in the United States is complex with different requirements for used oil generators, transporters, processors, and marketers (CFR, 2006).

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0045-6535/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.chemosphere.2007.01.070

The US Environmental Protection Agency (USEPA) presumes that used oil is to be recycled unless it is sent for disposal. In particular, used oil burned for energy recovery is subject to regulation as a hazardous waste, unless it is shown not to exceed allowable levels of certain metals (i.e., As, Cd, Cr, Pb), flash point, and total halogens (i.e., termed "on-specification" used oil) and is not mixed with a hazardous waste. However, because record keeping for burning on-specification used oil is not required for generators, it is difficult to estimate the amount of used oil burned for heating. Similarly, because ash generated from burning on-specification used oil is not typically regulated as a hazardous waste, its final disposition in the environment is uncertain.

When used oil is burned in a space heater (300–400 °C), resulting contaminants will partition to the air and ash residue. A limited risk assessment of the impact of used oil, burned in boilers and space heaters, on air quality has been conducted by the USEPA (1984). This USEPA study reported potential adverse human health effects, due to modeled airborne concentrations of hydrogen chloride and several metals (i.e., Ba, Pb, Cr, As, Cd). The ash residue will likely contain metal oxides, as well as various combustion by-products. One variable which may affect the ash residue is the concentration of chemicals added to the oil. For example, the presence of chlorinated organic solvents in used oil may affect the concentration of chlorinated species in the ash.

In particular, dioxin-like compounds are commonly formed via combustion and incineration processes (Czuczwa and Hites, 1986; Delistraty and Singleton, 2002). As a result, it is likely that used oil ash contains dioxin-like compounds, including PCDDs and PCDFs. Adverse effects of these compounds on both human health and ecological receptors have been extensively documented (Eisler, 1986; ATSDR, 1998; USEPA, 2000, 2003). Concentrations of dioxin-like compounds are typically expressed in terms of toxic equivalents (TEQs) of a well-characterized reference compound, i.e., 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD), with toxic equivalency factors (TEFs) specified by the World Heath Organization (WHO) (Van den Berg et al., 1998, 2006).

In addition to dioxin-like compounds, metals may also contribute to ash toxicity (Goyer and Clarkson, 2001; Paquin et al., 2003). Moreover, chemical analysis of a complex mixture, such as used oil ash, can be complemented with bioassay testing to provide additional information. In this regard, a standardized fish bioassay was selected which serves as a test to designate hazardous waste in Washington state (WDOE, 1999). This test evaluates acute toxicity which has been observed for both metals and dioxins (Jarvinen and Ankley, 1999; USEPA, 2006). Therefore, the purpose of this study was to evaluate TEQ (i.e., PCDDs, PCDFs), several metals (e.g., As, Cr, Pb), and fish toxicity in ash samples collected from space heaters burning used motor oil.

2. Methods

2.1. Sample collection and handling

Ash from space heaters which burn used motor oil was collected at 10 automotive repair shops in Washington state (USA). Heat output for these space heaters ranged from 135000 to 800000 BTU h^{-1}. Approximately 200 g of ash were collected from the combustion chamber of the space heater with a stainless steel spoon and placed in certified clean glass jars with Teflon lids. These samples were then stored at 4 °C in the dark until analysis.

For PCDDs and PCDFs, sample holding times followed USEPA Method 8290 which recommends that samples be held for less than 30 days prior to extraction (USEPA, 1994a). Although four samples were stored for 78 days prior to extraction, Method 8290 indicates PCDDs and PCDFs are very stable in a variety of matrices and that holding times may be as high as one year. In all cases, however, the time interval between extraction and analysis was within the 45 day requirement. With the exception of Hg, sample holding times for metals conformed with USEPA guidance (USEPA, 1996a). Metals were extracted and analyzed within the six month holding time. The holding time for Hg exceeded the recommended 28 days.

2.2. Analytical chemistry

Samples were analyzed for seven PCDD and 10 PCDF 2,3,7,8-substituted congeners with high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS), employing USEPA Method 8082 (USEPA, 1994a). Laboratory quality control tests were conducted, including analysis of blanks, duplicates, and spikes. Although the detection limit (DL) varied, depending on the physical state of the sample (e.g., moisture, interfering agents), the target DL range was 0.5–5 ng kg^{-1} (pptr) dry wt. for PCDDs and PCDFs.

Metals (except for Hg) were extracted by acid digestion of ash samples with USEPA Method 3050B (USEPA, 1996b) and analyzed with inductively coupled plasma-mass spectrometry (ICP-MS), employing USEPA Method 6020 (USEPA, 1994b). Analysis of Hg was performed with USEPA Method 7471A, using cold vapor atomic absorption (USEPA, 1994c). The mean and standard deviation (SD) of pH in ash were 7.3 and 2.9, respectively ($N = 10$), as measured by USEPA Method 9045C (USEPA, 1995). In addition, samples were oven-dried at 110 °C in order to express TEQ and metal concentrations on a dry wt. basis in ash. The mean and SD of moisture content in ash were 0.7% and 1.3%, respectively ($N = 10$).

2.3. Toxicity testing

For each ash sample, three replicates of 10 rainbow trout (*Oncorhynchus mykiss*) were exposed at two ash con-