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Determination of polychlorinated biphenyls and polychlorinated dibenzo-p-dioxins and dibenzofurans by pressurized liquid extraction and gas chromatography coupled to mass spectrometry in street dust samples

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ABSTRACT

Owing to massive pollution with polychlorinated biphenyls in the harbour area of Dortmund (Germany), several dust samples were taken from surfaces at industrial sites and analyzed by the North-Rhine Westphalian State Agency for Nature, Environment, and Consumer Protection (LANUV NRW). This report describes and validates a rapid approach to screening for the presence of polychlorinated biphenyls (PCBs) in street dust. Samples were collected by using a natural bristle brush and stainless steel scoops. Mass recovery of fine-particle sea sand (a dust surrogate) on asphalt and concrete surfaces was used as a criterion for the effectiveness of sampling. Better recoveries of sea sand were achieved on concrete than on asphalt surfaces. Furthermore, temperature optimization for a pressurized liquid extraction (PLE) method used to extract PCBs and polychlorinated dibenzodioxins and polychlorinated furans (PCDD/Fs) from street dust samples was developed and compared with Soxhlet extraction for the analysis of PCBs in real street dust samples. Toluene was used as the extraction solvent in both cases. During this study, a combination of toluene and PLE achieved better extraction efficiencies than Soxhlet extraction. Finally, the performance of the PLE method was evaluated by analysing NIST Standard Reference Material 1649a for PCB and PCDD/F concentrations. This demonstrated that the accuracy of the PLE method for the determination of both substance classes was satisfactory. In addition, concentrations of PCBs and PCDD/Fs in street dust samples from industrial sites are reported.

1. Introduction

In general, the term 'street dust' refers to the load of deposited dust on a paved surface. However, the term refers not only to dust that collects on surfaces next to a road, but also to dust that collects on other paved surfaces, such as at industrial sites. A critical aspect of street dust analysis is the threshold size of the dust particles considered. Yang et al. have examined particle sizes of <100 μm when determining levels of PCBs in street dust [4], whereas Irvine and Loganathan have analyzed PCB levels in particles as large as 250 μm [1]. However, a broader spectrum of particle sizes than was used in these studies needs to be sampled and analyzed to provide a comprehensive overview of PCB and PCDD/F burdens in street dusts. This overview is necessary to identify the size ranges of the particles that contribute most to the pollution, even if they do not necessarily make the largest contribution to the mass of the sample. Given that street dust is an excellent carrier and adsorbent for many organic and inorganic trace toxic analytes [2,3], the occurrence of diverse trace compounds in street dust samples has been investigated extensively. To that end, several sampling techniques for street dust samples have been developed. Irvine and Loganathan have used a stainless steel scoop to sample PCBs in street dust, and stored the sampled dust in pre-cleaned glass bottles prior to analysis [1]. A small paintbrush has also been used to collect street dust from street surfaces in order to determine levels of metals [2], and a vacuum cleaner was used to determine levels of polycyclic aromatic hydrocarbons (PAHs) in street dust [3]. A disadvantage of all these sampling methods is that they focus on the concentration of the analytes of interest in the sampled mass of dust. However, for the estimation of the total deposition load it is also important to know the area burden, which is the amount of sampled material on a certain sampling area. Despite its indispensability for these types of analyses, area burden has seldom been considered. The surface roughness of the sampling

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area plays a major role in determining the efficiency of a sampling method.

The present study involved the analysis of street dust samples for polychlorinated biphenyls (PCBs), as well as levels of polychlorinated dibenzodioxins and furans (PCDD/Fs). Due to recent massive pollution with PCB in the harbour area of the city of Dortmund, Germany, [7] the study focused on the analysis of PCBs. Despite the great deal of work on PCBs and PCDD/Fs in environmental analysis, surprisingly few studies have been reported so far that specifically deal with the determination of those organic pollutants in street dust [4]. In organic trace and ultra-trace analysis, several extraction techniques are used to isolate compounds of interest from solid matrices. Ever since the introduction of pressurized liquid extraction (PLE), this technique is often applied to environmental matrices. Conditions for PLE, such as the extraction temperature and extraction solvent, have been optimized [15–17,20–23]. Schantz et al. have used PLE to analyze PCBs in urban-dust standard reference material [5,17]. In their work, dichloromethane, acetonitrile and a mixture of n-hexane/acetone (1:1, v:v) were used for PLE of the reference material. For the determination of PCBs and polybrominated diphenylethers in house-dust samples, n-hexane was used as extraction solvent in PLE [15]. Yang et al. [4] have used supercritical fluid extraction for the extraction of PCBs in street dusts. Street dust samples investigated by Irvine and Loganathan were Soxhlet-extracted for the determination of PCBs [1]. Soxhlet extraction remains the standard method for routine analysis in many laboratories, despite the fact that its use is time consuming and requires large amounts of solvent. We therefore investigated the feasibility of simultaneous extraction and determination of PCBs and PCDD/Fs from street dust using PLE, with toluene as an alternative extraction solvent to those mentioned above.

When used as a PLE solvent, toluene is not often applied to the extraction of PCBs or other organic pollutants. However, for the determination of PCBs in sediments, Bandh et al. have found that the use of PLE with toluene enabled better extraction efficiencies than PLE with hexane/acetone (1:1, v:v) or even Soxhlet extraction, depending on sulphur and carbon contents in the matrix [21]. Toluene has been used for the extraction of PAHs during the evaluation of a diesel particulate matter standard reference material, and comparability of PLE and Soxhlet was demonstrated [17]. Toluene has also been used as a solvent to extract contaminated soil via PLE to determine levels of PCBs and PCDD/Fs. Contrary to the authors' expectations, toluene delivered unsatisfactory recoveries [22].

In addition to the economic advantages of using PLE, the application of PLE enables environmental matrices to be extracted at elevated pressures and temperatures. This accelerates the kinetics of analyte desorption from the matrix. Richter et al. have proposed that variation of the extraction temperature was the most effective optimization parameter [6]. The combined use of gas chromatography and mass spectrometry to separate and detect individual PCB congeners and the seventeen 2,3,7,8-chlorine substituted PCDD/F congeners has been studied intensively in the recent decades [8–10].

The aim of this study is firstly to establish a simple and quantitative sampling technique for street dust. To our knowledge, this is the first investigation of mass transfer during sampling. Second, by the development of an efficient PLE method for the determination of PCBs and PCDD/Fs in street dust samples enables the evaluation of whether it is possible to use PLE with toluene as extraction solvent instead of more costly and time-consuming Soxhlet extraction method. Owing to the equivocal results found in the literature, the extraction temperature was optimized to achieve the highest extraction efficiency. The method's performance was checked by analysing NIST Standard Reference Material (SRM) 1649a for certified PCB congeners and reference values for PCDD/F congeners. Finally, this study presents the first analysis of real street dust samples collected from industrial sites.

2. Materials and methods

2.1. Chemicals and materials

During development of the sampling and extraction methods, sea sand purchased from Merck (Darmstadt, Germany) was used as model matrix. The distributor reports that 90% of the sea-sand particle size ranges in size from 100 to 300 μm. Toluene, n-hexane, dichloromethane, and n-decane were used for the extraction and clean-up step for residue analysis, and all were of picograde quality, purchased from LGC Promochem (Wesel, Germany). H_2SO_4, NaOH and $AgNO_3$ used during the clean-up were purchased from Merck and were at analysis quality. The $^{13}C_{12}$- and native PCB and PCDD/F standards were purchased from Cambridge Isotopes Laboratories (Andover, USA). For the performance check of the analytical method, NIST Standard Reference Material (SRM) 1649a (Maryland, USA) was used. All PLE was performed using a Dionex ASE 200 system (Sunnyvale, USA).

2.2. Sampling technique

Quantitative sampling was tested on both concrete and asphalt surfaces that differed in surface roughness; i.e., the degree of unevenness elicited by gaps, holes, or channels in the surface. The asphalt ground corresponds more to real street sampling sites. Sea sand (1–50 g) was homogeneously distributed over 1 m^2 of the respective surfaces after they had been cleaned with a broom and a hand brush. The size range of the particles of sea sand corresponds well to that of the collected material (Section 3.3). Sampling was performed using a natural-bristle hand brush and a stainless steel scoop. The experiments were repeated five times, and the brushed sea sand was reweighed on a laboratory balance (accuracy ± 0.01 g). The brush and the stainless steel scoop were thoroughly cleaned between experiments, and reused.

2.3. Temperature optimization for the PLE of PCBs and PCDD/Fs from street dust

To develop the PLE method, 1–2 g of sea sand was weighed into a glass fibre thimble (16 mm × 50 mm; Whatman Schleicher and Schuell, Dassel, Germany) and spiked with 100 μL of $^{13}C_{12}$–PCB quantification standard mixture. The glass fibre thimble filled with the spiked sea sand was placed into a 22-mL PLE extraction cell for the extractions. For extraction temperatures ranging from 100 °C to 160 °C, the recovery rates of the individual $^{13}C_{12}$–PCB quantification standards were determined. Toluene was chosen as the PLE solvent, given its long-standing successful use as Soxhlet extraction solvent for the determination of PCBs and PCDD/Fs in several environmental matrices by our institute at LANUV NRW. Approximately 35 mL of toluene was required for PLE of each sample. The following extraction conditions were applied: extraction cycles, 1; extraction pressure, 110 bar; pre-heat time, 5 min; static extraction time, 5 min; flush volume, 60%; and purge time, 60 s. After the extraction process, 5 mL of n-decane was added as keeper to the crude extract, and the extract was subsequently concentrated to a 5-mL volume using a rotary evaporator. Before analysis and concentration via nitrogen flow to a final volume of 100 μL, $^{13}C_{12}$-2,2′,3,3′,4,4′-HexaCB (80 pg/μl; BZ #128) was added as a recovery standard. Concentration via nitrogen flow was performed between 80 and 90 °C. Therefore the extracts residue was transferred to a test tube and placed into a heating block. The analysis was performed in duplicate for each individual extraction temperature.