Environmental risk assessment of selected organic chemicals based on TOC test and QSAR estimation models

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ABSTRACT

Environmental risks of organic chemicals have been greatly determined by their persistence, bioaccumulation, and toxicity (PBT) and physicochemical properties. Major regulations in different countries and regions identify chemicals according to their bioconcentration factor (BCF) and octanol–water partition coefficient (Kow), which frequently displays a substantial correlation with the sediment sorption coefficient (Koc). Half-life or degradability is crucial for the persistence evaluation of chemicals. Quantitative structure activity relationship (QSAR) estimation models are indispensable for predicting environmental fate and health effects in the absence of field- or laboratory-based data. In this study, 39 chemicals of high concern were chosen for half-life testing based on total organic carbon (TOC) degradation, and two widely accepted and highly used QSAR estimation models (*i.e.*, EPI Suite and PBT Profiler) were adopted for environmental risk evaluation. The experimental results and estimated data, as well as the two model-based results were compared, based on the water solubility, *K*ow, *K*oc, BCF and half-life. Environmental risk assessment of the selected compounds was achieved by combining experimental data and estimation models. It was concluded that both EPI Suite and PBT Profiler were fairly accurate in measuring the physicochemical properties and degradation half-lives for water, soil, and sediment. However, the half-lives between the experimental and the estimated results were still not absolutely consistent. This suggests deficiencies of the prediction models in some ways, and the necessity to combine the experimental data and predicted results for the evaluation of environmental fate and risks of pollutants.

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Introduction

Because of the advancement of industrialization, more and more organic chemicals are being discharged into the environment, many of which have become major concerns recently because of their extreme toxicity or persistence in environment (Aksu, 2005). Common organic chemicals are used extensively in the chemical and pharmaceutical industries, food technologies, oil refineries, petrochemical works, dyeing and textile processes, and industrial and agricultural activities (Shahidi et al., 2015), and can exist in different environmental samples with diversified forms (Vörösmarty et al., 2010; Samecka-Cymerman et al., 2009; Elperin et al., 2011). Environmental risk of such compounds has aroused global concern, as they may not only be very persistent and very bioaccumulative (vPvB) and deleterious, but can also be transported through air, water, soil,

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sediment, and other environmental media far away from their original sources (Pavan and Worth, 2008).

Organic pollution owing to such compounds is of great harm to the environment and is a serious issue given their association with many health-related problems (Berezina et al., 2015). Both the fate and behavior of many organic chemicals in the environment depend largely on their physicochemical properties and environmental factors (Reid et al., 2000). Although the exact amount of organic pollutants produced in the world is indeterminate, it has been reported that there are at least 10,000 chemicals in current commercial production, with approximately 1000 being added each year (Mackay et al., 2006). Continuous increase in the production and extensive application of organic pollutants will intensify potential hazards to the environment and human health (Cachada et al., 2012). Organic compounds are distributed in many environmental media, having long half-lives. Pollutants with long half-lives will be present in some environmental media for a long time, which can lead to a wide distribution of such compounds (Schüürmann, 2004). They may accumulate and magnify greatly in the food chain and in individual organisms and have adverse effects on human health and the environment. However, little is known about their potential effects on the environment because of a lack of experimental data. In addition, organic pollutants can vary greatly in physical and chemical characteristics. Although toxicity data are adequate for some noted organic pollutants, data is sparse for most of these compounds and nonexistent for a few. For such chemicals, risk assessment is often impossible because their various toxicities, environmental fates, and health effects are largely undiscovered (Rücker and Kümmerer, 2012).

Furthermore, experimental testing of chemical compounds is usually costly and time-consuming, thus prediction models have played a significant role in remedying the shortage of data (Gramatica and Papa, 2003). Quantitative structure activity relationship (QSAR) models can predict biological activities by using variables of molecular structure (Liaw and Svetnik, 2015) and have the merit of only needing knowledge of chemical structure (Zhao et al., 2008). Such models search for mathematical relationships between chemical structures and activities. QSAR models immediately draw a conclusion that structurally similar chemicals generally show similar biological activities (Bradbury et al., 2004).

Bioconcentration is a process by which a specific chemical is absorbed by an organism from the surrounding environment merely *via* its respiratory and dermal surfaces. The degree to which bioconcentration occurs can be defined by the bioconcentration factor (BCF) (Arnot and Gobas, 2006). BCF is a crucial ecotoxicological indicator describing the trend of chemical compound concentration in a living organism and is an important parameter in environmental assessment (Gramatica and Papa, 2003). The BCF serves as the criteria for bioaccumulation when identifying pollutants that are hazardous to the environment (McGeer et al., 2003).

The fate of chemicals in the environment is constrained principally by their physical and chemical parameters (Mackay and Callcott, 1998), such as the octanol–water partition coefficient (K_{ow}) (Banerjee et al., 1980) and sediment sorption coefficient (K_{oc}) (Lu et al., 2008). K_{ow} can reflect the environmental fate of chemicals; the higher a chemical's K_{ow} value, the greater is the tendency for that chemical to partition to the organic phase. K_{oc} can appraise the relative tendency of chemicals to adsorb onto solid phases and the partitioning degree (Sun et al., 2016). K_{ow} and K_{oc} are of eminent importance for assessing the behavior and fate of organic pollutants in the environment, and they can be estimated using models based on quantum chemical descriptors (Dai et al., 1999).

Total organic carbon (TOC) concerns any chemical that contains carbon atoms except carbon dioxide and other related inorganic carbon substances and is the energy substrate for many microorganisms (Mook et al., 2012). The reaction kinetics could be calculated according to TOC results and be measured by Langmuir–Hinshelwood equation, and then the half-life for first-order kinetics could be calculated by TOC results (Da Silva et al., 2015).

The aim of this study was to assess the environmental fate and risk of select compounds using a combination of QSAR models and TOC-based half-life. According to the trophic magnification factors (TMFs) of the aquatic food web in Bohai in northern China, 39 compounds were selected. These compounds were screened using *in vitro* assays that measured the intrinsic clearance of liver microsomes from fish (weevers) and birds (quail) (Zheng et al., 2016). All 39 compounds showed significant trophic magnification in the food web.

Herein, prediction of water solubility (S_w), K_{ow}, K_{oc}, BCF, chronic toxicity value (ChV), and half-lives for the compounds in air, water, soil, and sediment was performed *via* two authoritative and widely used models, Estimation Programs Interface (EPI) Suite and persistence, bioaccumulation, and toxicity (PBT) Profiler. We compared the half-life results obtained from the two models with the laboratorial TOC half-lives. In addition, predictive parameters were compared between the two models for accuracy evaluation.

1. Materials and methods

1.1. Chemicals and devices

Environmental QSAR analysis models developed by the United States Environmental Protection Agency (US EPA) were used in this study. The EPI suite of models (EPI Suite™, Version 4.10, US EPA, Washington DC, USA) and the PBT Profiler (PBT Profiler™, Version 2.000, US EPA, Washington DC, USA, 2012) were freely available at http://www.epa.gov/oppt/exposure/pubs/episuitedl.htm and http://www.pbtprofiler.net, respectively. TOC was measured using an automatic TOC analyzer (TOC-Vcph, Shimadzu Corporation, Kyoto, Japan). Ultrapure water derived from a Millipore Milli-Q Gradient A10 (with TOC detector) purification system (Millipore, Billerica, MA, USA) was used for the preparation of all solutions. All reagents were of highest purity available and used without further purification. The organic chemicals (Appendix A Table S1) used in this study were purchased from J&K Scientific Ltd. (Beijing, China).

1.2. Estimation models

EPI Suite and PBT Profiler from the US EPA were employed to estimate the physicochemical properties and

environmental fate data of organic pollutants for QSAR analyses (Ying et al., 2007). The US EPA Office of Pollution Prevention and Toxics and the Syracuse Research Corporation developed EPI Suite. It is a windows-based suite of physicochemical property and environmental fate evaluation model and includes the following estimation programs: KOWWIN™, AOPWIN™, HENRYWIN™, MPBPWIN™, BIOWIN™, BioHCwin, KOCWIN™, WSKOWWIN™, WATERNT™, BCFBAF™, HYDROWIN™, KOAWIN, and AEROWIN™, and the fate models: WVOLWIN™, STPWIN™, and LEV3EPI™. ECOSAR™, which estimates ecotoxicity, is also included in EPI Suite™. In this study, we employed the level III fugacity model to assess half-life in various environmental compartments. It also can predict a diversity of indicators, including logKow, boiling point, melting point, vapor pressure, S_w, Henry's Law Constant, logKoc, and logBCF (Api et al., 2015; Eide-Haugmo et al., 2009).

PBT Profiler was developed as a screening tool to identify pollution prevention opportunities for chemicals in the absence of experimental data, and can be used to predict environmental persistence (half-life), BCF, and ChV according to the chemical structure. PBT Profiler estimates are designed for screening-level assessments to help identify pollution prevention opportunities for chemical substances (Abelkop et al., 2016; Gramatica et al., 2015). PBT Profiler determines ultimate biodegradation for water, soil, and sediment using the expert survey module in the BIOWIN estimation program.

1.3. Sampling and TOC determination

Sediment samples were collected with flasks in Haicang Bay, Xiamen, China. Sample treatment was conducted based on the Organization for Economic Cooperation and Development

Table 1 – Properties of 39 selected chemicals estimated using the US EPA Estimation Programs Interface suite (EPI Suite™ v4.10).

CAS No	S_W	logKow	logBCF	logKoc	Half-life (days)			
					Air	Water	Soil	Sediment
79-94-7	1.00E−03	7.20	2.30	5.43	3.62	180	360	1620.83
80-07-9	6.86E+00	3.90	2.30	3.46	18.25	60	120	541.67
98-07-7	2.17E+01	3.90	2.59	3.00	29.96	60	120	541.67
98-56-6	4.61E+01	3.60	2.56	3.21	44.58	60	120	541.67
115-32-2	7.77E−01	5.02	3.83	4.10	3.12	180	360	1620.83
117-08-8	1.59E+00	4.65	3.17	1.36	338.33	180	360	1620.83
119-47-1	1.24E−01	6.25	2.51	6.30	0.26	60	120	541.67
120-12-7	6.91E−01	4.45	3.05	4.21	0.27	60	120	541.67
127-90-2	1.84E−01	5.10	3.48	3.14	10.42	180	360	1620.83
632-58-6	8.92E+00	3.65	2.28	3.12	10.21	60	120	541.67
632-79-1	1.90E−02	5.63	3.21	1.01	437.50	180	360	1620.83
709-98-8	8.42E+01	2.88	1.87	2.25	2.83	60	120	541.67
1897-45-6	2.60E+01	3.66	2.02	3.02	1729.17	180	360	1620.83
2312-35-8	3.31E−01	5.57	3.09	4.56	0.18	60	120	541.67
3194-55-6	2.09E−05	7.74	2.93	4.99	2.13	60	120	541.67
13560-89-9	1.69E−08	11.27	0.73	7.68	0.47	180	360	1620.83
3864-99-1	2.63E−02	6.91	2.89	5.28	0.81	60	120	541.67
3896-11-5	6.84E−01	5.55	3.01	4.64	0.72	60	120	541.67
4130-42-1	2.12E+00	5.52	3.39	4.45	0.58	60	120	541.67
4419-11-8	6.94E−02	5.67	2.98	2.87	1.24	60	120	541.67
5915-41-3	5.54E+01	3.27	1.78	2.50	0.97	60	120	541.67
7287-19-6	2.66E+01	3.73	1.73	2.82	0.28	60	120	541.67
13472-08-7	4.91E+00	3.86	2.36	1.98	3.60	60	120	541.67
34256-82-1	4.74E+01	3.37	1.68	2.48	0.22	60	120	541.67
19666-30-9	5.27E−01	4.81	3.23	3.70	0.44	60	120	541.67
51630-58-1	6.10E−03	6.76	3.16	5.50	0.48	60	120	541.67
52315-07-8	1.56E−03	6.38	2.85	4.90	0.50	180	360	1620.83
52645-53-1	9.75E−03	7.43	2.76	5.08	0.46	60	120	541.67
66441-23-4	6.45E−01	4.95	2.21	4.22	0.32	60	120	541.67
76738-62-0	7.99E+01	3.36	2.16	2.97	0.64	60	120	541.67
91465-08-6	8.53E−04	6.85	2.69	5.53	0.32	180	360	1620.83
556-67-2	6.12E−02	6.79	3.88	4.16	10.58	37.5	75	337.50
40615-36-9	8.98E−02	5.74	3.77	5.33	0.19	60	120	541.67
1770-80-5	4.54E−04	7.25	2.47	4.54	0.72	180	360	1620.83
26040-51-7	1.98E−09	11.95	−0.041	5.94	0.49	60	120	541.67
3380-34-5	4.62E+00	4.66	3.04	4.37	0.66	60	120	541.67
2385-85-5	4.76E−04	7.01	3.76	5.55	4166.67	180	360	1620.83
101-02-0	2.35E−02	6.62	2.94	6.28	0.99	37.5	75	337.50
31570-04-4	2.85E−14	18.08	−0.049	11.33	0.45	180	360	1620.83

Kow: octanol–water partition coefficient; Koc: sediment sorption coefficient;
S_w: water solubility; BCF: bioconcentration factor.

(OECD) 301 Guidelines (OECD, 1994). The selected test substances were added to the sediment samples to a final concentration of 30 mg/L. Parallel blanks (without test substance) were prepared according to the same procedure. The laboratory determinations were performed in triplicate under aerobic conditions in flasks (250 mL) used as incubation reactors. The flasks were shaken on a shaker incubator (TS-211B, TENSUC, China) at 180 r/min at room temperature for 28 days. Within this period of the test, TOC determination was carried out every four days. The TOC content of the samples was determined using a TOC analyzer (TOC-Vcph, Shimadzu Corporation, Kyoto, Japan) equipped with a solid sample module (SSM-5000A, Shimadzu, Japan) and connected to a total nitrogen (TN) measuring unit (TNM-1, Shimadzu, Japan). The TOC analyzer was operated according to the manufacturer's instructions. TOC was determined *via* the dry combustion method (Nelson et al., 1996).

1.4. TOC degradation half-lives

As has been reported in previous literature (Banach-Szott et al., 2015; Da Silva et al., 2015; Wenzel et al., 1999), half-life was calculated based on TOC degradation. The reaction rate constant for the pseudo first-order reaction was calculated using the following Eq. (1):

$$kt = \ln(TOC_0/TOC_t) \tag{1}$$

where, k (day^{-1}) is the apparent reaction rate constant of the pseudo first-order reaction, t (day) is the time, TOC_0 (mg/L) is the initial ($t = 0$) TOC concentration, and TOC_t (mg/L) is the TOC concentration for the reaction time t (mg/L).

Then, the half-life ($T_{1/2}$) was calculated according to the following Eq. (2):

$$T_{1/2} = \ln 2/k \tag{2}$$

Table 2 – Properties of 39 selected chemicals estimated using the PBT profiler.

CAS No	S_W	logKow	logBCF	Fish ChV (mg/L)	Half-life (days)			
					Air	Water	Soil	Sediment
79-94-7	2.1E−03	7.20	4.00	1.6E−03	5.40	180	360	1600
80-07-9	2.4E+00	3.89	2.23	5.6E−01	28	60	120	540
98-07-7	5.3E+01	3.89	2.23	8.4E−02	46	60	120	540
98-56-6	2.9E+01	3.60	2.04	6.3E−01	67	60	120	540
115-32-2	8.0E−01	5.02	2.98	1.0E−02	4.60	180	360	1600
117-08-8	4.8E−02	4.64	2.73	1.3E−01	500	180	360	1600
119-47-1	2.0E−02	6.25	3.57	2.3E−04	0.39	60	120	540
120-12-7	4.3E−02	4.45	2.60	1.4E−01	0.40	60	120	540
127-90-2	1.5E+00	5.10	3.04	5.1E−02	15	180	360	1600
632-58-6	3.6E+03	3.64	0.51	9.7E + 00	15	60	120	540
632-79-1	1.6E−03	5.62	3.38	3.0E−02	670	180	360	1600
709-98-8	1.5E+02	3.07	1.69	4.4E−02	4.20	60	120	540
1897-45-6	8.1E−01	3.05	1.68	8.2E−01	2600	180	360	1600
2312-35-8	2.2E−01	5.00	2.96	2.6E−02	0.27	60	120	540
3194-55-6	8.6E−03	7.74	3.76	6.7E−04	3.20	60	120	540
13560-89-9	4.4E−08	11.20	2.04	NE	0.71	180	360	1600
3864-99-1	2.8E−01	6.91	4.00	1.3E−03	1.20	60	120	540
3896-11-5	2.6E+00	5.55	3.11	1.0E−02	1.10	60	120	540
4130-42-1	6.5E+00	5.52	3.08	1.5E−02	0.88	60	120	540
4419-11-8	9.6E−02	5.67	3.41	1.2E−02	1.90	60	120	540
5915-41-3	8.5E+00	3.21	1.28	2.6E−01	1.50	60	120	540
7287-19-6	3.3E+01	3.51	1.46	1.1E−01	0.42	60	120	540
13472-08-7	5.5E+00	3.85	2.20	2.9E−01	5.40	60	120	540
34256-82-1	2.2E+02	3.03	1.66	2.9E−01	0.32	60	120	540
19666-30-9	7.0E−01	4.80	2.83	8.0E−03	0.67	60	120	540
51630-58-1	2.0E−03	6.22	3.77	3.7E−05	0.71	60	120	540
52315-07-8	1.2E−01	6.94	2.99	5.7E−05	0.75	180	360	1600
52645-53-1	6.0E−03	6.50	2.70	9.6E−06	0.71	60	120	540
66441-23-4	9.0E−01	4.58	2.69	3.7E−02	0.50	60	120	540
76738-62-0	2.6E+01	3.20	1.52	3.4E−02	0.96	60	120	540
91465-08-6	5.0E−03	7.00	3.04	3.6E−05	0.46	180	360	1600
556-67-2	5.6E−02	6.74	4.11	2.0E−03	16	38	75	340
40615-36-9	4.4E−01	5.74	3.46	8.0E−03	0.28	60	120	540
1770-80-5	7.2E−03	7.25	4.00	2.0E−05	1.10	180	360	1600
26040-51-7	7.1E−08	11.90	1.11	NE	0.75	60	120	540
3380-34-5	1.0E+01	4.76	2.81	7.1E−02	1.00	60	120	540
2385-85-5	8.5E−02	6.89	3.20	2.0E−03	180	180	360	1600
101-02-0	7.1E−02	6.62	4.04	3.0E−03	1.50	38	75	340
31570-04-4	1.0E−12	18.00	0.51	NE	0.67	180	360	1600

NE: not estimated; *Kow*: octanol–water partition coefficient; ChV: chronic toxicity value.

1.5. Statistical analysis

TOC data were reported as the mean of three separate experiments ± SD. Microsoft Excel 2010 (Microsoft, Redmond, WA, USA) and SigmaPlot® 12.5 for Windows (Systat Software, Inc., San Jose, CA, USA) were used for all statistical analysis in this study. A one-way analysis of variance (ANOVA) with a Dunnett's post-hoc test was used to identify significant differences between logKow and logKoc, estimated using the US EPA EPI Suite. The data was fitted to a regression equation curve by means of SigmaPlot 12.5.

2. Results

2.1. Physicochemical properties

Tables 1 and 2 show the general physicochemical properties, including S_w, logKow, logKoc, logBCF, ChV, and half-life, of the 39 chemicals, as estimated using EPI Suite and PBT Profile, respectively. The 39 chemicals are divided into two categories (aliphatic and aromatic) (Appendix A Table S1).

2.2. TOC degradation half-life

Degradation of TOC was determined by using an automatic TOC analyzer, which can determine TN, total carbon (TC), inorganic carbon (IC), and TOC simultaneously. A first order kinetic model was used to describe the degradation behavior of the selected organic pollutants. The half-life for the target compounds was calculated according to Eqs. (1) and (2). The experimental half-lives according to TOC degradation of the selected chemicals are shown in Table 3. The half-life ranged from 6.87 ± 0.54 to 4284.59 ± 256.34 days.

2.3. Comparison with QSAR models

The predictive accuracy of EPI Suite and PBT Profiler was determined by comparing BCF and Kow. Fig. 1 shows the logKow and logBCF, calculated by the two models. The ratios are defined as EPI Suite/PBT Profiler. An EPI Suite/PBT Profiler ratio from 0.919 to 1.200 was found in the comparison of

logKow (Fig. 1a), whereas it ranged from −0.0961 to 4.4706 in the comparison of logBCF (Fig. 1b). In addition, the quantitative relationship between the logKow and logKoc estimated using the US EPA EPI Suite is illustrated in Fig. 2.

2.4. Estimated half-lives

Environmental fate models (EPI Suite and PBT Profiler) were used in this study for half-life prediction. Suggested environmental half-life values in air, water, soil, and sediment for the selected chemicals are presented in Tables 1 and 2. EPI Suite and PBT Profiler generated highly similar results for estimated half-lives of the 39 selected chemicals in water, soil, and sediment. However, they were not consistent with estimates of the half-lives in air.

3. Discussion

The S_w of an organic pollutant is one of the most significant physical properties controlling the distribution and fate of that chemical in the aquatic environment (Chiou et al., 1986). The Kow is of great importance in environmental fate research because of its utility in predicting biological and physical effects such as bioaccumulation, soil adsorption, and aquatic acute and chronic toxicity (Swanson et al., 1997). It has been applied to related environmental chemistry and toxicology research for 30 to 40 years. QSAR models based on Kow have been deemed very effective in exposure, hazard, and risk assessment. Recently, Kow has become an effectual, approved, and widely applied parameter in environmental risk assessment of organic contaminants. In the absence of experimental data, such prediction is especially effective (Hermens et al., 2013). Strong linear correlations exist between the two properties (logKow and logS_w), as stated in previous studies (Banerjee et al., 1980; Chiou, 2012). They are two of the most important parameters associated with the environmental behavior of hydrophobic organic chemicals (Pontolillo and Eganhouse, 2001).

As shown in Tables 1 and 2, S_w and Kow are relevant to other parameters such as Koc, BCF, and indices of biodegradability or toxicity. Chemicals with high logKow values have

Table 3 – Experimental half-life data of 39 selected chemicals in sediment calculated by $T_{1/2} = ln2/k$ based on TOC degradation test.					
CAS No.	$T_{1/2}$ (days)	CAS No.	$T_{1/2}$ (days)	CAS No.	$T_{1/2}$ (days)
79-94-7	60.32 ± 5.28	2312-35-8	18.57 ± 2.26	52315-07-8	32.53 ± 2.58
80-07-9	9.83 ± 1.75	3194-55-6	28.43 ± 3.47	52645-53-1	6.87 ± 0.54
98-07-7	39.49 ± 8.56	13560-89-9	18.26 ± 1.86	66441-23-4	15.27 ± 2.24
98-56-6	22.05 ± 3.88	3864-99-1	9.53 ± 1.05	76738-62-0	33.55 ± 2.05
115-32-2	24.88 ± 4.71	3896-11-5	12.09 ± 1.32	91465-08-6	36.97 ± 3.04
117-08-8	46.46 ± 7.43	4130-42-1	14.05 ± 1.38	556-67-2	4284.59 ± 256.34
119-47-1	79.26 ± 6.92	4419-11-8	39.48 ± 5.22	40615-36-9	12.59 ± 0.23
120-12-7	7.36 ± 1.35	5915-41-3	48.66 ± 4.83	1770-80-5	8.57 ± 1.65
127-90-2	19.00 ± 3.21	7287-19-6	88.48 ± 11.28	26040-51-7	31.80 ± 2.84
632-58-6	13.06 ± 1.26	13472-08-7	1094.34 ± 95.35	3380-34-5	114.57 ± 20.14
632-79-1	23.71 ± 3.25	34256-82-1	27.13 ± 2.58	2385-85-5	89.55 ± 8.54
709-98-8	15.93 ± 1.85	19666-30-9	23.83 ± 1.91	101-02-0	59.70 ± 2.65
1897-45-6	22.97 ± 3.50	51630-58-1	33.40 ± 4.36	31570-04-4	139.20 ± 9.51

Data are presented as mean ± SD; n = 3; CAS: chemical abstracts service.
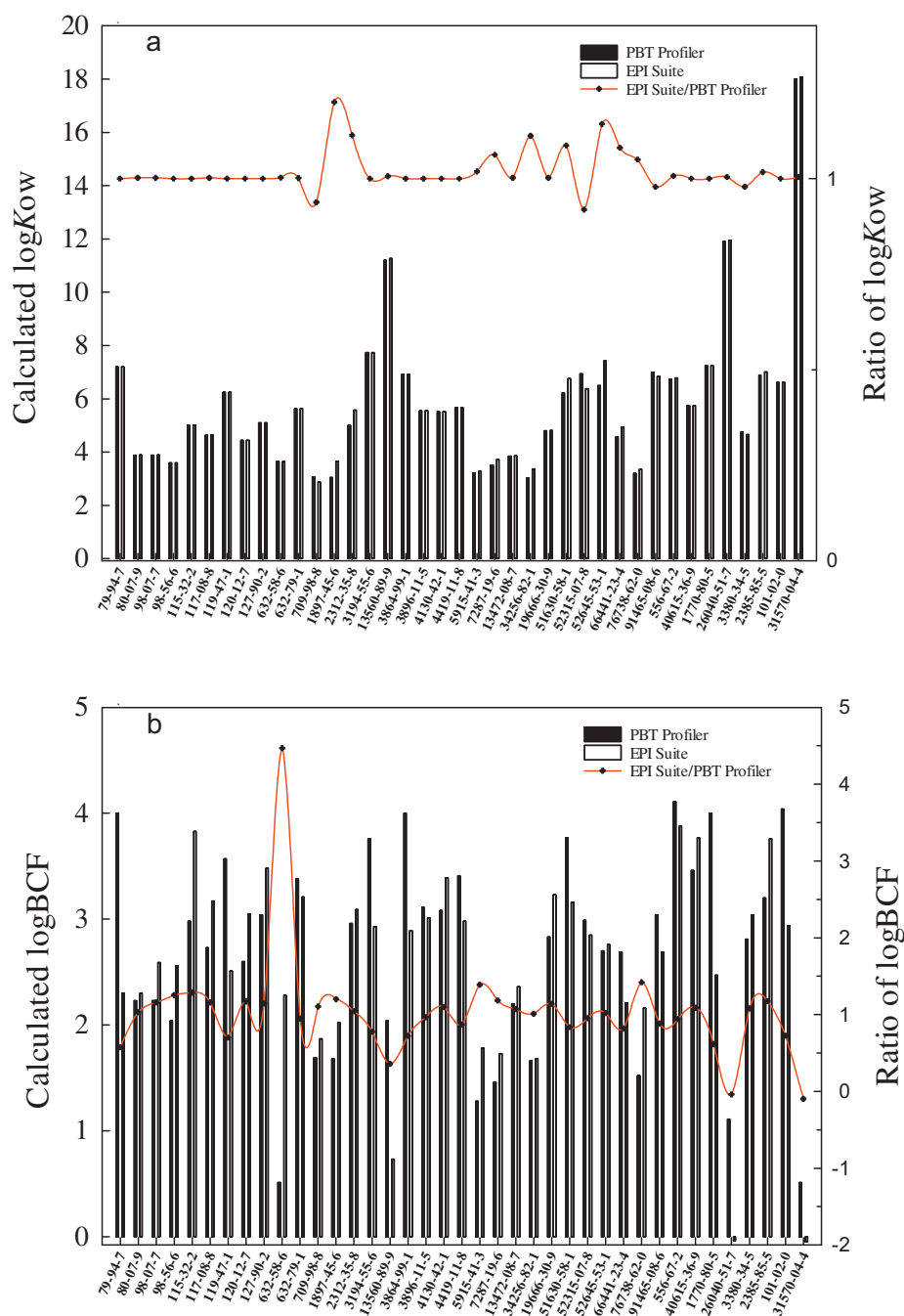
Fig. 1 – The comparison of Kow (a) and BCF (b) values between the two estimated models. The ratio was defined as EPI Suite/ PBT Profiler. PBT: persistence, bioaccumulation, and toxicity.

relatively poor solubility in water. High logKow values (≥6.0) imply that such chemicals have a tendency to partition to soil or sediment in the environment and have relatively high logBCF for most selected compounds, suggesting that these chemicals have the potential to concentrate in aquatic organisms. Kow is a useful parameter for predicting the BCF of organic compounds. A logKow value of 6.0 or greater is a key threshold for bioaccumulative chemicals. Lipophilic organic chemicals with logKow values (<5.0) can accumulate in adipose tissue to the maximum extent (Geyer et al., 1987) and are generally more toxic to fish (Swanson et al., 1997). Overall, in this work, at least 15 chemicals (38.46%) among

the model compounds have the ability to bioaccumulate, are harmful to fish, and therefore cause potential harm to the environment.

The two models were fairly accurate in predicting physico-chemical properties. An EPI Suite/PBT Profiler ratio from 0.919 to 1.200 was found in the comparison of logKow, whereas the ratio ranged from −0.0961 to 4.4706 in the comparison of logBCF. These ratios suggest that EPI Suite and PBT Profiler yielded similar results in estimating Kow and BCF. The models have been widely applied by the US National Institute of Health in assessing physicochemical properties (Sanderson et al., 2007).
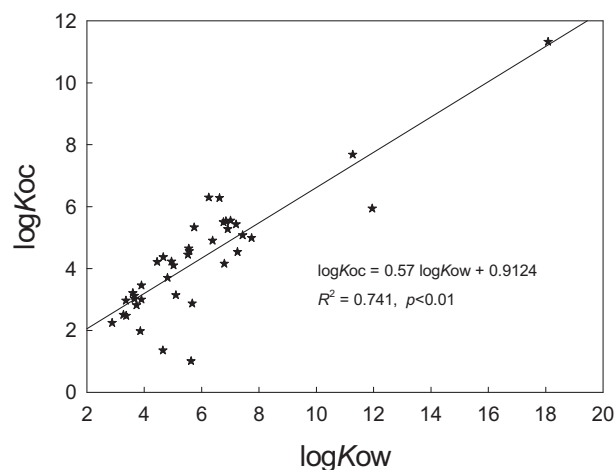
Fig. 2 – Quantitative relationship of 39 selected chemicals between the octanol-water partition coefficient and the soil sorption coefficient (logKow vs. logKoc) estimated using the US EPA EPI (Estimation Programs Interface) Suite.

Table 4 – Half-life data comparison of some standard chemicals.

CAS No.	This work	Others work	References
79-94-7	60.32 ± 5.28 days	60 days	Voordeckers et al., 2002
80-07-9	9.83 ± 1.75 days	About 12 days	Mathews et al., 1996
98-07-7	39.49 ± 8.56 days	4 weeks (anaerobic) 168 hr (aerobic)	Howard, 1991
1897-45-6	22.97 ± 3.50 days	3–6 days (in water) 30–60 days (in soil)	Caux et al., 1996
CAS: chemical abstracts service.			

However, there was a remarkable discrepancy between our experimental TOC degradation half-lives and the model-estimated half-lives. The two models obtained nearly the same half-lives for the 39 compounds in various environmental media with the exception of air. Although these models gave perfect results in the binary classification of half-lives, with general accuracy in the of 70%–80% range (Aronson et al., 2006), PBT Profiler calculated half-life in water, soil, and sediment by determining the ultimate biodegradation expert survey module of the BIOWIN estimation program, and EPI Suite estimated the half-lives based on the level III fugacity model. It is not reasonable to expect overall excellent performance from the selected models that rely simply on level III fugacity model or chemical structure (Jaworska et al., 2003; Walters et al., 2010). Surprisingly, the two fate models generated almost the same half-lives for the 39 compounds in various environmental compartments, probably because of their similarity in prediction mechanism. Biodegradation half-lives are extraordinarily variable parameters. Therefore, the estimated half-lives should not be used for the purpose of adequate environmental risk assessment unless the prediction mechanism and the accuracy improve (Aronson et al., 2006; Gouin et al., 2004). It is also can be concluded that there is an urgent need for continuing method development effort to provide credible data for risk assessment research (Walters et al., 2010).

To the best of our knowledge, this is the first time these 39 chemicals have been identified based on TOC test and QSAR estimation models. There is not enough data to compare with the data in similar analyses. Some data, under different conditions, can be used as a reference only. To evaluate the reliability of results, we cite four standard chemicals (79-94-7, 80-07-9, 98-07-7, and 1897-45-6) evaluated by others as examples. Table 4 shows the data comparison of the selected standard chemicals.

The OECD principles for model validation require defining the applicability domain (AD) for the QSAR models (Sahigara

et al., 2012). A previous study was carried out to characterize the AD of EPI Suite and to evaluate the performance of select AD assessment methods (Boethling and Costanza, 2010). Sahigara et al. (2012) used different approaches to define the AD of QSAR models, including EPI Suite. The results showed that all the implemented AD approaches had their own strengths and limitations and thus, it is up to the model builder to choose the most appropriate AD approach for his model. In general, the AD of EPI Suite is given as organic chemicals (Strempel et al., 2012). PBT Profiler is designed for discrete organic chemicals. Mixtures, inorganic chemicals, reactive chemicals, salts, high molecular weight compounds, chemicals with unknown or variable composition, surfactants, and fully fluorinated organics will not provide reliable results and should not be profiled. There is no doubt that OECD principles are absolutely essential for QSAR model design. Models that have been validated externally and internally can be considered reliable and applicable for both external prediction and regulatory purposes. Furthermore, the estimation models are continually improving as more data become available. The proposed models have been proved to fulfill the fundamental points set down by OECD principles for regulatory QSAR acceptability and could be used reliably as scientifically valid models in the REACH program (Gramatica, 2007).

4. Conclusions

EPI Suite and PBT Profiler models were adopted to predict environmental fate and health effects of the 39 chemicals in this study. Based on TOC degradation, the half-lives of the chemicals were tested simultaneously. The combined experimental results and estimated data were employed to evaluate the environmental risk. With regard to general physicochemical properties (i.e., Kow, Koc, and BCF), conservative use of QSAR models can generate reliable and conservative estimations of the environmental risk of chemicals. In addition, it was concluded that both models could yield a fair accuracy in measuring half-lives in environmental medium.

Indeed, our laboratorial TOC half-life values were far from the predictions of the models. This suggests some inadequacy of the QSAR models in environmental degradation assessment. The reason may be that the prediction mechanism of the models needs to be improved further for better evaluation of environmental fate and risk.

Undoubtedly, great progress has been made in developing estimation models for environmental chemical assessment. From the point of view of development of environmental chemistry, however, no model that can forecast every aspect of chemicals exists. Thus, the environmental risk of chemicals still often presents challenges. Models that have great precision and a better mechanism need to be developed and applied for environmental compound risk assessment. Finally, combining experimental data and predicted results is beneficial to environmental assessment.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.jes.2016.11.018.

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