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Alkylphenols and alkylphenol ethoxylates in dust from homes, offices and computer laboratories: Implication for personal exposure via inadvertent dust ingestion

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ABSTRACT

In the present study, the levels of alkylphenols (APs) and alkylphenol ethoxylates (APEs) in indoor dust of three different microenvironments were measured and daily intake via dust ingestion estimated. Alkylphenols and alkylphenol ethoxylates were extracted with the aid of sonication and analyzed by gas chromatography mass spectrometry after heptafluorobutyric anhydride derivatization. The concentration values of these pollutants ranged from 1918−10 935 ng g^{-1}; 343−12 438 ng g^{-1} and 1122 −15 324 ng g^{-1} in dust samples from homes, computer laboratories and offices, respectively. In all the microenvironment studied, *di*-NPE and *mono*-NPE were the most abundant isomers suggesting widespread use of NPE-based consumer products in the studied microenvironments. The daily exposure dose (DED) was estimated using min, mean and max concentrations of APs and APEs detected in respected microenvironments. The worst case scenario for the exposure of APEs was highest for toddlers at 146 ng kg^{-1} bw day^{-1} followed by teenagers at 11.3 ng kg^{-1} bw day^{-1} and adults at daily exposure of 8.53 ng kg^{-1} bw day^{-1}. Though the daily exposure doses are low, there is a cause for concern as these surfactants are not regulated in many developing countries and their use may be increasing.

1. Introduction

Non-ionic surfactants, such as alkylphenol ethoxylates (APEs), are among the most widely used classes of surfactants in detergents and emulsifiers. These surfactants are most frequently used in domestic, industrial and institutional applications, including paper production, pesticides formulations, leather and textile processing, and cleaning products [1–6]. Other uses of alkylphenols (APs) are in the preparation of antioxidants, curing agents, and heat stabilizers for polymer resins, and in some cases they are applied as an antioxidant itself [7]. The most important members of APEs are nonylphenol ethoxylates (NPEs) and octylphenol ethoxylates (OPEs), which account for approximately 80% and 20% of the total APEs production respectively [8–10]. Once released into the environment, APEs can degrade to short chain APEs (mono-tri) and alkylphenols (APs) such as octylphenol (OP) or nonylphenol (NP). These degradation by-products are persistent in the aquatic environment, bio-accumulative, and toxic to aquatic organisms [6]. NPs and OPs have been phased out in most developed countries and most of their uses are currently regulated [11]. However, in many developing countries such as those in Africa and Asia, no schedule has been made to reduce the use of NP and use of APEs in these countries may be increasing. For example, the production of NP in 2001 reached approximately 16 000 tons in China [12] increasing to 31 434 tons in 2011 [13].

Dust ingestion [14], air inhalation [15,16], dietary exposure via food and/or water intake [2,16] as well as skin contact [16] with products containing nonylphenol ethoxylates have been shown to be possible routes of human exposure to nonylphenol ethoxylates [2,14–16]. A number of studies have documented adverse effects associated with high level exposure to NPs. These effects include irritation of the lungs, digestive system, and irritation of the eye and

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skin [17,18]; other effects include antiandrogenic activity [17] and hepatotoxic effects [18,19]. Subsequently, the European Union has included NPs to the list of endocrine disrupting chemicals [20].

Dust from indoor environments can contain elevated concentrations of environmental contaminants and has been shown to be an important source of human exposure to several toxicants [21,22]. Recent studies have shown the significance of house dust as a medium and exposure route for endocrine disrupting compounds (EDCs) such as NPs and NPEs [14,15,23]. Indoor dust has been implicated as a receptacle and a concentrator of many organic contaminants; hence, levels of contaminants in indoor dust can be used as a proxy to assess the exposure potential to contaminants in the indoor environment [21]. A number of studies have shown the presence of NP and NPEs in settled dust [14,15,23–26]. However, the data with regards to the occurrence of these compounds in African house dust are not available. Therefore, the current study was undertaken to (i) assess for the first time, the levels of APs and APEs in different microenvironments (i.e. homes, offices and classrooms) in Africa; (ii) assess the magnitude of contamination by comparing results obtained with international data; and (iii) estimate occupational exposure to APs and APEs via dust ingestion.

2. Materials and methods

2.1. Materials

2.1.1. Standards and reagents

Derivatizing agent (heptafluorobutyric anhydride (HFBA)) was of analytical grade purchased from Sigma-Aldrich, South Africa. The solvents acetone and hexane used in the study were of gas chromatography (GC) grade and were used without further purification. Alkylphenols (NP, OP, *t*-BP, *t*-OP and *t*-NP) of analytical grade (purity 99.9%) were purchased from Laboratories of Dr Ehrenstorfer-Schäfers, Augsburg, Germany together with NPE (purity 96%), NPPE (purity 97%) and OPPE (purity 98%) of technical grade. Anhydrous sodium sulphate (purity 99.9%), granular powder was purchased from Merck, Florisil was purchased from Supelco, Bellefonte, USA while Helium as He 5.5 pure was purchased from Air Products South Africa, Vereeniging, South Africa.

2.1.2. Sampling

A total of 31 dust samples were collected from homes, n = 11, university students' computer laboratories, n = 12, and university staff offices, n = 8, between August and October 2012 in Durban, South Africa. Computer laboratory and office samples were collected with a LG 1600 W vacuum cleaner following the description of Harrad et al. [27]. The vacuum cleaner contained a dust unit which could easily be removed and emptied after each collection. Between each collection, it was cleaned with a disposable cloth wetted with iso-propanol. Samples from homes were obtained from the vacuum cleaner bags of each home collected under normal home use conditions as they reflect recently collected dusts and thereby provide an estimate of residential exposure to APs and APEs contamination [28]. All the sample collection bags were new and from the same manufacturer.

2.2. Methods

2.2.1. Extraction and clean-up

Non-dust particles, hair, and debris were hand-picked from all samples. All samples were homogenized by sieving through a 212-μm stainless steel sieve. About 0.5 g of dust sample was quantitatively weighed into a glass tube and 10 mL of 20% acetone in hexane was added and the content heated to 55 °C in an ultrasonic bath for 45 min. The procedure was repeated a second time without addition of fresh solvent. The extracts were centrifuged at 3500 rpm for 10 min, washed with 3 mL of 40% sulphuric acid. The aqueous phase was then extracted twice with 5 mL of hexane. The organic phases were combined and evaporated to ~2 mL for clean-up with Florisil.

Florisil was activated at 130 °C for 16 h and cooled in a desiccator before use. A 20 cm × 1 cm glass column was packed with 6 g of Florisil. Each column was topped with 0.8 g of anhydrous sodium sulphate and then wetted with 20 mL of the extraction solvent. Extracts were loaded onto columns just before the exposure of the sodium sulphate layer. AP and APEs were then eluted from the column with 65 mL of 50% acetone in hexane at a flow rate of 0.8 mL min^{-1}. The collected eluates were then evaporated to dryness under a gentle stream of nitrogen. The residue was reconstituted in hexane and derivatized with heptafluorobutyric anhydride as described in Chokwe et al. [29]. Prior to GC-MS analysis, an internal standard (50 μL of 0.5 mg L^{-1} Chrysene) was added to each sample.

2.2.2. Instrumental analysis

The heptafluorobutyric derivatives of alkylphenol ethoxylates were analyzed by Agilent 6890 GC equipped with 5975 mass selective detector (MSD) fitted with Agilent autosampler A7683. The GC separation was performed on a capillary column (Restek RTx-1614, film thickness 0.10 μm, 15 m × 0.25 mm I.D., (Chromspec cc South Africa)). Injections were made in the splitless mode with the injector temperature set at 280 °C. The injection volume was 1 μL. The GC temperature program conditions were as follows: initial temperature 50 °C, heated to 120 °C by a temperature ramp of 7.5 °C min^{-1} then 275 °C by a temperature ramp of 15 °C min^{-1} then finally heated to 300 °C (held for 2 min) by a temperature ramp of 25 °C min^{-1}. Helium was used as the carrier gas at a flow rate of 1.4 mL min^{-1} and a constant linear velocity of 62 cm s^{-1}. For the MS, the ion source and transfer line temperature were 150 and 300 °C, respectively and the ionization energy was 70 eV. APs and APEs mass spectra were obtained in full scan mode by injection of pure derivatized standards of APs and APEs in the range 220–800 amu. The m/z ions used for the quantification are presented in Table S1.

2.2.3. Quality assurance

Due to lack of certified reference materials, a spiking method was used to determine the recoveries of the analytes from method blank and field blank samples. Method blank samples were obtained (n = 3) by spreading anhydrous sodium sulphate on a pre-cleaned tiled floor. The floor was vacuumed following the same protocol as for real samples and the sample subjected to the analytical procedure. Dust obtained from ceiling board after renovation was used as a field blank. The dust was sieved through a 212 μm stainless steel sieve. Approximately 0.5 g of the method and field blank dust samples were spiked with 100 μL of 1 mg L^{-1} APs and 5 mg L^{-1} APEs standard solutions (corresponding to 200 and 1000 ng g^{-1} APs and APEs respectively) and subjected to the same extraction and clean-up procedures as for the real samples. The concentrations of APs and APEs in method blank were all below the limit of quantification and were treated as zero. However, the recoveries for spiked field blank samples were corrected for background concentrations of APs and APEs. The recoveries obtained ranged from 72–91% and 75–102% for field and method blank samples, respectively as presented in Table S2. Several other quality assurance measures were also routinely observed in this study and included running solvent blanks in between samples, analyzing samples in triplicates as well as analyzing test standard after every five samples. The quantification was accomplished using internal standard by relating the responses of alkylphenol and alkylphenol ethoxylates to the responses of Chrysene. The response factor was

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