Evaluation of contaminant retention in the soil of sustainable drainage systems: methodological reflections on the determination of sorption isotherms

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Abstract

Runoff infiltration in Sustainable Drainage Systems enables the interception of a part of urban contaminant fluxes owing to several processes. The soil’s ability to retain dissolved pollutants is generally assessed via sorption isotherms obtained from batch studies; however, the experimental points are not always in the same range as runoff concentrations. The present work (i) explores the consequences of modelling runoff–soil interactions from out-of-range equilibrium concentrations and (ii) proposes an improved method to ensure that experimental points fall within the desired range. Uncertainty analysis demonstrates that for a non-linear isotherm, using an extrapolated relationship may introduce significant biases in the ensuing estimations. Therefore, the proposed method consists of anticipating the equilibrium state of batch tests to accurately set the experimental conditions and reach appropriate concentrations. It is successfully applied to the determination of the sorption properties of copper and zinc onto three soils with different electrolyte solutions, as well as those of bisphenol A and three alkylphenols onto one soil. The contrasting affinities between the studied species and the soil materials could be related to their intrinsic properties and the soils’ pedological parameters, as well as the presence of salt or dissolved organic ligands which partially inhibited metal sorption.

Key words: batch tests, extrapolation, infiltration systems, metals, organic micropollutants, runoff

INTRODUCTION

Soil- and media-based Sustainable Drainage Systems (SuDS), which are primarily implemented for stormwater management, have been proven to offer interesting perspectives for the interception of runoff-generated contaminant fluxes (Napier et al. 2009), both in the particulate and the dissolved phases (LeFevre et al. 2014). Their retention capacities towards solute species, which originate from a combination of various physicochemical mechanisms (including charge-driven interactions with the soil matrix, coordination, chelation and surface precipitation), are often appraised via sorption isotherms, i.e., global, experimental relationships between solute concentrations and amounts sorbed onto...
the soil, at thermodynamic equilibrium (Tran et al. 2017). This approach has been widely used in the case of SuDS; practical applications of sorption isotherms include (i) comparing different materials used for SuDS design (Gülbaz et al. 2015; Huber et al. 2016), (ii) evaluating the overall amount of dissolved contaminants that can be retained by the media layer of existing bioretention facilities (Paus et al. 2014a), (iii) estimating the risks of metal transfer in roadside embankments (Kluge et al. 2014) and (iv) modelling contaminant behaviour within infiltration devices, including event-scale (Winiarski et al. 2013; Zhang et al. 2016) and long-term assessments (Li & Davis 2008; Quinn & Dussaillant 2014).

Batch experiments are among the most common approaches for the determination of sorption isotherms. A batch system consists of a suspension of soil in a given volume of electrolyte solution with a known initial concentration of the species of interest. The solution is maintained at a constant temperature with or without pH buffering. The final state of the system provides one point of the sorption isotherm, i.e., one pair \((C_{eq}, S_{eq})\) where \(C_{eq}\) and \(S_{eq}\) are, respectively, the dissolved and solid concentrations at equilibrium. Theoretical, continuous models are fitted to the series of experimental points. A significant number of batch studies have been published in the past decades concerning the sorption of metals onto various types of soils and specific sorbents in diverse physicochemical conditions (pH, ionic strength, or presence of organic ligands), and to a lesser extent, regarding the sorption of organic micropollutants (Delle Site 2001; Bradl 2004). Beyond the question of data availability, several reservations might be raised concerning the use of literature values (i.e., the fitted parameters of the curves) for the above-mentioned applications on SuDS. Among the different sources of uncertainty in the determination of sorption isotherms, some of which have been discussed by Huber et al. (2016) and Tran et al. (2017), the consistency between the range of equilibrium concentrations and the subsequently modelled situation should be questioned. In concrete terms, if an isotherm is supposed to describe the sorption mechanisms occurring between runoff contaminants and SuDS soil but equilibrium concentrations are not representative of runoff concentrations, then the ‘useful’ part of the curve will derive from an extrapolation (Fallou et al. 2016). For instance, equilibrium concentrations of metals in some cases lie between >1 mg·L\(^{-1}\) and 1 g·L\(^{-1}\) (Genc & Ulupinar 2010; Hararah et al. 2012) while their typical values in urban runoff are one to four orders of magnitude lower (Göbel et al. 2007). Although these ranges may be perfectly suitable for other contexts and types of water, the direct applicability of the isotherms to the case of SuDS soil is probably questionable.

Targeting equilibrium concentrations close to those observed in runoff brings about two difficulties in designing sorption experiments. First, equilibrium concentrations depend not only on the experimental conditions (initial concentration, solid/liquid ratio) but also on the sorption capacity of the soil, which precisely constitutes the unknown of the problem. In addition, equilibrium concentrations can only be measured if they exceed the limit of quantification of the analytical method employed. This second issue may particularly arise for organic micropollutants, frequently present at very low levels in urban runoff (Flanagan et al. 2018); their quantification therefore relies on complex analytical methods which are costly, time-consuming and require large volumes for analysis due to an extraction step.

As thoroughly discussed in the overview article of Bradl (2004), the sorption mechanisms of dissolved metals on soil constituents generally result in a Langmuir-type isotherm at low metal concentrations: in other words, sorption is linear at the very beginning of the curve, due to the absence of competition for sorption sites between solutes, then a concave shape appears as the soil’s sorption sites begin to be saturated. If the metal concentration increases further, surface precipitation may become the predominant retention process. Hence, as symbolized in Figure 1, the situation may be quite different according to the position of the experimental points and the ‘target’ range of concentrations. In the ideal configuration, experimental points match with typical runoff concentrations (a). However, if equilibrium concentrations happen to be too high, they can either be on the ‘plateau’ (b) or still in the linear part of the isotherm (c). In the former case, it cannot be guaranteed that the beginning of the isotherm is correctly represented. However, in the latter case, since the experimental points ‘capture’ the linear
trend, it is reasonable to consider that the observed slope is representative of the lower part of the curve. In the case of pollutants present at very low levels, targeting the linear region of the curve rather than real urban runoff concentrations can enable the use of simplified analytical methods for higher concentrations, thereby reducing the uncertainty, cost and time associated with analysis.

Therefore, the present work aims to explore (i) the potential bias induced by an inadequacy of the equilibrium concentration range and (ii) how experiments can be designed in order to ensure representative data. An improved experimental method is proposed in order to maximize the chance to reach appropriate concentrations. The approach relies on a parametric study of a batch system coupled with an a priori estimation of the soil’s retention capacities: this enables to theoretically anticipate the equilibrium state of the systems, and thus to adequately select the experimental conditions of the tests (initial concentrations and solid/liquid ratio). The interest and applicability of this method is investigated in the practical case of SuDS, examining two situations with different contexts and constraints:

• First, the sorption behaviour of two metals (copper and zinc) is evaluated for three SuDS soils, in the absence and in the presence of sodium chloride and dissolved organic acids.
• Then, the sorption behaviour of four organic micropollutants (bisphenol A (BPA) and several alkylphenols: 4-tert-octylphenol (4-t-OP), 4-nonylphenol (4-NP), and nonylphenol ethoxylate (NP10)) is examined for one soil.

These contaminants have been selected because they are ubiquitous in urban runoff, with different concentration levels, and constitute a contrasting panel of physicochemical properties (Flanagan et al. 2018). The addition of NaCl and organic acids illustrates the potential variability of metal retention processes due to either seasonal practices (deicing salt application) or natural generation of dissolved organic matter in the soil solution (Bäckström et al. 2004). The uncertainties associated with the extrapolation of a non-linear isotherm at low concentrations are then assessed and discussed.

MATERIALS AND METHODS

Soil materials

Study sites, sampling methodology and soil preparation

The characterized soils originated from three different infiltration devices in the Paris region (France). The first two sites are a newly constructed swale and a 4-year-old filter strip, both of which are located...
alongside a heavily trafficked highway (11,000 vehicles/day in each direction), and the third one is an infiltration basin with a relatively long operation time (~15 years) in a 2-ha residential catchment. The swale (site 1) is made up of a mixture of lime sand and topsoil, the filter strip (site 2) is made up of a silt loam soil, whereas the infiltration basin (site 3) was implemented upon the pre-existing soil (sandy clay loam). A 2-kg composite sample of uncontaminated filter media was collected prior to the construction of site 1. However, the soil of sites 2 and 3 was already partially contaminated due to the devices’ operation over several years: hence, in order to guarantee a minimal contamination of the collected samples, a preliminary field campaign was carried out to characterize the spatial variability of metal contents in the surface horizon (Tedoldi et al. 2017a). Subsequently, four subsamples were collected over a 15-cm depth in the least contaminated area of the facilities, assuming that the soil in this area was close to the initial state of the sites, so as to form 2-kg composite samples.

The soil samples were oven-dried (40 °C), gently broken by hand, then passed through a 2-mm nylon sieve. For all subsequent physicochemical analyses and batch tests, the required mass of soil was obtained by careful mixing and quartering. As regards the sorption experiments, soil 1 was characterized for metals and organics, whereas soils 2 and 3 were characterized for metals only.

Soil characteristics

All physicochemical analyses were carried out in a laboratory with COFRAC (French Accreditation Committee) certification. Soil pH was determined in a solution of soil and ultrapure water (volumetric ratio of 1:5) after 1 hour of equilibration (ISO 10390 2005). The carbonate content was determined by adding hydrochloric acid (4 M) and measuring the volume of CO₂ produced with a Scheibler apparatus (ISO 10695 2014). The fraction of organic carbon (f OC) was determined via dry combustion at 950 °C (ISO 10694 1995). The volatile matter content was calculated from mass difference after calcinating subsamples (~15 g) at 550 °C for 6 hours. So as to determine the cation exchange capacity (CEC), subsamples were saturated with ammonium (1 M), which was subsequently released by ion exchange with a NaCl solution (1 M) and analysed by spectrophotometry (NF X31-130 1999). Metal concentrations were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) after total acid digestion (HF + HClO₄), according to the standard NF X31-147 (1996). Concentrations of organic pollutants were evaluated for soil 1 following microwave extraction using ultra-performance liquid chromatography–tandem mass spectrometer. The geochemical background of soils 2 and 3 was estimated from deep soil sampling and analysis in previous assessments (Flanagan et al. 2017; Tedoldi et al. 2017b). In the following developments, all soil concentrations are expressed in milligrams per kilogram of dry matter.

Table 1 summarizes the main characteristics of the soil materials. Organic carbon and volatile matter classify in the following order: soil 1 < soil 2 < soil 3, which is probably linked to both the nature of the original soil and the operation time of the devices (increasing humus production at the soil surface). The order is the same for CEC and clay content, even if the measured values are quite comparable between soils 2 and 3. The three soils have an alkaline pH, which in the case of soil 1 is related to a high carbonate content (24% w/w), contrary to the other two materials for which total carbonates contents remain ~3%; their high pH values may be related to their ability to fix hydrogen cations. The fraction of the initial metal contents that could be attributed to either atmospheric or runoff-generated contamination was found to be low (Table 1).

Selection of the experimental conditions

Parametric study of a batch system

Each batch system consists of a mass M of suspended soil [kg] in a volume V of electrolyte [L] with an initial concentration Cᵢ of the species of interest [mg·L⁻¹] (the experiments are conducted in
monospecific solutions). As stated in the Introduction, the main objective of the proposed methodology is to ensure that equilibrium concentrations $C_{eq}$ [mg·L$^{-1}$] fall within the desired range, by anticipating the equilibrium state. Assuming, as a first approximation, that sorption can be accurately described by a linear model, the partition coefficient of which is referred to as $K_D$ [L·kg$^{-1}$], the expected $C_{eq}$ has an analytical expression (Equation (1)) which derives from a mass balance coupled with the equilibrium relationship $S_{eq} = K_D \cdot C_{eq}$.

$$C_{eq} = \frac{S_i + V}{M} \cdot \frac{C_i}{K_D + \frac{V}{M}}$$

(1)

where $S_i$ and $S_{eq}$ are, respectively, the initial and equilibrium contents on the soil [mg·kg$^{-1}$]. Figure 2 displays the theoretical values of $C_{eq}$ as a function of $K_D$ and $C_i$, for two different values of the $M/V$ ratio.

The purpose of the subsequent developments is to estimate a priori the order of magnitude of $K_D$, in order to set the experimental parameters $C_i$ and $M/V$ according to the 'target' concentrations. The latter will be defined with a different strategy for metals and organic compounds.

**A priori estimation of $K_D$ and selection of the initial concentrations**

**Metals.** In the case of metals, the objective was to obtain equilibrium concentrations covering the full range of concentrations expected in runoff, as presented in Figure 1(a). The estimation of $K_D$ was based upon the method proposed by Massoudieh & Ginn (2008), who assumed that equilibrium between runoff and surface soil had been reached in their study site: hence, they considered that the ratio between the metal content measured in the upper horizon ($S_{surface}$) and the dissolved concentration measured in runoff water ($C_{diss \ runof}$) could be retained as a $K_D$ value for

| Table 1 | Main physical and physicochemical properties of the characterized soils |
|-------------------------------|--------------------------|--------------------------|--------------------------|
| **Soil 1** | **Soil 2** | **Soil 3** |
| Texture (USDA classification) | Sandy loam | Silt loam | Sandy clay loam |
| Sand [%] | 72 | 10 | 47 |
| Silt [%] | 18 | 67 | 25 |
| Clay [%] | 10 | 23 | 28 |
| Bulk density [kg·dm$^{-3}$] ($N = 5$) | 1.5 ± 0.1 | 1.2 ± 0.1 | 1.1 ± 0.1 |
| Saturated water content [cm$^3$·cm$^{-2}$] ($N = 5$) | 0.36 ± 0.07 | 0.44 ± 0.04 | 0.47 ± 0.05 |
| Organic carbon ($f_{OC}$) [g·kg$^{-1}$] | 8.7 | 17.8 | 41.6 |
| Volatile matter [g·kg$^{-1}$] | 30 | 51 | 85 |
| CEC [cmol$_{-}$·kg$^{-1}$] | 5.1 | 11.8 | 13.6 |
| pH$_{water}$ | 8.7 | 8.7 | 8.2 |
| Carbonates [g·kg$^{-1}$] | 240 | 29 | 32 |
| Cu content (background) [mg·kg$^{-1}$] | 13 | 16 (14) | 15 (11) |
| Zn content (background) [mg·kg$^{-1}$] | 31 | 59 (48) | 72 (51) |
| BPA content [mg·kg$^{-1}$] | <0.01 | – | – |
| 4-t-OP content [mg·kg$^{-1}$] | <0.007 | – | – |
| 4-NP content [mg·kg$^{-1}$] | 0.15 | – | – |

The geochemical background of soils 2 and 3 is indicated in brackets. The concentration of NP-10 is not available.
their modelling approach:

$$K_D = \frac{S_{\text{surface}}}{C_{\text{diss}}^{\text{runoff}}}$$  \hspace{1cm} (2)

In the present work, the maximum surface contents of copper and zinc were available from the preliminary investigations in sites 2 and 3. As to site 1, the short operation time of which did not enable the same approach, another 4-year-old filter strip alongside the same highway, constructed with a very similar material, was used as a surrogate (Flanagan et al. 2017). However, the problem with the term $S_{\text{surface}}$ in Equation (2) is that the measured contents in the solid phase result from both solute sorption onto the soil and sediment accumulation at the surface, the former being the only element of interest. It was thus assumed that the fraction of $S_{\text{surface}}$ attributable to sorption equalled the dissolved fraction in runoff, as a result of which $K_D$ could also be estimated as the ratio of total concentrations. Although this hypothesis might be not totally accurate, it will be shown to be sufficient to determine an order of magnitude of the partition coefficient. Typical literature values of the total runoff concentrations were considered – corresponding to equivalent land uses, i.e., 100 $\mu$g·L$^{-1}$ for copper and 400 $\mu$g·L$^{-1}$ for zinc in both sites 1 and 2 (Göbel et al. 2007) and 50 $\mu$g·L$^{-1}$ for copper and 200 $\mu$g·L$^{-1}$ for zinc in site 3 (Bressy et al. 2014).

The calculated $K_D$ ($2\times10^3$ L·kg$^{-1}$ for zinc and $4\times10^3$ L·kg$^{-1}$ for copper) are represented with vertical lines in Figure 2. For the sorption experiments, the target concentrations were $\leq400$ $\mu$g·L$^{-1}$ for zinc and $\leq100$ $\mu$g·L$^{-1}$ for copper. Combining the $K_D$ predictions and the curves displayed in Figure 2, the $M/V$ ratio was set to 5 g·L$^{-1}$ in order to avoid excessive initial concentrations, and the retained range for $C_i$ was 0–3 mg·L$^{-1}$ for copper and 0–6 mg·L$^{-1}$ for zinc with soils 1 and 2, and 0–10 mg·L$^{-1}$ for copper and 0–20 mg·L$^{-1}$ for zinc with soil 3.

**Organic micropollutants.** Contrary to metals, equilibrium concentrations of organic micropollutants corresponding to realistic values in urban runoff were not targeted, since the studied compounds are usually found at low levels, i.e., [BPA] and [alkylphenols] $\leq1$ $\mu$g·L$^{-1}$ (Flanagan et al. 2018). Quantification in this range typically requires an extraction step and analysis by high performance
liquid chromatography coupled to tandem mass spectrometry (HPLC-MS/MS), which is expensive and time-consuming due to the many steps in the analytical process (filtration, extraction, injection, integration). As it can reasonably be assumed that the low concentrations observed in runoff for these pollutants are well below the transition from the linear to the non-linear behaviour of the isotherm (Delle Site 2001), the choice was made to target higher concentrations and to verify a posteriori that the experimental points were still in the linear part of the curve (Figure 1(c)). This allowed the use of a simplified but more robust analytical method, which eliminates the need for an extraction step. Hence, all organic compounds were analysed by direct injection of water samples in HPLC-UV (UV detection at 228 nm) (Chunshan et al. 1990; Bernacka et al. 2009). The limit of detection of BPA and NP10 was 20 μg·L⁻¹, and those of 4-NP and 4-t-OP were 35 and 80 μg·L⁻¹, respectively, so the target equilibrium concentrations were chosen accordingly. The subsequent method was the same as for metals, i.e., the expected $C_{eq}$ were estimated from various initial concentrations ($C_i$) and for different values of the $M/V$ ratio, as a function of the a priori $K_D$ of the soil relative to each compound.

For organic molecules, it is common practice to estimate a $K_D$ value from an organic carbon partition coefficient ($K_{OC}$) and the soil’s fraction of organic carbon ($f_{OC}$) according to Equation (3) (Delle Site 2001):

$$ K_D = K_{OC} \cdot f_{OC} $$  

Previsouly reported log $K_{OC}$ values vary in the range 2.06–3.59 for BPA (U.S. National Library of Medicine 2018), 3.44–4.03 for 4-t-OP (UE 2005) and 4.70–5.60 for 4-NP (Bergé et al. 2012); however, data availability appeared to be nonexistent for NP10. Considering the fraction of organic carbon in soil 1 (8.7 g·kg⁻¹), this corresponds to $K_D$ values of 1–34 L·kg⁻¹ for BPA, 24–93 L·kg⁻¹ for 4-t-OP and 436–3,460 L·kg⁻¹ for 4-NP.

Combining $K_D$ estimations and predicted equilibrium concentration curves, the $M/V$ ratio was set to 100 g·L⁻¹. The retained range for $C_i$ was 0.2–3.0 mg·L⁻¹ for BPA and 1–10 mg·L⁻¹ for 4-t-OP, 4-NP and NP10. The same experimental conditions as those for 4-NP were chosen for NP10 due to the lack of available knowledge about this molecule.

**Experimental procedure**

Details on all reagents used in the experiments are provided in Table S1, Supplementary material. As specified above, metal sorption was investigated in the three soils whereas the sorption behaviour of organic micropollutants was assessed for soil 1 only. Seven different initial concentrations were considered for metals and five for BPA and alkylphenols. All sorption tests were preceded by a 24-hour pre-equilibration phase, during which a suspension of 5.00 ± 0.01 g of dry soil was incorporated in the electrolyte solution under constant agitation (500 rpm); the volume of solution was different for metals and organics, according to the retained $M/V$ ratio (1 L and 50 mL, respectively). The electrolyte solution corresponded to diluted mineral water (Evian and ultrapure water, volumetric ratio of 1:10), the composition of which approximately mimicked runoff composition – as reported by Göbel et al. (2007). This will be hereafter referred to as the ‘reference condition’, since two additional electrolyte solutions were tested for metals.

All experiments were carried out in non-competitive conditions (i.e., individual contaminants in each batch system), considering duplicates for metals in the reference condition, and single runs in the other cases. At the beginning of the experiments, the batch systems were spiked with stock solutions of the reagent of interest to reach the desired initial concentrations $C_i$. Aliquots were collected after 24 hours of equilibration, and underwent a different preparation according to the contaminant considered, as described in the subsequent paragraphs. The temperature was maintained at...
21 ± 2 °C, and the pH of the solution was not buffered; it was measured in each batch system at the beginning and at the end of the experiments.

Blank samples (soil without addition of contaminants) and spike samples (contaminants without addition of soil), were also considered so as to check the absence of experimental biases or interferences, such as adsorption onto the bottles or sample contamination. None of these effects was observed.

Reaction kinetics were determined by collecting aliquots after different contact times (2, 20, 40, 60 min, 2, 4, 6, 8, 24 and 48 hours), which confirmed that equilibrium was reached within the 24-hour duration of the experiments. The results are presented in the Supplementary material.

Metals

The tests were undertaken in high-density polyethylene bottles. At the end of the experiments, the aliquots were collected with a polyethylene syringe, filtered at 0.45 μm with a cellulose acetate syringe filter (Whatman), acidified with 0.3 mL HNO₃ (65%), then stored in polyethylene tubes at 4 ± 1 °C prior to analyses by ICP-AES. Two additional series of tests were carried out with soils 1 and 3, adding (i) 1.0 g·L⁻¹ of sodium chloride and (ii) 10 mg·L⁻¹ of humic acids to the electrolyte solution prior to the pre-equilibration phase. These values were chosen in accordance with the measurements of Bäckström et al. (2004) in the soil solution of roadside infiltration systems; the NaCl concentration is also consistent with the experimental conditions retained by Paus et al. (2014b) to investigate the effects of road salt on metal mobility in bioretention systems.

Just before metals were added, the pH was 7.6 ± 0.1, 7.6 ± 0.1 and 7.5 ± 0.1 for soils 1, 2 and 3, respectively; in the final state, it was 7.6 ± 0.2, 7.5 ± 0.1 and 7.4 ± 0.2, respectively.

Organic micropollutants

The tests were performed in glass bottles, in a controlled room (21 °C) and in the dark to avoid any photodegradation of organic compounds. Prior to the tests, all glassware was washed using TFD-4 detergent (free of any trace of bisphenol A or alkylphenols), rinsed with purified water (Milli-RO Millipore) and calcined at 500 °C for 2 hours. Stock solutions of organic compounds were prepared in methanol to favour their dissolution (<5% methanol to avoid any influence on the sorption processes). Sodium azide (Roth, >99%), a biocide, was added to each batch sample at a concentration of 200 mg·L⁻¹ to limit the biodegradation of organic compounds (Navarro et al. 2009; Liao et al. 2014; Liping et al. 2014). At the end of the experiments, the collected aliquots were filtered on binder-free glass microfibre filters (GF/F Whatman) before analysis by HPLC-UV.

The pH of the solution was 8.0 ± 0.1 at the beginning and at the end of the experiments.

Data analysis: sorption isotherms

For each batch system, the sorbed amount of contaminant ∆S [mg·kg⁻¹] was calculated from a mass balance:

\[ \Delta S = \frac{(C_i - C_f)V}{M} \]  

(4)

where \( C_f \) is the concentration in the collected aliquot (which corresponds to \( C_{eq} \) for the sorption tests) [mg·L⁻¹]. The solid content was then calculated as \( S_{eq} = S_i + \Delta S \) where \( S_i \) is the initial content of the soil [mg·kg⁻¹]. The data are available online (Tedoldi et al. 2019).

The experimental relationships between \( C_{eq} \) and \( S_{eq} \) were fitted with the three most common theoretical models, namely, the linear (Equation (5a)), Langmuir (Equation (5b)) and Freundlich
(Equation (5c)) isotherms:

\[ S_{eq} = K_D \cdot C_{eq} \]  
\[ S_{eq} = S_{max} \frac{K_L \cdot C_{eq}}{1 + K_L \cdot C_{eq}} \]  
\[ S_{eq} = K_F \cdot C_{eq}^n \] 

where \( K_D \) is a solid–liquid partition coefficient \([\text{L}\cdot\text{kg}^{-1}]\), \( S_{max} \) is the maximum (monolayer) sorption capacity of the sorbent in Langmuir’s formalism \([\text{mg}\cdot\text{kg}^{-1}]\), \( K_L \) is a scale parameter \([\text{L}\cdot\text{mg}^{-1}]\), \( K_F \) is the Freundlich constant \([\text{mg}^{1-n}\cdot\text{kg}^{-1}\cdot\text{L}^n]\) and \( n (\leq 1) \) is a shape parameter \([-]\). Other significant relationships can be found in the literature to model the sorption isotherms, such as the Redlich–Peterson, Sips, Toth or Koble–Corrigan equations, all of which introduce three parameters (Foo & Hameed 2010). Considering the number of data points, it was decided to use a parsimonious approach and to retain models with one or two parameters. All parameters were fitted via a non-linear optimization technique with a quadratic error criterion.

**RESULTS AND DISCUSSION**

**Sorption isotherms**

**Metals**

Figure 3 presents the sorption isotherms of copper and zinc for the three soil materials in the reference conditions, i.e., without sodium chloride or humic acids, and Figure 4 displays the sorption isotherms of zinc onto soils 1 and 3, in varying physicochemical conditions. Whatever the electrolyte solution, the linear model (Equation (5a)) satisfactorily fitted the experimental data for copper in the range of equilibrium concentrations \((\leq 60 \mu\text{g}\cdot\text{L}^{-1}\) for soils 1 and 2 and \((\leq 320 \mu\text{g}\cdot\text{L}^{-1}\) for soil 3). Conversely, the concavity of the curve was visible for zinc at equilibrium concentrations >100 to 200 \(\mu\text{g}\cdot\text{L}^{-1}\),

![Figure 3](https://iwaponline.com/bgs/article-pdf/1/1/1/597946/bgs0010001.pdf)
as a result of which the best fit was achieved with either a Freundlich or a Langmuir equation (Equations (5b) and (5c)). The parameters of the fitted models are summarized in Table 2 for both metals.

**Figure 4** | Sorption isotherms of zinc onto (a) soil 1 and (b) soil 3, in the three different experimental conditions (reference, 1.0 g L⁻¹ of sodium chloride, and 10 mg L⁻¹ of humic acids): experimental points and adjusted theoretical models.

**Table 2** | Parameters of the sorption isotherms for metals onto the three soil materials

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<thead>
<tr>
<th>Soil 1</th>
<th>Copper</th>
<th>Zinc</th>
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<tbody>
<tr>
<td>Ref.</td>
<td>$K_D$</td>
<td>$n$</td>
</tr>
<tr>
<td>NaCl</td>
<td>$9.8 \times 10^3$</td>
<td>0.98</td>
</tr>
<tr>
<td>HAb</td>
<td>$1.4 \times 10^4$</td>
<td>0.96</td>
</tr>
<tr>
<td>HA³</td>
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<th>Zinc</th>
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<td>0.98</td>
</tr>
<tr>
<td>NaCl</td>
<td>$6.1 \times 10^3$</td>
<td>0.99</td>
</tr>
<tr>
<td>HAb</td>
<td>$6.1 \times 10^3$</td>
<td>0.96</td>
</tr>
<tr>
<td>HA³</td>
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<tr>
<th>Soil 3</th>
<th>Copper</th>
<th>Zinc</th>
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<tbody>
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<td>0.99</td>
</tr>
<tr>
<td>NaCl</td>
<td>$6.1 \times 10^3$</td>
<td>0.96</td>
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<tr>
<td>HAb</td>
<td>$4.8 \times 10^3$</td>
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</tbody>
</table>

- Sodium chloride and humic acids both limited zinc sorption onto soils 1 and 3, as demonstrated by the graphs and the adjusted parameters $K_F$ and $S_{max}$, which reflect the soil/metal affinity, and vary in the order reference > NaCl > humic acids (Table 2). The influence of NaCl on the sorption isotherm became visible at concentrations $C_{eq} \geq 100$ to 200 μg L⁻¹; this occurred at $C_{eq} \geq 100$ to 400 μg L⁻¹ with humic acids. For copper, the partition coefficient $K_D$ was ~20% lower in the presence of humic acids, for both soils. However, NaCl did not seem to influence copper sorption onto soil 3, at least at a concentration of 1 g L⁻¹, and for soil 1, this metal even appeared to be slightly better removed from the aqueous solution in the presence of NaCl.

- Essentially, the retention of solute metals in soils is attributable to three classes of processes: (i) non-specific, charge-driven interactions with negative surfaces of the soil matrix such as clays; (ii) coordination or chelation bonds formed with surface functional groups, especially due to the soil organic matter; and (iii) precipitation (Tedoldi et al. 2016). The importance of the first two categories of
mechanisms is generally appraised through the soil’s CEC and organic/volatile matter fraction, respectively, which in the present case range in the order soil 1 < soil 2 < soil 3. This sequence also corresponds to the retention of zinc (Figure 3(b)), as observed in previous batch studies (Sastre et al. 2007). Nevertheless, as can be seen in Figure 3(a), the retention potential of copper onto the three soil materials decreased in the opposite order (soil 1 ≈ soil 2 > soil 3), indicating the prevalence of an additional retention mechanism.

Soils 1 and 2 are characterized by high pH, and high carbonate content for the former one (Table 1). This is likely to favour Cu hydrolysis and precipitation (mainly in the form CuCO₃), which occur at a lower pH than for zinc (Calvet 2013), as confirmed by Genç-Fuhrman et al. (2007) with speciation calculations on PHREEQC. This interpretation is also supported by the fact that increasing ionic strength (with the addition of NaCl) led to higher copper removal from the batch systems with soil 1, while zinc removal was lessened, in accordance with the theory of ion exchange (Sposito 2008). In view of this, Huber et al. (2016) suggested that undertaking sorption experiments at pH 5 would prevent all precipitation mechanisms and isolate the contribution of metal adsorption onto the soil surface. Yet, stormwater runoff from traffic areas is generally characterized by a near neutral pH (Göbel et al. 2007) which tends to an equilibrium with the soil pH during infiltration, thus precipitation could also participate in metal retention in SuDS; therefore, performing sorption experiments without using a buffer to control the pH may be suitable as well to investigate and quantify the thorough retention mechanisms. Additionally, Genç-Fuhrman et al. (2007) considered that a low pH value may influence the heavy metal speciation in a way not realistic for stormwater.

**Organic micropollutants**

Figure 5 presents the sorption isotherms of the four organic compounds on soil 1. In accordance with the pursued objective, the linear part of the isotherm was indeed visible for all micropollutants. However, when considering the entire range of equilibrium concentrations, curves showed concavity and were best described by non-linear models. The corresponding parameters are given in Table 3. Substantial differences were obtained between the four organic compounds, the sorption of which

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**Figure 5** | Sorption isotherms of organic micropollutants for soil 1: experimental points and adjusted theoretical models: (a) non-linear relationships in the complete range of equilibrium concentrations, (b) linear isotherm at low concentrations.
decreased in the order NP10 > 4-NP > 4-t-OP > BPA, as reflected by the differences between the parameters $K_F$ or $S_{\text{max}}$.

The high retention of the previously uncharacterized NP10 can be explained by its high molecular weight (centred on 660 g·mol$^{-1}$) and long-chain ($n = 10$) molecular structure compared to the other compounds. As to the other compounds, the order is consistent with the reported behaviour and $K_{OC}$ values from the literature. 4-NP and 4-t-OP have similar molecular structures, but 4-NP is an isomeric compound while 4-t-OP corresponds to a single structure, which could explain the higher retention observed for 4-NP, i.e., by the adaptation of the 4-NP isomers to multiple types of sorption sites (Navarro et al. 2009).

### Interest of the proposed experimental approach

**Agreement of equilibrium concentrations with the ‘target’ values**

The main purpose of the developed methodology was to ensure that the obtained isotherms could be accurately used for modelling a situation with usual runoff concentrations. For copper, the a priori estimates of $K_D$ differed by less than an order of magnitude from the a posteriori values (Table 2). As a result, equilibrium concentrations ranged from 0 to 60 $\mu$g·L$^{-1}$ in the first two cases and 0 to 320 $\mu$g·L$^{-1}$ in the third one, which, overall, fell within the target range. As for zinc, despite the unsuitability of the linear model to describe the whole isotherms, a $K_D$ value $\gamma$, referred to as ‘$K_{D,\text{ini}}$’ in Table 2, could still be determined in the lower part of the curves (first 4 to 5 points), where the linear trend was valid. The initial slope was equal to 2.7, 13 and $6.8 \times 10^3$ L·kg$^{-1}$·mg$^{-1}$ for soils 1, 2 and 3, respectively, while the estimated $K_D$ fell between 2 and $8 \times 10^3$ L·kg$^{-1}$. This relative agreement enabled the isotherms to be fitted with equilibrium concentrations $\leq 600$ $\mu$g·L$^{-1}$, except for the extreme point of each isotherm.

For organic compounds, the lowest experimental points fell within the linear part of the isotherm (Figure 1(c)). Extrapolating the observed linear trend to the very beginning of the curve may be used to represent sorption at runoff concentrations, considering that the $K_{D,\text{ini}}$ value remains valid at lower concentrations. Just like for metals, these values (Table 3) were relatively consistent with the pre-estimations derived from literature data. The a posteriori values of the organic carbon partition coefficient ($K_{OC}$) for each molecule, calculated from Equation (3), are also presented in Table 3.

### Uncertainty analysis

Ensuring that isotherms are representative of the concentrations observed in the field constrains the design of batch experiments. To understand why it is important to do so, the present section aims to better characterize the uncertainties which affect an interpolated and an extrapolated $C - S$ relationship. A stochastic method was carried out, the reference case of which corresponded to the isotherm of zinc onto soil 3 (referred to as ‘$\varphi$’ in the subsequent developments), considered as the ‘true’
relationship for this soil. Random variables were used to mimic sorption experiments leading to different intervals of equilibrium concentrations $[C_{\text{low}_{\text{min}}}, C_{\text{low}_{\text{max}}}]$ and $[C_{\text{high}_{\text{min}}}, C_{\text{high}_{\text{max}}}]$, the first one being representative of usual runoff concentrations ($C_{\text{low}_{\text{min}}} = 10 \, \mu \text{g} \cdot \text{L}^{-1}$ and $C_{\text{low}_{\text{max}}} = 400 \, \mu \text{g} \cdot \text{L}^{-1}$), and the second one requiring an extrapolation of the isotherm ($C_{\text{high}_{\text{min}}} = 0.5 \, \text{mg} \cdot \text{L}^{-1}$ and $C_{\text{high}_{\text{max}}} = 20 \, \text{mg} \cdot \text{L}^{-1}$).

For each range, the following procedure was applied 2,000 times:

1. Seven values $C_{\text{sim}_{\text{eq}}_{\text{i}}}$ were randomly sampled from a uniform distribution $U([C_{\text{min}}, C_{\text{max}}])$, to simulate the reached equilibrium concentrations in the seven batch systems.

2. The corresponding sorbed contents were evaluated according to Equation (6):

$$S_{\text{sim}_{\text{eq}}_{\text{i}}} = \varphi(C_{\text{sim}_{\text{eq}}_{\text{i}}}) + e_i$$

where $e_i \sim N(0, \sigma^2)$ is an error term which represents the experimental uncertainties: for each soil, the residuals between the experimental points and the reference isotherm were tested for normality (Shapiro–Wilk test, $p > 0.5$) and the residual standard error was calculated; the average value of $\sigma = 40 \, \text{mg} \cdot \text{kg}^{-1}$ was retained for the present analysis.

3. A Langmuir isotherm was fitted to the series of points $(C_{\text{sim}_{\text{eq}}_{\text{i}}}, S_{\text{sim}_{\text{eq}}_{\text{i}}})$ with the same optimization technique as described in the Material and methods section.

The 2,000 iterations enabled the computation of 95% confidence intervals for the sorption isotherm, considering the two different ranges of concentrations (Figure 6).

This figure illustrates the link between the range of experimental points and the magnitude of the resulting uncertainties. In the case equilibrium concentrations are $\leq 0.4 \, \text{mg} \cdot \text{L}^{-1}$ (pale envelope), the fitted isotherm has a satisfying accuracy in this range – which meets the objective set considering metal sorption in SuDS – but may be inappropriate to model the soil’s behaviour at higher concentrations. The opposite configuration occurs when the experimental points lie in a high range (dark envelope), leading to a poor precision in the presently targeted part of the curve (i.e., at low concentrations). The differences can be further exemplified by comparing the retardation factors in a

![Figure 6](https://iwaponline.com/bgs/article-pdf/1/1/1/597946/bgs0010001.pdf)
saturated soil. When modelling reactive transport in a homogeneous media, this parameter, which intervenes in the advection–dispersion equation, corresponds to the ratio between the migration velocity of a non-reactive tracer and the migration velocity of the considered species (subject to sorption). It is calculated as:

\[
R = 1 + \frac{\rho}{\theta_s} \frac{\partial S_{eq}}{\partial C_{eq}}
\]  

(7)

where \( \rho \) is the soil’s bulk density and \( \theta_s \) is the saturated water content. Because of the concavity of the curve, the derivative \( \frac{\partial S_{eq}}{\partial C_{eq}} \) has been estimated as the initial slope, describing the sorption behaviour at low concentrations. The value of \( R \) is thus expected to lie between 15,000 and 18,000 when the isotherm is interpolated. Conversely, this range turns out to be 11,000–33,000 when it is extrapolated from high concentrations: in other words, metal breakthrough may be predicted to occur twice too soon or twice too late compared to what it actually does. Hence, regarding the practical case of contaminant transfer in SuDS soil, the proper representation of solute transport appears to be critically dependent upon a careful determination of the isotherm, as long as an empirical approach is retained for sorption. Otherwise, the interest of refining the description of the system and processes (e.g., accounting for non-equilibrium flow, particulate transport or non-uniform infiltration at the soil surface) may be questioned in view of the uncertainties generated by the inaccurate \( C/S \) relationship.

Possible alternatives for the pre-estimation of sorption isotherms

The results emphasized the importance of pre-estimating whenever possible the sorption capacities of the characterized soil materials in order to reach the desired final state of the batch systems. However, previously contaminated samples, such as those for metals in the present study, are not always available. When they are not, alternative approaches are required to pre-estimate the soil’s retention capacities. The first option would be to carry out two-step sorption experiments, the first one being a preliminary assessment aimed to refine the expected range of \( K_D \) and to optimally set the subsequent experimental conditions. For this first step, two or three batch systems, each one differing by an order of magnitude in \( C_i \), are likely to be sufficient.

However, as this approach may turn out to be quite onerous and time-consuming, especially to analyse organic micropollutants at low concentrations, it would be useful to indirectly assess \( K_D \) or any other parameter of the sorption isotherm. For organic compounds, this can be suitably done using the parameters \( K_{OC} \) and \( f_{OC} \) as shown in the present study. Similarly, attempts have been made to demonstrate correlations between basic pedological properties and the soil’s sorption capacities towards metals (Sastre et al. 2007), or even to establish pedotransfer functions (Horn et al. 2005; Vega et al. 2010). Soil pH, clay content, CEC and organic matter content were proven to constitute quite good predictors of the sorption coefficient(s) for metals. Equation (8) provides an example of such a relationship, reported by Minasny & Perfect (2004), which supposedly describes the sorption of zinc on any ordinary soil with \( R^2 = 0.85 \):

\[
\ln S_{eq} = \frac{0.714}{n} \ln C_{eq} - 1.66 + 1.25 \ln \text{CEC} + 0.258 \ln \text{pH} + 0.117 \ln f_{OC} - 0.398 \ln \text{Clay}
\]  

(8)

where \( \text{CEC} \) is the cation exchange capacity [mmol·kg\(^{-1}\)], \( f_{OC} \) is the organic carbon content [%] and \( \text{Clay} \) is the mass fraction of clay [%]. Given the soil properties summarized in Table 1, it can be verified that this relationship leads to an underestimation of the experimental data by approximately one
order of magnitude, for the three soils we studied: the predicted values of $K_F$ would be 96, 214 and 230 mg$^{1\text{n}}$·kg$^{-1}$·L$^{-1}$, respectively, while the actual values are 950, 1,280 and 2,390 mg$^{1\text{n}}$·kg$^{-1}$·L$^{-1}$ (Table 2).

While such equations present an indubitable interest for approximating a soil’s retention capacities – for example, within the present methodology, they may help define the experimental conditions – the estimation they provide is however too uncertain to fully replace a direct, site-specific characterization of a soil. A source of noise in these pedotransfer functions may be the variety of contexts and experimental conditions used in establishing sorption isotherms. Therefore, developing application-specific pedotransfer functions may help overcome these problems; this would require generating and/or gathering isotherm data within an appropriate range of equilibrium concentrations according to the purpose pursued. In the case of SuDS, the present approach maximizes the chance of reaching metal concentrations typical of urban runoff.

**CONCLUSIONS**

Sustainable Drainage Systems significantly contribute to urban pollution control through filtration and sorption of runoff-generated contaminants. The soil’s ability to retain dissolved species is commonly appraised via sorption isotherms which are fitted from batch systems. In this context, the aim of this study was (i) to explore the consequences of modelling runoff–soil interactions from out-of-range equilibrium concentrations and (ii) to propose an improved method to ensure that experimental points fall within the desired range. An uncertainty analysis demonstrated that if non-linearity already occurs in a concentration range typical of stormwater runoff, then extrapolating the sorption isotherm may introduce significant biases. The experimental approach which was proposed relied on an a priori estimation of the soil’s retention properties, which enabled the anticipation of the final state of the batch systems, thus allowing for an appropriate selection of the initial concentrations and solid/liquid ratio. This method has been successfully applied to investigate the sorption behaviour of two metals on three soil materials with contrasting characteristics, and four organic micropollutants on one soil only. Both sorption isotherms and kinetics could be determined and fitted with widespread albeit parsimonious theoretical models.

The soils’ retention capacities towards zinc appeared to be correlated to their organic matter content and CEC; however, this was not the case for copper, because the high pH of the first two materials tended to favour its precipitation. The presence of dissolved organic ligands in the batch systems, at realistic values for the soil solution, partially inhibited metal sorption (~20% lesser), so did NaCl for zinc only. These two observations have noteworthy implications for the retention and release of metallic contaminants in SuDS soil. The affinity of organic micropollutants with the soil classified in the order NP10 > 4-NP > 4-t-OP > BPA, as expected from the comparison of their $K_{OC}$ and molecular structures. As regards kinetic aspects, most of the sorption processes could be considered instantaneous, indicating that contaminant retention might be efficient even with a low contact time between soil and infiltrating water. This may be verified and further investigated via column experiments.

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