# ESTIMATION OF PHYSICOCHEMICAL PROPERTIES OF 22 ORGANO-PHOSPHATE ESTERS AND EVALUATION OF THEIR OVERALL PERSISTENCE AND LONG-RANGE TRANSPORT POTENTIAL

Hidetoshi Kuramochi [1]*, Hidetaka Takigami[1], Martin Scheringer [2], and Shin-ichi Sakai [3]

[1]Center for Material Cycles and Waste Management Research, National Institute for Environmental Studies, Tsukuba, Ibaraki 305-8506, Japan; [2] Institute for Chemical and Bioengineering, Swiss Federal Institute of Technology, ETH Zurich, HCI G127, CH 8093 Zurich, Switzerland; [3] Environment Preservation Research Center, Kyoto University, Yoshida-Honmachi, Sakyo-ku, Kyoto 606-8501, Japan

## 1. Introduction

Recently, research and development of non-PBDE (polybrominated diphenyl ether) flame retardants have received increasing attention due to prohibition on the marketing and use of some PBDEs by the Stockholm Convention and phaseout of decabromodiphenyl ether in the United States as well as EU. Understanding the environmental fate and mechanism of contamination of these alternatives to PBDEs requires knowledge of their physicochemical properties such as vapor pressure and 1-octanol/water partition coefficient. In our previous works (e.g. refs 1 and 2), we have measured physicochemical properties of various brominated flame retardants (BFRs) and some organophosphorous flame retardants (PFRs). However, it is very time consuming to measure the properties of all flame retardants. We should therefore know the approximate value of each property and then select some of the PFRs to be the foci of studies concerned with environmental contamination issues such as persistence and long-range transport. We have estimated the properties of BFRs by two estimation methods and then found out some POP-like BFRs[3]. For PFRs, there are some papers reporting the estimated properties[4,5]. However, nobody knows if the estimated values are reasonable or not.

In this work, first, we tried to predict the physicochemical properties of 22 organophosphate esters (OPEs), which are widely used as PFRs, using some estimation tools such as EPI Suite and SPARC. We discuss the estimates in terms of the partitioning characteristics of the compounds as well as their estimated performance. Furthermore, we used EPI Suite to estimate the degradation half-lives of the compounds in each environmental medium. From the combination of estimated properties and half-lives, the overall persistence (Pov) and long-range transport potential (LRTP) of all the OPEs were calculated with OECD Pov and LRTP Screening Tool. Some compounds were selected as POP-like OPEs on the basis of their high persistence and LRTP values.

## 2. Materials and methods

*2.1. Chemicals:* In this study, we selected 22 organophosphate esters (Table 1) from early work on non-PBDE BFRs and PFRs[5]. Our previous studies[6,7] have reported some properties of five compounds: TPHP, TMPP, PBDPP, PBDMPP, BPA-BDPP)

Table 1 Organophosphate esters calculated in this study

| Abbrevi-ation | Mw/ g·mol$^{-1}$ | Name | Abbrevi-ation | Mw/ g·mol$^{-1}$ | Name | Abbrevi-ation | Mw/ g·mol$^{-1}$ | Name |
|---|---|---|---|---|---|---|---|---|
| TMP | 140.08 | Trimethyl phosphate | TCEP | 285.49 | Tris(chloroethyl) phosphate | TTBNPP | 1018.46 | Tris(tribromoneopentyl) phosphate |
| TEP | 182.16 | Triethyl phosphate | TCIPP | 327.56 | Tris(2-chloroisopropyl) phosphate | IPPP | 216.17 | Isopropyl phenyl phosphate |
| TPP | 224.24 | Tri-n-propyl phosphate | TDCPP | 430.9 | Tris(2,3-dichloropropyl) phosphate | TPHP | 326.29 | Triphenyl phosphate |
| TIBP | 266.32 | Tris(isobutyl) phosphate | TDCIPP | 430.9 | Tris(1,3-dichloroisopropyl) phosphate | TMPP | 368.37 | Tris(methylphenyl) phosphate |
| TNBP | 266.32 | Tri-n-butyl phosphate | CMP-BCEP | 582.99 | 2,2-Bis(chloromethyl)-1,3-propanediol bis[bis(2-chloroethyl) phosphate] | TIPPP | 452.52 | Tris(4-isopropylphenyl) phosphate |
| TBOEP | 398.48 | Tris(2-butoxyethyl) phosphate | CMP-BCMEP | 639.1 | 2,2-Bis(chloromethyl)-1,3-propanediol bis[bis(2-chloro1-methylethyl) phosphate] | PBDPP | 574.46 | Resorcinol bis(diphenyl phosphate) |
| TEHP | 434.64 | Tris(2-ethylhexyl) phosphate | TDBPP | 697.61 | Tris(2,3-dibromopropyl) phosphate | PBDMPP | 686.67 | Resorcinol bis[di(2,6-dimethylphenyl) phosphate] |
| | | | | | | BPA-BDPP | 692.63 | Bisphenol A bis(diphenyl phosphate) |

*2.2. Estimation of physicochemical properties:* The physicochemical properties calculated in this study were vapor pressure ($p_i$), water solubility ($S_w$), the 1-octanol/water partition coefficient ($K_{ow}$), and the air/water partition coefficient ($K_{aw}$). The last two partition coefficients, in particular, are required for the evaluation of overall persistence and long-range transport potential (vide infra). We used EPI Suite (version 4.11)[8] and SPARC[9] as the estimation tool. The principles of estimation differ between the tools. EPI Suite is basically composed of fragment methods, while SPARC is based on linear free energy relationships. In order to suggest a more appropriate tool for estimating physicochemical properties, we calculated the deviation between measured values and the values estimated with each tool.

*2.3. Estimation of half-lives in the environment:* Half-lives in each environmental medium ($t_{air,\ 1/2}$, $t_{water,\ 1/2}$, and $t_{soil,\ 1/2}$) were also required for the estimation of Pov and LRTP. All half-lives were calculated with EPI Suite. $t_{water,\ 1/2}$, and $t_{soil,\ 1/2}$ were calculated according to a correction table[10] and the assumption $2 \cdot t_{water,\ 1}/2$[11], respectively.

*2.4. Estimation of Pov and LRTP:* Given the two estimated partition coefficients and three half-lives, the OECD Pov and LRTP Screening Tool (version 2.2)[12] calculated the Pov (days) and LRTP of a chemical. The tool provides two kinds of LRTPs as output: a characteristic travel distance (CTD) in kilometers and a transfer efficiency (TE) as a percent value. The Pov is a measure of time scale for degradation of the chemical in the environment. The CTD is the distance from the source point to the point at which the concentration of the chemical is 37% of the concentration at the source. The TE is equated to the ratio of the flux (deposition) onto a target region to the flux (emission) from the source region. OPEs with high Pov and LRTP values were extracted and identified as POP-like compounds by comparing their Pov and LRTP values with the analogous values of POP-PBDEs and the reference lines indicating POP-like[13].

## 3. Results and discussion

Figures 1a–1d show plots of individual properties estimated by EPI Suite and SPARC, with the compounds sorted on the basis of molecular weight. Basically, $p_i$, $S_w$, and $K_{aw}$ decreased with an increase in molecular weight, whereas $K_{ow}$ increased. OPEs with halogens have higher $S_w$ and $p_i$, and lower $K_{ow}$.

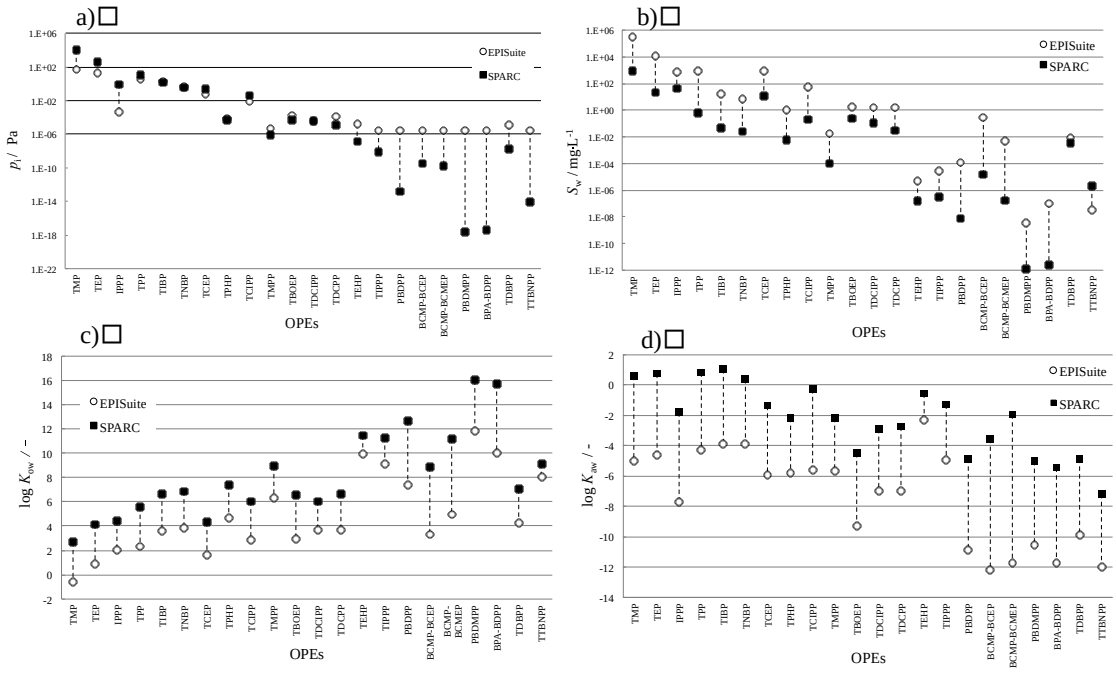


Fig. 1. Phsycochemical propeties of 22 OPEs estimated by EPI Suite and SPARC. Open circle: EPI Suite; solid square: SPARC.

Compared the results between both tools, there was not large difference in the $p_i$ estimation for the OPEs with molecular weight lower than 440 g·mol$^{-1}$, while the estimates for the OPEs with the higher molecular weight significantly differed. Especially, the estimates for such OPEs by EPI Suite might be not reasonable due to a constant $p_i$ value as a function of molecular weight. In the case of the other properties, the profiles from the individual tools qualitatively seem to be similar. However, the estimates by EPI Suite were higher or lower than those by SPARC by three orders of magnitudes or high. These large differences lead to the question of which tool provides a better estimate of $K_{ow}$ as well as $K_{aw}$. The estimates were therefore compared with the measured values as shown in Figs 2a–2d. These figures demonstrated that EPI Suite is excellent for estimating the physicochemical properties of OPEs. However, it should be noted that EPI Suite overestimated $p_i$ for OPEs with a high molecular weight.

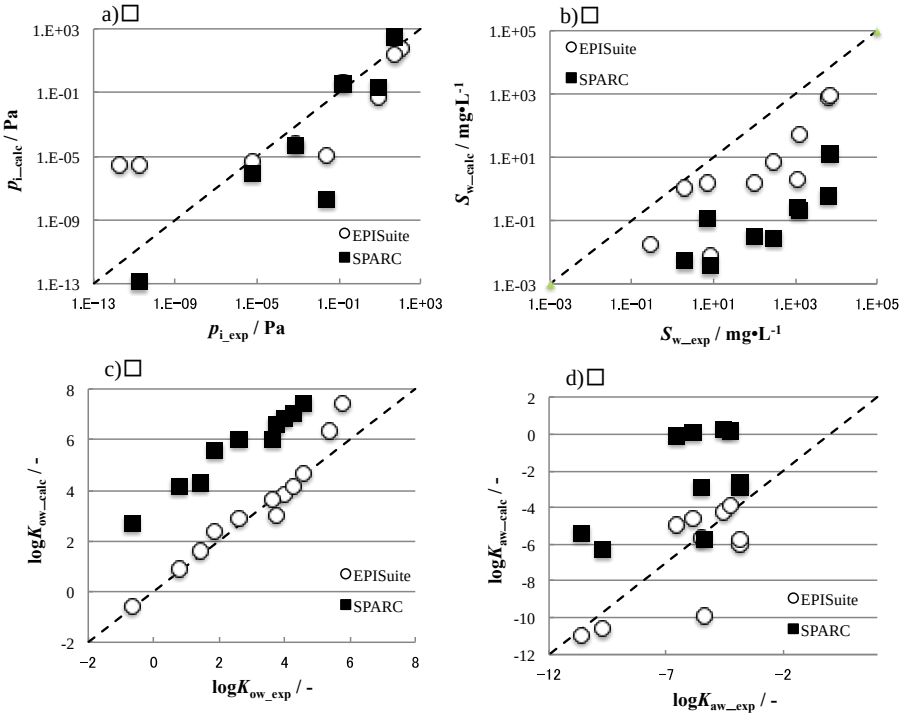


Fig. 2. Comparison of phsycochemical propeties of OPEs estimated by EPI Suite and SPARC with their literature values (measured values). Dotted line: perfect fit.

To estimate Pov and LRTP, three half-lives ($t_{air,\ 1/2}$, $t_{water,\ 1/2}$, and $t_{soil,\ 1/2}$) were calculated by EPI Suite. The $t_{air,\ 1/2}$ values of OPEs were in most cases less than 2 days. Hence, the present OPEs are expected to exhibit low LRTP. In contrast, most of the OPEs with molecular weights higher than 400 g·mol$^{-1}$ had $t_{water,\ 1/2}$ values longer than 2 months and $t_{soil,\ 1/2}$ values longer than 6 months. Based on these estimated values, such OPEs are expected to persist in the environment.

The estimated results for Pov and two LRTP parameters (CTD and TE) are shown in Figs. 3a and 3b. The vertical and horizontal lines in Figs. 3a and 3b define the criteria for POP-like characteristics. The regions in the upper-right quadrants of these graphs denote POP-like characteristics, and the regions in the lower-left quadrants denote low persistence and LRTP. In comparison with the results for non-PBDE BFRs, the number of OPEs with low persistence and LRTP is larger than that of non-PBDE BFRs. However, the Pov and LRTP values for TTBNPP, BCMP-BCMEP, TIPPP, PBDMPP, and BPA-BDPP lie in the upper-right quadrants or above three POP-PBDEs (BDE-47, -99, and -153). These selected OPEs are considered to be POP-like. Therefore, their

properties should be experimentally clarified, and then their Pov and LRTP should be re-evaluated with experimental data.

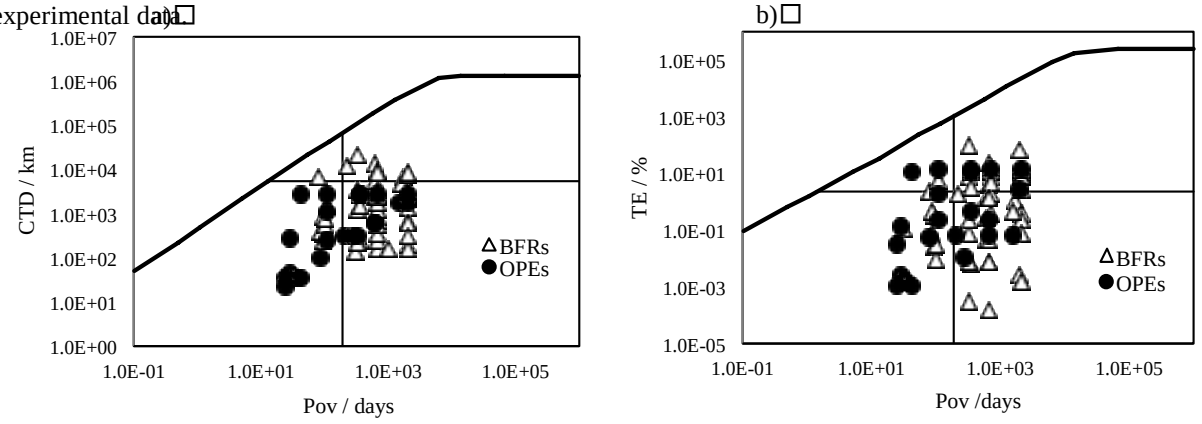


Fig. 3. Pov and LRTP (CTD and TE) of 22 OPEs calculated by the OECD Pov & LRTP Screening Tool using property data from EPISuite. Open triangle: 3 PBDEs (BDE-47, -99, and -153) and non-PBDE BFRs; solid circle: OPEs. a) Pov vs. CTD, b) Pov vs. TE

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