Drinking water recontamination in distribution networks: the case of bisphenol A release from epoxy resins

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Abstract
Monitoring and management of drinking water distribution networks (DWDNs), including possible release from materials in contact with drinking water (DW), have been stressed as crucial to avoid DW re-contamination leading to a potential increase of human health risk. Recent scientific studies and regulations clearly highlighted the release of bisphenol A (BPA) from plastic materials used to renovate DWDNs pipelines as one the major hazardous events. Lab tests on three epoxy resins were designed with the Design of Experiments (DoE) method to calibrate a migration model. In order to predict water quality variation in DWDNs, the migration model was combined with a hydraulic model, through EPANET-MSX, and validated in relevant environmental conditions, in collaboration with an Italian water utility. The model allowed to simulate BPA propagation in the DWDN identifying the most vulnerable areas and permitting to customize a site-specific monitoring and intervention plan to minimize the risk.

Keywords
BPA migration tests; design of experiment (DoE); drinking water distribution network (DWDN); epoxy resins; fate modelling; human health risk

INTRODUCTION

Drinking water distribution networks (DWDNs) can cause a relevant deterioration of water quality reaching the tap, with potential human health risk for users (Bruchet et al., 2014). Raising concern has been demonstrated on the release of bisphenol A (BPA), a known endocrine disruptor, from epoxy resins, that are widely used for relining of damaged DWDN pipes (Palmiotto et al., 2015).
Since recent guidelines and regulations on drinking water supply (e.g. EU Parliament, 2018) indicate a new approach for water system management based on the health risk prevention through the whole supply chain, the control of drinking water quality along DWDNs is recommended.
To achieve this goal, in this study, a modelling tool for prediction of BPA release from epoxy resins and fate in DWDNs was developed to evaluate the human health risk and guarantee the optimal DWDN management. Data for model calibration and validation refer to an Italian case study.

MATERIAL AND METHODS

Lab-scale migration tests were performed according to the standard BS EN 12873-2:2005, to calibrate the BPA release model. Lab migration tests were performed on three commercial epoxy resins, characterized by different components formulation, free BPA content and relining technique. Lab tests were designed with the Design of Experiments (DoE) method in order to build a BPA release model as a function of the combination of residual chlorine concentration (0, 0.06, 0.2, 0.34, 0.4, 1 mg/L) and water chemical stability, evaluated as aggressivity index (AI = 11.5, 11.8, 12.5, 13.2, 13.5), to simulate water quality conditions in different locations of the DWDN. Tests lasted about 180 days to account for both short and long-term release. Migration model was validated with literature data, verifying its validity through the Normalized Mean Square Error (NMSE).
An already existing EPANET hydraulic model of the studied DWDN was used, simulating a hydraulic scenario of the average water consumption. EPANET-MSX (Multi-Species eXtension) was used to implement the chlorine decay and BPA release kinetics within the studied DWDN.

Data on renovated pipes sizes and lengths were provided by the water utility. BPA diffusivity and degradation coefficients were taken from the literature (Niesner and Heintz, 2000). A monitoring campaign was carried out from April 2019 to February 2020 to collect data about BPA concentration in the area of the studied DWDN close to two installed epoxy resins.

RESULTS AND CONCLUSIONS

Migration tests showed that, independently from the resin and water conditions, the BPA release can be well described (R^2 between 0.78 and 0.99) by a model combining two first-order kinetics (Eq. 1):

$$BPA(t) = a \cdot e^{b \cdot t} + c \cdot e^{d \cdot t} \quad \text{(Eq. 1)}$$

where BPA(t) [µg/L] is the BPA concentration at time t [h]; $a+c$ [µg/L] represents the BPA concentration at time 0 (BPA_0); b and d [h^{-1}] are the parameters of the first order kinetics. In literature there are no models describing BPA release in water from epoxy resins. However, a first order kinetics equation was already used to describe the release of BPA or other compounds from plastic materials (Fan et al., 2014). BPA release model for resin R1, tested in contact with deionized water and tap water, without residual chlorine and with chlorine concentration at 1 mg/L, is reported in Figure 1a.

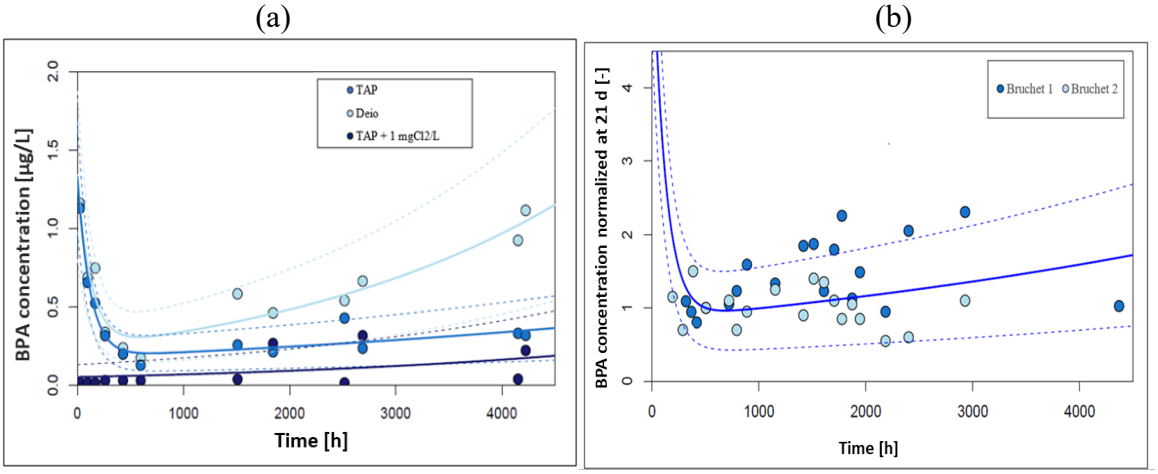

Figure 1. BPA release over time: (a) model calibration: dots correspond to the experimental data with resin R1 as a function of the tested water matrix; (b) model validation of the normalized BPA release in tap water without chlorine: dots correspond to literature data (Bruchet et al., 2014). Solid lines indicate the estimated model, dashed lines represent the models 95% confidence intervals.

BPA concentration decrease after the instantaneous maximum concentration peak up to about 25 days can be well described according to a first order kinetics: the rate of this decay is indicated by the parameter b, which is negative. The initial peak can be attributed to an incomplete polymerization of the resins, seen as surface outcrops of all the parts that make up the mixture and that have not finished reacting, including free BPA. It can be assumed that the BPA concentration decrease is due to the decrease in the amount of free BPA which can leach in water. After around 25 days, the BPA concentration tends to increase again, probably due to material deterioration, again according to a first order kinetics; in fact, the parameter d of the model is positive.

The model on the release of BPA over time in tap water was validated compared to data found in literature (Bruchet et al., 2014). As different surface-to-volume ratio were tested in these two studies, BPA release data were normalized with respect to BPA concentration at 21 days, given in common in these two studies. The output of the validation (Figure 1b) shows that the model is well suited to the experimental data by Bruchet et al., being almost all the validating data points within the 95% confidence interval of the calibrated model, as confirmed by the low NMSE value of 0.17.

An important factor affecting BPA release is the resin free BPA content. In fact, the greater BPA release was found for resin R1 that, due to its formulation and to the lower cross-linking degree, has higher free BPA content (92.1±3.8 µg/g) compared to resin R2 (66.3 µg/g) and R3 (66.0 µg/g). This result has important implications for water utilities. In fact, the measurement of free BPA content in the epoxy resin is fast and can be a first indication for the selection of the best resin to be

installed.
The results of the previous step have shown that both water AI, being deionized water more aggressive than tap water, and chlorine concentration have an effect on BPA release (Figure 1a). Consequently, their combined effect was studied, exploiting the potential of DoE, on: (i) BPA_0 concentration (ii) BPA integral migration (BPA_IM), estimated integrating the BPA leaching model over the tested period. In fact, the initial BPA concentration is fundamental to describe the worst condition and to support water utilities in evaluating potential exceedance of the regulation limit proposed in the European drinking water directive (2.5 µg/L). Moreover, since BPA has chronic health effects on human health, it is fundamental to evaluate the influence of water characteristics on the total BPA mass in water in case of long-time exposures. The resulting models for the two responses as a function of chlorine concentration (mg/L) and water AI (-) (reported in Figure 2) are:

$$BPA_0 = 48.1 - 1.37\,[Cl_2] - 7.27\,AI + 0.28\,AI^2 \quad \text{(Eq. 2)}$$

$$Mass\_BPA = 1026 - 161.5\,[Cl_2] - 64.5\,AI \quad \text{(Eq. 3)}$$

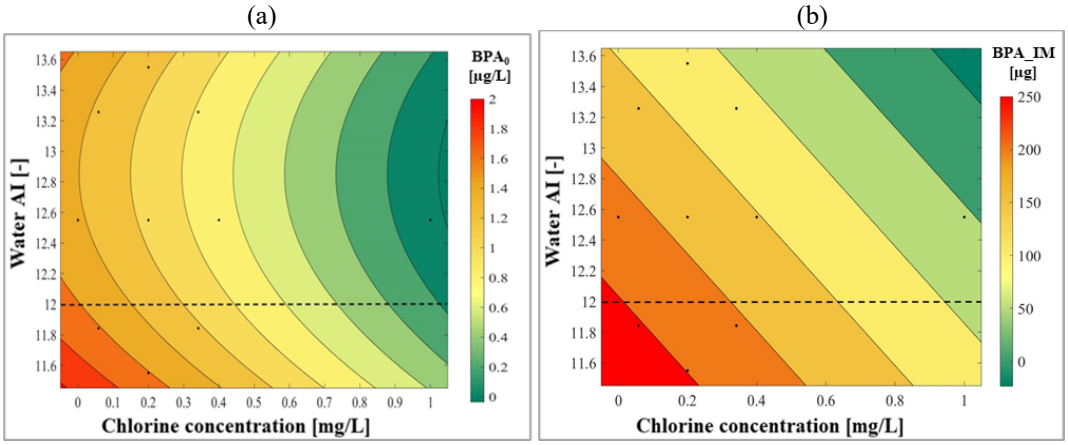

Figure 2. Contour plot of (a) initial BPA concentration, BPA_0 (µg/L), (b) BPA integral migration, BPA_IM (µg), as a function of chlorine concentration and water AI.

Both BPA_0 concentration and the BPA integral migration decrease linearly with increasing chlorine concentration. Several researchers justified the inverse proportion between BPA and chlorine concentrations in water, addressing their reaction to form chlorination by-products of BPA, such as trichlorophenol (TCP) and chloro-bisphenols BPA (Bruchet et al., 2014). To verify this assumption, free BPA content in the epoxy resin before and after the tests has been analyzed. The reduction in resins free BPA content (in the range of 20.7-25.4 µg/g) was found to increase linearly with chlorine concentration, in contradiction with the trend found looking only at BPA concentration in water (Eq. 2 and Eq. 3). Therefore, this is a confirmation that the actual BPA release from epoxy resins is not decreasing with chlorine concentration, but the released BPA is then transformed in its chlorination by-products, causing a reduction in BPA concentration found in water. This evidence suggests that all chlorination by-products should be monitored, in addition to the potentially released resin components, to assess the actual risk to human health in chlorinated water. Aggressive water (AI<12) was found to intensify the release in BPA, therefore, it is important to evaluate the water stability of the area where the epoxy resins should be installed. Finally, the initial BPA concentration was found to be more affected by the chlorine concentration, while water AI has more influence on the integral BPA migration over the whole tested period.
BPA fate through the DWDN close to two pipes renovated with epoxy resins was modelled (Fig. 3).

(a) (b) (c)

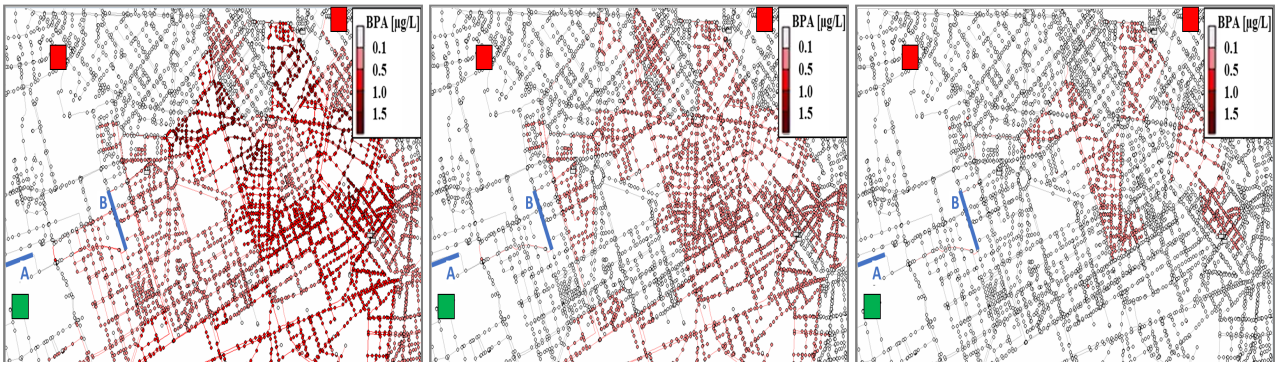

Figure 3. Modelled BPA concentration (µg/L) through a real DWDN in the area close to two epoxy resins (orange segments) as a function of the time from installation after: (a) 5 days; (b) 30 days; (c) 100 days. The DWTP serving the water passing through the renovated pipelines is reported as a green square. Red squares represent DWTPs serving adjacent areas.

Throughout the simulated period, BPA concentration in the affected area ranged from 0 to a maximum of 1.65 µg/L, with median concentration of 0.68 µg/L. Samples collected through a monitoring campaign in the area showed BPA concentrations ranging from below the LOQ (0.015 µg/L) to 0.792 µg/L. The lower measured maximum concentration, compared to the simulated one, is probably due to the fact that the field monitoring campaign started after 290 days from the epoxy resins installation. Therefore, the initial BPA release peak, that is included in the model simulation, was not detected in the monitoring campaign. Both the simulated and measured BPA concentrations in the studied area do not exceed the proposed EU regulation limit (2.5 µg/L). However, it is important to consider that water utilities usually adopt safety factors for planning hazards preventive control measures; in particular, an attention threshold and an alarm threshold, set to 60% and 80% of the regulation limit respectively, are usually used respectively to increase the frequency of monitoring campaign and to stop the operations implementing corrective actions. The maximum achieved concentration in the simulation is 1.65 µg/L, corresponding to 66% of the regulation limit, highlighting the need for frequent sampling and monitoring in the analysed area.
This model, proposed for the first time in literature, is a supporting tool in planning the monitoring campaign identifying the most vulnerable areas in which human health risk is potentially higher. For example, it is interesting to observe (Figure 3) that there are areas close to the installed resins that are characterised by a low risk, because they are likely served by other adjacent DWTPs. Finally, this tool is useful to customize site-specific monitoring and intervention plan and simulate possible future relining scenarios in order to assess and minimize the risk.

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