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Occurrence and exposure evaluation of perchlorate in outdoor dust and soil in mainland China

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HIGHLIGHTS

- High perchlorate levels were found in soil and outdoor dust samples from China.
- Exposure to perchlorate via soil does not exceed the US EPA reference dose.
- People can be at risk at the sites with high dust perchlorate concentrations.
- Dust may be an important perchlorate exposure pathway and needs further study.

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ABSTRACT

A total of 98 paired soil and outdoor dust samples were collected across mainland China for survey of perchlorate. Perchlorate was detected in all of the soil and outdoor dust samples. High levels of perchlorate were found in soil, ranging from 0.001 to 216 mg/kg in Northern China and from 0.001 to 25.8 mg/kg in Southern China. Even higher perchlorate concentrations were detected in dust samples, with concentrations ranging from 0.132 to 5300 mg/kg in Northern China, and from 0.270 to 3700 mg/kg in Southern China. This is the first known report of perchlorate in dust samples. The high perchlorate levels in soil and dust may raise concern on the potential risk for organisms and human. The daily perchlorate intakes were evaluated based on our measured perchlorate concentrations via inhalation, ingestion, and dermal contact of soil and dust for both children and adults, respectively. In general, the exposure from soil does not appear to lead to perchlorate intakes exceeding the US EPA reference for both children and adults. However, children can be at risk from exposure to perchlorate via dust, and it needs considerable concern for both children and adults at the sites with high dust perchlorate concentrations. After comparison with other possible exposure pathways, such as from drinking water, we suggested that dust may be an important potential source of perchlorate exposure in China, and further study is needed, especially for indoor dust.

1. Introduction

Perchlorate is widely known as an oxidant or ignitable source in solid rocket propellants and munitions, or used in fireworks, roadside flares, and air bag inflation systems (Urbansky, 1998). More and more literature reported anthropogenic sources of perchlorate in drinking water, groundwater, surface water, and soil, with concentrations ranging from below 0.1 μg/L to 35 μg/L in drinking water (Quinones et al., 2007; Kannan et al., 2009; Blount et al., 2010), from below 0.1 to 22.1 μg/L in groundwater (Kannan et al., 2009; Wu et al., 2010), from below 0.1 to 2300 μg/L in surface water (Kosaka et al., 2007; Kannan et al., 2009; Wu et al., 2010), and from below 1 to 13 μg/kg in soil (Rao et al., 2007; Jackson et al., 2010; Ye et al., 2013). It was also reported in wet precipitation samples from the US (Parker et al., 2008; Rajagopaian et al., 2009) and China (Ye et al., 2013), at a concentration up to 24.4 μg/L in Montezuma. Besides anthropogenic sources, perchlorate can be formed naturally in the atmosphere or co-exists in sodium nitrate deposition (Michalski et al., 2004; Dasgupta et al., 2005), and naturally occurring perchlorate was found up to 200 μg/L in groundwater from Southern High Plains and 1.7 mg/kg in caliche sample from Death Valley in the US (Rajagopalan et al., 2006; Rao et al., 2007; Jackson et al., 2010). Furthermore, several studies found that perchlorate could be accumulated by plants readily (Yu et al., 2004; Jackson et al., 2005; Voogt and Jackson, 2010). Therefore, it is regarded as a new threat to the ecosystem and human beings (Shi et al., 2007).

Perchlorate can inhibit the uptake of iodide by the thyroid gland, and consequently reducing the production of thyroid hormones (Wolff, 1998). Therefore, perchlorate contamination has become an important environmental issue in connection with human health. The levels of

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perchlorate in human samples have been well documented, including human blood, saliva, breast milk, and urine, with concentrations ranging from below 0.1 to 160 μg/L (Kirk et al., 2005; Caldwell et al., 2006; Blount et al., 2007; Kannan et al., 2009; Oldi and Kannan, 2009; Zhang et al., 2010). Previous studies indicated that both water and food could act as exposure sources to human beings (Sanchez et al., 2005; Blount et al., 2010; Lee et al., 2012). Several studies revealed that soil and outdoor dust may act as carriers of pollutants from human activities or atmospheric deposition (Christoforidis and Stamatis, 2009; G.T. Shi et al., 2011). They are regarded as potential exposure sources to human, especially for children, who have higher frequency of hand-to-mouth activities (Glorennec et al., 2012). Furthermore, soil could also act as a potential exposure source of perchlorate for wildlife, vegetables, and crops (Smith et al., 2004; Jackson et al., 2005; Shi et al., 2007).

However, to date, only few studies focused on the occurrence of perchlorate in soil, and very few from China (Rao et al., 2007; Jackson et al., 2010; Ye et al., 2013). No information is available regarding the concentrations of perchlorate in dust. Therefore, the objectives of this study were to investigate perchlorate levels in soil and outdoor dust in China and to assess related risk to Chinese people. To do so, 98 paired soil and outdoor dust samples from mainland China (one from Hong Kong) were sampled to evaluate perchlorate concentrations and human exposure by ingestion, inhalation, and dermal contact of soil and outdoor dust for both children and adults. To our knowledge, this is the first report of the perchlorate levels in dust around the world. The results expand knowledge concerning the presence and distribution of perchlorate in China, and add new information on the exposure route of perchlorate to human.

2. Materials and methods

2.1. Chemicals and reagents

Perchlorate was procured from Sigma-Aldrich (St. Louis, MO, USA). The $^{18}O_4$-labeled perchlorate used as internal standard (IS) was obtained from Cambridge Isotope Laboratories (Andover, MA, USA). Formic acid was of HPLC grade and purchased from Tianjin Guangfu Fine Chemical Research Institute, China. HPLC-grade methanol was obtained from CNW Technologies GmbH (Germany). Milli-Q water was used throughout the study.

2.2. Sample collection and preparation

A total of 98 paired soil and outdoor dust samples were collected in China during February to March in 2013 around Chinese Traditional Spring Festival. The sampling sites covered most regions of China, except for Macau and Taiwan. The locations are shown in Fig. 1, and the detailed descriptions of the sampling sites are given in Table S1 in Supporting Information. China is officially divided into northern and southern parts along Yangzi River (http://www.xzqh.org/quhua/), and accordingly, the two municipalities directly under the Central Government, Beijing and Tianjin, and 14 provinces, Inner Mongolia, Xinjiang, Hebei, Gansu, Ningxia, Shanxi, Shaanxi, Qinghai, Shandong, Henan, Anhui, Liaoning, Jilin, and Heilongjiang are assigned to Northern China, and the remains are recognized as Southern China in this study (Fig. 1). Northern China is usually more arid than Southern China, and has less precipitation, and hence, the difference in perchlorate levels was compared between Northern China and Southern China.

Settled dust on exterior window sill or building surface above 1 m of ground was sampled using a hand-held brush and a paper. Simultaneously, soil sample was collected using a polypropylene plastic (PP) tube near the dust sampling site, and 4 sub-samples of topsoil (0–3 cm) were taken and then mixed thoroughly to obtain a bulk sample for each sampling site. Each brush, paper, and PP tube was used only once at each sampling site. All the samples were preserved in sealed polyethylene packages separately to avoid contamination; subsequently the samples were transported to the laboratory. They were then air dried, sieved, transferred to clean PP bottles, and stored at −20 °C until analysis.

2.3. Sample extraction and analysis

Soil samples (0.5 g) were extracted in a 15 mL PP tube with 5 mL of Milli-Q water (Ye et al., 2013). For sampling sites, S48 and S98, 2 mL of Milli-Q water was used instead of 5 mL due to the low perchlorate concentrations in these soil samples. Dust samples (0.02 g) were extracted in a 15 mL PP tube with 10 mL of Milli-Q water. Prior to extraction, the IS was spiked, and the concentration of the IS in each sample was 20 μg/L. Tubes were shaken for 2 h, and an aliquot of 0.7 mL extract was transferred into a 1.5 mL PP centrifuge tube after standing, and centrifuged at 15,000 r/min for 10 min and the supernatant was collected.

Analysis was performed on LC–MS/MS (Agilent Technologies, USA) using the method developed by Li and George (2005), with minor modifications. Briefly, LC–MS/MS equipped with an electrospray ionization interface was operated in negative ion mode. Nitrogen (with a purity of 99.9%) was used as desolvation gas, with a manipulating temperature of 350 °C. The flow rate was 10 L/min, and the nebulizing gas pressure was 50 psi. The capillary voltage was 4000 V. The separation column was an Athena C18-WP column (4.6 mm × 150 mm, 3 μm) (CNW Technologies GmbH, Germany). The mobile phase was an isocratic flow of 90/10 of 0.1% formic acid water solution/methanol at a flow rate of 0.4 mL/min. The LC separation was set to 10.5 min. The column was kept at 30 °C. The injection volume was 20 μL, and injection was performed by an autosampler. The retention time of perchlorate and the IS was ~7.5 min. Detailed parameters for MRM are given in Table S2.

2.4. Quality assurance and quality control

Quantification was performed by two internal calibrations, which were established with 8 low levels of perchlorate standard solutions ranging from 0.2 to 10 μg/L, and 9 relative high levels of perchlorate standard solutions ranging from 10 to 1000 μg/L. All of the standard solutions were dissolved in water, and the concentration of the IS was 20 μg/L. The limit of quantification (LOQ) was 0.16 μg/L, and defined as a value corresponding to a signal-to-noise ratio of 10. Recoveries and matrix effects were investigated using soil and dust samples from 6 different sources by triplicate after spiking the native perchlorate standard at five different levels, and the results are shown in Table S3. A group of standard solutions including low (0.5 μg/L), middle (5 μg/L), and high (50 μg/L) levels of perchlorate was injected with each batch of 20 samples. Precision and accuracy of the analysis, reported as recoveries and relative standard deviation (RSD), are given in Table S3. Procedural blanks were performed using the same procedure as for the samples. Both procedural blank and reagent blank were prepared and analyzed with each batch of 20 samples, and none of the target chemical was found in the blanks. Calibration curves were prepared for each batch of 100 injections, and the RSD of the slope was within 3%.

2.5. Statistical analysis

Statistical analyses were conducted using SPSS 17.0 software program (SPSS Inc., Chicago, IL). Descriptive statistics and box chart were used to characterize the levels of perchlorate in the soil and dust samples. Data sets of perchlorate concentrations were normally distributed when natural logarithm transformed (Kolmogorov–Smirnov test), and ln-transformed data were used in the parametric statistical analysis. Pearson correlation coefficient was calculated to assess the potential relationship between the soil and dust perchlorate levels from mainland