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Phthalate and PAH concentrations in dust collected from Danish homes and daycare centers

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ABSTRACT

As part of the Danish *Indoor Environment and Children's Health* (IECH) study, dust samples were collected from 500 bedrooms and 151 daycare centers of children (ages 3 to 5) living on the island of Fyn. The present paper reports results from the analyses of these samples for five phthalate esters (diethyl phthalate (DEP), di(n-butyl) phthalate (DnBP), di(isobutyl) phthalate (DiBP), butyl benzyl phthalate (BBzP), di(2-ethylhexyl) phthalate (DEHP)) and three PAHs (pyrene, benz[a]anthracene (B[a]A) and benzo [a]pyrene (B[a]P)). The three PAHs and DEHP were detected in dust samples from all sites, while DEP, DnBP, DiBP and BBzP were detected in more than 75% of the bedrooms and more than 90% of the daycare centers. The dust mass-fractions of both phthalates and PAHs were log-normally distributed. With the exception of DEP, the mass-fractions of phthalates in dust were higher in daycare centers than homes; PAH mass-fractions in dust were similar in the two locations. There was no correlation among the different phthalates in either homes or daycare centers. In contrast, the PAH were correlated with one another – more strongly so in homes ($R^2 = 0.80–0.90$) than in daycare centers ($R^2 = 0.28–0.45$). The dust levels of several phthalates (BBzP, DnBP and DEHP) were substantially lower than those measured in a comparable study conducted 6–7 years earlier in Sweden. Although usage patterns in Denmark differ from those in Sweden, the current results may also reflect a change in the plasticizers that are used in common products including toys. PAH levels were roughly an order of magnitude lower than those measured in Berlin and Cape Cod residences, suggesting that the Danish sites are less impacted by motor vehicle emissions.

1. Introduction

Phthalate esters and polycyclic aromatic hydrocarbons (PAHs) are among the most frequently encountered indoor pollutants. For the purposes of this paper we consider them to be semi-volatile organic compounds (SVOCs); this is based on their vapor pressures at room temperature (Weschler and Nazaroff, 2008). The phthalate esters have primarily indoor sources: higher molecular weight species are used as plasticizers and lower molecular weight species are used as solvents/carriers in personal care products. In contrast, PAHs have both outdoor and indoor sources, reflecting their formation during combustion. Outdoor sources include motor vehicle exhaust, incineration and heating with fossil fuels; they are also emitted from heavier fractions of petroleum such as roofing tars and asphalt. Indoor sources include smoking, cooking and gas-fired appliances. Human exposure to phthalates rose sharply after World War II as peacetime usage of PVC exploded. They were first identified in indoor environments in the early 1980s (Weschler, 1980, 1984) and have since been measured in numerous surveys of indoor environments (Pöhner et al., 1997; Øie et al., 1997; Butte et al., 2001; Becker et al., 2002, 2004; Clausen et al., 2003; Kersten and Reich, 2003; Rudel et al., 2003; Fromme et al., 2004a; Becker et al., 2004; Morgan et al., 2004; Bornehag et al., 2005; Hwang et al., 2008; Kolarik et al., 2008a; Abb et al., 2009).

Humans have been exposed to PAHs since "the dawn of man". PAHs have been extensively measured in indoor settings (e.g., Mukerjee et al., 1997; Pöhner et al., 1997; Chuang et al., 1999; Wilson et al., 2001, 2003; Hansen et al., 2001; Camann et al., 2002; Rudel et al., 2003; Fromme et al., 2004b; Maertens et al., 2004; Morgan et al., 2004; Robertson et al., 2005; Ong et al., 2007;

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Mannino and Orecchio, 2008; Naspinski et al., 2008). Comparisons of dust concentrations (mass-fractions) reported in the cited studies indicate that, for measurements conducted over the past decade, the levels of phthalates in indoor dust tend to be 3–5 orders of magnitude higher than those of PAHs.

Both phthalates and PAHs have been linked to adverse health effects. Starting in the early 2000s, the potential for various phthalates to serve as endocrine disruptors has received considerable attention (e.g., Mylchreest et al., 2000; Duty et al., 2003, 2005; Hauser and Calafat, 2005; Rudel and Perovich, 2009). For PAHs, the major health concern has been cancer. Several are known or suspected carcinogens, most notorious among these being benzo[a]pyrene (B[a]P) and benz[a]anthracene (B[a]A). The specific health concern that has driven the present study is the dramatic increase in allergies and asthma among children in developed countries (Beasley et al., 2003). In the late 1990s it was suggested that phthalates might be contributing to this observed increase (Øie et al., 1997). A number of studies have now made associations between children's indoor exposure to phthalate esters or PVC and the risk of allergy and asthma (Jaakkola et al., 1999; Øie et al., 1999; Jaakkola et al., 2000; Bornehag et al., 2004; Jaakkola et al., 2004; Kolarik et al., 2008b). Jaakkola and Knight (2008) have recently conducted a systematic review of phthalates from PVC products and the development of allergies and asthma. While PAHs have not been directly associated with allergies and asthma, preliminary evidence suggests that traffic-derived PAHs may increase the risk for asthma-related symptoms in children (Miller et al., 2004; Perera et al., 2009). Numerous studies have linked traffic related pollution to asthma and allergic diseases (van Vliet et al., 1997; Morris et al., 2000; Venn et al., 2001; Nicolai et al., 2003; Zmirou et al., 2004; McConnell et al., 2006; Jerrett et al., 2008; Salam et al., 2008). It is known that PAHs are major constituents of motor vehicle exhaust and can be used as markers for exposure to traffic-derived pollution (Oda et al., 2001). While their production by multiple combustion processes means that their presence is not uniquely indicative of motor vehicle exhaust, levels of PAHs can be used to establish upper bounds on potential exposure to traffic related pollution in indoor environments.

The ongoing Danish *Indoor Environment and Children's Health (IECH)* study is a multiyear investigation of potential associations between different indoor environmental factors and children's health, especially allergies and asthma (Clausen et al., 2009). It has three parts: i) a questionnaire survey distributed to 17,500 families on the Danish island of Fyn that have children between ages 1 and 5 (Toftum et al., 2009a); ii) a case-base study, designed using information from the survey, totaling 500 children–200 "cases" with asthma/allergies and 300 randomly selected "bases" and iii) a day-care center intervention study. During the second part of this study, detailed investigations were conducted in the homes and daycare facilities of the 500 children designated as either "case" or "base" (Toftum et al., 2009b). The investigations included the collection of dust samples from the children's bedrooms and the daycare centers they attended. These dust samples have subsequently been analyzed for five phthalate esters and three PAHs – the subject of the present paper. The IECH study builds on the earlier Swedish DBH (Dampness in Buildings and Health) study, which found associations between selected phthalate ester concentrations in dust samples collected from children's bedrooms (346 homes) and asthma and allergies in the children (Bornehag et al., 2004). More recently a similarly designed study has found associations between selected phthalates in dust from children's homes in Bulgaria and the children's allergic symptoms (Kolarik et al., 2008b).

The aim of the present paper is threefold: to report the mass-fraction of the targeted phthalate esters and PAHs measured in dust samples collected from children's bedrooms ($n = 500$) and daycare centers ($n = 151$) on the island of Fyn, Denmark; to examine potential correlations among levels of these SVOC pollutants in children's bedrooms and daycare facilities; and to compare the results with levels reported in other studies to derive a sense of variations over place and time. To our knowledge, in terms of the number of buildings sampled, this is the largest study of its kind to date. In reporting these results we remind the reader that an SVOC in an indoor environment is simultaneously present in the gas phase, associated with airborne particles, associated with settled dust and sorbed to all indoor surfaces (Weschler et al., 2008; Weschler and Nazaroff, 2008; Xu and Little, 2006; Xu et al., 2009, 2010). The mass-fraction of an SVOC in settled dust provides information on its anticipated concentration in other indoor compartments and can be used to estimate human exposure via multiple pathways including inhalation, ingestion and dermal sorption.

2. Methods

2.1. Dust collection

Dust was collected from non-floor surfaces in the children's bedrooms using a phthalate-free ALK dust filter (ALK-Abelló A/S, Hørsholm, Denmark) mounted in a holder connected to a vacuum cleaner. The filter holder as well as the sampling nozzle was constructed of phthalate-free materials. Collection of dust from plastic surfaces and textiles was avoided. In 2% of homes a second dust sample ("duplicate") was collected. In 5% of the homes (randomly chosen) a field blank was collected.

2.2. Chemical analysis

Prior to sampling, the virgin filters were pre-conditioned, weighed and assigned an ID number. The loaded filters or blanks were returned to the laboratory (shipped at ambient temperature) where they were conditioned, weighed, wrapped in aluminum foil and re-packed in their original bag. The net dust mass on the loaded filters ranged from 43 to 1396 mg. Of the total filters that were analyzed, 33 (5%) were field blanks, 12 were duplicates, and 42 were laboratory blanks.

The target compounds for chemical analyses were diethyl phthalate (DEP), di(n-butyl) phthalate (DnBP), di(isobutyl) phthalate (DiBP), butyl benzyl phthalate (BBzP), di(2-ethylhexyl) phthalate (DEHP), and the PAHs pyrene, benz[a]anthracene (B[a]A) and benzo[a]pyrene (B[a]P). Analyses were performed by gas chromatography–mass spectrometry (GC–MS) on an Agilent Technologies 6890 N GC System equipped with a 7683 Series Autoinjector and a 5975 XL Mass Selective Detector. The analytical capillary column was BPX – 5 (5% phenyl polysilphenylene siloxane), 25 m, 0.22 mm i.d., 0.25 μm film thickness; ultra-high purity helium was used as the carrier gas.

The dust samples were extracted and analyzed in a manner similar to that described by Rudel et al. (2003). The samples were spiked with isotopically labelled internal standards diethyl phthalate-d_4, di(n-octyl) phthalate-d_4, chrysene-d_{12}, benzo[a]pyrene-d_{12} (surrogate recovery standards) prior to analysis. The recoveries were 0.90 ± 0.19 for diethyl phthalate-d_4, 1.01 ± 0.19 for di(n-octyl) phthalate-d_4, 0.95 ± 0.17 for chrysene-d_{12} and 0.94 ± 0.19 for benzo[a]pyrene-d_{12} in all samples and blanks.

The spiked dust samples were equilibrated for 30 min at room temperature and then extracted in an ultrasonic bath 2×30 min using 2×15 ml of n-hexane with 6% diethyl ether. The combined extracts were concentrated to approximately 5 ml. A 250 μL aliquot was analyzed after adding 1,2,3,4-tetrachloronaphthalene as an injection standard. The target compounds were quantified