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Persistent and emerging pollutants in the blood of German adults: Occurrence of dechloranes, polychlorinated naphthalenes, and siloxanes

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ABSTRACT

Human biomonitoring is a valid method to determine exposure, identify time trends, and monitor the effects of restrictions and measures. To characterize the recent exposure of Germans to persistent or emerging substances, we analyzed 4 dechloranes, 33 polychlorinated naphthalenes (PCNs), and 3 cyclic volatile methyl siloxanes (cVMS) in 42 plasma samples. The samples were collected from blood donors on a random selection.
The median values of both Dechlorane Plus (DDC-CO) isomers were 1.23 ng/g l.w. for *anti*- and 0.77 ng/g l.w. for *syn*–DDC-CO. The two other dechloranes were found at lower levels. The median level of $\sum$ — PCNs was 575 pg/g l.w. (range: 101–1406 pg/g l.w.). On average, the levels of PCNs in plasma were dominated by the congeners CN73, CN66/67, and CN51, which were responsible for approximately 71% of the total amount of PCNs. The cVMS octa-, deca-, and dodecamethylcyclotetrasiloxane could be determined in only some samples, with maximum values of 0.73, 0.48, and 0.79 μg/l, respectively.
Regarding dechloranes, our results are similar to those from other western countries but slightly lower than results from China. The levels of PCNs in German blood are similar to those observed in the U.S.A., but considerably lower than those reported for Korea. Using a preliminary TEF (toxic equivalency factor), the mean TEQ of the 9 quantifiable PCNs in Germany was low (0.36 pg TEQ/g l.w.). The PCN levels in our study group are lower compared to previous studies.

1. Introduction

Persistent organic pollutants (POPs) are organic compounds that distribute widely throughout the environment, accumulate in fatty tissues, biomagnify in food webs, and are toxic to humans and wildlife. In 2001, the Stockholm Convention listed the first twelve POPs recognized as causing adverse effects on humans and the ecosystem. Polychlorinated naphthalenes (PCNs) are substances proposed for listing under the Stockholm Convention. Due to their high potential to cause environmental and health concerns, POPs require continuous monitoring. Human biomonitoring of POPs in blood is a valid method to determine recent exposure, identify time trends, and monitor the effects of restrictions and measures (NRC, 2006). Recently, some other organic substances that are produced in large quantities have attracted scientific interest, such as dechloranes and methyl siloxanes. However, data on human exposure to these substances are still very limited and require investigation.

Hexachloronorbornene-based flame retardants, commonly known as dechloranes, have been used for decades in electrical wires, cable coatings, computers, furniture, and other applications (Xian et al., 2011). Dechlorane Plus® (IUPAC-name: 1,2,3,4,7,8,9,10,13,13,14,14-dodecachloro-1,4,4a,5,6,6a,7,10,10a,11,12,12a-dodecahydro-1,4,7,10-dimethanodibenzo[*a*,*e*]cyclooctene), first used as a substitute for the pesticide Mirex, is a high-production volume chemical that consists of two isomers (*syn* and *anti*). In the technical mixture, the *anti*-isomer accounts for approximately 75% of the total isomers (Sverko et al., 2011). Little is known about the production volumes of Dechlorane 602 and Dechlorane 603, but their use in polymeric products has been documented (Sverko et al., 2011). Since 2006, dechloranes were observed at higher concentrations in sediments and fish collected from the Great Lakes compared to other lakes (Shen et al., 2010). Xian et al. (2011) summarized the sources and environmental behaviors of dechloranes and concluded that long-range atmospheric transportation of dechloranes occurred, indicating a global presence. Recent scientific literature, although limited, has shown a low toxicity of dechloranes, particularly affecting the liver (US-EPA, 2011). Nevertheless, data gaps exist, and a comprehensive risk assessment is still lacking.

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PCNs are a mixture of potentially 75 different congeners with one to eight chlorine atoms. Their physical–chemical properties vary considerably; tetra- to octa-CNs are lipophilic, and their water solubility and vapor pressure both decrease with an increasing degree of chlorination (UNEP, 2013). Historically, they have been used in many applications, including the use as wood preservatives and additives to paints and engine oils (UNEP, 2013). Although PCNs have been banned for several decades, their release is still possible, primarily from past applications and products. By deposition of such products from thermal processes as waste incineration, through evaporation from contaminated soil, and as impurities from PCB-containing devices, PCN are released to the environment (Domingo, 2004; UNEP, 2013). The toxicological profile of PCNs is not well characterized, but, due to their interaction with the cytosolic Ah receptor (AhR), exposure to PCNs could result in a pattern of biochemical and toxic responses typical for dioxin-like compounds (WHO, 2001; Falandysz et al., 2014).

Cyclic volatile methyl siloxanes (cVMS) are possibly persistent in the environment and have the potential to accumulate in aquatic organisms and biomagnify in food-chains (EC/HC, 2008a,b,c). cVMS may be emitted into the environment from industrial processes that use these compounds to form silicone polymers and co-polymers and from blending, formulating and packaging operations (EC/HC, 2008a,b,c; Wang et al., 2013). In addition to polymer synthesis, typical applications include cosmetics, personal care products, cleaning agents, and surface treatment agents (Dudzina et al., 2014). For all cVMS studied to date, the liver and, to a lesser extent, the lung have been identified as the target organs, but there are some indications from animal experiments that tumors (D5) and impaired fertility may also be critical effects (EC/HC, 2008a,b,c).

To date, only few studies have analyzed the presence of the above-mentioned substances in human blood. In Germany, recent data on the body burden of the general population are lacking. Therefore, the objectives of our study were to determine 4 dechloranes (Dechlorane Plus® [*syn*- and *anti*-DDC-CO], Dechlorane 602 [DDC-DBF], and Dechlorane 603 [DDC-Ant]), 33 PCNs consisting of tetra- to octa-congeners, and 3 cyclic volatile methyl siloxanes (cVMS) (octamethylcyclotetrasiloxane [D4], decamethylcyclopentasiloxane [D5], and dodecamethylcyclohexasiloxane [D6]) in German blood samples.

All of the abbreviations used in the text follow the structure suggested by Bergman et al. (2012). The chemical structure is given in Fig. 1.

2. Materials and methods

2.1. Study group and sampling

The Bavarian Red Cross Blood Donation Service was requested to collect blood samples of the general population on a random selection. Samples were obtained from healthy blood donors living in Munich and the surrounding areas in the winter in 2013 and 2014. The blood was freshly collected by the Bavarian Red Cross Blood Donation Service. After venipuncture, each sample was centrifuged to obtain the plasma fraction and stored without preservatives at −20 °C until analysis. Because of the high risk of field and laboratory contamination, several measures were undertaken to minimize potential contamination of samples prior to their distribution to our partners. The plasma samples were carefully defrosted in a special room in our laboratory, which was intensively ventilated overnight and then closed approximately 2 h before sample handling. The technical personnel wore CAT III chemical-protective coveralls, mouthguards, and powder-free nitrile gloves during the division of samples into subsamples for the different laboratories, which was conducted over a single session. On the day of sample handling, the personnel did not use any personal care products such as deodorants, hair and skin products, soaps, and cosmetics. All of the samples were prepared in a laminar flow workbench under clean-room conditions to minimize contamination from the indoor air. Afterwards, the samples were again deep-frozen and sent to the laboratories under cooled conditions.

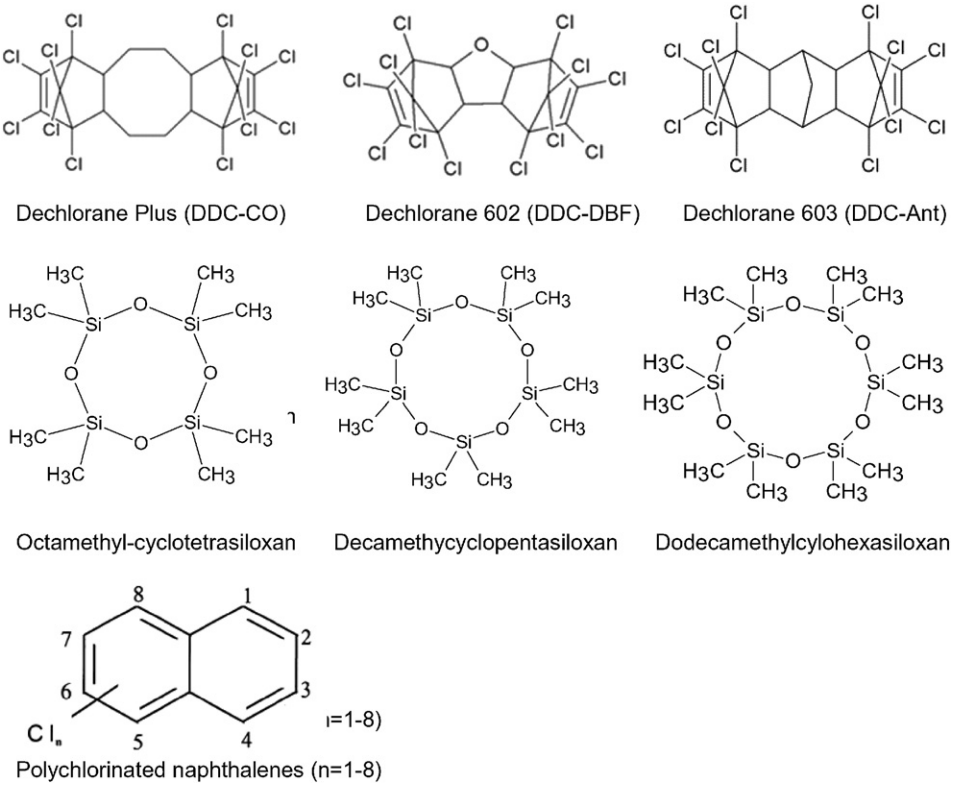

Fig. 1. Chemical structures of the target analytes.