Title of research project: Bioaccessibility evaluation of halogenated and organophosphorus flame retardants by physiologically-based extraction test with Tenax bead: Application to settled dust from e-waste and end-of-life vehicle processing workshops in northern Vietnam

Project members:

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Purposes:

In our previous studies, informal e-waste recycling and end-of-life vehicle (ELV) processing activities in northern Vietnam have been characterized as potential emission sources of HFRs and OPFRs (Tue et al., 2013; Takahashi et al., 2017; Hoang et al., 2022). Although human exposure and risk assessment of dust-bound flame retardants were included in these studies, such estimations were drawn from the hypothesis that HFRs and OPFRs in dust are 100% bioaccessible. To avoid overestimation of potential risk, evaluating bioaccessibility of FRs from dust is critically important. In this project, concentrations and bioaccessibility of legacy and emerging FRs will be examined in settled dust samples collected from informal waste and vehicle processing workshops in northern Vietnam by both chemically- and physiologically-based extraction methods, followed by gas chromatography-tandem mass spectrometry (GC-MS/MS) quantification. To our knowledge, this is among the first studies to characterize the bioaccessibility of HFRs and OPFRs related to informal processing of e-waste, plastic waste, and vehicles.

Methods:

Settled dust samples were collected from Bui Dau e-waste recycling areas (Hung Yen Province) and Thuyen ELV processing areas (Bac Giang Province), northern Vietnam. Concentrations of HFRs and OPFRs in dust samples were determined by using methods described elsewhere (Hoang et al., 2022a). In brief, the dust samples will be extracted with hexane/acetone (1:1, v/v) mixture using a SE-100 solvent extractor (Mitsubishi Chemical Analytech, Japan). The extracts will be separated into 2 portions for HFR and OPFR analysis. The HFR portions will be spiked with ^{13}C-labeled surrogates, and cleaned up by using gel-permeation chromatography, solid-phase extraction (SPE), and activated silica gel chromatography. The OPFR portions were spiked with ^{13}C-labeled surrogates and purified by using appropriate SPE cartridges. Before instrumental analysis, labeled internal standards will be added into clean extracts to monitor surrogate recovery. HFRs were determined using a GC-MS/MS system (7890A series and 7000 GC/MS Triple Quad; Agilent Technologies, USA) with an Rtx-1614 column (15 m × 0.25 mm × 0.1 μm; Restek, USA). OPFRs were determined using the same GC-MS/MS instrument with a DB17-HT column (30 m × 0.25 mm × 0.15 μm; Agilent Technologies, USA).

Ingestion bioaccessibility of HFRs and OPFRs in dust samples will be investigated by using in vitro physiologically based extraction method with Tenax bead assisted sorption (Fang and Stapleton, 2014). Bioaccessible concentrations of HFRs and OPFRs in dust will be determined by incubation extracting the samples with simulated digestive fluids (e.g., gastric, intestinal, and colon fluids) and assisted sorptive Tenax beds. Combination of chemically- and physiologically-based concentrations and physiochemical properties can provide relevant information about bioaccessibility and "realistic" exposure risk of HFRs and OPFRs in dust. The validity and applicability of the Tenax bead-assisted sorptive physiologically based method and influencing factors (e.g., nature of target compounds and dust matrices) in evaluating bioaccessibility of HFRs and OPFRs will be also discussed.

Results:

Bioaccessibility of HFRs and OPEs in the waste processing dust samples is presented in Fig. 1. The bioaccessibility of PBDEs and other HFRs was relatively low, ranging from 0% to 14% without a clear difference between compounds. Our results were in good agreement with those reported by previous studies, showing low bioaccessibility of hydrophobic FRs under different *in vitro* conditions (He et al., 2018; Wannomai et al., 2020). These values were markedly lower than those reported by some earlier works (Abdallah et al., 2012; Fang and Stapleton, 2014), probably due to the differences in extraction methods, dust particle sizes, and dust matrix properties. Bioaccessible fractions of BDE-209 were higher in the ELV dust (3%–13%) than in the e-waste dust (0.5%–0.9%), while the remaining HFRs showed higher bioaccessibility in the e-waste dust. Lower bioaccessibility of almost HFRs in the ELV dust was largely due to their lower total concentrations, resulting in bioaccessible levels lower than the MDLs. Information about bioaccessibility of DPs is still limited. These CFRs were generally not bioaccessible in PBET experiments without Tenax absorption sink (He et al., 2018; Wannomai et al., 2020). Higher bioaccessibility of *syn*-DP over *anti*-DP was observed in the e-waste dust (median 6% and 3%) and the SRM 2585 dust (25% and 18%). Meanwhile, *anti*-DP exhibited higher bioaccessibility in the ELV dust (median 8%) than *syn*-DP (bioaccessible concentrations < MDLs), largely due to lower *syn*-DP concentrations in the whole dust and the digestive phases.

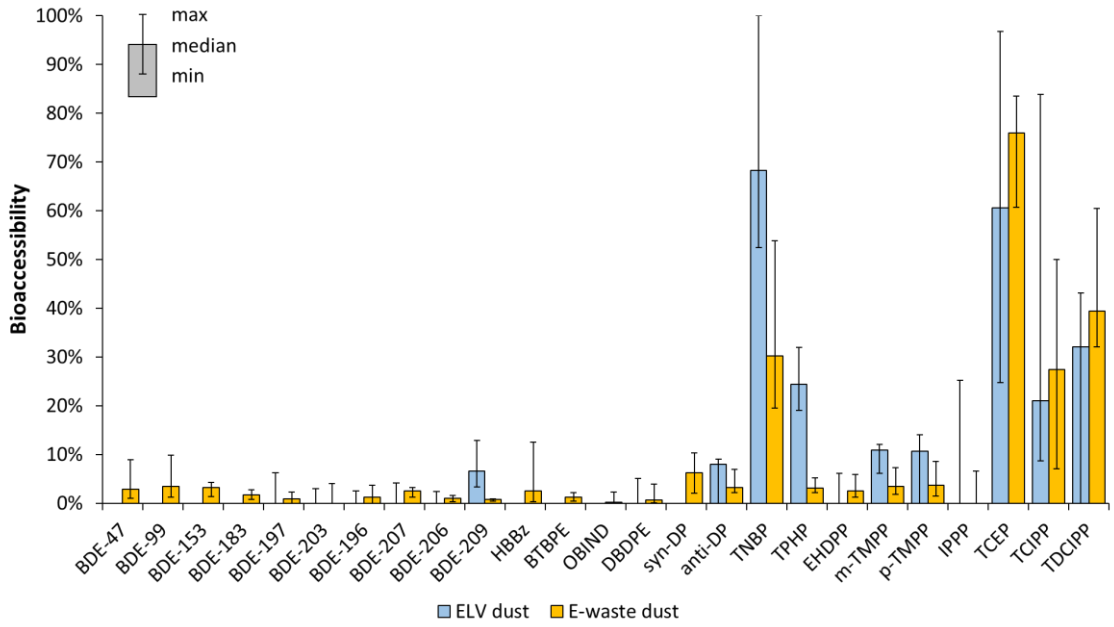

Fig. 1. Bioaccessibility of HFRs and OPEs in the ELV and e-waste dust samples.

Bioaccessibility of OPEs was generally higher than that of HFRs in our dust samples. The median bioaccessible fractions were the highest for TCEP (66%; 25%–97%), followed by tri-*n*-butyl phosphate (TNBP: 52%; 19%–100%), TDCIPP (37%; 0%–60%), and TCIPP (29%; 7%–84%). The remaining non-Cl-OPEs had quite lower bioaccessibility (0%–32%). Interestingly, bioaccessibility of non-Cl-OPEs was higher in the ELV dust than in the e-waste dust, while bioaccessibility of Cl-OPEs was not significantly different between the two areas. For examples, median bioaccessibility values of TNBP, TPHP, and tris(methylphenyl) phosphates (*m*- and *p*-TMPP) in the ELV dust were 68%, 24%, and 11%, respectively; while these values derived for the e-waste dust were only 24%, 3%, and 3%. Unlike HFRs, bioaccessibility of OPEs in the SRM 2585 sample were within the range measured in our waste processing dust samples. TCEP, TCIPP, TDCIPP, and TNBP also exhibited high bioaccessibility from dust in other *in vitro* studies (Fang and Stapleton, 2014; He et al., 2018; Guo et al., 2019; Wannomai et al., 2020).

Conclusion:

Gastrointestinal bioaccessibility of various legacy and alternative flame retardants and plasticizers was assessed in workplace dust samples from Vietnamese e-waste and ELV processing sites by using Tenax-assisted physiologically-based extraction test. Our results are in good agreement with previous studies, showing higher bioaccessibility of Cl-OPEs (e.g., TCEP, TCIPP, and TDCIPP) and short-chain alkyl OPEs (e.g., TNBP) compared to hydrophobic BFRs (e.g., PBDEs, HBBz, BTBPE, and DBDPE) and CFRs (e.g., DPs). Specific dust matrices containing large amounts of micronized plastics or oily materials can affect bioaccessibility of HFRs and OPEs, especially less polar substances. Bioaccessible fractions of PBDEs, DPs, and non-Cl-OPEs were higher in the ELV dust than e-waste dust, while bioaccessibility of polar Cl-OPEs did not show significant difference between the two areas. Pollutants associated with plastic debris may be hardly eluted and absorbed in gastrointestinal tract. In contrast, oily materials

containing OPEs or serving as extractant of dust may enhance mobility of HFRs and OPEs. Daily uptake doses of HFRs and OPEs in dust were estimated, indicating quite low health risks for both e-waste and ELV workers. Additional investigations on absorption behaviors and impacts of organic pollutants in workplace dust should be performed for multiple chemical classes and exposure pathways with relevant extraction methods.

Future challenges:

Comparison of human levels of OPEs and HFRs is still challenging, and other exposure pathways (i.e., dietary and inhalation) and metabolism of these substances should be considered. In addition, the variability of dust matrices, especially those with specific compositions, and the discrepancies between their behavior in the dynamic digestive system as compared to the static in vitro digestion tests remain as uncertainty factors for the application of practical bioaccessibility values for risk assessment.

Publication:

Anh Quoc Hoang, Nguyen Minh Tue, Akitoshi Goto, Ryogo Karyu, Le Huu Tuyen, Pham Hung Viet, Hidenori Matsukami, Go Suzuki, Shin Takahashi, Tatsuya Kunisue. Bioaccessibility of halogenated flame retardants and organophosphate esters in settled dust: Influences of specific dust matrices from Vietnamese informal e-waste and end-of-life vehicle processing areas. Submitted to Science of the Total Environment (under review).

References:

Abdallah, M.A.E., et al., 2012. http://doi.org/10.1039/c2em30690e.

Fang, M., Stapleton, H.M., 2014. https://doi.org/10.1021/es503918m.

Guo, H., et al., 2019. https://doi.org/10.1016/j.scitotenv.2018.09.340.

He, R.W., et al., 2018. https://doi.org/10.1016/j.envres.2017.12.014.

Hoang, A.Q., et al., 2022. https://doi.org/10.1016/j.envpol.2022.119809.

Takahashi, S., et al., 2017. https://doi.org/10.1007/s10163-016-0571-3.

Tue, N.M., et al., 2013. http://dx.doi.org/10.1016/j.envint.2012.11.006.

Wannomai, T., et al., 2020. https://doi.org/10.1016/j.chemosphere.2020.126632.