Modelling of the release of organic compounds from polyethylene pipes to water

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ABSTRACT

The use of polyethylene pipes in the distribution network causes contamination of the drinking water. The contaminants are a mixture of phenols, quinones, antioxidants and short polyethylene chains that in general have a functional polar oxygen group. With the use of the film-layer theory and a mass balance for a pipe, an equation is derived to compute the outlet concentration from a given pipe. The equation indicates that if the water in a pipe has a turbulent flow, the water becomes significantly more contaminated by the migrants, compared to water with a laminar flow. The maximum concentration of contaminants is predictable, and is equal to the product of the migrants' concentration in the polymer and its partition coefficient at the polymer and water interface. E.g. the maximum obtainable concentration of a stabilizer, as Irganox® 1010, in drinking water exposed to PE pipes used in Denmark is between 0.2 and 0.3 mg/L if no reaction of the added antioxidant has taken place in the pipe extrusion step.

Key words | antioxidants, diffusion, drinking water, hydraulics, phenols, polyethylene (PE) pipes

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NOMENCLATURE

A	Area of the inner surface of the pipe [m²]
$c_{w,i,\text{int}}$	Mass concentration of species i at the water interface [kg/m³]
$c_{w,i}$	The overall mass concentration of species i in the water [kg/m³]
$c_{w,\max,i}$	The maximum obtainable mass concentration of species i in the water [kg/m³]
$c_{w,out,i}$	The mass concentration of species i in the pipe outlet [kg/m³]
$c_{p,i,\text{int}}$	Mass concentration of species i in the polymer interface [kg/m³]
$c_{p,i}$	The mass concentration in the polymer [kg/m³]
$c_{w,in,i}$ and $c_{w,out,i}$	Mass concentration of species i in the inlet and outlet of the pipe [kg/m³]
d_{inner}	Inner pipe diameter [m]
$D_{w,i}$	Diffusion coefficient of species i in water [m²/s]
$D_{p,i}$	Diffusion coefficient of species i in the polymer [m²/s]
$K_{w/p,i}$	Partition coefficient of species i at the interface between the water and polymer phase [-]
k_1	First order rate constant [s⁻¹]
k_i	Mass-transfer coefficient [m/s]
$k_{ln,i}$ and $k_{loc,i}$	Logarithmic mean and local mass-transfer coefficient [m/s]
L	Length of pipe [m]
Q	Volume flow rate [m³/s]
r	Radius from the centre of pipe [m]
Δr_p	Thickness of the film-layer in the polymer [m]
Δr_w	Thickness of the film-layer in the water phase [m]
R_{inner}	Inner pipe radius [m]
t	Time [s]
$t_{1/2}$	Half-life [s]

v	Flow velocity. $(v = 4Q / (\pi \cdot (d_{inner})^2))$ [m/s]	
J_i	The mass flux of species i through the interface [kg/(m^2 s)]	

GREEK LETTERS

ρ	The water density [kg/m^3]
μ	The water viscosity [kg/(m s)]

DIMENSIONLESS GROUPS

Re	Reynolds number [-]
Sc_i	Schmidt number [-]
Sh_i	Sherwood number [-]

INTRODUCTION

The use of polyethylene (PE) pipes in drinking water distribution networks and household installations causes a contamination of the consumer's tap water. This was shown by Anselme *et al.* (1985, 1986), Brocca *et al.* (2002) and Skjevrak *et al.* (2003) who found phenols and quinones in water exposed to either high density PE (HDPE) pipes or cross-linked PE (PEX) pipes. Compounds such as esters, aldehydes, ketones, terpenoids and aromatics are known to migrate as well, and may be a growth media for micro-organisms in for example biofilms (Skjevrak *et al.* 2003).

More than 100 different organic compounds are found to migrate to water from polyethylene materials like HDPE and PEX (Anselme *et al.* 1985, 1986; Ho *et al.* 1994; Brocca *et al.* 2002; Skjevrak *et al.* 2003; Koch 2004; Nielsen *et al.* 2005).

The identified migrants can be grouped as follows:

1. Additives like antioxidants.
2. Degradation products formed by radical reaction of the antioxidants.
3. Broken PE chains that in general have a functional polar oxygen group (e.g. esters & aldehydes).

Two types of PE pipes are used in the drinking water network; HDPE pipes in the distribution mains and service pipes, and PEX in the household installations as hot and cold water pipes. HDPE pipes are manufactured by extruding PE granulates with stabilizers as antioxidants, and PEX is manufactured by cross-linking PE granulates in connection with the extrusion step. There are three principal technologies for cross-linking; peroxide method, reactive silane method and beta irradiation method (Water Panel 2004).

The small PE chains are formed in the extrusion step of a PE pipe due to e.g. high temperatures, mechanical forces and oxygen. By adding antioxidants to the PE granulate, the concentration of broken chains is decreased, but degradation products of the antioxidants are formed, which are often aromatic compounds like phenols and quinones (Pospíšil *et al.* 2002). In the cross-linking step of PEX pipes, by-products of the antioxidants may be formed. The antioxidants are also added to increase the material's service life (Gedde & Ifwarson, 1990; Hassinen *et al.* 2004).

The antioxidants, like Irganox® 1010, have been shown to migrate from *PE granulate* to water by Anselme *et al.* (1986), and Gandek *et al.* (1989) showed that antioxidants migrate from linear-low density PE (LLDPE), low density PE (LDPE) and HDPE used for *food packaging* to water. It has not yet been shown that non-reacted antioxidants will migrate from *PE pipes* to water. This can either be due to the fact that the antioxidants have reacted into degradation products in the extrusion step of the pipe, the analytical methods used were inappropriate, or that this has not yet been investigated.

In a field study, the increase in contaminant concentration in water exposed to PE pipes in a distribution system was measured (Nielsen *et al.* 2005). The conclusions in this project were based on the rate of migration being directly proportional to the residence time. Therefore, the sampling locations were placed in the outer region of the distribution network, where the water had a high residence time due to the low water consumption. The precise reason for the assumption stating that the migration is directly proportional to the residence time is not mentioned, but it could be gathered from the model used to determine migration of additives from food packaging polymers to the food. The model used in the Practical Guide (2003) is taken from the book entitled *The Mathematics of Diffusion*, Crank (1970). The concentration of the migrant in this model is assumed to be equally distributed in the surrounding media i.e. no boundary layer resistance

exists. This means that the main chemical parameters of importance are the migrants' diffusion coefficient in the polymer and its partition coefficient at the interface. This assumption is shown to be valid for good solvents as corn oils, but for water as the extracting media, mixing is shown to be of importance for antioxidant migration (Limm & Hollifield 1995).

Mixing of water takes place when vortices exist, as when the drinking water has a turbulent flow in the network. This is expected to be the case in main pipelines where the flow rate is high and has a turbulent flow. Sieder & Tate (1936) studied the effect of mixing for fluids flowing in a pipe, by making a correlation between flow rates in the laminar and turbulent domain and heat-transfer. This can be altered into a similar mass-transfer correlation (Bird *et al.* 2002). With the use of the correlation by Sieder and Tate (1936), the relationship between flow rate and contaminant concentration can be evaluated.

The purpose of this paper is to derive an expression for the outward diffusion of organic compounds from PE pipes to water. This information can subsequently be applied to calculate the concentration of organic compounds in the water. Using literature data, the effect of

turbulent and laminar flow can be compared, and the physical and chemical parameters that have an effect can be elucidated.

MIGRATION THEORY

Film-layer theory

The flux, J_i, of contaminants from the polymer to the water phase is computed by Fick's first law of diffusion on each side of the interface (subscript: int). This differential expression is shown in Equations (2) and (3). With the use of the film-layer theory a linear concentration profile at the interface is introduced. This causes a small uncertainty but is a good guideline when modelling migration rates (Wesselinger & Krishna 2000; Bird *et al.* 2002). In Figure 1 the concentration profile, with and without the film-layer, is illustrated. The expressions for the flux in the film-layer are shown to the right in Equations (2) and (3). $D_{p,i}$ and $D_{w,i}$ are the diffusion coefficients of species i in the polymer and the water, respectively. Δr_p and Δr_w are the thicknesses of the film-layer in the polymer and water, respectively. The equilibrium concentrations at the interface are connected to the partition coefficient, $K_{w/p,i}$, in Equation (1). $c_{w,i,\text{int}}$ and $c_{p,i,\text{int}}$ are the concentrations of species i at the water and the polymer interface, respectively.

$$K_{w/p,i} = \frac{c_{w,i,\text{int}}}{c_{p,i,\text{int}}} \tag{1}$$

$$J_i = D_{p,i} \frac{\partial c_{p,i}}{\partial r_p}\bigg|_{\text{int}} \approx \frac{D_{p,i}}{\Delta r_p}(c_{p,i} - c_{p,i,\text{int}}) \tag{2}$$

$$J_i = D_{w,i} \frac{\partial c_{w,i}}{\partial r_w}\bigg|_{\text{int}} \approx \frac{D_{w,i}}{\Delta r_w}(c_{w,i,\text{int}} - c_{w,i}) \tag{3}$$

The thickness of the boundary layer in the water depends on the movement of the water, i.e. an enhanced level of mixing reduces the magnitude of Δr_w. This link is in the film-layer theory expressed by the mass-transfer coefficient, k_i, which is equal to $D_{w,i} / \Delta r_w$. By introducing k_i in
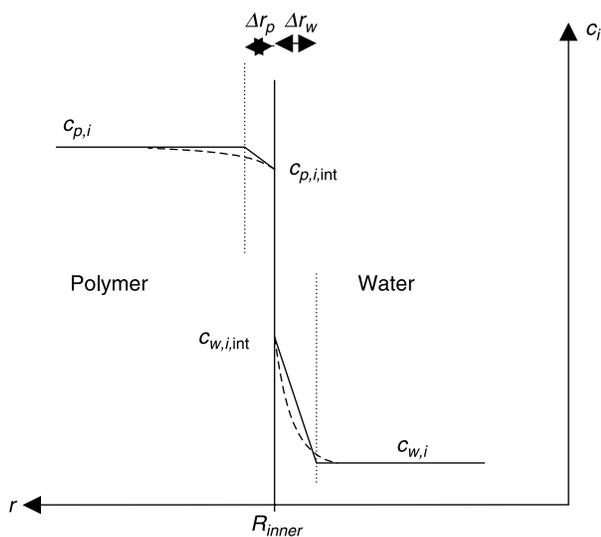

Figure 1 | Concentration profile at the interface between polymer and water phase. The solid line is the estimated profile used in the film-layer theory. The dashed line is the true concentration profile. r is the radius from the centre of pipe and R_{inner} is the inner radius of the pipe.

Equation (3), Equation (4) is obtained.

$$J_i \approx k_i(c_{w,i,\text{int}} - c_{w,i}) \tag{4}$$

Using Equations (1), (2) and (4), the overall flux at the interface can be derived into Equation (5).

$$J_i = \frac{k_i(c_{p,i}K_{w/p,i} - c_{w,i})\frac{D_{p,i}}{\Delta r_p}}{\frac{D_{p,i}}{\Delta r_p} + k_iK_{w/p,i}} \tag{5}$$

In an experiment by Limm & Hollifield (1995) it was shown that the antioxidant migration from polymers to corn oils was independent of the level of mixing. According to the model mentioned earlier by J. Crank (1970), the rate of migration depends on the migrants' diffusion coefficient in the polymer and the partition coefficient at the interface. This means the magnitude of the mass-transfer coefficient is unimportant in Equation (5), and $D_{p,i} / \Delta r_p \ll k_i K_{w/p,i}$. The high solubility of the antioxidants in corn oils leads to this derivation.

For migration from polymers to water, Limm & Hollifield (1995) experimentally showed that the effect of mixing has influence on the rate of migration. This means the magnitude of $k_i \cdot K_{w/p,i}$ is of importance in Equation (5), i.e. the magnitude of $k_i \cdot K_{w/p,i}$ is equal to or smaller than $D_{p,i} / \Delta r_p$. This must be associated with the low solubility of the antioxidants in water. For new pipes the thickness of Δr_p is infinitesimally small from which Equation (5) can be rewritten into Equation (6). The change of Δr_p over time reduces the validity of Equation (6) due to the "aging" of the pipe, and the magnitude of the error depends strongly on the given migrant and the flow conditions.

$$J_i = k_i(c_{p,i}K_{w/p,i} - c_{w,i}) \tag{6}$$

Mass-transfer correlation and outlet concentrations in pipes

Correlations in transport phenomena from a solid phase to a moving phase are widely investigated in the literature. The comprehensive book by Bird, Stewart and Lightfoot (2002) has reviewed existing correlations for heat-transfer from a pipe to a moving fluid. The majority of the correlations originate from Sieder & Tate (1936) who have collected data for fluids as water and oils with different viscosities. In Bird *et al.* (2002) it is shown that heat-transfer and mass-transfer

correlations can be linked, if a number of criteria are fulfilled. For migration from PE-pipes to water the following are of particular importance:

- The migrant is weakly soluble in water i.e. the molar fraction at the interface is approximately zero.
- Low diffusivity of the migrant in water.
- Small net mass-transfer rates i.e. no significant transport of water molecules into the material.
- No chemical reaction of the migrants takes place.

In the correlations, three dimensionless groups are introduced; Sherwood, Reynolds and Schmidt numbers (see the list of nomenclatures for specifications of the parameters):

Sherwood number	Reynolds number	Schmidt number
$\mathrm{Sh}_i = \frac{k_i d_{inner}}{D_{w,i}}$	$\mathrm{Re} = \frac{\rho v d_{inner}}{\mu}$	$\mathrm{Sc}_i = \frac{\mu}{\rho D_{w,i}}$

With the use of these groups it is possible to correlate the rate of migration (Sherwood number), with the flow rate (Reynolds number), and the physical property of the fluid (Schmidt number).

For flow in pipes, there are two areas of interest, laminar and turbulent flow. Laminar flow, Re < 2100, is characterised by smooth movement of particles in layers without mixing, and turbulent flow, Re > 8000, is a state where the particles move in many directions while being transported along the pipe. In-between the laminar and the turbulent domains, a momentary change can take place depending on friction on the pipe surface and external vibrations on the pipe. For example, if the pipe surface is rough, a turbulent flow may begin at low flow rates and if a mechanical force affects the pipe, the generated vibrations will cause a turbulent flow. For Reynolds numbers higher than 8000 it is practically impossible to retain a laminar flow.

The laminar flow has two time domains of importance: 1) The time period where the particles arrange in a hyperbolic order and the maximum water velocity is obtained in the centre of the pipe, e.g. when the water momentarily goes from stagnant condition to a given laminar flow. This domain is called the inlet zone because it is also valid for fluids entering a pipe with a velocity
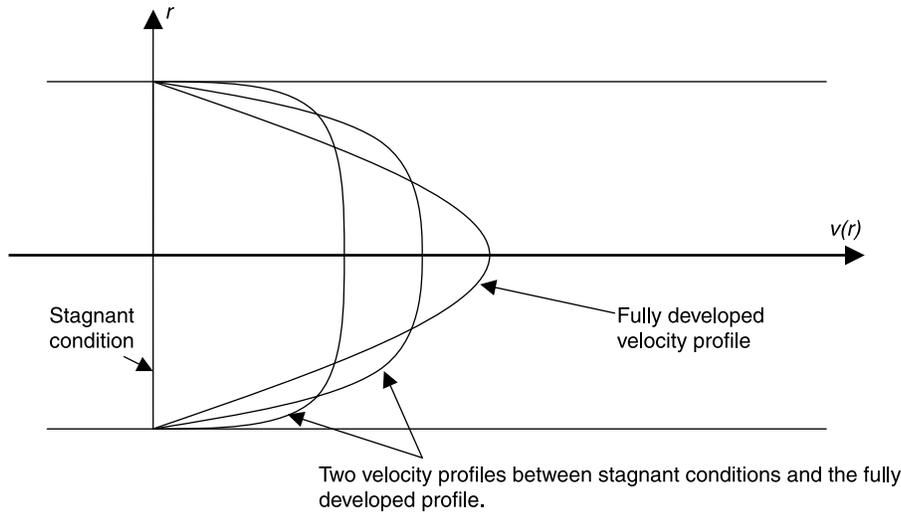
Figure 2 | The Velocity, *v(r)*, profile of water in a pipe, going suddenly from a stagnant state to a laminar flow of a given flow rate.

profile independent on position. Figure 2 illustrates the change in velocity profile over time. 2) The velocity profile is fully developed i.e. no change in velocity of the particles. This takes place when $t > 0.035 \cdot (d_{inner})^2 \cdot \rho/\mu$ or when the fluid has flown $L > 0.035 \cdot d_{inner} \cdot Re$.

Equation (7) is the logarithmic mean mass-transfer correlation for the inlet zone with a laminar flow that is valid with an uncertainty of 20% for $Re \cdot Sc_i \cdot d_{inner}/L > 10$. For lower values of $Re \cdot Sc_i \cdot d_{inner}/L$ the mass-transfer coefficient is significantly underestimated.

$$Sh_{\ln,i} = 1.86 \left(Sc_i \frac{\rho \cdot d_{inner}^2}{\mu \cdot t} \right)^{1/3} \tag{7}$$

When the laminar flow is fully developed the local mass-transfer coefficient is correlated as shown in Equation (8).

$$Sh_{loc,i} = 3.657 \tag{8}$$

At turbulent flow conditions, the logarithmic mean mass-transfer correlation shown in Equation (9) is valid for $L/d_{inner} > 60$. However, for L/d_{inner} between 10 and 60 the Reynolds number has to be higher than 20,000 before the correlation in Equation (9) is valid.

$$Sh_{\ln,i} = 0.026 \, Re^{0.8} Sc_i^{1/3} \tag{9}$$

The subscripts ln and *loc* in Equations (7), (8) and (9) describe how to compute the outlet concentration, $c_{w,out,i}$,

of a given pipe. *loc* means local mass transfer and the coefficient is valid in Equation (8). But for ln it is the logarithmic mean concentration difference that correlates (i.e. the overall mass transfer coefficient and the outlet concentration are computed with the use of Equation (10)). $J_{\ln,i}$ is the overall flux to the media flowing along the pipe over time. With the use of a mass balance for a pipe, Equation (11), an expression for the outlet concentration is obtained in Equation (12). Here the pipe area is rewritten as an expression of the inner diameter and pipe length.

$$J_{\ln,i} = \frac{(K_{w/p,i} \cdot c_{p,i} - c_{w,in,i}) - (K_{w/p,i} \cdot c_{p,i} - c_{w,out,i})}{\ln(K_{w/p,i} \cdot c_{p,i} - c_{w,in,i}) - \ln(K_{w/p,i} \cdot c_{p,i} - c_{w,out,i})} \cdot$$
$$k_{\ln,i} \tag{10}$$

$$c_{w,out,i} - c_{w,in,i} = J_{\ln,i} \cdot A/Q \tag{11}$$

$$\frac{K_{w/p,i} \cdot c_{p,i} - c_{w,out,i}}{K_{w/p,i} \cdot c_{p,i} - c_{w,in,i}} = \exp\left(-\frac{k_{\ln,i} \cdot \pi \cdot d_{inner} \cdot L}{Q} \right) \tag{12}$$

When the mass transfer coefficient is local, the outlet concentration is also expressed by Equation (12). In which $k_{\ln,i}$ becomes $k_{loc,i}$.

RESULTS AND DISCUSSION

With the use of the derived Equation (12) and the correlations for, k_i, Equations (8) and (9), for computing

the outlet concentration from a PE pipe, six parameters are of interest. Flow rate, pipe length and inner pipe diameter are the three important physical parameters. The migrant concentration in the pipe material, its partition coefficient at the interface between the PE matrix and water, and its diffusion coefficient in water are the important chemical parameters. From the consumer's point of view, it is worth noting that the maximum obtainable concentration, $c_{w,\max,i}$, of a given compound in the drinking water is predictable. It is the product of the concentration of the species in the PE matrix at the interface, $c_{p,i}$, and its partition coefficient, $K_{w/p,i}$, as shown in Equation (13). This is derived from Equation (6) where the water is saturated when the flux, J_i, is zero.

$$c_{p,i} \cdot K_{w/p,i} = c_{w,\max,i} \tag{13}$$

The magnitude of the partition coefficient is related to the solubility of a given compound in water and the PE matrix, respectively. This means that the value for the small broken PE chains is higher than for example the large antioxidants. And these chains will be removed from the matrix rather quickly, but the migration of antioxidants

will last for the lifetime of the pipe. The literature concerning experimental determination of partition coefficient at a polymer water interface is limited to two articles, Gandek et al. (1989) and Bertoldo and Ciardelli (2004). In Figure 3 the partition coefficients are shown at different temperatures for different materials. A general tendency is that the partition coefficient is of a magnitude between 10^{-5} to 10^{-3} and has an average of $1.55\cdot10^{-4}$. It is not possible to make an obvious correlation between the magnitude of $K_{w/p,i}$ and temperature, because the solubility decreases in both the polymer and water with decreasing temperature (Laidler & Maiser 1999). This means that if the solubility in the polymer has a smaller change than the water solubility with a given temperature decrease, $K_{w/p,i}$ will decrease.

As an example, the maximum possible concentration of Irganox® 1010 in the drinking water can be determined. $c_{p,i}$ is often between 1500 and 2000 mg pr. kg PE in Danish pipes before the extrusion step (Water Panel 2004). This means, the maximum possible concentration of Irganox® 1010 in the drinking water is between 0.2 and 0.3 mg/L.

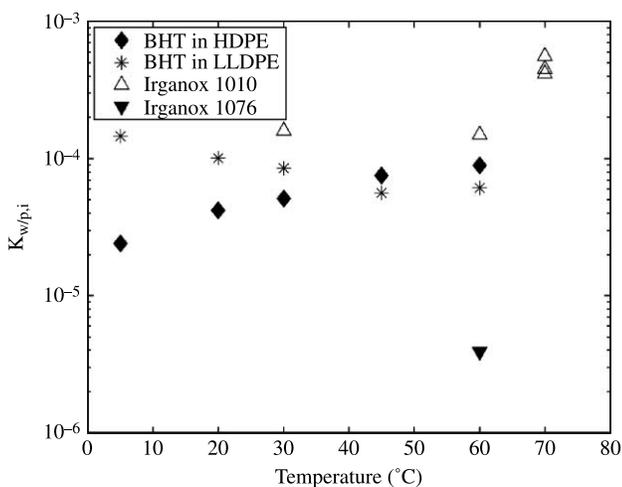By introducing the parameter $c_{w,\max,i}$ in Equation (12) and by assuming that the inlet concentration equals zero,

Figure 3 | Partition coefficients, $K_{w/p,i}$, for BHT, Irganox® 1010 and Irganox® 1076 versus temperature, experimentally determined by Gandek et al. (1989) and Bertoldo & Ciardelli (2004). $K_{w/p,i}$ is for BHT measured at both a HDPE/water and a LLDPE/water interface, respectively. Irganox® 1076 is measured at a LDPE/water interface, and Irganox® 1010 is measured on LDPE, polypropylene and two copolymers of ethylene-propylene.
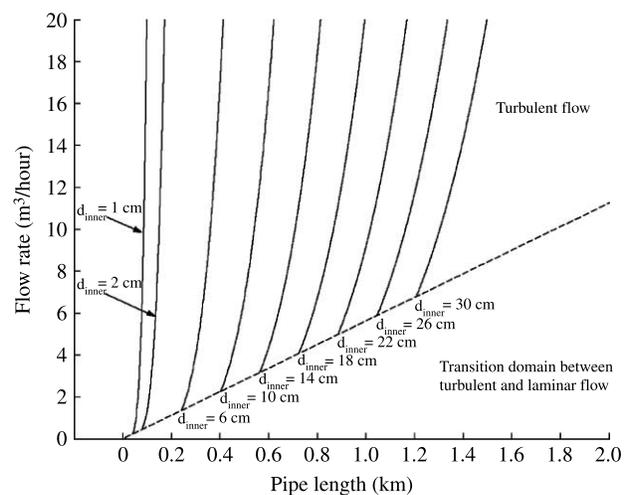

Figure 4 | Effect of turbulent flow with different pipe diameters. The figure illustrates the relationship between flow rate, inner pipe diameter and length of pipe to obtain 50% of maximum concentration of contaminants in water. The migrants' diffusion coefficient is 10^{-9} m²/s, the water density is 1000 kg/m³ and the viscosity is 0.001 kg·m⁻¹·s⁻¹.
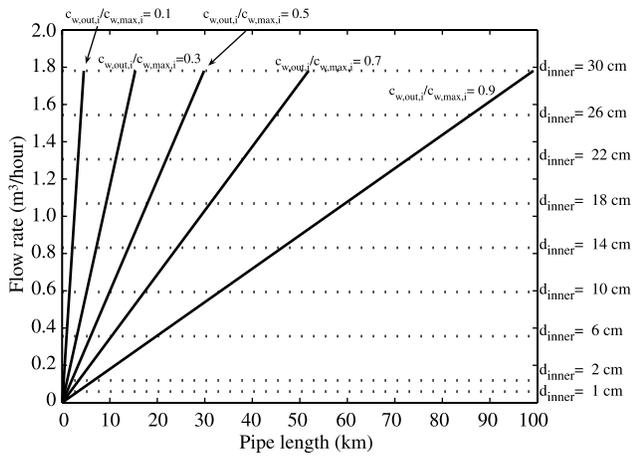
Figure 5 │ Effect of laminar flow. The figure illustrates the outlet concentration of a pipe, with a given flow rate and length. It is valid for all possible inner diameters. The horizontal lines indicate the maximum flow rate possible in a pipe with the indicated inner diameter before entering the transition domain between laminar and turbulent flow. The migrants' diffusion coefficient is 10^{-9} m^2/s, the water density is 1000 kg/m^3 and the viscosity is 0.001 kg·m^{-1}·s^{-1}.

Figure 6 │ Outlet concentration for two migrants with a diffusion coefficient of 10^{-9} and 10^{-10} m^2/s, respectively, versus residence time in a pipe with an inner diameter of 20 cm, and a length of 1 km. The change in flow domain can occur momentarily in the transition domain. The dotted line for the laminar flow is the maximum obtainable outlet concentration if the water velocity changes momentarily from zero to a given velocity. The water density is 1000 kg/m^3 and the viscosity is 0.001 kg·m^{-1}·s^{-1}.

Equation (14) is derived. This equation determines the contaminant saturation, $c_{w,i}/c_{w,\max,i}$, at a given place in a pipe.

$$\frac{c_{w,i}}{c_{w,\max,i}} = 1 - \exp\left(-\frac{k_i \cdot \pi \cdot d_{inner} \cdot L}{Q}\right) \tag{14}$$

The dimensionless concentration, $c_{w,i}/c_{w,\max,i}$, which is equal to $c_{w,i}/(K_{w/p,i}\cdot c_{p,i})$, in Equation (14) indicates that the outlet concentration is directly proportional to the migrant's concentration in the polymer.

With the use of the mass-transfer correlation for turbulent, Equation (9), and laminar flow, Equation (8), in Equation (14), Figures 4 and 5 are produced. Figure 4 illustrates the relationship between flow rate, pipe diameter and length of pipe to obtain 50% of $c_{w,\max,i}$ for all migrants with a diffusion coefficient of 10^{-9} m^2/s. This figure indicates that for turbulent flow an increased diameter will decrease the outlet concentration, and an increased flow rate decreases the outlet concentration. Figure 5 illustrates the relationship between flow rates, pipe length and outlet concentration for all pipe diameters. The horizontal dotted lines indicate the maximum flow rate (Reynolds number equals 2100) for a given pipe before entering the transition domain between laminar and turbulent flow. By comparing the two figures, it is seen that turbulent flow causes a higher contamination of the water compared to laminar flow.
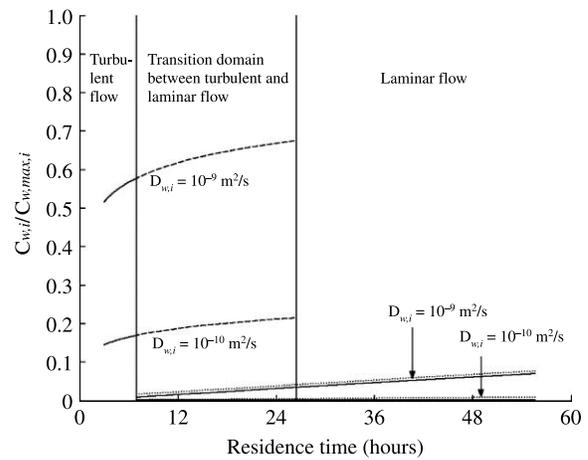
Figure 6 gives a practical example illustrating the relationship between residence time and outlet concentration for two migrants with a diffusion coefficient of 10^{-9} and 10^{-10} m^2/s in water. The pipe has a length of 1 km and an inner diameter of 20 cm, and when going from turbulent to laminar flow the outlet concentration decreases significantly. However, the magnitude of the diffusion coefficient is also of importance. The diffusion coefficient is typically in the range between 10^{-10} and 10^{-9} m^2/s in water, and due to Stokes–Einstein equation, the actual size of the migrant is of importance, i.e. the larger the molecule the smaller the diffusion coefficient (Laidler & Meiser 1999). There are no experimental data for diffusion coefficients of antioxidants in water. Nonetheless, the shape of the degradation products are comparable with benzene, which according to Nazaroff and Alvarez-Cohen (2000) has a diffusion coefficient of $1.0 \cdot 10^{-9}$ m^2/s at 25°C. For the same reason, this diffusion coefficient is used in the computations to make Figures 4 and 5.

A momentary change in water velocity with a laminar flow will cause a slow change in velocity profile and mass-transfer coefficient. Equation (7) correlates the change in Sherwood number with time when the velocity changes momentarily from stagnant to a laminar flow. In the example in Figure 6 a dotted line is shown in the laminar domain. This line is the maximum obtainable outlet concentration if the

Table 1 | First order rate constant, k_1, for hydrolysis of antioxidant in water and its half-life, $t_{1/2}$, at a given temperature. The rate constants are experimentally determined by Gandek *et al.* (1989)

Antioxidant	Temperature	k_1	$t_{1/2}$
BHT	60°C	$(7.7 \pm 0.8) \cdot 10^{-6}$ s^{-1}	1.0 ± 0.1 days
BHT	45°C	$(3.2 \pm 1.7) \cdot 10^{-6}$ s^{-1}	2.9 ± 1.5 days
BHT	30°C	$(0.25 \pm 0.02) \cdot 10^{-6}$ s^{-1}	32 ± 2 days
BHT	20°C	$(0.37 \pm 0.10) \cdot 10^{-6}$ s^{-1}	22 ± 6 days
BHT	5°C	$(0.23 \pm 0.16) \cdot 10^{-6}$ s^{-1}	48 ± 35 days
Irganox® 1076	60°C	$0.35 \cdot 10^{-6}$ s^{-1}	23 days
Irganox® 1010	60°C	$0.31 \cdot 10^{-6}$ s^{-1}	26 days

water changes momentarily from stagnant to a laminar flow with a given flow rate. The concentration converts afterwards against the solid line. The effect of frequently changing flow rates in the distribution network does not cause a significant change in contaminant concentration compared to that caused by a change in flow domain.

With the use of the derived Equation (12), it is possible to determine the outlet concentration from a new pipe, provided that the different parameters are known. In this equation one assumption is made: The migrant is unaffected by the change of environment, e.g. the migrant does not react with oxygen or hydrolyse.

However, reaction of the antioxidants in water does take place. Table 1 shows experimentally determined half-life times for the first order hydrolysis of the antioxidants; butylated hydroxytoluene (BHT), Irganox® 1076 and Irganox® 1010 determined by Gandek *et al.* (1989). This table indicates that the antioxidants have a half-life of more than 20 days. The normal residence time for water in the distribution network is below 3 days, i.e. reactions of the antioxidants can be ignored. This means that the drinking water probably will contain non-reacted antioxidants if they are found to migrate from PE pipes.

Lundbäck *et al.* (2006) showed that aerobic conditions increase the migration of antioxidants from PE pipes to water, compared to anaerobic conditions. This is attributed to a degradation of stabilizers due to antioxidants' reaction with oxygen in the water phase. The experiment performed by Lundbäck *et al.* (2006) does not make it possible to determine a specific rate of oxidation i.e. it is not possible to conclude whether the antioxidants oxidise in the water before reaching the consumers' tap.

CONCLUSIONS

An equation for computing the outward diffusion of organic compounds in new PE pipes is derived. The equation indicates that the contaminant concentration in the pipe, its diffusion coefficient in water and its partition coefficient are the chemical parameters which have an effect on the contaminant concentration in water exposed to PE pipes. The physical parameters of importance are found to be the pipe diameter, flow rate and length of the pipe.

The flow rate of the water is of significant importance, because at high flow rates the flow may become turbulent and rates of migration increase significantly compared to water with a laminar flow. This means that in water which changes from laminar to turbulent flow, an increased contaminant concentration in the outlet of a given pipe can be expected. In such a case, a decrease in residence time will not decrease the outlet concentration, on the contrary. At a given flow rate and pipe length, the outlet concentration from pipes with a laminar flow is independent of the pipe diameter, while in the turbulent domain, an increased diameter will decrease the outlet concentration. A momentary change in velocity of water is shown not to cause a significant change in contaminant concentration compared to a change in flow domain (laminar vs. turbulent).

The maximum concentration of a migrant in water flowing in a PE pipe is the product of the migrants' partition coefficient and its concentration in the polymer matrix. By using this, it is possible to estimate that the maximum concentration of Irganox® 1010 in drinking water exposed to PE pipes in Denmark is between 0.2 and 0.3 mg/L. This is valid if no reaction of the added antioxidant takes place in the pipe extrusion step.

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