

Fugacity Analysis of Polycyclic Aromatic Hydrocarbons between Microplastics and Seawater

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Abstract – Recently, the accumulation of plastic debris in the marine environment has become a great concern worldwide. Although plastics are biologically and chemically inert, plastic debris has been suspected of causing adverse effects on ecosystems due to the increase in reactivity by size reduction and/or micropollutants associated with plastics. Because of the high sorption capacity of microplastics toward organic micropollutants, it is suspected that microplastics may play roles in the distribution and fate of micropollutants. In order to quantitatively evaluate the “net flow” of environmental contaminants in water-plastic-organism systems, a fugacity analysis was conducted using concentrations of polycyclic aromatic hydrocarbons (PAHs) in open oceans and in polyethylene as a representative material of plastic debris. Ratio of fugacity in polyethylene to that in seawater showed a decreasing trend with increasing partition coefficient between polyethylene and seawater ($K_{PE/sw}$). This indicates that phase equilibrium between polyethylene and seawater is not attained for higher molecular weight PAHs. Disequilibrium of high molecular weight PAHs suggests that transfer from seawater to plastic debris is thermodynamically driven and the role of plastic debris as a vector to transfer them to living organisms would be minimal. However, additives may slowly migrate from plastics into the environment causing potentially serious effects on ecosystems.

Key words – microplastics, polycyclic aromatic hydrocarbons (PAHs), bioaccumulation, fate, fugacity, partitioning

1. Introduction

In recent decades, the accumulation of plastic debris in the marine environment has raised significant concerns (Moore

et al. 2001, 2008; Thompson et al. 2004; Barnes et al. 2009; Ivar do Sul and Costa 2014). Although plastics are regarded as being inert, potentially harmful effects on marine ecosystems are suspected to be caused by the increased reactivity of smaller broken-down plastic particles (Bhattacharya et al. 2010; von Moos et al. 2012; Lee et al. 2013) and/or the chemical contaminants associated with plastic debris (Teuten et al. 2009).

Major plastic materials identified in monitoring studies have been polyethylene, polypropylene, and polystyrene (Hidalgo-Ruz et al. 2012). They are plastic materials that have been produced in large quantities over the past 50 years (Andrady and Neal 2009). These plastic materials may contain additives intentionally incorporated to enhance the desired engineering properties, or contain environmental contaminants, such as persistent organic pollutants (POPs), due to the high sorption capacity of plastic materials. Because of the high partition or distribution coefficient between plastic and water, the concentration of many hazardous chemicals was found to be higher than that in water (Lee et al. 2014; Velzeboer et al. 2014). This aspect raised concerns that plastics may deliver hazardous chemical substances from water to living organisms (Teuten et al. 2009). In other words, the existence of small plastic debris may be considered to accelerate the rate of transport of hydrophobic organic chemicals to living organisms. For example, Bakir et al. (2014) showed that the rate of desorption of hydrophobic organic contaminants such as phenanthrene, DDT, and diethylhexyl phthalate under simulated gut conditions was enhanced, and suggested that enhanced mass transport may contribute to the role of

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ingested plastic particles as a “vector” for hydrophobic organic chemicals.

However, higher concentrations of hydrophobic organic chemicals (HOCs) in plastic phase than those in water do not necessarily mean that micro- or nano-sized plastic particles contribute to bioaccumulation of HOCs through the food chain. Biomagnification occurs when the fugacity of a chemical of a predator is maintained at a greater level than that of the prey and the environment, because HOCs are absorbed but not utilized in the body, whereas the organic matter of prey is used for new cells or for energy production (Gobas et al. 1999). Because plastics are not digested and not absorbed through the intestinal tract, the transfer process of HOCs from the ingested plastic particles to the body is different from HOCs contained in prey. In addition, the concentration of plastic particles in the marine environment may not be sufficiently high to contribute to the overall intake rate of HOCs compared with other processes, such as absorption through the gills and via food (Gouin et al. 2011).

Fugacity represents the “escaping tendency” of a chemical from its confined phase (Mackay 2001) normally described in the unit of pressure. Chemicals in a phase with higher fugacity flow to another phase with lower fugacity to attain phase equilibrium. Thus, analyzing the fugacity of the chemical in different environmental media should be useful in estimating the direction of net chemical flow from one phase to another (Lohmann et al. 2009; Ma et al. 2013). In these studies, the fugacity ratio between water and air was used to evaluate the direction of the global transport of HOCs.

In this study, a fugacity analysis was performed for eight polycyclic aromatic hydrocarbons (PAHs) as examples of HOCs that are not intentionally added to plastics, to evaluate the direction of net flow of PAHs in the marine environment. Polyethylene (PE) was chosen as the model plastic phase because partitioning of PAHs between PE and seawater has been intensively studied. Monitoring data for PAHs in plastic debris were obtained from the literature and they were converted to fugacity using partition coefficients. Fugacity in seawater was estimated from literature values reported in the open oceans that were not likely to be affected by point or non-point sources nearby. The fugacity ratio of the two phases was then computed and differences in fugacity ratio for PAHs with different hydrophobicity were compared in order to judge the degree of equilibration and the net direction of the chemical flow driven by thermodynamic partitioning.

2. Data Collection and Fugacity Analysis

Model plastic phase and pollutants

Polyethylene was chosen as a surrogate plastic material because it is the most widely used plastic material (Plastics Europe 2015) and most abundantly identified in marine debris (Hidalgo-Ruz et al. 2012). In addition, partitioning properties of PAHs between polyethylene and water are well-documented in the literature (Huckins et al. 1993; Müller et al. 2001; Booij et al. 2003; Adams et al. 2007; Cornelissen et al. 2008; Fernandez et al. 2009; Perron et al. 2009; Smedes et al. 2009; Hale et al. 2010; Bao et al. 2012; Fries et al. 2012; Lee et al. 2014). PAHs were chosen as model environmental pollutants because physico-chemical properties such as Henry’s law constant, partition coefficients, required for the calculation of fugacity, are well-documented in the literature and monitoring data in seawaters and for polyethylene are available as individual chemicals. Thus, eight PAHs (phenanthrene (PHE), fluoranthene (FLU), anthracene (ANT), pyrene (PYR), chrysene (CHR), benzo[*a*]pyrene (BaP), dibenz[*a,h*]anthracene (DBaH), benzo[*ghi*]perylene (BghiP)) were chosen. The range of hydrophobicity and molecular size of the selected PAHs almost covers that of 16 priority PAHs by US EPA. The logarithm of the partition coefficient between PE and seawater ($\log K_{PE/SW}$) ranged from 4.44 (for PHE) to > 7.87 (for DBaH) (Lee et al. 2014).

Data collection

Reported values of the concentration of the selected PAHs in polyethylene debris collected in the field were obtained from publications filed in SCOPUS between January 2000 and March 2015. The combinations of keywords used in the screening are listed in Table 1. Because researchers use different terminology, the individual names of PAHs or “polycyclic aromatic hydrocarbons” were combined with “microplastics”, “debris”, “resin pellets”, “pellets”, or “polyethylene”. Ideally, seawater concentrations of PAHs

Table 1. Keywords used for searching publication from SCOPUS

Medium	Keyword
Microplastics	“microplastics”
	“resin pellet”
	“debris” and individual names of PAHs
	“pellet” and individual names of PAHs
Seawater	“polyethylene” and individual names of PAHs
	“seawater” and individual names of PAHs
	“seawater” and “polycyclic aromatic hydrocarbons”

Table 2. Polyethylene/water partition coefficients and the Henry's law constants used for the calculation of fugacity

PAHs	log H (H in L atm mol ⁻¹)	log K _{PE/sw} (K _{PE/sw} in L kg ⁻¹) ^a
Phenanthrene (PHE)	-2.64 ^b	4.44
Fluoranthene (FLU)	-2.88 ^b	5.52
Anthracene (ANT)	-2.52 ^b	4.77
Pyrene (PYR)	-3.01 ^b	5.57
Chrysene (CHR)	-3.64 ^b	6.39
Benzo[a]pyrene (BaP)	-4.01 ^b	7.17 ^c
Dibenzo[a,h]anthracene (DBahA)	-5.51 ^d	7.87 ^c
Benzo[ghi]perylene (BghiP)	-4.96 ^e	7.61 ^c

^aValues taken from Lee et al. (2014) using third-phase partitioning method, ^bfrom Lee et al. (2012), ^cindicates partition coefficients that might be underestimated because of incomplete equilibrium, ^dfrom Odabasi et al. (2006), ^efrom ten Hulscher et al. (1992)

should be used for water samples collected at the same sites where plastic debris was collected. However, to the best of our knowledge, no published paper has reported concentrations of individual PAHs in both phases at the same sampling sites.

Of the 14 references that reported concentrations of PAHs in polyethylene or plastic pellets collected in seawater, or on beaches, five publications (Frias et al. 2010; Hirai et al. 2011; Karapanagioti et al. 2010, 2011; Mizukawa et al. 2013) indicated that PAH concentration was measured in polyethylene pellets or fragments. Because all data from Karapanagioti et al. (2010) are also included in their later publication (Karapanagioti et al. 2011), data from Karapanagioti et al. (2011) were used in the following analysis. Seven publications reported only the total concentration of PAHs in the plastic phase. Two other publications reported the concentration of individual PAHs chosen in isolated pellets, without the identification of plastic type (Fisner et al. 2013a, 2013b). However, the concentration of PAHs from those two studies was also included in the analysis because most of plastic pellets isolated were polyethylene or polypropylene (Rios et al. 2007, 2010; Hidalgo-Ruz et al. 2012).

Table 3 summarizes median, 25, and 75 percentile values of measured concentrations of eight selected PAHs in plastic pellets or fragments, information about the sample collection sites and the sample size. A blank field appears when the concentration was not measured. Sample collection sites include open oceans (Hirai et al. 2011) and beaches (Karapanagioti et al. 2010, 2011; Frias et al. 2011; Hirai et al. 2011; Fisner et al. 2013a, 2013b). Because there were many values of PAH concentration in isolated plastic particles below the detection limit, the calculated median and 25 percentile values were represented as n.d. for certain PAHs. For all studies, the reported concentration of PAH was obtained by pooling

isolated plastic particles to minimize piece-to-piece variation. Because the mass of pooled plastic particles for chemical analysis was different among those studies, the same weight was given to the median values from single articles for fugacity analysis.

It is thought that plastic fragments and pellets remain for a long time in open seawater due to regional/global circulation systems based on their abrasion and weathering status (Browne et al. 2007; Barnes et al. 2009). Thus, the fugacity of PAHs in plastic debris should be compared with that of PAHs in seawater samples that represent the global baseline level of PAHs. Keyword combinations of “seawater” and the name of individual PAHs or “polycyclic aromatic hydrocarbons” yielded more than 600 publications. Among them, nine references (Nizzetto et al. 2008; Fuoco et al. 2009; Lohmann et al. 2009, 2013; Berrojalbiz et al. 2011; Wu et al. 2011; Chizhova et al. 2013; Ma et al. 2013; Monteyne et al. 2013) were selected to give representative levels of PAH in open oceans after excluding monitoring values near oil spill sites or places where the levels were likely to be affected by point and nonpoint sources of PAHs including harbors, ports, coastal areas, and lagoons.

In Table 4, sample size, sampling location, and reported values of concentrations in seawaters are summarized. Median, 25 and 75 percentile values were calculated as mentioned above for PAH concentration in plastic particles. Chizhova et al. (2013) reported only maximum, minimum and mean concentrations for seven PAHs (FLU, ANT, PYR, CHR, BaP, DBahA, and BghiP) in the East Sea (Sea of Japan), without reporting raw data for each concentration. Thus, mean values were taken instead of median values for the following analysis. Monteyne et al. (2013) provided concentrations of eight selected PAHs from the North Sea. Values obtained from the sample collected 8 km away from

Table 3. Concentrations of individual PAHs in plastic debris reported in the literature and the sampling sites

Reference	Fisner et al. (2013a)	Fisner et al. (2013b)	Frias et al. (2010) ^a	Hirai et al. (2011)	Karapanagioti et al. (2011)	Mizukawa et al. (2013)
PHE	0.0057 (0.0038, 0.0088)	0.046 (0.017, 0.155)	0.0555 (0.0238, 0.0871)	0.018 (N.D., 0.063)	0.027 (0.010, 0.034)	0.043 (0.023, 0.089)
FLU	0.0052 (0.0031, 0.0088)	0.040 (0.009, 0.082)	0.0556 (0.0212, 0.0900)	0.009 (N.D., 0.050)	0.010 (0.008, 0.067)	0.008 (0.003, 0.016)
ANT	0.0116 (0.0045, 0.0191)	0.009 (0.005, 0.028)	0.0086 (0.0075, 0.0096)	0.002 (N.D., 0.011)	0.006 (0.002, 0.029)	0.003 (0.001, 0.019)
PYR	0.0057 (0.0029, 0.0086)	0.083 (0.009, 0.387)	0.1497 (0.0448, 0.2546)	0.008 (N.D., 0.052)	0.007 (0.006, 0.029)	0.005 (0.002, 0.011)
CHR	0.0159 (0.0063, 0.0220)	0.194 (0.063, 0.321)	0.0957 (0.0293, 0.1621)	N.D. (N.D., 0.021)	0.032 (0.012, 0.085)	0.009 (0.004, 0.020)
BaP	0.0069 (0.0041, 0.0132)	0.026 (0.003, 0.140)	N.D. (N.D., N.D.)	N.D. (N.D., 0.001)	0.004 (0.003, 0.014)	0.0008 (N.D., 0.0024)
DBahA	0.0068 (0.0039, 0.0160)	0.013 (N.D., 0.041)	-	-	-	-
BghiP	0.239 (0.155, 0.433)	-	0.0343 (N.D., 0.0686)	0.001 (N.D., 0.002)	0.008 (0.002, 0.012)	0.001 (0.001, 0.004)
Sample collection site(s)	Santos Bay (Brazil)	Santos Bay (Brazil)	Cresmina beach Fonte da Telha beach (Portugal)	Kugenuma beach, Japan Odaiba beach, Japan Seal beach, USA Tonkin Bay, Vietnam Marbella beach, Costa Rica Central Pacific Gyre, North Pacific SEA Pacific Cruise, North Pacific SEA Caribbean Cruise, Caribbean Sea	Kato Achaia beach, Vatera beach, Loutropygos beach, Aegina island (Greece)	Matosinhos beach Costa Nova beach Vieira de Leiria beach Alcobaça beach Gamboa beach Guincho beach Algés beach São Torpes beach Bordeira beach (Portugal)
# of samples	10	30	2	23	4	9

Median values of the concentration of the individual PAHs in plastic debris are listed with the 25 and 75 percentile values in parentheses except for ^aFrias et al. (2010) where only two samples were analyzed. All values are in the unit of mg/kg

Table 4 Concentration of selected PAHs in seawater from open oceans reported in the literature with sampling locations

Reference	Berrojabliz et al. (2011)	Chizhova et al. (2013)	Fuoco et al. (2009)	Lohmann et al. (2009)	Lohmann et al. (2013)
PHE	1.37×10^{-7} (6.93×10^{-8} , 1.98×10^{-7})	-	6.50×10^{-8} (3.60×10^{-8} , 9.10×10^{-8})	2.32×10^{-8} (1.60×10^{-8} , 3.63×10^{-8})	N.D. (N.D., 7.37×10^{-8})
FLU	6.29×10^{-8} (3.64×10^{-8} , 9.36×10^{-8})	6.30×10^{-7}	4.90×10^{-8} (2.40×10^{-8} , 6.75×10^{-8})	2.48×10^{-8} (1.77×10^{-8} , 3.81×10^{-8})	2.18×10^{-8} (1.58×10^{-8} , 2.63×10^{-8})
ANT	5.40×10^{-9} (3.40×10^{-9} , 1.31×10^{-8})	3.40×10^{-7}	7.00×10^{-9} (4.50×10^{-9} , 1.05×10^{-8})	2.75×10^{-10} (2.10×10^{-10} , 3.63×10^{-10})	N.D. (N.D., N.D.)
PYR	3.03×10^{-8} (1.57×10^{-8} , 7.08×10^{-8})	1.30×10^{-6}	2.30×10^{-8} (1.70×10^{-8} , 3.15×10^{-8})	9.50×10^{-10} (6.70×10^{-10} , 1.58×10^{-9})	6.59×10^{-8} (4.84×10^{-8} , 8.24×10^{-8})
CHR	1.41×10^{-8} (8.00×10^{-9} , 2.39×10^{-8})	3.60×10^{-8}	8.00×10^{-9} (6.00×10^{-9} , 1.15×10^{-8})	-	N.D. (N.D., N.D.)
BaP	1.00×10^{-9} (1.00×10^{-10} , 3.30×10^{-9})	1.60×10^{-8}	3.00×10^{-9} (2.00×10^{-9} , 4.00×10^{-9})	-	-
DBahA	1.50×10^{-9} (1.00×10^{-10} , 4.20×10^{-9})	3.90×10^{-8}	4.00×10^{-9} (3.00×10^{-9} , 5.00×10^{-9})	-	-
BghiP	1.70×10^{-9} (1.20×10^{-9} , 3.10×10^{-9})	4.20×10^{-8}	5.00×10^{-9} (3.50×10^{-9} , 6.00×10^{-9})	-	-
Sample collection site (s)	Catalan Sea, Mediterranean West Basin, Mediterranean Sicily Strait, Mediterranean Ionian Sea, Mediterranean Libyan Sea, Mediterranean Aegean Sea, Mediterranean Cretan Sea, Mediterranean Black Sea, Mediterranean	East Sea (Japan Sea), Pacific	Ross Sea, Antarctica	North Atlantic Arctic	Rhode Island Sound, Antarctica Gulf Stream, Antarctica Warm eddy in Sargasso Sea, Antarctica North Equatorial Current, Antarctica Amazon plume, Antarctica North Equatorial Counter Current, Antarctica South Equatorial Current, Antarctica Benguela Current, Antarctica
# of sample	43	13	13	22	56

Table 4. Continued

Reference	Ma et al. (2013)	Monteyne et al. (2013)	Nizzetto et al. (2008)	Wu et al. (2011)
PHE	7.40×10^{-9} (4.30×10^{-9} , 1.47×10^{-8})	1.60×10^{-6} (1.40×10^{-6} , 1.80×10^{-6})	4.10×10^{-7} (2.24×10^{-7} , 5.30×10^{-7})	6.07×10^{-6} (5.08×10^{-6} , 7.64×10^{-6})
FLU	3.80×10^{-9} (2.48×10^{-9} , 1.14×10^{-8})	7.40×10^{-7} (4.90×10^{-7} , 1.50×10^{-6})	5.44×10^{-8} (2.38×10^{-8} , 1.06×10^{-7})	8.15×10^{-7} (6.03×10^{-7} , 1.22×10^{-6})
ANT	1.00×10^{-9} (8.00×10^{-10} , 1.85×10^{-9})	1.60×10^{-7} (8.00×10^{-8} , 1.70×10^{-7})	1.88×10^{-8} (8.80×10^{-9} , 3.66×10^{-8})	6.00×10^{-7} (5.03×10^{-7} , 7.93×10^{-7})
PYR	5.85×10^{-9} (2.83×10^{-9} , 1.20×10^{-8})	5.00×10^{-7} (9.30×10^{-8} , 1.10×10^{-6})	8.42×10^{-8} (7.60×10^{-8} , 1.45×10^{-7})	6.70×10^{-7} (4.15×10^{-7} , 8.48×10^{-7})
CHR	1.95×10^{-9} (6.75×10^{-10} , 2.83×10^{-9})	6.40×10^{-8} (2.60×10^{-8} , 8.20×10^{-8})	-	3.00×10^{-8} (N.D., 1.38×10^{-7})
BaP	2.50×10^{-10} (1.00×10^{-10} , 5.50×10^{-10})	1.70×10^{-8} (N.D., 3.40×10^{-8})	N.D. (N.D., N.D.)	N.D. (N.D., N.D.)
DBahA	1.10×10^{-10} (N.D., 3.38×10^{-10})	1.30×10^{-8} (4.00×10^{-9} , 1.40×10^{-8})	-	N.D. (N.D., N.D.)
BghiP	1.65×10^{-10} (3.75×10^{-11} , 4.08×10^{-10})	1.10×10^{-8} (4.00×10^{-9} , 1.10×10^{-8})	6.00×10^{-10} (N.D., 8.00×10^{-10})	N.D. (N.D., N.D.)
Sample collection site(s)	from the East China Sea to the High Arctic (33.23N–84.5N), Pacific	5 miles from the Belgian coastal harbours, Mediterranean	from 49°20'N (Bremerhaven, Germany) to 24°50'S (Cape Town, South Africa), Atlantic	Western Taiwan Strait, Pacific
# of sample	18	3	15	24

Median values of the concentration of the individual PAHs in seawater are listed with the 25 and 75 percentile values in parentheses. N.D. = not determined. All values are in the unit of mg/L. PHE = phenanthrene, FLU = fluoranthene, ANT = anthracene, PYR = pyrene, CHR = chrysene, BaP = benzo[a]pyrene, DBahA = dibenz[a,h]anthracene, BghiP = benzo[ghi]perylene

the coastline of Belgium were taken. All other values along the coastline were excluded in the analysis. In Nizzetto et al. (2008) a few values that were reported as “not quantifiable” were excluded in the calculation of median values. As was the case with the PAH concentration in plastic particles, median values from single references had the same weight in the following fugacity analysis.

Calculation of fugacity from reported concentrations

The fugacity of PAHs in seawater (f_{sw} , atm) was calculated by multiplying the seawater concentration (C_{sw} , mol/L) with the Henry’s law constant (H , L atm/mol):

$$f_{sw} = C_{sw} H \quad (1)$$

Fugacity of PAHs in polyethylene (f_{PE}) was calculated by equation (2).

$$f_{PE} = C_{PE} H / K_{PE/sw} \quad (2)$$

where C_{PE} represents PAH concentration in polyethylene or plastic debris (mol/kg) and $K_{PE/sw}$ represents the partition coefficient between polyethylene and seawater (L/kg). The salting-out effect on the Henry’s law constant was neglected because salt concentration in seawater was shown not to have a very significant effect (Endo et al. 2012; Lee et al. 2014). In addition, the effects of the Henry’s law constant were cancelled because fugacity ratio (f_{PE}/f_{sw}) was used in the following analysis.

In the case where the plastic phase was not identified (Fisner et al. 2013a, 2013b), fugacity of PAH in plastic debris was calculated by partition coefficients between polyethylene and seawater ($K_{PE/sw}$) because PE has higher production volume than PP.

3. Results and Discussion

PAHs in plastic debris

In general, higher concentrations of PAH were monitored near Santos Bay (Fisner et al. 2013a, 2013b) (Table 3). This would be likely due to potential sources of PAHs in Santos Bay located near Santos harbor and Cubatão industrial complex which is a center for the petrochemical and metal industry of Brazil. Hirai et al. (2011) used PE pellets collected from many places across the world, including open ocean and beaches. For other studies, PE pellets were mostly isolated on beaches and their median values reported were mostly within one order of magnitude (Frias et al. 2010;

Hirai et al. 2011; Karapanagioti et al. 2011; Mizukawa et al. 2013).

PAHs in open oceans

As shown in Table 4, it is not surprising that the reported concentration of PAHs in seawaters has a much larger variation than that in plastic debris, because seawater samples are likely to be more affected by local sources of PAHs. Median values of the selected PAHs in open oceans have varied within approximately three orders of magnitude. It is difficult to choose one representative baseline value in open oceans for individual PAHs, because reported values from selected publications represent concentrations in diverse sites and sampling dates. For example, the median values for PYR were reported in all the selected references and ranged from 9.5×10^{-10} to 1.3×10^{-6} mg/L. Concentrations of PAHs tend to be higher in seawater samples collected closer to major industrialized areas (Wu et al. 2011; Chizhova et al. 2013; Monteyne et al. 2013) than in remote oceans (Lohmann et al. 2009; Ma et al. 2013; Nizzetto et al. 2013), implying the potential influences of industrial activities. The PHE/ANT ratio in seawater samples of the selected studies ranged from 7.4 to 84. Because crude oils are characterized by a high PHE/ANT ratio (Neff et al. 2000, 2005), the seawater samples were not likely to have been affected by the direct influence of crude oil spill events.

Thus, median values of the concentration of PAHs in seawater from each reference were used for the calculation of the fugacity ratio, whereas the median of the median values of the concentration in plastic debris from each reference were used.

Fugacity analysis

Figure 1 compares calculated fugacities of PAHs in polyethylene (f_{PE}) and those in seawater (f_{sw}) from each literature. Values of fugacities are summarized in Table A1, Appendix. The fugacity calculated by Lohmann et al. (2009) using seawater concentrations (Fig. 1d) for PHE, ANT, FLU, and PYR and by Ma et al. (2013) (Fig. 1f) for all selected PAHs, were consistently higher than values obtained using seawater concentrations in other publications. As mentioned above, the seawater samples studied by Lohmann et al. (2009) and Ma et al. (2013) included Arctic waters that might be less affected by any anthropogenic sources of PAHs, such as river outflow, ship ballast water, and other potential point sources. Because values of individual PAH concentration

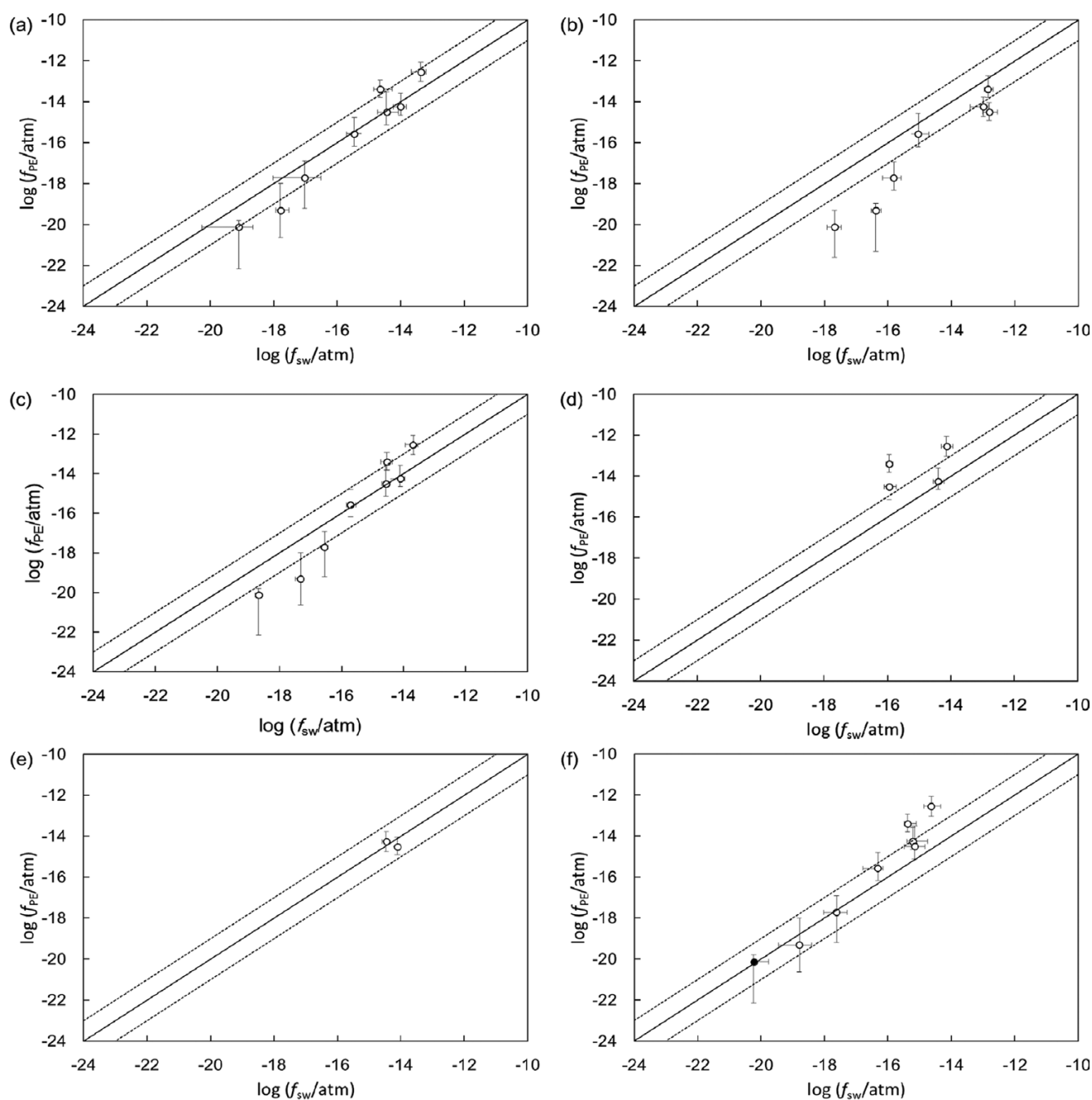


Fig. 1. Comparison between the logarithm fugacity of PAHs in polyethylene debris ($\log f_{PE}$) and that in seawater ($\log f_{SW}$). Median fugacity of each PAH in PE was used, whereas median fugacity values of PAHs in seawater were taken from (a) Berrojakbiz et al. (2011), (b) Chizhova et al. (2013), (c) Fuoco et al. (2009), (d) Lohmann et al. (2009), (e) Lohmann et al. (2013), (f) Ma et al. (2013), (g) Monteyne et al. (2013), (h) Nizzetto et al. (2008), and (i) Wu et al. (2011). Solid lines represent 1:1 relationship (i.e., phase equilibrium) and dashed lines represent 10:1 and 1:10 relationship. Horizontal and vertical error bars denote the 25th and 75th percentiles of calculated fugacities of PAHs in PE and seawater. Filled circles indicate that 25th percentile values were not detected

were not collected at the same sites, it is not desirable to compare calculated fugacities directly. However, a clear tendency revealing that fugacity ratio decreases with increasing

$\log K_{PE/SW}$ in most studies evaluated provides a meaningful insight (Fig. 2). Diffusion coefficients of PAHs decrease with increasing molecular weight and partition coefficient

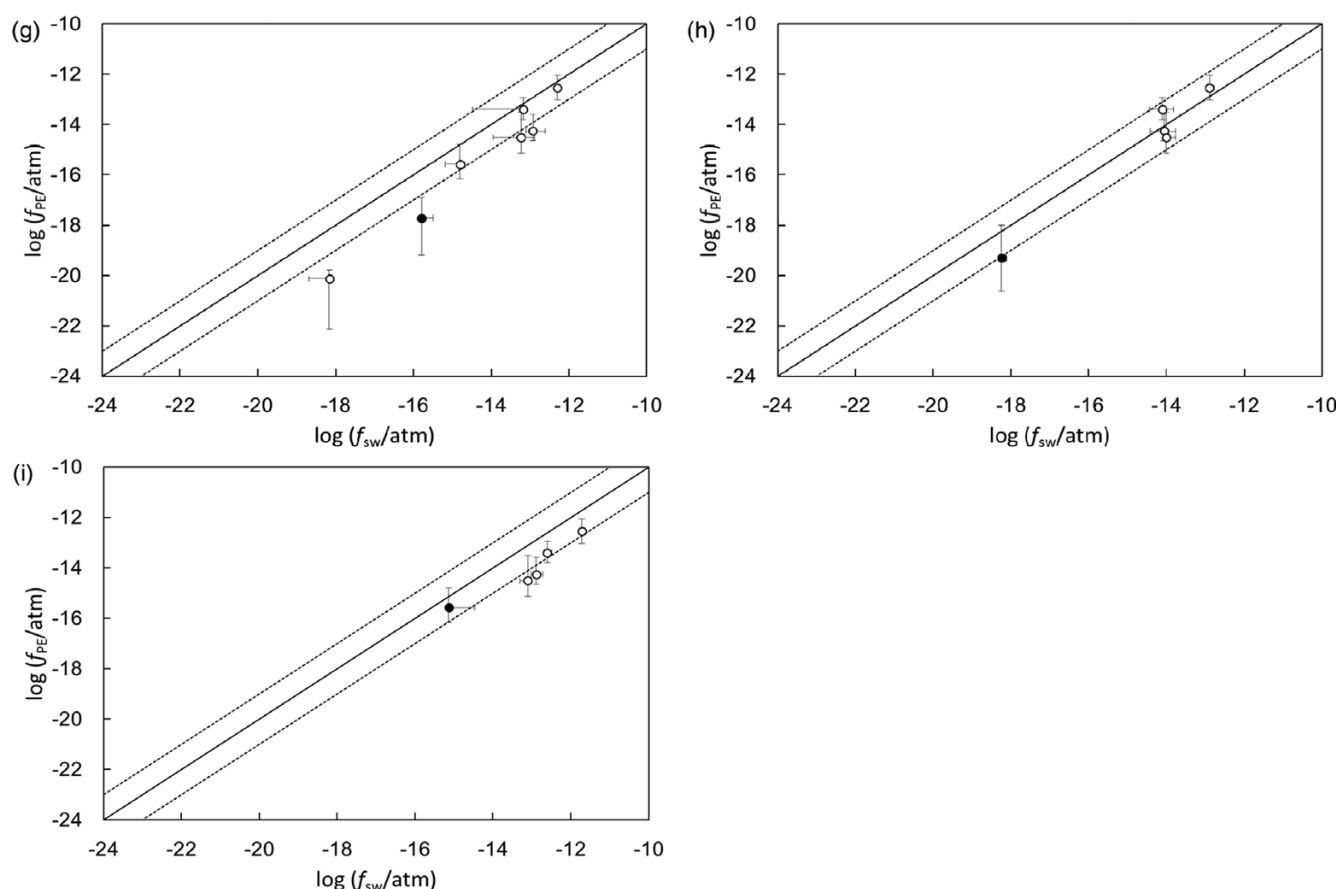


Fig. 1. Continued

(Rusina et al. 2007, 2010; Lohmann 2012). Because the time required to attain thermodynamic phase equilibrium increases with increasing $K_{PE/SW}$, as well as decreasing the diffusion coefficient in PE, more hydrophobic and larger PAHs such as BaP and DBaH are not likely in phase equilibrium between PE debris and seawater. Because PAHs are not intentionally included in PE, the longer time required for phase equilibrium makes them slowly flow to PE debris from seawater.

Implications for plastic debris on the transport of organic contaminants

Although the fugacity analysis in this study was limited to eight selected PAHs and one plastic material, a clear tendency in the changes in the fugacity ratio was observed with increasing $\log K_{PE/SW}$. Because PAHs are ubiquitous and in general not directly added to plastic materials during manufacture, relatively lower fugacity for more hydrophobic PAHs in plastic particles indicate net absorption of those PAHs from water to plastic

debris. This could be explained by a high partition coefficient and slow internal diffusion of more hydrophobic organic chemicals. This might be similar for other anthropogenic chemicals not intentionally added to the plastic matrix although further validation is required.

The roles of plastic particles as “vectors” for anthropogenic chemicals would be also limited because the net direction of chemical flow is likely from seawater to plastic debris especially for more hydrophobic and thus more bioaccumulative organic chemicals. Fugacity is also the driving force for bioaccumulation processes (Gobas et al. 1999). Although the increased rate of chemical transfer from plastic particles to water was observed in a few laboratory studies (Bakir et al. 2014), it should be noted that the fugacity of test chemical species in plastic phase was much higher than in water because test chemicals were initially spiked in plastic particles. It is unlikely that hydrophobic chemicals flow against the fugacity gradient if the fugacity of a chemical in plastic phase is lower than that in water. However, chemical additives in plastic material

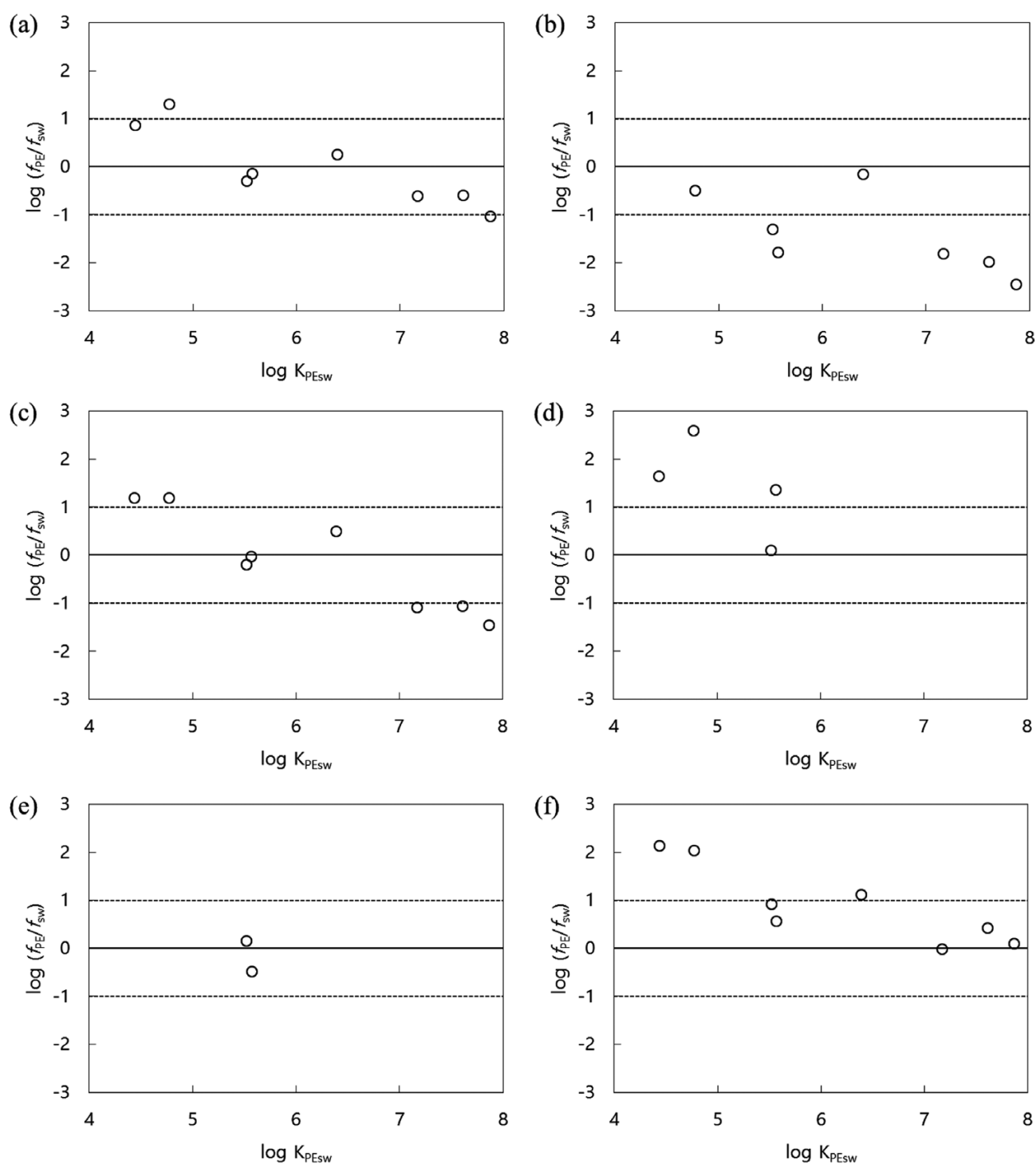


Fig. 2. Relationships between the logarithm of the fugacity ratio ($\log(f_{PE}/f_{SW})$) and $\log K_{PEsw}$. Median fugacity of each PAH in PE was used, whereas median fugacity values of PAH in seawater were taken from (a) Berrojbiz et al. (2011), (b) Chizhova et al. (2013), (c) Fuoco et al. (2009), (d) Lohmann et al. (2009), (e) Lohmann et al. (2013), (f) Ma et al. (2013), (g) Monteyne et al. (2013), (h) Nizzetto et al. (2008), and (i) Wu et al. (2011). Solid lines represent $f_{PE}/f_{SW}=1$ (i.e., phase equilibrium) and dashed lines represent 0.1 and 10

should have a much higher fugacity in the plastic phase than fugacity in seawater for long time and plastic debris may be

important sources of those chemicals in bioaccumulation processes in the marine environment.

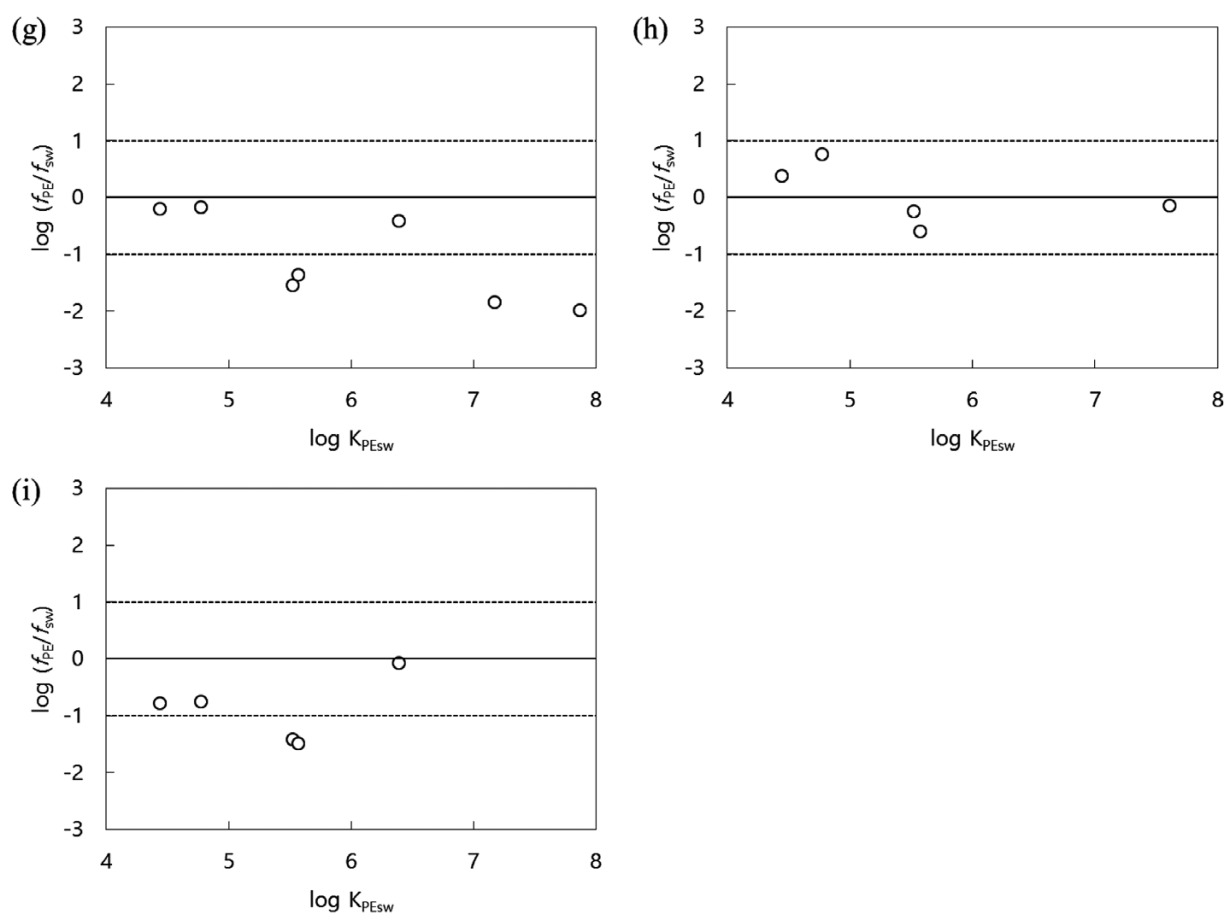


Fig. 2. Continued

4. Conclusion

Fugacity analysis on 8 selected PAHs showed a clear tendency that the ratio of fugacity in polyethylene to that in seawater decreased with increasing partition coefficient between polyethylene and seawater ($K_{PE/SW}$). This suggests that time for phase equilibrium between polyethylene debris and seawater would be longer for more hydrophobic and higher molecular weight PAHs. The results imply that the net direction of intermedia transport of hydrophobic anthropogenic pollutants other than plastic additives would be from seawater to marine plastic debris, although the analysis was limited to 8 PAHs and further confirmation is required.

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