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TESTING PHENANTHRENE DISTRIBUTION PROPERTIES OF VIRGIN
PLASTIC PELLETS AND PLASTIC ERODED PELLETS FOUND ON LESVOS
ISLAND BEACHES (GREECE)

by

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ABSTRACT

Plastic pellets have been characterized as toxic pollutant carriers throughout the world oceans and coastal zones. However, their sorptive properties are not yet well understood. In the present study, virgin pellets and plastic eroded pellets (PEP) are used to elucidate their distribution characteristics through distribution kinetic studies. Distribution occurs through diffusion into the pellet for all materials (polyethylene, polyoxymethylene, and PEP) except polypropylene (PP). Although diffusion into the polymer happens with similar rates for both freshwater and saltwater external solutions, apparent diffusion is dependent on the solution salinity because it results in higher equilibrium distribution coefficients. Distribution coefficient into the PEP is higher and diffusion is slower than into the virgin materials. This is attributed to increased crystallinity of the PEP due to weathering. PP demonstrates diffusion rates that are increased by salinity and is apparently faster than into the other polymers suggesting a surface diffusion process.

KEYWORDS: plastic pellets, polyethylene, phenanthrene, distribution kinetics, diffusion, polypropylene

INTRODUCTION

Plastic pellets are a known solid waste widely found throughout the coastal zones all over the world (Gregory, 1977; Shiber, 1979; 1987; Galgani et al., 1995; Galil et al., 1995; Minchin, 1996; Debrot et al., 1999; Andradi, 2000; Galgani, 2000; Mc Dermid and McMullen, 2004). They are the raw materials for plastic products and are accidentally or intentionally released in the marine environment during transportation or plastic production (Ryan, 1988; ITF, 1988). Those that have lower density than water float on the ocean surface and easily end up on beaches (Gregory, 1977). During their journey on the ocean surface, they are in contact with the ocean enriched surface layer or are found coated with tar (Shiber, 1987; Karapanagioti and Klontza, 2006). Being an organic medium they should attract hydrophobic contaminants when present in the surrounding solution. Hydrophobic distribution of organic micropollutants has been observed onto polypropylene pellets when tested as potential adsorbents (Rice and Gold, 1984), onto polyethylene strips when tested as potential passive sampling devices (Müller et al., 2001; Lohmann et al., 2005; Pascall et al., 2005; Komarova et al., 2006) and onto polyoxymethylene strips used as a solid phase extraction medium (Jonker and Koelmans, 2001). Plastic pellets are carriers of toxic pollutants found on their journey from the release point to the sampling point (either on the sea or the beach surface) (Mato et al., 2001).

Previous studies have shown that several marine organisms such as seabirds, turtles, etc. ingest the plastic pellets found on the water or sand surface (Bourne and Imber, 1982; Sileo et al., 1990; Blight and Burger, 1997; Mc Cauley and Bjorndal, 1999). Once the polluted plastic pellets are ingested, the contaminants might be transferred to the body of the organism (Ryan et al., 1988). A positive correlation

between the mass of plastic pellet ingested and contaminants found in the organism fat tissue has been reported (Ryan et al., 1988; Bjorndal et al., 1994).

Mato et al. (2001) observed high distribution coefficients for polychlorinated biphenyls (PCBs) onto polypropylene pellets collected from the sea surface. Additionally, they performed distribution experiments with virgin materials in baskets drifting on the sea surface. After a six-day exposure period, they observed that: (a) distribution coefficients increased over time and (b) the final experimental distribution coefficients were two orders of magnitude lower than those measured for the pellets collected from the sea surface suggesting that equilibrium was not reached in this time period.

Mato et al. (2001) proposed three potential reasons for eroded pellets to demonstrate different distribution behavior than the virgin pellets. The first reason is the increase in surface area due to polymer weathering that would increase the effective diffusivity. The other reasons are the increase in polarity and crystallinity for the weathered pellets that would decrease distribution coefficient and rate according to Mato et al. (2001). Endo et al. (2005) also conducted an extensive field work including PCB analysis of pellet samples from 47 beaches in Japan. Concentrations were highly variable among particles but no clear relationships between crystallinity, weathering and PCB concentrations were found. The observations in these two last studies suggest that the distribution mechanisms of organic contaminants onto weathered plastic pellets are not yet well understood.

The hypothesis of the present study is that a detailed kinetic distribution experiment would elucidate the sorptive behavior of different plastic pellets. The objectives of the present work are as follows: a) study the phenanthrene distribution long-term equilibrium and kinetics of i) the virgin plastic pellets obtained from local

plastic producers and ii) the plastic eroded pellets found in Lesvos island beaches in order to determine differences in the sorptive behavior of the various material; and b) determine the effect of salinity on these sorptive behaviors. Such information can be used in toxicological studies to determine the contaminant mass transfer from the pellet to the organism or in monitoring studies that pellets can be used as organic micropollutant tracers. Phenanthrene that is used in the present study as a model compound, is a polycyclic aromatic hydrocarbon (PAH) commonly found as an aquatic contaminant (Law et al., 1997; Kalf et al., 1997) and widely used in distribution studies (Young and Weber, 1995; Kleineidam et al., 1999; Karapanagioti et al., 2000).

MATERIALS AND METHODS

Materials

Plastic eroded pellets (PEP) were collected from different sandy beaches around Lesvos island. Samples were found on the sand surface and were taken from the high tide line as well as from the berm of the beach. All samples were cleaned with a paper tissue to remove sand and were visually separated by morphology. PEPs were dry and no biofilm was observed visually. Virgin polyethylene (PE) and polypropylene (PP) pellets were obtained from local industrial plastic producers. Virgin polyoxymethylene (POM) pellets were obtained from Aldrich. All pellets were 2-3 mm in diameter except PP which were smaller (2 mm).

Phenanthrene (> 99.0%) was used as the model sorbate. Phenanthrene was from FLUKA. It was dissolved in methanol (> 99.8% from Merck) to a 1 g/L stock solution that was kept in the refrigerator and in the dark.

Distribution Experiments

Solutions used in batch studies were prepared in synthetic freshwater (FW) with 44 mg/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 14 mg/L CaSO_4 , and 17 mg/L NaHCO_3 and in synthetic saltwater (SW) with 31 g/L NaCl , 10 g/L $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.04 g/L NaHCO_3 . The synthetic water solutions were spiked with the methanol stock solution in order to add phenanthrene in specific concentrations. Methanol in the test solution was always less than 1%; below this percentage cosolvent effects can be neglected (Schwarzenbach et al., 2003). Sodium azide (NaN_3) was added at a concentration of 200 mg/L to minimize bacterial growth and thus biodegradation during batch studies. All distribution kinetic experiments were conducted in triplicate in 120 mL amber glass vials with Teflon-coated septa. The mass-of-sorbent-to-solution ratios for each sample are presented in Table 1. For each triplicate sample, a corresponding triplicate blank sample was also prepared with the same phenanthrene solution as the sample but without the polymer pellet. The concentration measurements of the triplicate blank samples were monitored along with the corresponding triplicate samples and were used as the initial concentration of the corresponding triplicate samples in order to account for any losses to the bottle or due to the measurement procedure. The initial phenanthrene concentration was 100 $\mu\text{g/L}$ (11% of the FW phenanthrene solubility and 8% of the SW phenanthrene solubility in order to prevent any phase distribution phenomena due to salinity). The bottles were stored at room temperature (around 23 ± 2 °C) in the dark and shaken periodically (once a day in the first week and weekly thereafter). Measurements were taken at various time intervals (e.g., 1, 5, 8, 15, 35, 56, 73, 102, 144, 202 days). A triplicate sample is considered to reach

equilibrium when the last two measurements (at least 15 days apart) are statistically the same.

Aqueous phenanthrene concentrations were measured by a Perkin-Elmer LS-50B Luminescence Spectrometer using a quartz cuvette and excitation/emission wavelengths of 252/347 nm, respectively. Three to four mL of each sample were entered in the cuvette and the phenanthrene solution concentration was measured in the spectrometer. After the measurement was recorded the sample from the cuvette was returned to the original sample. Fresh calibration standards were used each time measurements were taken. Losses in phenanthrene mass due to sample handling during measurements ranged between 0.9-7% for experimental periods of 100-200 days, respectively. These losses were taken into account in the mass balance equation since phenanthrene 'initial' concentrations (blank sample solution concentrations or in other words nominal initial concentrations) were measured on every sampling occasion. Triplicate blank samples with sorbent and synthetic water only were monitored for desorption of natively bound solutes. However, no measurable concentration of phenanthrene was detected in the solution.

DATA ANALYSIS

Experimental Data Transformation

The linear isotherm model was employed in the present study to evaluate distribution isotherms. It relates the mass of chemical sorbed per unit mass of solid (q_e) [$\mu\text{g}/\text{Kg}$] to the equilibrium solute concentration (C_e) ($\mu\text{g}/\text{L}$) by the following equation:

$$q_e = K_d C_e \quad (1)$$

where K_d (L/Kg) is the distribution coefficient. K_{da} is defined as the apparent distribution coefficient measured at a given time and not necessarily at equilibrium. The equilibrium solute concentration (C_e) was directly measured on every sampling occasion. The mass of chemical sorbed per unit mass of solid (q_e) was determined for each sampling occasion through the following mass balance equation:

$$q_e = (C_o - C_e) V / m \quad (2)$$

where C_o is the initial concentration or the average phenanthrene solution concentration of the triplicate blank samples that correspond to the triplicate samples (in other words nominal initial concentration), V is the sample solution volume and m is the mass of the polymer pellet. Both V and m were recorded during sample preparation.

Some of the saltwater kinetic batches did not reach equilibrium during the time course of the experiment. In order to calculate the equilibrium K_d in saltwater, a modification of the Setschenow equation proposed in Schwarzenbach et al. (2003) was used:

$$K_{d\text{ SW}} = K_{d\text{ FW}} 10^{K_s [\text{salt}]} \quad (3)$$

where $K_{d\text{ SW}}$ and $K_{d\text{ FW}}$ are the distribution coefficients in saltwater (SW) and freshwater (FW), respectively, K_s is the Setschenow constant (0.272 for phenanthrene) and $[\text{salt}]$ is the total salt molar concentration in the solution equal to 0.5 M for seawater (Schwarzenbach et al., 2003).

Model Methods

The distribution kinetic results are explained using Fick's 2nd law in spherical coordinates:

$$\frac{\partial C}{\partial t} = \frac{D_a}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C}{\partial r} \right) \quad (4)$$

where C is the solute concentration, t is the time, r is the distance from the center of the sphere and D_a is the apparent diffusion coefficient.

If the distribution isotherm is linear and the initial and boundary conditions known, analytical solutions to the Fick's 2nd law exist. Distribution experiments in batch reactors (bath of limited volume; Grathwohl, 1998) can be described with the following conditions:

$C = 0$ at the beginning of the experiment ($t=0$) inside the pellet ($0 < r < \alpha$)

$C = C_{eq}$ at the end of the experiment ($t=\infty$) at the surface of the pellet

$\partial C / \partial r = 0$ after the beginning of the experiment and in the pellet center ($r=0$)

where C_{eq} is the phenanthrene aqueous concentration at equilibrium and α is the pellet radius.

The analytical solution given by Crank (Grathwohl, 1998), describes the mass of phenanthrene in the pellet (M) after time t over the same mass at equilibrium (M_{eq}) as follows:

$$\frac{M}{M_{eq}} = 1 - \sum \frac{6\beta(\beta+1)}{9+9\beta+q_n^2\beta^2} \exp\left[-q_n^2 \frac{D_a t}{\alpha^2}\right] \quad (5)$$

where β is the ratio of the phenanthrene mass in solution to the phenanthrene mass in the pellet at equilibrium (calculated from the experimental results at equilibrium e.g. mass of phenanthrene in solution is calculated through the phenanthrene aqueous concentration at equilibrium and the volume of the solution), q_n is an analytical coefficient calculated, $D_a t / \alpha^2$ is a dimensionless number also known as Fourier number.

In the present study, values of β in Equation 5 were relatively small ($\beta = 0.14-11$) resulting in $(D_a t / \alpha^2)$ values lower than 0.1 for the time needed to reach equilibrium. These low Fourier numbers allow the use of a short-term approximation (Equation 6) (Grathwohl, 1998):

$$\frac{M}{M_{eq}} = 6 \left(\frac{1}{\beta} + 1 \right) \sqrt{\frac{D_a t}{\pi \alpha^2}} \quad (6)$$

At non-equilibrium conditions phenanthrene sorptive uptake can be described by the ratio of the apparent distribution coefficient (K_{da}) to the distribution coefficient at equilibrium (K_d) as follows (Grathwohl, 1998):

$$\frac{K_{da}}{K_d} = \frac{\beta}{\frac{1+\beta}{M/M_{eq}} - 1} \quad (7)$$

The advantage of Equation 7 compared to the previous Equation 6 describing the short term approximation is that the solution is independent of the different values of β and allows comparison of the sorptive uptake at different solid-to-solution ratios in batch experiments (Grathwohl, 1998).

The fitting parameter in the analytical solution employed in the present study is D_a . In an Excel spreadsheet, K_{da}/K_d ratios were calculated through Equations 6 and 7 and were compared to experimental K_{da}/K_d ratios for the experimental measurement times. The D_a value chosen is the one that minimizes the error given in Equation 8:

$$error = \sum \frac{\left(average_measured \frac{K_{da}}{K_d} - model \frac{K_{da}}{K_d} \right)}{\left(model \frac{K_{da}}{K_d} \right)^2} \quad (8)$$

that is the sum, of the mean of (K_{da}/K_d ratios measured) minus (K_{da}/K_d ratios predicted by the model) over the (K_{da}/K_d ratios predicted by the model) squared, for all measurement occasions.

For model result interpretation, D_e is defined as the effective diffusion coefficient independent of the distribution coefficient of each material that equals $D_e = D_a / K_d \rho$ (where ρ is the particle density) and the effective diffusion rate independent of the particle radius is defined as D_e / α^2 .

RESULTS AND DISCUSSION

Material Characterization

Material characterization of PEPs found on the Lesvos island beaches is presented elsewhere (Karapanagioti and Klontza, 2007). The most important aspects of material characterization in relation to the present study include the following observations: a) 61% and 21% of PEPs had similar appearance to virgin PE and PP pellets respectively; and b) PEPs color was not indicative of the degree of weathering of each pellet. Both white (or similar to the virgin material color) and yellow PEPs demonstrate similar distribution kinetics. Thus, yellow color of PEPs does not indicate a higher degree of weathering that would lead to a different kinetic behavior compared to the white PEPs (similar D_e/α^2 values). 9% of the PEPs would float in an isopropyl alcohol solution of 0.95 g/mL whereas virgin PE and PP as well as PEPs that had similar appearance to virgin PE and PP would sink (Karapanagioti and Klontza, 2007). In the present study, PEPs used in the kinetic experiments were chosen from the bulk solution that resulted from PEPs that appeared like PE and PP. PEPs with lighter density, PEPs that had an orange color, or PEPs with tar stuck on them were not used in the experiments (Karapanagioti and Klontza, 2007). In the present work, it was intended to use PEPs of average appearance (that is 66% of total PEPs collected).

Equilibrium distribution results

Table 1 presents the K_d values obtained at the end of the kinetic experiments. The value for each material represents the average of the triplicate measurements during the last two sampling occasions when values were not statistically different for each material. Among the virgin polymers, PP had the lower K_d value (270 L/Kg), one order of magnitude lower compared to K_d values for PE and POM. PE demonstrated a K_d value 1.7 times higher than that of POM. This was probably due to the oxygen present in the polymer chain of POM. PE K_d value in the present study was lower by a factor of 3 compared to the value reported for PE (27000 L/Kg) in Lohmann et al. (2005). This difference could be attributed to the cleaning method using solvents employed in Lohmann et al. (2005). One of the PEP samples had a low K_d value (1400 L/Kg) and the other one a higher value (11000 L/Kg) than PE. Obviously the two PEPs chosen for the distribution experiment were not of the same material, although the 2 pellets that were used demonstrated similar density and morphological characteristics.

Table 1 also presents the K_d values calculated for the virgin pellets and the values experimentally obtained for the PEPs in SW. Based on the Setschenow equation (see Equation 3), phenanthrene K_d was expected to increase by a factor of 1.4 in a solution with seawater salinity (Schwarzenbach et al., 2003). In the present study, salinity was expected to increase partitioning into the polymer. PP reached equilibrium in the SW experiment and the K_d value obtained from the experiment (410 ± 140) was not statistically different from the value calculated based on the K_d value in the FW experiment and the Setschenow equation (380; see Table 1). One of the 3 PEPs used in the SW experiment demonstrated a slightly lower K_d value than PE

and the other 2 both demonstrated a K_d value (statistically the same) higher than PE by a factor of almost 2. In this case, 2 out of 3 PEPs used in the SW experiment were made of the same material although all 3 pellets that were used demonstrated similar density and morphological characteristics.

Mato et al. (2001) observed K_d values for PCBs in SW and for marine eroded PP 0.1-1 log units lower than each tested compound (PCB) K_{ow} value and for virgin PP 2 log units lower than the K_d values for marine eroded PP. In the present study for phenanthrene, log K_d in SW for virgin PP was 2.7 and log K_{ow} was 4.6 (Montgomery and Welkom, 1990); a difference of 1.9 log units. Thus, the observed K_d in the present study was similar to K_d pattern reported by Mato et al. (2001) for virgin pellets but lower than the reported results for marine eroded PP. The PEPs in the present work demonstrated a range of equilibrium log K_d values in SW of 4.1-4.4; K_d values close to the phenanthrene K_{ow} value.

Distribution kinetics

Figures 1a and 1b present distribution kinetic data for all sorbents in FW and SW solutions, respectively. PP appeared to reach equilibrium after 20-40 days whereas the rest of the sorbents required more than 80 days for reaching equilibrium. On the first day in SW, all sorbents demonstrated similar sorptive capacities. In FW, 1 out of 2 and in SW, 2 out of 3 PEPs (or 3 out of 5 (60%) altogether) demonstrated similar distribution kinetic behavior as PE. This is consistent with conclusions based on morphological observations that 61% of PEPs look like PE (Karapanagioti and Klontza, 2007). The PEPs demonstrating a different behavior was probably different polymer materials with lower distribution coefficients.

Figures 2a and 2b present the distribution kinetic data for PE in both FW and SW solutions and the same data normalized with the K_d equilibrium along with the analytical model fitted lines, respectively. In Figure 2a, on the first day, salinity increased the distribution coefficient for PE. Then, the kinetics in both solutions appeared to follow a similar pattern until the last measurement where the distribution in SW continued to increase (from $11,000 \pm 500$ to $14,000 \pm 1,000$) compared to distribution in FW (from 8700 ± 900 to 9600 ± 1100), which remains the same as in the previous measurement. It seems that salinity drives phenanthrene out of the solution but it does not affect intrapolymer diffusion rate. In Figure 2b, distribution in FW reached equilibrium faster and attained the value of 1 earlier than in SW. This happened because salinity increased the distribution coefficient (K_d equilibrium), although it did not affect intrapolymer diffusion.

Experimental results were simulated well by the analytical model short-term approximation (Equation 6; see Figure 2b). In the present study, the early data were not used in the model fitting process since they followed a different behavior than the rest of the data. Evidence of phenanthrene diffusion within the POM pellet interior was presented in a previous study using microprobe laser desorption laser ionization mass spectrometry ($\mu\text{L}^2\text{MS}$) to measure phenanthrene at different depths in the POM pellets (Ahn et al., 2005).

In Table 2, D_a values obtained from the analytical model simulations and calculated D_e/α^2 based on the distribution coefficient and polymer density are presented. D_a is the apparent diffusion coefficient that is a measure of overall concentration change in the solution. D_e/α^2 is the effective diffusion rate that is independent of distribution coefficient and polymer radius and is a means of comparing materials of various radii and distribution coefficients. D_e/α^2 is the rate

with which the solute diffuses into each material regardless of its properties. For example, a large radius or a higher distribution coefficient would result in a slower D_a regardless of the actual rate within the sorbent material. In environmental studies, D_a is a relevant property of the pellets since it measures the disappearance of the phenanthrene from the solution whereas in polymer science, D_e/α^2 is more relevant.

D_a value for PE was similar with that for POM but was higher by a factor of 3 than the value for PP. D_e/α^2 values showed that actual diffusion into PE is faster than in the other polymers and was not affected by salinity. Based on these observations, phenanthrene diffused into the polymer with similar rates in both solutions but D_a demonstrated different values due to different distribution coefficients among materials and in SW. In other words, phenanthrene diffused into the polymers at the same rate but in SW its diffusion appeared slightly slower because it had to reach a higher K_d value at equilibrium.

POM D_e/α^2 value was slightly affected by salinity whereas PP D_e/α^2 value was highly affected by salinity (increased by almost one order of magnitude). POM demonstrated a lower effective diffusion rate than PE probably due to its higher crystallinity (see discussion in the next subsection).

For PEPs, apparent diffusion was slower – except for the pellet with the lower distribution coefficient (PEP2 in FW). Actually in SW, PEP diffusion rate was slower. This could be due to changes in morphology caused by weathering. Weathering increases polyethylene crystallinity (Satoto et al., 1997; Guadagno et al., 2001) and density (Gulmine et al., 2003). D’Aniello et al. (2000) observed slower diffusion for PP with increased crystallinity. As described in the polymer science literature review in Young and Weber (1995), polymers with increased crystallinity are expected to have slower diffusion kinetics and increased distribution coefficient

for organic sorbates. These two sorptive behavior characteristics were observed for the weathered pellets when compared to virgin PE tested in the present study. This comparison is possible only in kinetic experiments or when distribution equilibrium is reached. For measurements of contaminant concentrations in field pellets there is no indication where each pellet may be on the kinetic curve at the time of sampling. This explains why a clear relationship between weathering and crystallinity and PCB concentration was not found in Endo et al. (2005).

Polypropylene (PP) Sorptive Behavior

Polypropylene K_d values were lower than PE by at least one order of magnitude. This is consistent with observations reported by Endo et al. (2005) and by Mato cited in Endo et al. (2005). The present study attempts to explain these observations using the kinetic experiment results.

Figure 3 presents the distribution kinetic data for PP in both FW and SW solutions. The presence of salinity resulted in higher K_{da} values in SW for the same sampling time suggesting that distribution on PP is directly dependent on the solution chemistry. For the other polymers diffusion into the interior was the limiting kinetic factor and thus, diffusion into the polymer was not dependent on the presence of salinity (see K_{da} values after Day 1 in SW and FW for PE in Figure 2a and D_e/α^2 values in Table 2).

The fast diffusion coefficient for PP compared to the other polymers suggested that phenanthrene diffused onto the PP surface through a partitioning mechanism and not in the PP interior. If this is true then the diffusion depth was less than the pellet radius. For this reason, D_e/α^2 values are also presented in Table 2. When comparing

the effective diffusion rates in FW, distribution into PP was a slower process than in the other polymer materials tested. Also PP was the only polymer where the D_e/α^2 value increased due to salinity. Thus, distribution into PP was affected by the solution chemistry (salinity in the present study). Similar results were observed in a study using PP pellets as sorbents to remove organics from water solution; pyrene appeared to be able to diffuse only to some extent into the PP particle (Rice and Gold, 1984b).

Similar differences between PE and PP have been observed in photo-degradation studies (Shyichuk et al., 2005). Degradation of PE reached all depths proportionally to the exposure time. PP showed higher degradation at the upper subsurface layers and much lower degradation than PE in the rest of the particle. PE and PP can be found in different types and structures (e.g. isotactic and atactic PP) that demonstrate varying surface properties based on the production method (Zhang et al., 1997). In the present study, the types of structures for each pellet is not known and thus, it is not prudent to make specific hypotheses on why the different distribution behaviors were observed. Some general conclusions can be drawn based only on the general formulas of PE, POM, and PP, and general observations such as: PE and POM show chain folding domains (Vancso et al., 1994), PE shows random surface structure (Zhang et al., 1997), POM includes hexagonal crystals (Vancso et al., 1994) and PP demonstrates small groups on the surface whereas the main molecule lies flat to optimize interactions with the underlying chains (Zhang et al., 1997). It can be assumed that PE and POM allow solute diffusion through their loose packing whereas PP allows interaction of solutes only with the exposed surface groups and not inside the stable bulk material. Pascall et al. (2005) suggested that the greater the distance between the polymeric chains the easier it is for the chemicals to diffuse into the matrix of the polymer.

CONCLUSIONS

The most important conclusions of the present study are the following:

- PP had a lower distribution coefficient than PE and POM.
- PE and POM demonstrated intrapolymer diffusion limited distribution. Distribution kinetics depended on the diffusion into the polymer and the final distribution coefficient in both water solutions.
- Diffusion into the polymer was not affected by salinity but seemed slower because the system had to reach a higher distribution equilibrium coefficient in SW than in FW.
- Distribution onto the PP pellets was a surface diffusion process affected by solution salinity.
- PEPs demonstrated higher distribution coefficient and slower distribution kinetics probably due to diffusion into weathered polymer that had increased crystallinity.

The present work explains why pellets found on the same beach demonstrated different concentrations of contaminant (Endo et al., 2005). However, a similar study with well-characterized PEPs will provide more evidence on how different degrees of weathering affect the intra polymer diffusion and surface diffusion.

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FIGURE CAPTIONS

Figure 1 Phenanthrene distribution kinetic results in synthetic (a) freshwater (FW) and (b) saltwater (SW). PE: polyethylene; PP: polypropylene; POM: polyoxymethylene; PEP: plastic eroded pellets; K_{da} : apparent distribution coefficient measured at a given time

Figure 2 a) Phenanthrene distribution kinetic results for polyethylene (PE) in synthetic freshwater (FW) and saltwater (SW). K_{da} : apparent distribution coefficient measured at a given time. b) Phenanthrene distribution kinetic experimental results and analytical model predictions for polyethylene (PE) in synthetic freshwater (FW) and saltwater (SW). K_{da} : apparent distribution coefficient measured at a given time over K_d : distribution coefficient at equilibrium. Solid and dashed lines are the model predictions for the freshwater and saltwater, respectively

Figure 3 Phenanthrene distribution kinetic results for polypropylene (PP) in synthetic freshwater (FW) and saltwater (SW). K_{da} : apparent distribution distribution coefficient measured at a given time.

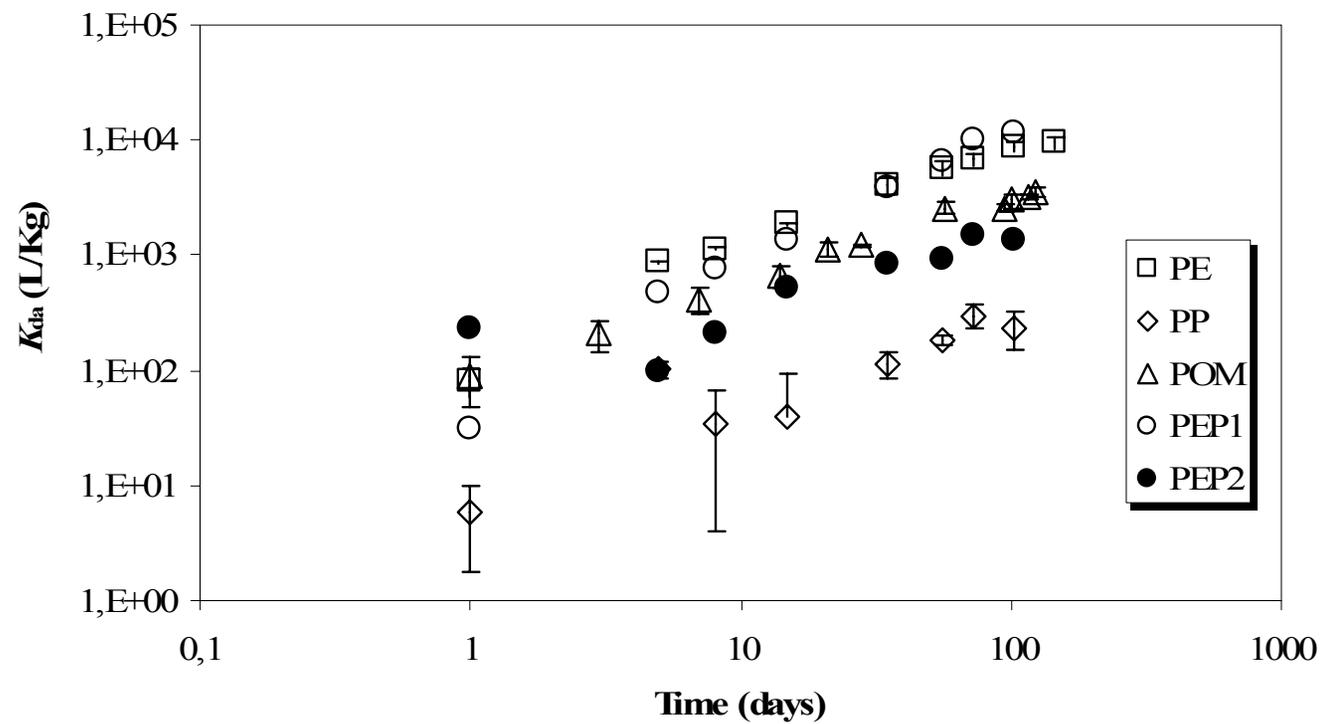


Figure 1a

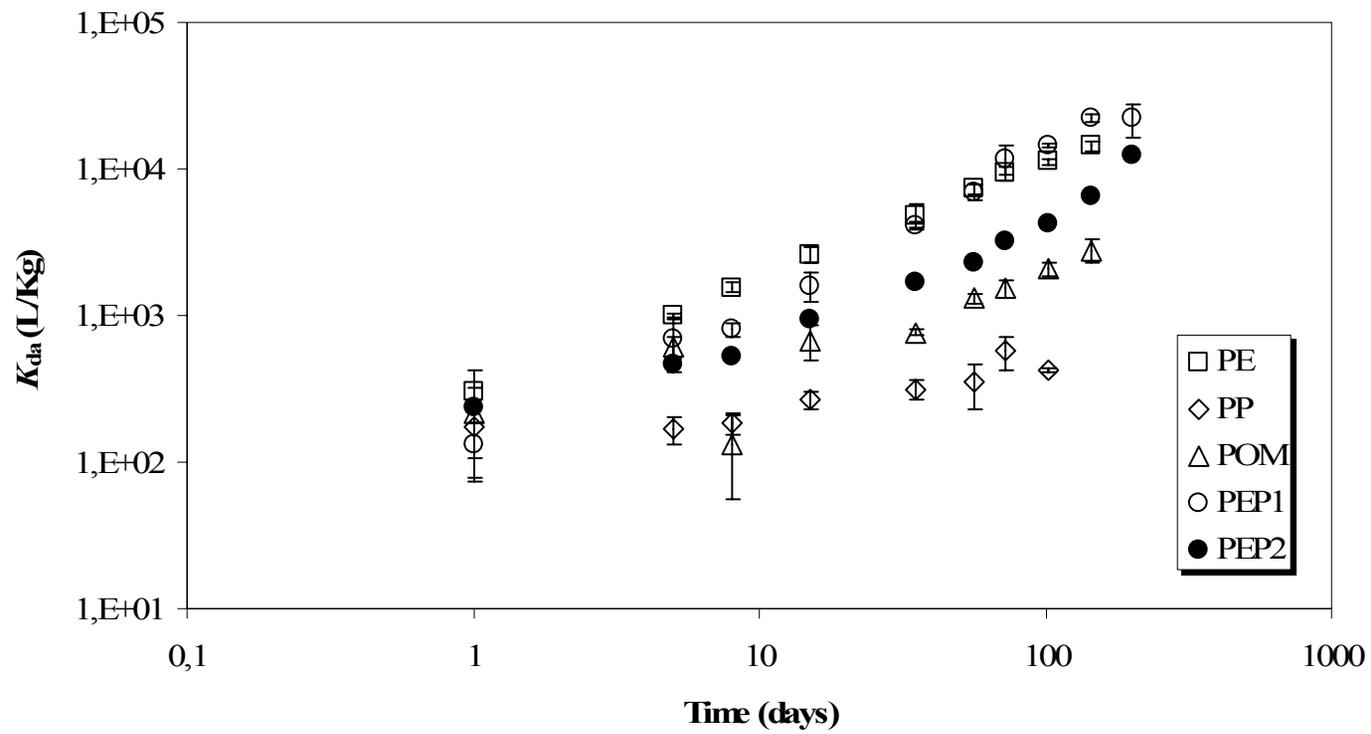


Figure 1b

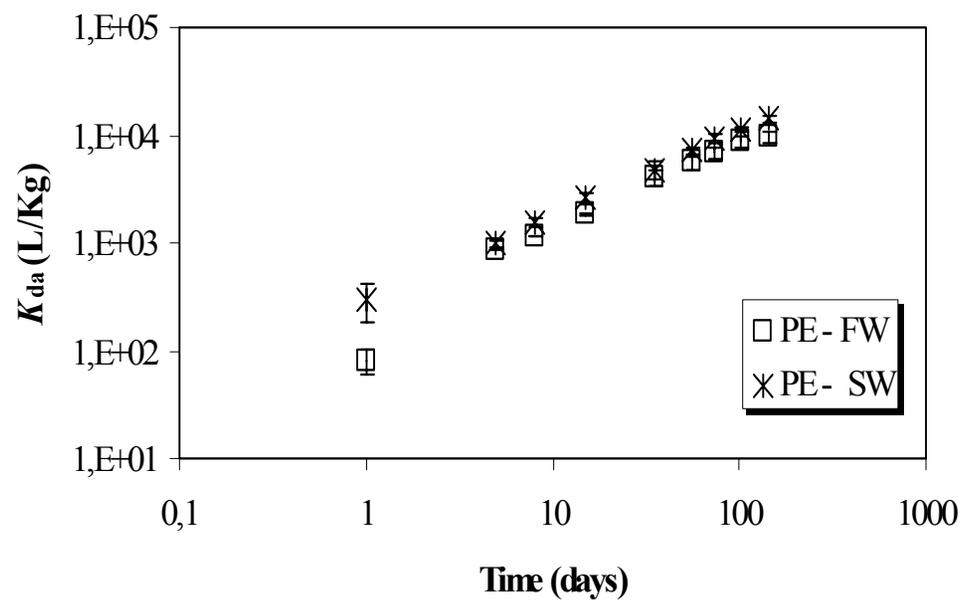


Figure 2a

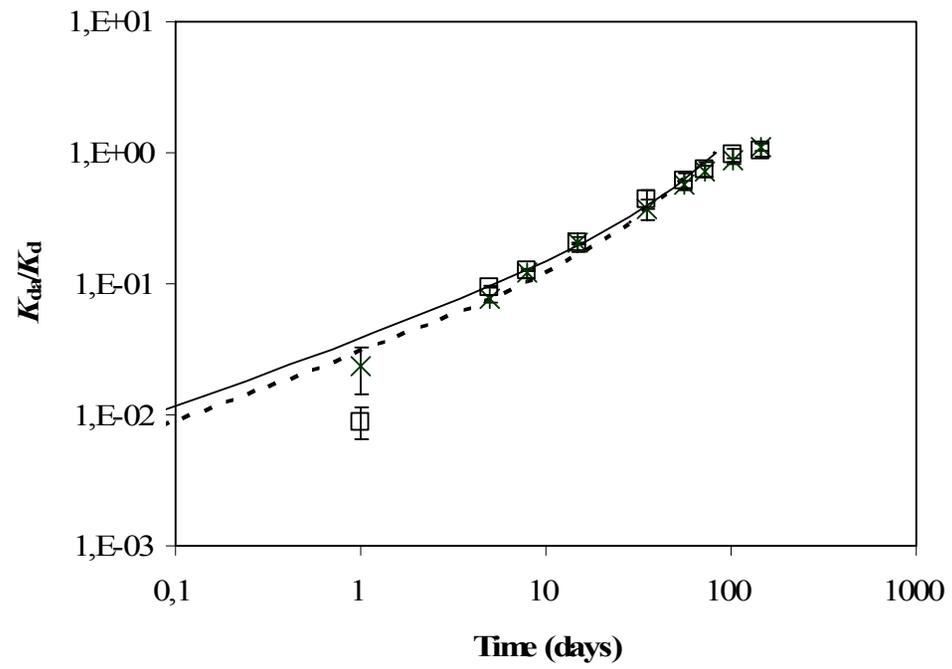


Figure 2b

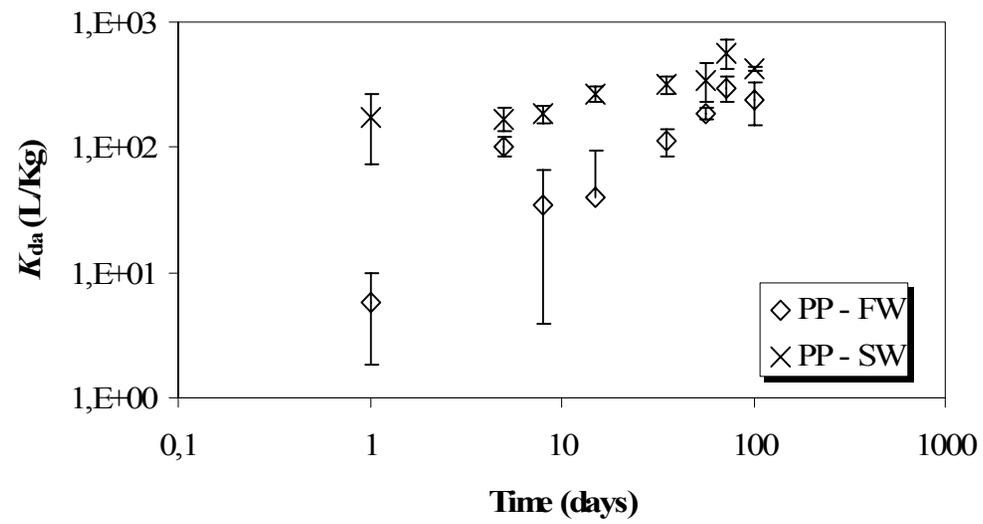


Figure 3

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Table 1 Distribution coefficients for the different pellet types.

Sorbents	m/V (mg/mL)	K_{dFW} (L/Kg)	Duration of the experiments (Days)	K_{dsw} (L/Kg)
PE	0.24	9200 \pm 1000	144	13000
PP	0.25	270 \pm 80	102	380 (420 ^a \pm 140)
POM	0.15	5300 \pm 860	164	7400
PEP	0.32	1400 \pm 120 11000 \pm 1300	102	>12000 ^b , 22000 ^a \pm 3300

PE: polyethylene; **PP:** polypropylene; **POM:** polyoxymethylene; **PEP:** plastic eroded pellets; m/V : average ratio of pellet mass per solution volume; K_{dFW} : distribution coefficient in **FW:** synthetic freshwater. Values were determined using the last two measurement occasions at the end of the kinetic experiments in freshwater solution (FW) using whole pellets (6 points); K_{dsw} : distribution coefficient in **SW:** synthetic saltwater. Distribution coefficients in saltwater solution (SW) were calculated using the K_{dFW} values and the Setschenow equation; Mean \pm standard deviation

^aThese samples reached equilibrium at the end of the experiments; thus, these values were experimentally determined; ^bThis sample did not reach equilibrium at the end of the experiments; this value was the last measurement

Table 2 Kinetic distribution properties based on analytical modeling

Sorbent	Solution	α	β	C_e	D_a	D_e/α^2	T	error
	Water	(cm)		($\mu\text{g/L}$)	(cm^2/s)	(1/s)	(90%)	
PE	FW	0.14	0.46	34	3 E^{-11}	1 E^{-5}	70	0.0553
PP	FW	0.10	11	105	9 E^{-11}	2 E^{-6}	40	0.8610
POM	FW	0.15	0.40	21	2 E^{-11}	7 E^{-6}	110	0.8202
PEP1	FW	0.14	0.23	18	9 E^{-12}	5 E^{-6}	70	0.1601
PEP2	FW	0.14	2.5	70	1 E^{-10}	7 E^{-6}	90	0.6345
PE	SW	0.14	0.30	23	2 E^{-11}	1 E^{-5}	70	0.0964
PP	SW	0.10	10	104	3 E^{-10}	1 E^{-5}	25	0.0724
POM	SW	0.15	0.88	46	1 E^{-11}	6 E^{-6}	450	0.5334
PEP1	SW	0.14	0.14	12	3 E^{-12}	3 E^{-6}	95	0.1552
PEP2	SW	0.14	0.25	20	4 E^{-12}	2 E^{-6}	195	0.0375

PE: polyethylene; **PP:** polypropylene; **POM:** polyoxymethylene; **PEP:** plastic eroded pellets; **FW:** synthetic freshwater or **SW:** synthetic saltwater; α : particle radius; β : the ratio of the phenanthrene mass in solution to the phenanthrene mass in the pellet at equilibrium; C_e : expected phenanthrene aqueous concentration at equilibrium; D_a : apparent diffusion coefficient (value chosen to minimize model error); D_e/α^2 : effective diffusion rate; **T (90%):** time required to reach 90% equilibrium expressed in days; **Error:** the $\sum[(\text{mean of measurement} - \text{model prediction}) / \text{model prediction}]^2$ of all measurements