



Diffusion of chemicals from the surface of pipe materials to water in hydrodynamic conditions: applications to domestic drinking water installations

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Abstract

Domestic plumbing installations inside buildings could be a source of deterioration of drinking water quality. Organic materials in contact with drinking water could introduce organoleptic properties changes due to the diffusion of organic compounds from the pipe surface to the drinking water. Therefore, to limit the presence of organic substances in drinking water, some European countries implement regulations based on migration tests carried out in static condition. In France an “Attestation of Sanitary Conformity” (ASC) has been created. Indeed, materials in contact with water are evaluated to check the accordance with specific migration limits. However, despite the ASC, some materials release chemical compounds in the domestic networks and some organoleptic problems persist in operating conditions.

The objective of this study is to determine a relationship between the amount of compounds migrating to tap water and the operating parameters such as temperature, flow rate and geometry of the network. Different organic materials were experimentally tested in terms of chemical release in water in dynamic pilot units. Transfer kinetic curves of organic micropollutants were determined in various operating conditions. Models of mass transfer in solids were applied and diffusion coefficients were obtained and compared to those found in literature. The innovative character of the study is to develop an experimental and numerical



approach to estimate organic pollutant concentration present in water networks taking into account the influence of real conditions.

Keywords: drinking water, plumbing installations, mass transfer, diffusion coefficient, partition coefficient, pipes.

1 Introduction

Since the 1980s, a part of old pipes used in domestic plumbing are replaced by plastic pipes. The trend is to choose, in particular, PEX (reticulated polyethylene) materials in individual domestic installations because of its flexibility and its application in cold and hot water networks [1]. However, the degradation of chemical and organoleptic water quality has been ascertained when these materials are used. The main causes are the dissolution of polymer additives, the desorption of compounds resulting from the degradation of the materials and permeation of external compounds through the pipe [2, 3].

The evolution of the organic quality of drinking water in domestic plumbing is of major interest. Many papers have been published concerning the identification of organic compounds migrating from PEX into the water [4–6] and the evolution of organic compounds in drinking water [5]. Nonetheless, few studies dealt with the influence of operating conditions in the migration of compounds from the organic materials to the water. A full scale study on an office building network made with copper pipe and brass components showed that the leaching of lead, copper and molybdenum increase with the water temperature and that the stagnation areas caused the accumulation of pollutants [8]. The risk of leaching and dead volume exists in the case of organic material too. Aware of the problem of pollution of the drinking water due to organic materials, the competent authorities established a regulation for all the organic materials intended to come into contact with drinking water. The transfer of compounds from materials to the water does not be a danger to human health or do not change significantly the chemical and organoleptic characteristics of drinking water.

In France, in order to limit the migration of organic compounds from monolayer, multilayer and composite materials into drinking water, an “Attestation of Sanitary Conformity” (ASC) has been created. To obtain the ASC, the materials are tested by approved laboratories to verify the accordance with specific migration limit (SML) and with the positive list of chemicals allowed. These tests are made in static conditions during 48 hours and are not representative of real utilizations.

The first objective of this paper is to study the influence of domestic plumbing operating conditions on the migration rate and migration kinetics of organic compounds from PEX material to water. This work has been carried out on an inert experimental device able to represent the operating conditions as temperature and flow rate. The migration has been measured over time with a TOC-meter. The second objective is to model the migration regardless of the operating conditions using the second Fick’s law and the determination of diffusion coefficient, partition coefficient and initial concentration of migrating compounds through experimental analysis, literature and additional chemical analysis.



2 Theory

2.1 Physic of migration in organic materials

The way of migration occurring in water depends on the properties of the polymer and the migrating compounds. The migrating compounds move through the polymer by distorting polymer chains. Therefore, the size and the shape of migrating compounds is important as well as the capability of the polymer chains to be distorted. This last parameter depends on the polymer properties such as density, crystallinity, degree of cross-linking. The glass transition temperature of the polymer (T_g) is also important. Below T_g , the polymer chains are rigid and the motion of migrating compounds is more difficult while, above T_g , the polymer is in a rubber-like state, the polymer chains are more flexible and the migrating compounds can move more easily. In general, the higher the temperature, the higher the migration rates [9].

At the interface between material and water, the extraction of migrating compounds depends on its thermodynamic properties such as polarity and solubility. Indeed, a migrating compound having a low solubility in water would rather remain in the polymer than migrate into the water [10].

2.2 Modelling approach

Several approaches exist and the choice depends on the parameters of the problem. When the number of migrating compounds is large, a general approach is preferred rather than a specific approach. For the same reasons and for its very high difficulty, the microscopic approach is often set aside in favour of macroscopic approach, even if it could give very exact results. Most migration models assume that migration is a deterministic process [11]. Nevertheless, differences may appear between experiments and modelling for some different reasons (heterogeneity in materials, variation of temperature, etc.) and a stochastic approach could be judicious for a large the number of experiments. The modelling of migration is widely used in alimentary plastic packaging. The models developed are compatible with the transfer of migrating compounds from pipe into water.

2.2.1 Diffusion equations

The diffusion of migrating compounds through a polymer to the water can be described by the Fick's equations, in a deterministic approach. The second Fick's law (one dimension), eqn (1), is written as

$$\frac{\partial c_p}{\partial t} = D_p \frac{\partial^2 c_p}{\partial x^2} \quad (1)$$

where c_p is the concentration of migrating compounds in the polymer (mg.kg^{-1}), D_p the diffusion coefficient in the polymer ($\text{m}^2.\text{s}^{-1}$), t the time (s) and x the axial position in the polymer (m).

The solutions of eqn (1) depend on the underlying assumption for the characteristics of the problem.

All the solutions proposed have two main parameters for migration prediction: a diffusion coefficient and a partition coefficient. The setting of both parameters



allows the prediction of the migration into water for each combination of migrant and polymer [12].

2.2.2 Diffusion coefficient

The diffusion coefficient D_p is a property which indicates the facility with which a compound can move through a polymer by diffusion. Many models to estimate diffusion coefficient have been proposed, none of them is a truly predictive diffusion model but they can lead to good estimation depending of assumptions. When it relates to materials in contact with drinkable water, the number of migrating compounds is very high and each one has a specific diffusion coefficient in the material. In these cases, the easiest way is to consider an overall diffusion coefficient which is a weighted average diffusion coefficient of every migrating compound in the material [13].

2.2.3 Partition coefficient

The partition coefficient K_p is the ratio of concentrations of a compound between polymer and water at equilibrium, as written in eqn (2).

$$K_p = \frac{c_{p,eq}}{c_{w,eq}} \quad (2)$$

with $c_{p,eq}$ the concentration of compounds in polymer at equilibrium (mg.kg^{-1}) and $c_{w,eq}$ the concentration of compounds in water at equilibrium (mg.kg^{-1}). The partition coefficient for a specific compound is a function of the thermodynamic properties of the polymer, the water quality and the compound characteristics. In practice, the determination of the partition coefficient is difficult and a lot of methods have been developed using electronic, steric or molecular orbital parameters [14].

3 Materials and methods

3.1 Compounds migration test

The migration tests were carried out on a device capable of reproducing the operating conditions of a domestic water installation (migration bench). The device includes a pump, a flowmeter and a heater system and is shown in Figure 1. The experimental unit is made with glass and Teflon to guarantee the innocuousness of the system and prevent pollution of the water by the material constituting the test rig.

During the migration test, the inner surface of the material was in contact with ultrapure water. Five litres of water flowed in the system at adjustable temperature and flow rate; the water temperature could be set between $30 \pm 1^\circ\text{C}$ and $50 \pm 1^\circ\text{C}$ and the flow rate (written as velocity) between 0.15 and 1.5 m.s^{-1} in a pipe with inner diameter of 16 mm (corresponding to a Reynolds number ranging from 2400 to 24000). The outlet pressure is the atmospheric pressure. Prior to the migration test, the sample (PEX pipe) were rinsed with tap water during 30 min and then rinsed 3 times with test water (ultrapure water). Immediately after this washing, the pipe was fixed to migration device to begin the experiment.

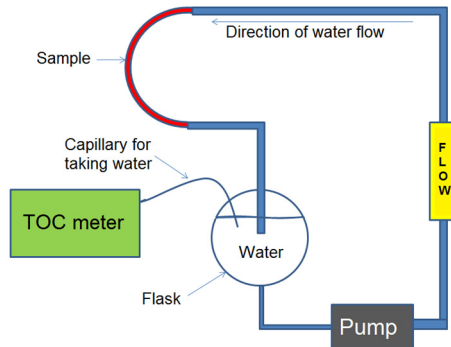


Figure 1: Scheme of migration bench.

The evolution of the concentration of organic and inorganic compounds in the water was followed through TOC measurement using a TOC-meter (TOC-VCSH, Shimadzu). This tool allowed an overall tracking of the migration and was not discriminating against the compounds present in the water. Ten measures of TOC were made successively every day the first week and every three or four days after that for a period up to 3 months. A control migration test was also performed by using a Teflon pipe as a sample.

3.2 Samples and water

PEX-b material pipes were employed as sample during the study. PEX-b consisted of cross-linked polyethylene through the Silane method. Pipe piece have a length of 1.5 m, an internal diameter of 16 mm and a thickness of 1.1 mm. The samples used were obtained directly from the manufacturer, and then the types and the quantities of additives present in the material were unknown. The pipes (BETAPEX-RETUBE, Comap, France) can be used in sanitary hot and cold water system, as shown in the technical opinion ATEC 14/11-1688 (CCFAT France). The pipes were fixed to the migration bench with captive nut and a polymeric circumferential seal guarantee watertightness

Ultrapure water was used as reference water for the study. The initial rate of TOC (Total Organic Carbon) in the water was lower than 0.1 mg.L^{-1} ; these properties ensure a better detection of the migration of compounds, particularly during the first days of the experiments.

3.3 Modelling the migration

The main purpose of this part is to model the kinetic of compounds migration from the material to the water. The model developed is implemented in AKTS-SML Software. This simulation tool is available for monolayer materials. The migration phenomena are evaluated through general, macroscopic and deterministic approach and are based on a solution of second Fick's law (eqn (3)) [12].

$$M_{L,t} = A c_{p,0} \rho_p d_p \alpha \left[1 - \exp\left(-\frac{D_p t}{d_p^2 \alpha^2}\right) \operatorname{erfc}\left(\frac{\sqrt{D_p t}}{d_p \alpha}\right) \right] \quad (3)$$

$$\text{with } M_{L,t} = \frac{1}{V_p} (c_{p,0} - c_{p,t}) \text{ and } \alpha = \frac{1}{K_p} \frac{V_L}{V_p}.$$

And where $M_{L,t}$ represents the mass of compounds which have migrated (mg), A the exchange area (m^2), $c_{p,0}$ the initial concentration of migrating compounds in the material (mg.kg^{-1}), $c_{p,t}$ the concentration of migrating compounds in the material at time t (mg.kg^{-1}), ρ_p the material density (kg.m^{-3}), d_p the material thickness (m), t the time (s), D_p the diffusion coefficient ($\text{m}^2.\text{s}^{-1}$), V_L the volume of water (m^3), V_p the volume of polymer (m^3) and K_p the partition coefficient.

Several data are then required to model the migration kinetics. Some of them are easy to get, e.g. the thickness, the density, the volume of material and the volume of water. The others need to be evaluated with complementary chemical analysis, bibliographical information or experimental data. The initial concentration of migrating compounds has been determined with microwave assisted extraction in polar and protic solvents on PEX samples, the diffusion coefficient has been determined by analysis of migration curves and partition coefficient have been estimated through some assumptions explained below.

3.3.1 Estimation of initial concentration of migrating compounds in the material

The material used for the test has been cut into 25 μm thick slices using a microtome. The samples have been put in different solvents under microwave treatment for 48h. The microwave assisted extractions on very thin chips allow the extraction of the additives from the material very quickly [15]. Polar protic solvents have been used to be under the same conditions as those used in experimental extraction with water. It was methanol and water/acetic acid mixing. Then, the chips have been recovered and dried. The difference in mass of chips weighed at the beginning and at the end of the extraction has given the quantity of compounds extracted from the material and therefore the initial concentration of migrating compounds in the material.

Table 1 gives the initial concentration of additives estimated with methanol and acetic acid.

Table 1: Estimation of initial concentration of additives in the material.

| Solvent | Initial concentration of extracted migrating compounds $c_{p,0}$ (mg.kg^{-1}) |
|-------------------------------|--|
| Water + acid acetic (3% vol.) | 4800 \pm 1200 |
| Methanol | 5100 \pm 1000 |

The values found are almost similar with the two solvents and moreover correspond to the initial value of additives traditionally used by manufacturers [12]. The migration model is not very sensitive to the initial concentration of additives, then the choice has been made to fix $c_{p,0} = 5000 \text{ mg.kg}^{-1}$.

3.3.2 Determination of the diffusion coefficients

The diffusion coefficients have been determined from experimental data and mathematical analysis (Table 3). A Taylor-expansion of $\exp \frac{D_p t}{d_p^2 \alpha^2}$ and $\text{erfc} \frac{\sqrt{D_p t}}{d_p \alpha}$

have been made in eqn 3 after verification of criteria and have led to eqn (4). The criteria mentioned above are:

1. K_p must equal to about 1.
2. $d_p \alpha \gg \sqrt{D_p t}$.

The first criterion can be accepted for high velocity of water in the pipe. The flow is turbulent throughout the complete range of operating velocities. The water flowing in the pipe puts shear stresses on the wall of the pipe and the higher the velocity, the high the wall shear stresses (Table 2 shows the value of wall shear stresses as a function of velocity of water in a pipe having the same geometry as in experiments) [16].

Table 2: Wall shear stresses as a function of velocity of water.

| Velocity of water (m.s ⁻¹) | Wall shear stress (Pa) |
|--|------------------------|
| 0.15 | 0.29 |
| 0.6 | 2.27 |
| 1.5 | 7.71 |

When the velocity of water is high enough, the wall shear stress could be strong enough to physically extract the migrating compounds, therefore assuming $K=1$. The second criterion can be verified through a quick numerical analysis. The diffusion coefficient in rubber polymers are between 10^{-10} and 10^{-12} cm².s⁻¹ at 30–50°C, the time of experimentations are about 2 months (6.10^6 s), α is about 56 in the configuration of migration bench used, therefore $\frac{\sqrt{D_p t}}{d_p \alpha}$ is between 10^{-3} and 10^{-5} .

$$M_{L,t} = \frac{2}{\sqrt{\pi}} A c_{p,0} \rho_p (D_p t)^{1/2}. \quad (4)$$

Then the experimental value of migration measured with the migration bench for high velocity of water (>0.6 m.s⁻¹) have been plotted against \sqrt{t} . The straight line obtained has a slope equal to $\frac{2}{\sqrt{\pi}} A c_{p,0} \rho_p D_p^{1/2}$ which allows the determination of D_p .

Table 3: Determination of diffusion coefficients at different temperatures.

| Temperature (°C) | Diffusion coefficient (cm ² /s) |
|------------------|--|
| 30 | $2.5.10^{-13}$ |
| 40 | 2.10^{-12} |
| 50 | 4.10^{-12} |

This corresponds to common value for diffusion of large migrating compounds in rubber polymer. As a comparison, the values of diffusion coefficient in LDPE at 23°C is $5.2.10^{-12}$ cm².s⁻¹ for 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate (Irganox 1076, CAS: 2082-79-3), $5.82.10^{-12}$ cm².s⁻¹ for 2,2-Thiodiethyl-bis-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate] (Irganox 1035, CAS: 41484-35-9) [13].



3.3.3 Estimation of partition coefficient

The choice has been made to use simple approach to estimate the partition coefficient, particularly because of the migrating compounds are unknown. The migrating compounds are assumed to have a low solubility in the water. Then, in first approximation, K_p is assumed to be equal to 1000 for low water velocity when the wall shear stress is too low to have an impact on the extraction of compounds at the interface [14]. However, K_p is assumed to be equal to 1 for high water velocities ($>0.5 \text{ m.s}^{-1}$), when the wall shear stress is high enough to extract physically the migrating compounds at the interface.

4 Results and discussion

4.1 Experiments

Before migration experiments even start, the innocuousness of migration bench has been verified by using an inert Teflon pipe as reference. The concentration of TOC has been very close to 0 during two months, proving that no pollution with organic matters comes from the migration bench.

4.1.1 Influence of temperature on migration

Figure 2 shows the concentration of TOC in water over time as a function of temperature and for a velocity of water of 0.6 m.s^{-1} . As expected, the water temperature has a strong impact on migration phenomena. The migrating compounds have been able to move more easily in the more flexible polymer chains as the temperature of the pipe increases.

4.1.2 Influence of water velocity on migration

Figure 3 shows the concentration of TOC in ultrapure water over time as a function of velocity of water at 30°C and 50°C . Some assumptions could be formulated to explain the influence of the velocity on the migration kinetics. The water velocities considered herein are not high enough to have a real impact on the structure of the material. Therefore, at a same temperature, the diffusion coefficient of migrating compounds in the material is the same for each velocity of water. The water velocity could have an influence on the extraction of migrating compounds at the interface between material and water. When the velocity of water is high enough, the wall shear stress could be strong enough to have an impact on the extraction of organic compounds at the surface.

Thus, for very slow velocity of water, the exchange could be determined by chemical equilibrium of migrating compounds concentration between material and water. For higher velocity, the migrating compounds could be physically extracted by the friction of water at the surface of the pipe.

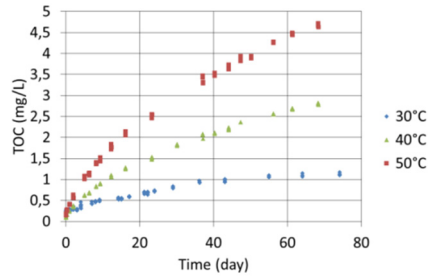


Figure 2: Influence of temperature on migration phenomena.

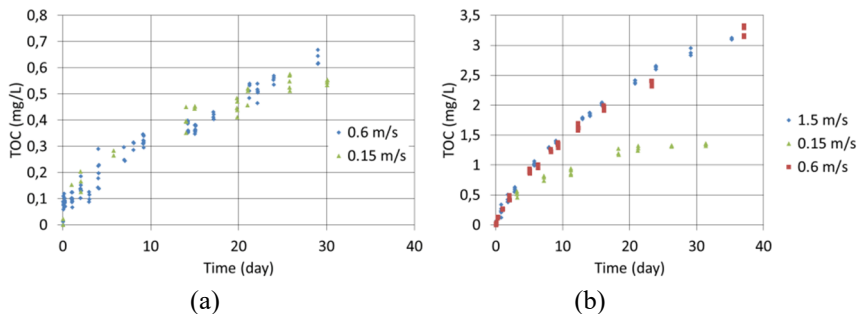


Figure 3: Influence of velocity of water on migration phenomena at 30°C (a) and 50°C (b).

4.2 Modelling

The experimental and modelling evolutions of concentrations of organic matters in the water are compared over time in order to evaluate the modelling method (Figure 4). The diffusion coefficients (Section 3.3.2) and initial concentration of migrating compounds (Section 3.3.1) have been used for the implementation of the model. The partition coefficient has been fixed at 1 for velocity of water equal to 1.5 and 0.6 $\text{m}\cdot\text{s}^{-1}$ and 1000 for velocity equal to 0.15 $\text{m}\cdot\text{s}^{-1}$.

The methodology has allowed to evaluate and to predict the migration phenomena with a good accuracy in these scenarios. The difficulties to measure experimentally the migration in hydrodynamic condition during a long time have not allowed experimentations conducted longer than 3 months. In this way, the robustness of the model has not been test for a longer time. Nevertheless, these results constitute a consistent step in the comprehension of migration phenomena in hydrodynamic conditions.

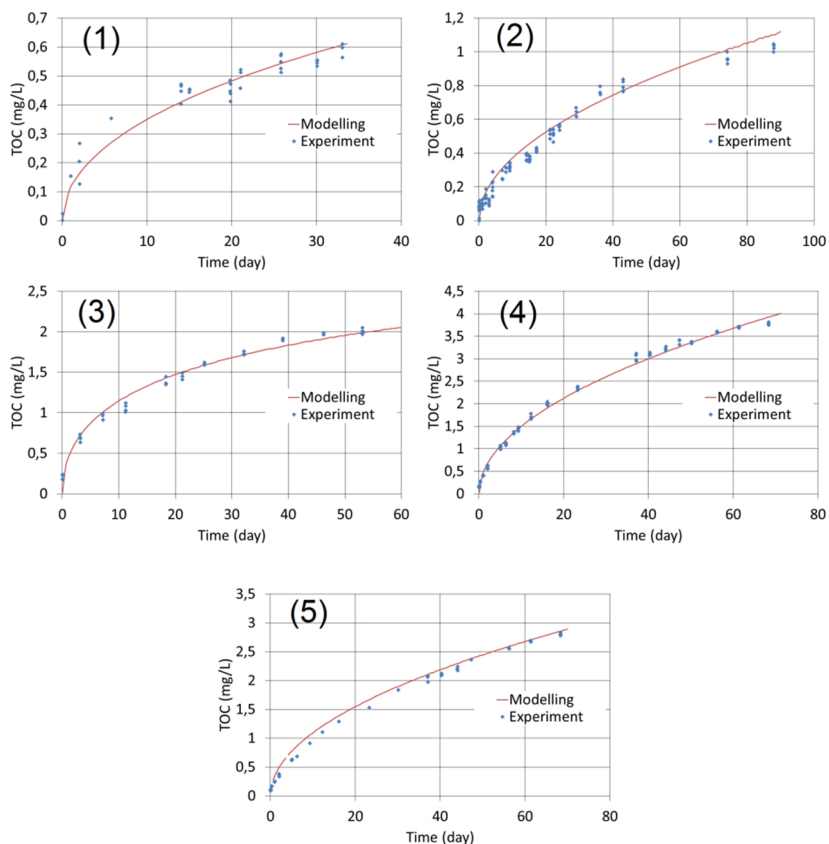


Figure 4: Modelling of migration phenomena in hydrodynamic conditions at different water temperatures and water velocities: (1) 30°C and 0.15 m.s⁻¹, (2) 30°C and 0.6 m.s⁻¹, (3) 50°C and 0.15 m.s⁻¹, (4) 50°C and 0.6 m.s⁻¹(same that 1.5 m.s⁻¹), (5) 40°C and 0.6 m.s⁻¹.

5 Conclusion

The study has shown that temperature and water velocity have an impact on migration phenomena. It has been assumed that, above certain velocities, the water flow could create a friction on the pipe wall which extracts physically the migrating compounds at the interface material/water.

A model has been developed to estimate the migration under realistic operating conditions (temperatures and water velocities) in a domestic installation. The model arguably gives satisfaction on its testing field. It assesses migration through the determination of diffusion and partition coefficients. The temperature has an impact on the diffusion coefficient and the water velocity on the partition coefficient. The diffusion coefficients have been determined using analysis on

experimental data and the partition coefficient has been estimated through assumptions about the solubility of migrating compounds in the water and the mechanical action of water flowing on the exchange surface.

This modelling methodology has a special interest to link mass transfer of organic pollutants to hydrodynamic pattern in a domestic installation. It will be possible, from this approach to evaluate the contribution of pipe materials to water quality in real conditions.

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