



Sorption of Organophosphorus Flame Retardants on Settled Dust

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INTRODUCTION

Why It Is Important

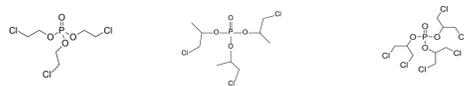
- Semi volatile organic compounds (SVOCs), e.g. flame retardants, phthalates, perfluorinated compounds (PFCs), and polychlorinated biphenyls (PCBs), are among several identified chemicals under review by U. S. Environmental Protection Agency (EPA)
- Aligns with the need to develop risk assessments and policy decisions to minimize exposures and protect human health
- Fill critical knowledge gaps for standard and reliable methods to characterize SVOC sources and sinks and to predict the SVOC emissions and transport in the indoor environment

SVOCs: Flame Retardants

- Flame retardants (FRs) are used to meet flammability standards (hard plastics, spray foam application, polyurethane foam, electronic, mattress, textile, carpet, etc.)

Table 1. Organophosphate FRs (OPFRs)

CAS RN	Chemical Name	Synonyms
115-96-8	Ethanol, 2-chloro-, phosphate	TCEP
13674-84-5	2-Propanol, 1-chloro-, 2,2',2''-phosphate	TCPP
13674-87-8	2-Propanol, 1,3-dichloro-, phosphate	TDCPP



- Exposure pathways: inhalation; dermal contact; ingestion
- Fate and transport mechanisms in the indoor environment are needed for exposure assessment and risk management
 - Multiple mass transfer mechanisms: material/air; dust/air; dust/material; material/material
 - Critical parameters: material/air partition coefficient (K_{ma}); solid-phase diffusion coefficient (D_s); Sorption rate constant (k_a , k_d)

OPFRs Sorption on Settled Dust

- Inhalation exposure to gas phase SVOCs becomes less important when the solid-air partition coefficient becomes larger
- Dust is an important sink for indoor air pollutants
 - Small in size and large surface area-to-volume ratio
 - Settle on source or non-source surfaces
 - Be re-suspended, allowing them to contribute to inhalation
- Differences between airborne particles and settled dust
 - Settled particles are usually larger in size
 - May contain more earthen (crustal) and less organic carbon
 - Settled dust has longer time to contact with indoor air
 - SVOC concentrations in the dust can be higher

MATERIALS and METHODS

Small Chamber Test Design

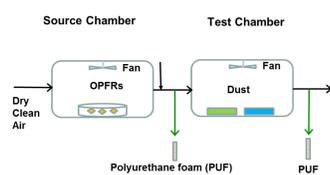


Figure 1. Schematic of the air flow between two chambers

Chamber Testing

- Constant OPFR gas phase emissions
- House dust (HD) from household vacuum cleaner bags, irradiated to eliminate microbiological activity, sieved with 150 μm sieve, and then conditioned at 160°C for 5 minutes to remove quantifiable TCEP, TCPP, and TDCPP before use.
- Arizona Test Dust (ATD) was purchased from Powder Technology, Inc.
- Gas phase OPFRs directed from the source chamber to the empty test chamber to "coat" the chamber wall for more than 20 days to minimize the chamber wall sink effect prior to test
- Each piece loaded with 0.2 g of dust as evenly as possible
- Seven dust rails placed in the small chamber
- Dust rails removed from the chamber at different times and the dust collected and extracted to determine its OPFR content
- Air sampling at the mixing T-connector and the test chamber lid with PUF 600 mL/min at volume of 50 - 360 liters
- Quality assurance and quality control

Table 2. OPFR source settings in the OPFR source chamber

OPFRs	Cup Materials	Cup Size (ID, cm x Depth, cm)	Temperature (°C)	Emission Rate \pm %RSD, $\mu\text{g}/\text{h}$, (n=57)
TCEP	Teflon	5.08 x 0.83	24.6	0.12 \pm 16.5
TCPP	Teflon	5.07 x 0.81	24.6	0.43 \pm 11.3
TDCPP	Aluminum	5.07 x 0.79	67	0.045 \pm 19.8

\pm %RSD-Relative standard deviation

Table 3. Dust chamber test conditions

Parameters	T1-ATD (\pm %RSD)	T2-HD (\pm %RSD)
Dust loading on each tray, g	0.2	0.15
Chamber air change rate, h-1	1.1 (\pm 0.8)	1.1 (\pm 1.1)
Temperature, C	23.3 (\pm 0.1)	23.3 (\pm 0.1)
Relative humidity, %	53.2 (\pm 1.7)	54.2 (\pm 1.8)
Test duration, h	507	412

Analytical Methods

- Organic carbon and elemental carbon (OC/EC) contents and particle properties were analyzed.
- Dust and PUFs extracted with 1:1 methylene chloride/ethyl acetate
- Analyzed on gas chromatography/mass spectroscopy (GC/MS)
- GC Internal standard (d_{27} -tributyl phosphate), extraction recovery check standard (d_{15} -triphenyl phosphate)
- Quality assurance and quality control

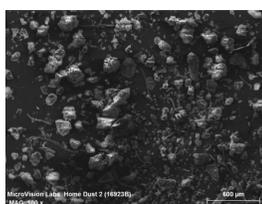
RESULTS and DISCUSSION

Dust Analysis

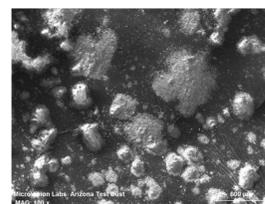
Table 4. Selected properties of the two dust samples tested

Property	House Dust	Arizona Test Dust
Weight by volume, g/mL ^a	0.938 \pm 0.008	0.723 \pm 0.016
Surface area, m ² /g ^{a, b}	3.60 \pm 0.02	10.32 \pm 0.02
Particle size - mean, μm ^{b, c}	67.88 \pm 0.21	4.35 \pm 0.01
Particle size - range, μm ^{b, c}	5.5 to 220	0.5 to 10
Particle size - 90%, μm ^{b, c}	164.54	8.31
Particle size - 50%, μm ^{b, c}	44.22	3.67
Particle size - 10%, μm ^{b, c}	11.58	0.97
Total carbon, % (w/w) ^d	20.83 \pm 0.48	1.03 \pm 0.13
Organic carbon, % (w/w) ^d	20.11 \pm 0.56	1.03 \pm 0.13

a. d Arithmetic mean \pm standard deviation (SD) a(n=2), d(n=4)
b. Analyzed by a commercial analytical laboratory
c. Weighted mean \pm standard deviation (SD) (n=2)



House Dust (HD)



Arizona Test Dust (ATD)

Dust Sorption Concentrations

- Sorption concentration in the dust collected increased steadily over time as a result of the air/dust partition.
- The ATD absorbed 1-4 times more OPFR than the HD
- The chamber air concentration dropped at the beginning but gradually went up after approximately 200 hours for both ATD and HD

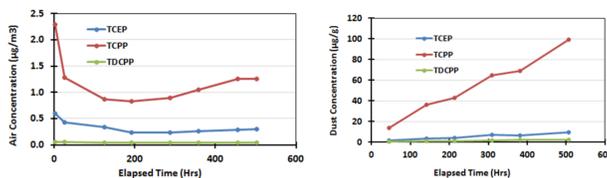


Figure 2. OPFR concentrations in the chamber air (left, $\mu\text{g}/\text{m}^3$) and ATD (right, $\mu\text{g}/\text{g}$) during Test 1.

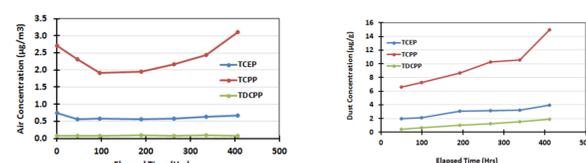


Figure 3. OPFR concentrations in the chamber air (left, $\mu\text{g}/\text{m}^3$) and HD (right, $\mu\text{g}/\text{g}$) during Test 2.

Sorption Rate

- The time-averaged sorption rate (R_D , $\mu\text{g}/\text{g}/\text{h}$) between exposure time 0 and t is calculated by the concentration measured on dust at the exposure time divided by the exposure time, t (h).
- Normalized sorption rate R_D^* ($(\mu\text{g}/\text{g}/\text{h})\text{dust}/(\mu\text{g}/\text{m}^3)\text{air}$):

$$R_D^* = \frac{R_D}{\bar{C}_a}$$

where \bar{C}_a is the time-averaged concentration in the chamber air between exposure time 0 and t ($\mu\text{g}/\text{m}^3$)

- Sorption rate decreased over time for both ATD and HD
- TCPP with the highest air concentration had the highest sorption rate.
- TDCPP with the lowest vapor pressure had the highest normalized sorption rate for HD

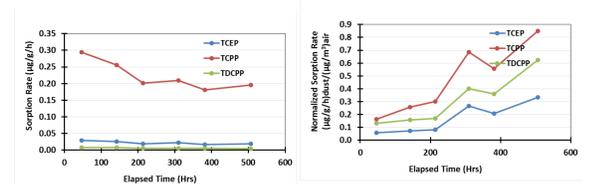


Figure 4. Sorption rate (left, $\mu\text{g}/\text{g}/\text{h}$) and normalized sorption rate of OPFRs in ATD test (right, $(\mu\text{g}/\text{g}/\text{h})\text{dust}/(\mu\text{g}/\text{m}^3)\text{air}$)

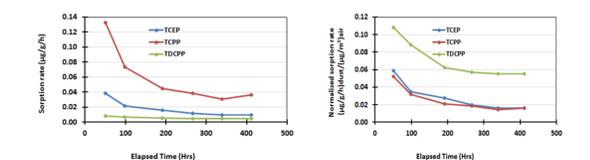


Figure 5. Sorption rate (left, $\mu\text{g}/\text{g}/\text{h}$) and normalized sorption rate of OPFRs in house dust test (right, $(\mu\text{g}/\text{g}/\text{h})\text{dust}/(\mu\text{g}/\text{m}^3)\text{air}$)

CONCLUSIONS

- The sorption of OPFRs from air by the dust is affected by the physiochemical properties of the dust, such as size, origin, shape, density, porosity, etc.
- The sorption favors the less volatile chemicals during dust/air partition
- The data will be used to further understand the mass transfer mechanisms of dust/air partitioning
- More work is underway to better characterize the factors that affect the degree of sorption of OPFRs on dust
- The results will help to accurately estimate indoor exposures and develop strategies that enlighten risk assessments

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