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Occurrence of carbazoles in dust and air samples from different locations in Germany

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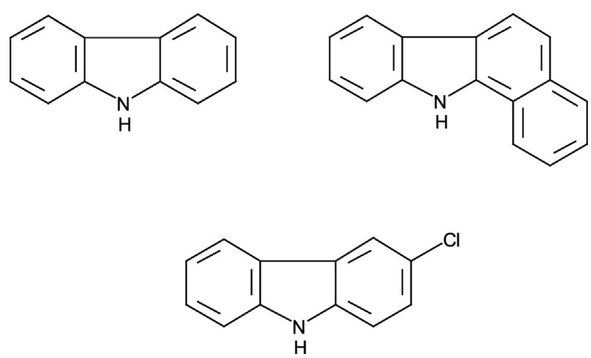
HIGHLIGHTS

- Carbazole and halogenated carbazoles have natural and anthropogenic sources.
- Dust samples were collected from residences, daycare centers, and schools.
- Carbazoles were observed in nearly all dust samples, especially in schools.
- In air samples, all analytes were quantified at low levels.

GRAPHICAL ABSTRACT



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ABSTRACT

9H-carbazole is generated from incomplete combustion of diverse fossil fuels and biomass, in tobacco smoke and from industrial processes, while halogenated carbazoles have natural and anthropogenic sources.
We analyzed 9H-carbazole and 14 halogenated carbazoles in dust samples from 14 schools, 13 daycare centers, and 13 residences, as well as 5 indoor air samples from residences in Munich, Germany. Overall, we present first data of various carbazoles in different indoor environments without visible combustion sources.
The median (95th percentile) values of the halogenated analytes mainly detected in the entire study group were 10.3 ng/g (308 ng/g) for 9H-carbazole, 13.3 ng/g (735 ng/g) for 3,6-dichloro-9H-carbazole, 6.2 ng/g (159 ng/g) for 1,3,6-tribromo-9H-carbazole, and 1.2 ng/g (21.1 ng/g) for 2,7-dibromo-9H-carbazole. For most of the target analytes, the highest concentrations were observed in dust samples from schools, and the lowest were found in residences. In the air samples, all analytes were found only at low levels, with median values of 7.7 pg/m^3 for 9H-carbazole and 6.1 pg/m^3 for 2,3,6,7-tetrachloro-9H-carbazole.
For 9H-carbazole, “typical” and “high” non-dietary intake of children through dust ingestion using median and 95th percentile values were calculated to be 0.03 ng/kg b.w. and 1.1 ng/kg b.w. daily, respectively.
Due to limited toxicological information and exposure data for other relevant pathways (e.g., dietary intake), the risk assessment is inconclusive. Nevertheless, there are indications that 9H-carbazole has

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carcinogenic properties and that halogenated carbazoles have dioxin-like toxicities. Therefore, further research is essential.

1. Introduction

9H-carbazole is released into the environment via emissions from waste incineration (Ishikawa et al., 2005), combustion of biomass (Glarborg et al., 2003), tobacco smoke (Hoffmann et al., 1968), production of synthetic dyes (Parette et al., 2015), and aluminum manufacturing, as well as rubber, petroleum, and coal combustion (IARC, 1983; Aydin et al., 2014). Additionally, it can be isolated from precursors found in explosives and propellants during combustion (Goerner, 2010). Overall, it can be assumed that carbazoles occur in emissions of all incomplete combustion processes of nitrogen-containing organic matter and from thermal processes that are also able to form polychlorinated analogs (Altarawneh et al., 2009). Halogenated carbazoles have natural and anthropogenic sources. They can be formed in environmental media by different chemical reactions, such as enzymatic halogenation of carbazoles (Altarawneh and Dlugogorski, 2015) and in the manufacture of halogenated indigo dyes (Parette et al., 2015). Other sources include the use of chloroaniline herbicides and intentionally synthesized bromocarbazoles for photo- and semiconductors (Chen et al., 2016), as well as the use of tribromoaniline, which is used in dyes and polymers and as a flame retardant (Bindra and Narang, 1995).

In an undisturbed sediment core collected in 2001 from the Lippe River in Germany, carbazoles were quantified and found to date back approximately 50 years (Heim et al., 2004). The concentration observed varied from 11 to 172 ng/g d.w. for 9H-carbazole and 7 to 147 ng/g d.w. for benzocarbazole (BenzoCZ). The brominated carbazole 1,3,6,8-tetrabromo-9H-carbazole (1368-BCZ) was detected for the first time in sediment cores from Lake Michigan in 2004, indicating that the concentration peaked between 1920 and 1935 (Zhu and Hites, 2005). Thereafter, various publications have reported carbazole levels in marine and freshwater sediments from Greece, Canada, China, and Germany (Grigoriadou and Schwarzbauer, 2011; Guo et al., 2014; Pena-Abaurrea et al., 2014; Wu et al., 2016; Chen et al., 2016; Wu et al., 2017). The highest concentrations observed were for 9H-carbazole, BenzoCZ, and 3,6-dichloro-9H-carbazole (36-CCZ), with concentration ranges from 0.4 to 312 ng/g d.w., 0.02 to 4.2 ng/g d.w., and 4.3 to 100 ng/g d.w., respectively.

Reischl et al. (2005) found 3-chloro-9H-carbazole (3-CCZ) and 36-CCZ for the first time in many of 200 soil samples collected between 1991 and 2004 in Germany. In 22 soil samples collected in 2004 near an industrial area in Greece, halogenated carbazoles were observed in some samples, with levels ranging from 5 to 110 ng/g d.w. for monochlorocarbazole and 9 to 3500 ng/g d.w. for 36-CCZ (Grigoriadou and Schwarzbauer, 2011). In a recent study from Germany, the humic layer and other different soil horizons were analyzed in 86 forest soil samples (Mumbo et al., 2016). Here, the concentrations of the most abundant analytes, CZ, 36-CCZ, and 36-BCZ, ranged from 0.6 to 268 ng/g d.w., 0.4 to 68 ng/g d.w., and 0.2 to 20 ng/g d.w., respectively. For sum of four azarenes concentrations are higher in industrialized regions of Europe than in Bangkok (Bandowe et al., 2014). In a study performed in China, CZ was quantified in 6 surface soil samples from suburban areas and 20 dust samples from paved roads (Wei et al., 2015). 9H-carbazole was found with mean levels of 7.5 ng/g d.w. in soil and 235 ng/g d.w. in road dust, which indicate the importance of human activity for 9H-carbazole enrichment. Under natural conditions, 3-CCZ and 36-CCZ are not readily degradable (Tröbs et al., 2011).

No epidemiological information is available for carbazoles so far. Toxicological data are very limited and are restricted to 9H-carbazole. 9H-carbazole was shown to be non-mutagenic in various tests and showed low acute toxicity (IARC, 2013). In the only available carcinogenicity study, 100 mice were fed a pellet diet containing 9H-carbazole for 22 months (Tsuda et al., 1982). A statistically significant increase in the incidence of hepatocellular and forestomach tumors was found in both sexes and in all groups. The IARC stated that there is sufficient evidence that 9H-carbazole is carcinogenic in experimental animals, but the mutagenic mechanism is unknown (IARC, 2013). IARC classifies 9H-carbazole as possibly carcinogenic to humans (group 2B). No classification is available so far for BenzoCZ and other halogenated substances.

The study aimed to extend the data base for exposure to different carbazoles and to obtain the first indications of exposure in the indoor environments of schools, daycare centers, and residences. Overall, 15 carbazoles (see Table 1) were measured in 5 indoor air samples from residences and in 40 settled dust samples in three of the aforementioned indoor spaces. This study is a sub-project of the LUPE 3 (Länderuntersuchungsprogramme, LUPE) and LUPE 4 studies, for which previous results have been reported (Fromme et al., 2013, 2015).

2. Materials and methods

2.1. Study area/participants

The investigation was carried out in 14 elementary schools, 13 daycare centers, and 13 residences in Munich, Germany. Daycare centers and schools were contacted by the study group or by the local health authorities. After consenting to participate, the facility managers and residents received detailed information regarding the study. All rooms were naturally ventilated.

2.2. Sampling

Air sampling of PM_{10} was conducted only in 5 residences with a medium volume sampler using a flow controlled pump operating at a constant flow of 2.3 m^3/h for 24 h (Derenda, Teltow, Germany). Sample volumes were calculated from elapsed time indicators and flow measurements before sampling with calibrated rotameters. The sampler was placed in the center of the residential living room, and resident presence was optional. After sampling, the filters were stored refrigerated in airtight glass jars until analysis.

Dust samples were collected by slowly vacuuming the floors for approximately 5 to 10 min using a dust filter holder (ALK-Abello Arzneimittel GmbH, Wedel, Germany) mounted on a sampler connected to a vacuum cleaner. To avoid heterogeneity, larger particles and sand deposits were removed, but the dust was not sieved.

2.3. Analysis of carbazoles in indoor air and dust

2.3.1. Chemicals and materials

The native standards, including 9H-carbazole, 2-bromo-9H-carbazole, 3-bromo-9H-carbazole, and 3,6-dibromo-9H-carbazole, were obtained from AK Scientific (purity > 98.7%, Union City, CA, USA). 11H–Benzo[*a*]carbazole was from Chiron (0.2 mg/ml, purity > 99.5%, Trondheim, Norway). 1,3,6,8-Tetrachloro-9H-carbazole, 2,3,6,7-tetrachloro-9H-carbazole, 3,6-dichloro-9H-carbazole, 3-chloro-9H-carbazole, 1,3,6-tribromo-9H-carbazole, 1,3,6,8-tetrabromo-9H-carbazole, 1-bromo-3,6-dichloro-9H-carbazole, and 1,8-dibromo-3,6-dichloro-9H-carbazole, as well as the isotope-labeled standard $^{13}C_{12}$–3,6-dichloro-9H-carbazole, were supplied by Wellington Laboratories (Guelph, Ontario, Canada) at 50 μg/ml concentrations (purity > 98%) in nonane with 10% toluene. Carbazole-d_8 of 99% purity was from CDN Resource