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Occurrence of perchlorate in indoor dust from the United States and eleven other countries: Implications for human exposure

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ABSTRACT

Perchlorate is a widespread environmental contaminant and potent thyroid hormone disrupting compound. Despite this, very little is known with regard to the occurrence of this compound in indoor dust and the exposure of humans to perchlorate through dust ingestion. In this study, 366 indoor dust samples were collected from 12 countries, the USA, Colombia, Greece, Romania, Japan, Korea, Pakistan, Kuwait, Saudi Arabia, India, Vietnam, and China, during 2010–2014. Dust samples were extracted by 1% (v/v) methylamine in water. Analyte separation was achieved by an ion exchange (AS-21) column and analysis was performed by high performance liquid chromatography–tandem mass spectrometry (HPLC–MS/MS). The overall concentrations of perchlorate in dust were in the range of 0.02–104 μg/g (geometric mean: 0.41 μg/g). The indoor dust samples from China contained the highest concentrations (geometric mean: 5.38 μg/g). No remarkable differences in perchlorate concentrations in dust were found among various microenvironments (i.e., car, home, office, and laboratory). The estimated median daily intake (EDI) of perchlorate for toddlers through dust ingestion in the USA, Colombia, Greece, Romania, Japan, Korea, Pakistan, Kuwait, Saudi Arabia, India, Vietnam, and China was 1.89, 0.37, 1.71, 0.74, 4.90, 7.20, 0.60, 0.80, 1.55, 0.70, 2.15, and 21.3 ng/kg body weight (bw)/day, respectively. Although high concentrations of perchlorate were measured in some dust samples, the contribution of dust to total perchlorate intake was <5% of the total perchlorate intake in humans. This is the first multinational survey on the occurrence of perchlorate in indoor dust.

1. Introduction

Perchlorate is both a naturally occurring (Rao et al., 2010; Urbansky et al., 2001) and man-made chemical, widely used as an oxidant in rocket fuel, missiles, flares, fireworks, and automobile air bag inflators (Motzer, 2001). Anthropogenic sources are thought to be the major sources of perchlorate in the environment. Perchlorate has been reported to occur in human bodily fluids, such as saliva, breast milk, serum, and urine (Blount et al., 2009; Eguchi et al., 2014; Oldi and Kannan, 2009). Perchlorate has the ability to inhibit the uptake of iodide at 30 times greater affinity than iodine itself by the sodium/iodide symporter (NIS) (Tonacchera et al., 2004), which results in the disruption of thyroid hormone production in animals and humans (Blount et al., 2006; Chen et al., 2014; Dohán et al., 2007; Gilbert and Sui, 2008; Wu et al., 2010; York et al., 2003). A decreased thyroid hormone level has been

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shown to adversely affect neurodevelopment in mammals, human fetuses, infants, toddlers, and children (Charatcharoenwitthaya et al., 2014; Mendez and Eftim, 2012; Wu et al., 2012; York et al., 2003).

Perchlorate is also recognized as a persistent and pervasive contaminant (Fisher et al., 2000; Motzer, 2001). It can accumulate in leafy vegetables and reach humans through the food chain (Lee et al., 2012; Sanchez et al., 2006; Voogt and Jackson, 2010). The United States Environmental Protection Agency (USEPA) has proposed an oral reference dose (RfD) of 0.7 μg perchlorate/kg body weight (bw)/day (Greer et al., 2002; Zewdie et al., 2010).

Assessing sources of human exposure to perchlorate is a subject of considerable interest among various environmental and public health agencies throughout the world. Thus far, perchlorate has been reported to occur in drinking water (Blount et al., 2010; Kannan et al., 2009; Wu et al., 2010), foodstuffs (Lee et al., 2012; Wang et al., 2009), and outdoor dust particles (Gan et al., 2014). The current estimates of exposure to perchlorate, extrapolated from blood or urine biomonitoring studies in the USA and China, suggested values that exceed the RfD in many cases, especially for infants and toddlers (Zhang et al., 2010). Because perchlorate is a water-soluble contaminant present in fertilizers, it was believed that agricultural produce was the major source of human exposure to this chemical. However, perchlorate is also used in many products in the indoor environment, including bleach, matches, and pharmaceutics (Zewdie et al., 2010). Despite this, no earlier studies have reported the occurrence of perchlorate in indoor dust.

Indoor dust can be a significant source of human exposure to contaminants such as polybrominated diphenyl ethers (PBDEs) (Rudel et al., 2003; Lorber, 2008; Wu et al., 2007) and ingestion of indoor dust has been shown to be an important exposure pathway to environmental chemicals, especially for infants and toddlers (Johnson-Restrepo and Kannan, 2009; Guo and Kannan, 2011; Liao et al., 2012). Determination of perchlorate levels in indoor dust and the assessment of human exposure doses through the ingestion of dust are imperative to the assessment of risks and for the development of strategies to mitigate exposures. In this study, we conducted a multinational survey of perchlorate levels in 366 indoor dust samples collected from 12 countries (two American, two European, and eight Asian countries). Perchlorate exposures via dust ingestion for various age groups (infants, toddlers, children, teenagers, and adults) were calculated on the basis of the measured concentrations. This is the first study to report the occurrence of perchlorate in indoor dust from several countries.

2. Materials and methods

2.1. Chemicals

Ammonium perchlorate (>99.9%) and methylamine (40 wt.% solution in water) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Isotope-labeled sodium perchlorate ($Cl^{18}O_4^-$, >90%) was purchased from Cambridge Isotope Laboratories (Andover, MA, USA). Milli-Q water was obtained from an ultrapure water system (Barnstead International, Dubuque, IA, USA). All other reagents used in the study were analytical grade.

2.2. Sample collection

From 2010 to 2014, 366 dust samples were collected from single or multiple cities in 12 countries, including Athens, Greece (2014, $n = 30$); Iasi, Romania (2012, $n = 23$); Albany, New York, USA (2014, $n = 30$); Cartagena, Colombia (2014, $n = 39$); Kumamoto, Nagasaki, Fukuoka, Saitama, and Saga, Japan (2012, $n = 22$); Ansan and Anyang, Korea (2012, $n = 40$); Faisalabad, Pakistan (2011–2012, $n = 24$); Kuwait City (2013, $n = 34$); Jeddah, Saudi Arabia (2014, $n = 31$); Patna, India (2014, $n = 30$); Hanoi, Thai Binh, and Hungyen, Vietnam (2014, $n = 33$); and Beijing, Guangzhou, and Shanghai, China (2010–2011, $n = 30$). Bedrooms and living rooms of homes and apartments (all countries), offices (Korea, Vietnam, and Japan), laboratories (Korea and Vietnam), and cars (Kuwait) were selected for sampling. Floor dust samples were obtained from vacuum cleaner bags in each of the sampling sites, with the exception of samples from China and India, which were obtained by sweeping the floor. All samples were sieved through a 150 μm sieve, homogenized, packed in clean aluminum foil, and stored at 4 °C until analysis.

2.3. Sample preparation

Dust samples were extracted and analyzed by following the method described elsewhere, with some modifications (Gan et al., 2014). Briefly, 50 mg of sample was accurately weighed and transferred into a 15 mL polypropylene (PP) conical tube. Samples were then spiked with 5 ng of ^{18}O-perchlorate, as an internal standard. The dust samples were extracted with 5.0 mL of 1% methylamine in water by shaking in an orbital shaker (Eberbach Corp., Ann Arbor, MI, USA) for 30 min. The mixture was centrifuged at 4,500 ×*g* for 5 min (Eppendorf Centrifuge 5804, Hamburg, Germany), and the supernatant was transferred into a new PP tube. The extract was purified by passage through an Envi-Carb cartridge (250 mg/3 mL; Supelclean, Bellefonte, PA, USA), preconditioned with 5 mL of water. The purified extract was filtered through a 0.2 μm regenerated cellulose membrane filter (Phenomenex, Torrance, CA, USA) prior to analysis by liquid chromatography–tandem mass spectrometry (LC–MS/MS).

2.4. Instrumental analysis

Samples were analyzed with a Waters 2695 high performance liquid chromatograph (HPLC) (Waters Corporation, Milford, MA, USA) and Micromass Quattro tandem mass spectrometer (MS/MS) in the negative electrospray ionization mode with multiple reaction monitoring. Chromatographic separation was achieved with a 250 mm × 2 mm IonPac AS-21 anion-exchange column (Dionex, Sunnyvale, CA, USA). An isocratic mobile phase of 20 mM aqueous methylamine was used at a flow rate of 300 μL/min. Perchlorate was monitored by the mass transition of m/z 99 → m/z 83 for $^{35}ClO_4$ and m/z 101 → m/z 85 for $^{37}ClO_4$. The ratio of the peak areas of $^{35}ClO_4^-$ to $^{37}ClO_4^-$ was monitored, and a ratio of 3.12 ± 25% was considered acceptable. The cone voltage and the collision energy were 40 V and 22 V, respectively. The perchlorate internal standard ($Cl^{18}O_4^-$) was monitored by a mass transition of m/z 107 → m/z 89. Limit of quantitation (LOQ) for perchlorate in indoor dust was 0.02 μg/g, which was calculated based on the lowest concentration in the calibration that produced a signal-to-noise ratio of 10; the average weight of samples taken for analysis and the concentration/dilution factors were included in the calculation of LOQ.

2.5. Quality assurance and quality control

Quantification was performed by two internal calibrations, which were established at six low concentrations of perchlorate standard solutions ranging from 0.2 to 10 μg/L, and at six high concentrations ranging from 10 to 500 μg/L. The correlation coefficient of the calibration (r) curve was 0.999. Calibration standards were injected daily before and after the injection of a batch of samples. For samples with responses greater than the linear range, extracts were diluted with water and reanalyzed. All of the standard solutions were prepared in water, and the spiked concentration of the internal standard (^{18}O-ClO_4) was 1.0 μg/L. The injection of 10 μL of 0.2 μg/L standard yielded a signal-to-noise ratio of 10. Recoveries and the presence of matrix effects for dust samples were tested in triplicate by spiking the native perchlorate standard at three different levels (1.0, 10, and 100 μg/L), and the results are presented in Table S1. The recoveries of perchlorate spiked into each of the samples ranged from 89% to 101%.