

Projet LIFE ADSORB

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Life Adsorb Task B3 – deliverable B3.01

Lab studies for the evaluation of the adsorption properties of the filter substrates Rainclean[®], sand and sediment

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2 INTRODUCTION

Road runoff, and in particular runoff from heavily trafficked roads such as urban outskirts, is an important vector of organic or metallic micropollutants that contributes to the degradation of aquatic environments and undermines the achievement of good ecological status under the European Water Framework Directive.

The LIFE-ADSORB project (LIFE17 ENV/FR/000398), targets the implement and testing of a vertical flow reed bed filter, whose innovative design allows mechanical filtration but also adsorption of dissolved micropollutants on a specific substrate, thus promoting their subsequent degradation. The focus of the project is on reducing organic and mineral micropollutants in road runoff, especially suspended solids (SS), metals, hydrocarbons and other environmentally toxic substances (phthalates, alkylphenols, perfluorinated compounds, etc.).

Task B3.1 aims at evaluating in the lab the capacity of Rainclean®, the adsorbent material implemented in the LifeAdsorb red bed filter prototype, for the adsorption of a range of heavy metals and organic micropollutants, as well as their potential of ulterior desorption when submitted to clean water flow. Based on a series of batch and column tests, this work is needed to :

- Assess the maximal pollutant load that the Rainclean can fix before breakthrough under the functioning conditions of the filter and thus evaluate its expected life time
- Establish the parameters of adsorption kinetic and isotherm laws, which will be used for the modelling work in task B2

3 THEORETICAL BACKGROUND

3.1 Road runoff pollution

Numerous studies (Clark et al., 2006; Göbel et al., 2007) have highlighted the extent of pollution from urban wet weather discharges. In particular, runoff from high-traffic roads and pavements carries high pollution loads and requires specific treatment. Road runoff carries a variety of organic and mineral contaminants, including priority pollutants targeted by the Water Framework Directive and other more emerging ones (Markiewicz et al., 2017; Wicke et al., 2021). Indeed rainwater, when it reaches the ground, washes away the surfaces over which it flows and erodes/corrodes the surface materials. Primary sources of road runoff contamination include (Müller et al., 2020; Revitt et al., 2014) exhaust gases; abrasion of tires, brakes and other car parts; automotive fluids such as windscreen washers, engine oils, brake fluids and coolants; leaching from metallic or polymeric bodywork parts; leaching from pavement coating or painting...

Road runoff contamination is widely documented for metals and aliphatic and polycyclic aromatic hydrocarbons (Huber et al., 2016; Lee and Bang, 2000; Legret and Pagotto, 1999), but significant concentrations of other organic micropollutants originating in particular from consumables, fluids and car bodies have also been reported, such as phthalates or alkylphenols

(Björklund et al., 2009; Gasperi et al., 2022). Based on the results from the Roulépur project (Gasperi et al 2022), on four roads and parking lots with various urban contexts and traffic levels, the following micropollutants families were found to be particularly relevant for road runoff contamination and were chosen as reference pollutants to be considered in the LifeAdsorb project : trace metals (As, Cd, Cr, Cu, Ni, Pb, V, Zn), aliphatic and polycyclic aromatic hydrocarbons (PAHs), phthalates, alkylphenols (octylphenol and nonylphenol), bisphenol A.

Many factors impact the production of run-off pollution and the increase in pollutant concentration: the physical characteristics of sites (type and intensity of land use, degrees of impermeability); the type and intensity of human activity; climatic characteristics (intensity, duration of rainfall, period of dry weather preceding rainfall). This explains the great variability in the quality of runoff and the discharged loads from one place to another, and for a same place from one rain event to another. The extent of contamination varies according to the level of daily traffic and traffic conditions. According to Huber et al 2016, it is of particular concern in the case of congested and heavily trafficked roads.

Although suspended solids (TSS) are generally recognized as the main vector of stormwater contamination, recent studies focusing on road runoff temper this assumption (Helmreich et al., 2010; Huber et al., 2016; Kayhanian, 2012). TSS from runoff includes a large fraction of fine particles for which treatment by decantation is insufficient. In addition, dissolved pollution can be significant for certain metals (Cd, Ni, Cu, Zn) as well as certain low hydrophobic organic micropollutants (bisphenol A, alkylphenols, low molecular weight phthalates). The distribution of contamination between the dissolved and particulate phases is also highly variable from one rainfall event to another (Helmreich et al 2010).

Table 1 and Table 2 summarize the ranges of total and dissolved event mean concentrations measured on the four experimental sites of the Roulépur project, for the micropollutants targeted in LifeAdsorb. These tables underline the importance of dissolved concentrations for some of the contaminants, as well as their wide range of variation. For cases of heavy traffic roads, with high runoff contamination levels, treatment of this dissolved-phase contamination is a necessity that is insufficiently taken into account in conventional stormwater treatment systems. Standard stormwater treatment devices mainly target particulate pollutants, which are removed based on settling and physical filtration. In order to removed the dissolved phase of contaminants, adsorption processes have to be targeted. In the LifeAdsorb biofilter prototype, this relies on the implementation, within the filtration layer of a reed bed filter of and adsorbant media.

Table 1 : range of events mean concentrations (EMC), and distribution between dissolved and particulate fraction, measured during the Roulépur project on four road/parking sites in Paris conurbation – case of trace metals

		As (µg/l)	Cd (µg/l)	Cr (µg/l)	Cu (µg/l)	Ni (µg/l)	Pb (µg/l)	V (µg/l)	Zn (µg/l)
Total concentration	Minimum – maximum EMC	0.25 - 37	0.01 - 4.8	1.4 - 192	7 - 871	0.7 - 51	1.2 - 243	1.7 - 189	16 - 1650
	Range of site median EMCs	0.64 - 4.9	0.08 - 0.28	4.5 - 44	17 - 249	3.0 - 23	6.3 - 55	5.0 - 26	53 - 600
Dissolved concentration	Minimum – maximum EMC	0.14 - 6.8	0.01 - 0.16	0.2 - 10.6	2.6 - 251	0.2 - 13	0.1 - 3.9	0.5 - 58	2.4 - 362
	Range of site median EMCs	0.2 - 1.0	0.03 - 0.04	0.3 - 1.1	5.8 - 35	0.5 - 3.0	0.2 - 0.8	1.0 - 4.1	9.8 - 49
Particle bound fraction (%)	Minimum - maximum	14 - 93	10 - 100	42 - 100	19 - 98	22 - 100	77 - 100	42 - 98	36 - 98
	Range of site medians	39 - 86	79 - 100	93 - 100	54 - 91	71 - 100	96 - 99	62 - 94	64 - 95

Table 2 : range of events mean concentrations (EMC), and distribution between dissolved and particulate fraction, measured during the Roulépur project on four road/parking sites in Paris conurbation – case of organic micropollutants

		16PAHs (ng/l)	BPA (ng/l)	OP (ng/l)	NP (ng/l)
Total concentration	Minimum – maximum EMC	359 - 13300	86 - 5900	32 - 1830	79 - 2560
	Range of site median EMCs	840 - 4190	207 - 1690	65 - 720	120 - 1760
Dissolved concentration	Minimum – maximum EMC	22 - 210	61 - 4630	19 - 1010	43 - 4490
	Range of site median EMCs	61 - 86	171 - 1400	28 - 400	77 - 480
Particle bound fraction (%)	Minimum - maximum	59 - 100	3 - 74	15 - 93	15 - 98
	Range of site medians	92 - 99	11 - 36	48 - 72	29 - 71

3.2 Adsorption theory

Definition of adsorption

Adsorption is a phase transfer process that is widely used in practice to remove substances from fluid phases (gases or liquids). It is a surface phenomenon by which atoms, ions or molecules from a fluid attach themselves to a solid surface. It can also be observed as natural process in different environmental compartments. The term adsorption was first proposed by Kayser in 1881 to differentiate between gas condensation at the surface and gas adsorption, the process in which gas molecules enter the mass. The solid material that provides the surface for adsorption is referred to as adsorbent; the species that will be adsorbed are named adsorbate. By changing the properties of the liquid phase (e.g. concentration, temperature, pH) adsorbed species can be released from the surface and transferred back into the liquid phase. This reverse process is referred to as desorption (Worch, 2012).

The difference between adsorption and absorption

As explained before, the term adsorption describes the enrichment of adsorbates on the surface of an adsorbent. In contrast, absorption is defined as transfer of a substance from one bulk phase to another bulk phase (Figure 1). Here, the substance is enriched within the receiving phase and not only on its surface. In natural systems, some materials with complex structure can bind substances from the aqueous phase on their surface but also in the interior of the material. The uptake of organic solutes by the organic fractions of soils, sediments, or aquifer materials is a typical example for such complex binding mechanisms. In such cases, it is not easy to distinguish between adsorption and absorption. Therefore, the more general term sorption is preferred to describe the phase transfer between the liquid and the solid in natural systems. The term sorption comprises adsorption and absorption. Moreover, the general term sorption is also used for ion exchange processes on mineral surfaces.

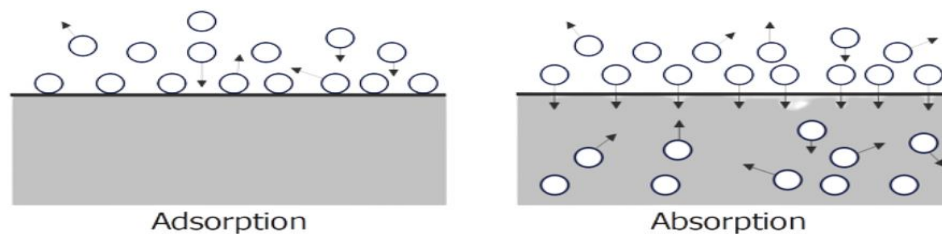


Figure 1 : substance transfer in adsorption and absorption

Type of adsorption

In most types of water and wastewater treatment practice, two primary driving forces result in the adsorption of a solute from a solution onto a solid phase.

The first driving force is related to the lyophobic (solvent disliking) character of the solute. The most important factor for the intensity of adsorption is the solubility of a dissolved substance. A hydrophilic substance likes the water system and tends to stay there. Hence, it is less adsorbable on a solid phase. Contrarily, a hydrophobic substance tends to be adsorbed rather than staying in water. Complex organic contaminants, such as humic acids have both hydrophobic and hydrophilic groups, so that the hydrophobic part of the molecule is adsorbed, whereas the hydrophilic part tends to stay in the solution.

The second driving force for adsorption is the affinity of the solute for the solid due to electrical attraction of the solute to the solid. This type of adsorption can occur as a result of Van Der Waals

attraction or chemical interaction with the adsorbent. These forces result due to the high affinity of the solute for the particular solid.

Table 3 : difference between physisorption and chemisorption

Properties	Physisorption	Chemisorption
Coverage	Mono or multilayer	Monolayer
Nature of bonding	Physical (Van der Waals) (dipole-dipole interactions, dispersion forces, induction forces)	Chemical (chemical reactions between the adsorbate and the surface sites)
Adsorption Enthalpy	> 50KJ/mol	> 50 kJ/mol
The process in temperature	Favoured by a decrease in temperature	Favoured by an increase in temperature
Desorption	Total	difficult
Specificity to adsorption sites	Nonspecific	Very Specific (depends on the nature of the bonds forming)
Adsorption rate	Rapid	Very variable, often slow
Desorption	Easy by reduced pressure or increased temperature	Difficult – high temperature is required to break bonds

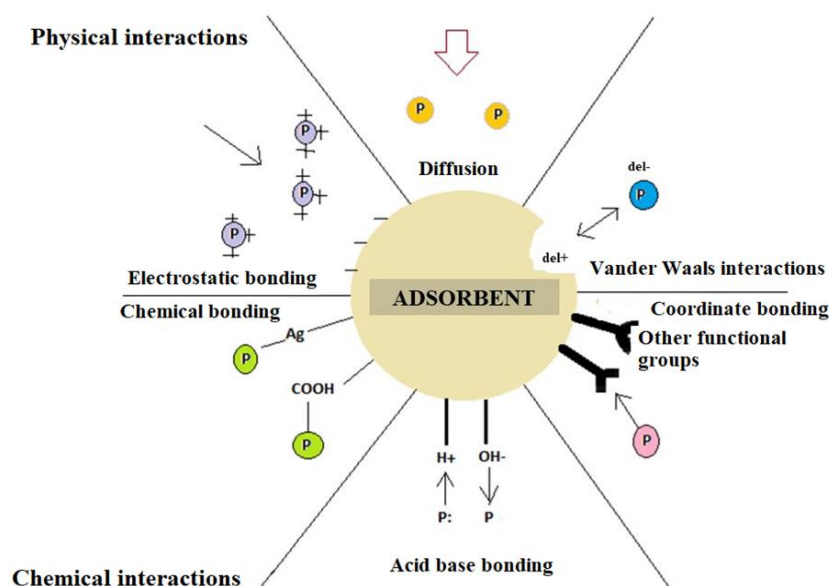


Figure 2 : Various forms of adsorbent-adsorbate interactions

Different forms of adsorbent-adsorbate interactions are explained in Figure 2 (Natarajan et al., 2022). Depending on the value of the adsorption enthalpy, adsorption can be categorized as physical adsorption (physisorption) or chemical adsorption (chemisorption). The physical adsorption is caused by Van Der Waals forces (dipole-dipole interactions, dispersion forces, induction forces), which are relatively weak interactions. They are primarily responsible for the sorption of hydrophobic, non-ionic compounds (Filep et al., 2021). The adsorption enthalpy in the case of physisorption is mostly lower than 50 kJ/mol. Chemisorption is when the adsorbate undergoes chemical interaction with the adsorbent. It involves an exchange of electrons between specific surface sites and solute molecules, a chemical bond being formed. Chemically adsorbed adsorbates are not free to move on the surface or within the interface, and

the interaction energies are therefore in the order of magnitude of reaction enthalpies (> 50 kJ/mol). It has to be noted that the differentiation between physisorption and chemisorption is widely arbitrary, and the boundaries are fluid (Worch, 2012).

Description of adsorption processes

The adsorption equilibrium is the basis of all adsorption models. Knowledge about the adsorption equilibrium is a precondition for the application of both kinetic and dynamic adsorption models. To predict adsorption dynamics, information about adsorption equilibrium as well as about adsorption kinetics is necessary. These general principles of adsorption theory are not only valid for single solute adsorption but also for multisolute adsorption, which is characterized by competition.

The equilibrium relationship is typically considered at constant temperature and expressed in the form of the adsorption isotherm as shown in the equation (1)

$$q = f(c) \quad T = \text{constant} \quad (1)$$

q is the mass-related adsorbed amount, c , the adsorbate concentration, T , the temperature.

The adsorption kinetics describes the time dependence, t , of the adsorption process, which means the increase of the loading with time or, alternatively, the decrease of liquid-phase concentration with time.

$$q = f(t) \quad c = f(t) \quad (2)$$

The adsorption rate is typically determined by slow mass transfer processes from the liquid to the solid phase. Adsorption within the frequently used fixed-bed adsorbers is not only a time dependent but also a spatial-dependent process. The dependence on time (t) and space (z) is referred to as adsorption dynamics or column dynamics.

$$q = f(t, z), \quad c = f(t, z) \quad (3)$$

Figure 4 shows the main constituents of the practice-oriented adsorption theory and their interdependences.

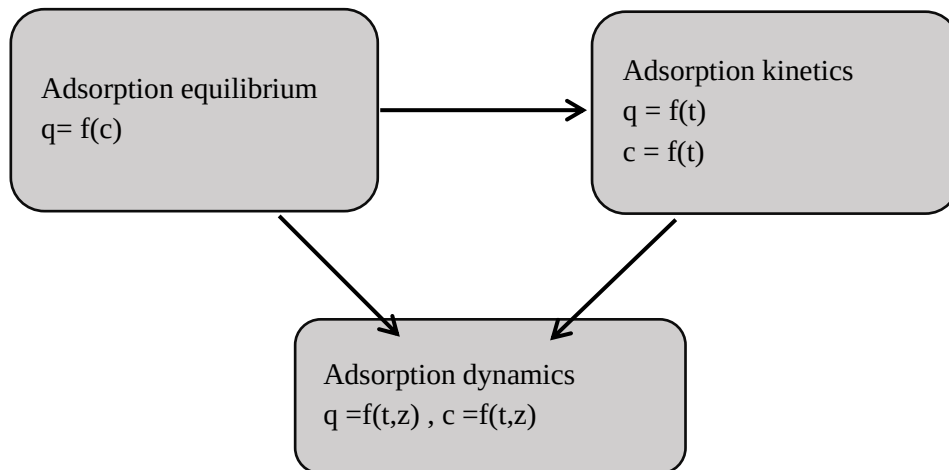


Figure 3 : Elements of the adsorption theory.

3.2.1 Adsorption kinetics

Adsorption kinetics has made it possible to determine (1) the initial speed of adsorption of a pollutant on an adsorbent as well as (2) the time of contact necessary between the adsorbate and the adsorbent for the thermodynamic equilibrium between the solid phase and the liquid phase to be reached.

A mass of adsorbent (m) and a solution with a known concentration of the studied compound (Ci) are put in contact. The kinetics are carried out at room temperature in perfectly agitated flasks using a rotary agitator. The initial concentration (C0) is measured, and the time (t0) corresponds to the moment of contact between the adsorbent and the adsorbate. The concentration in the liquid phase is measured over time until the equilibrium level is reached. The solid/liquid separation is performed by simple decantation.

3.2.1.1 Pseudo-first-order kinetics and pseudo-second-order kinetics

The kinetics of adsorption can usually be represented by two models: pseudo-first-order kinetics (PFO) or pseudo-second-order kinetics (PSO).

Table 4 :Expressions of PFO and PSO kinetic models

Model	Differential equation	Solution	Linearised equation
PFO	$\frac{dq_t}{dt} = k_1(q_e - q_t)$	$q_t = q_e(1 - e^{-k_1 t})$	$\ln(q_e - q_t) = \ln q_e - k_1 t$
PSO	$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$	$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}$	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$

with

q_t : pollutant mass adsorbed per unit mass of sorbent at time t (in mg/kg)
q_e : pollutant mass adsorbed per unit mass of sorbent at equilibrium (in mg/kg)
k₁ in min⁻¹ and k₂ in kg.mg⁻¹.min⁻¹ adsorption kinetic constants

3.2.1.2 Instantaneous adsorption

An initial rapid "instantaneous" adsorption can also be observed at t = 0, which can be modeled by the following equations:

$$q_t = q_i + (q_e - q_i)(1 - e^{-k_1 t}) \quad \text{PFO with initial instantaneous adsorption}$$

$$q_t = q_e - \frac{q_e - q_i}{1 + k_2 t(q_e - q_i)} \quad \text{PSO with initial instantaneous adsorption}$$

Where q_i is the pollutant mass that adsorbs very quickly at t=0 per unit mass of sorbent

3.2.1.3 Weber-Morris or IPD model

The kinetics of intra-particle diffusion adsorption mechanism (Weber-Morris or IPD model, Ghibate et al., 2021) can be described as follows: $q = k_d \sqrt{t} + C_d$

where k_d is the IPD rate constant (mg/(g min^{1/2})) and C is a constant for any experiment (mg/g).

3.2.2 Adsorption isotherms

Adsorption isotherms are experimental curves that allow the characterization of thermodynamic equilibrium of adsorption by showing the amount of adsorbate that can be adsorbed by the adsorbent

(q_e) in relation to the equilibrium concentration of the adsorbate in fluid phase (C_e). These are critical parameters in the adsorption system design.

Adsorption isotherms are generally expressed by mathematical equations. These mathematical expressions are usually obtained from experiments performed in static reactors.

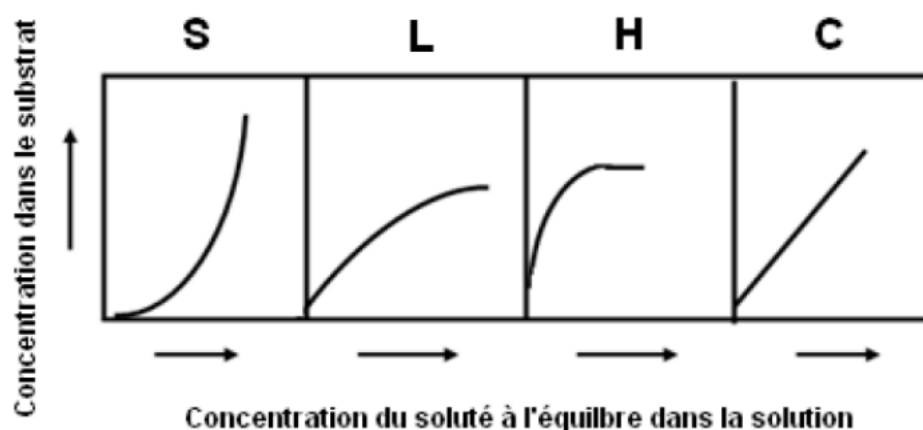
In a batch adsorption test, an adsorbent dosage (m) is mixed with a certain volume (V_0) of a solution at an initial solute concentration (C_0) in flasks that are perfectly stirred. Different adsorbent dosages are placed into contact with a solution containing known solute concentration. Thus, when equilibrium is reached, different values of equilibrium concentrations (C_e) are obtained, and the adsorption capacities (q_e) are calculated according to the following equation:

$$q_e = \frac{(C_i - C_e)V}{m}$$

where q_e is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg.g^{-1}), C_i and C_e are the initial and equilibrium concentrations (mg.L^{-1}) of adsorbate, respectively, V is the volume (L) and m is the mass (g) of the adsorbent.

3.2.2.1 Adsorption isotherm classification

Experimentally, we distinguish four main classes of adsorption isotherms: class S (Sigmoid), class L (Langmuir), class H (High affinity) and class C (Constant partition). Below, are schematized, these different isotherms with brief definitions.



The S-type isotherm is characteristic of monofunctional organic molecules with moderate intermolecular attractions. This S-type curve expresses the competition between the solute and the solvent for the occupation of adsorption sites present on the solid phase at low solute concentrations. The L-type isotherm is the most common one and is identified by the formation of a monolayer of adsorbate on the surface of the adsorbent. These L-type curves can be described by the Langmuir or Freundlich equations. H-type isotherms describe a very high affinity of the solute for the adsorbent. In this case, the solute molecules in the initial dilute solution are virtually all adsorbed on the solid adsorbent. Finally, the type C isotherm represents linear partitioning between the liquid and solid phases, corresponding to a linear model.

3.2.2.2 Linear isotherm

In this model, the quantity adsorbed at equilibrium is directly proportional to the adsorbate concentration remaining in the solution. This type of curve is expected when working at low solute concentration without reaching saturation of the adsorption sites. It can be written as

$$q_e = K_D C_e$$

where: q_e is the amount adsorbed per specific amount of adsorbent (mg.g^{-1}), C_e is the equilibrium concentration of the solution (mg.L^{-1}) and K_D is the liquid/solid partition factor (L.g^{-1}).

3.2.2.3 Langmuir Isotherms

The Langmuir-type isotherms remain to be the most widely used for practical applications. The Langmuir isotherm for pure component adsorption is

$$q_e = \frac{q_m k_L C_e}{1 + k_L C_e}$$

where: q_e is the amount adsorbed per specific amount of adsorbent (mg.g^{-1}), C_e is the equilibrium concentration of the solution (mg.L^{-1}), K_L is the Langmuir constant and q_m is the maximum amount of metal ions required to form a monolayer (mg.g^{-1}).

3.2.2.4 The Freundlich Isotherm Model

The Freundlich isotherm assumes that the adsorption occurs on a heterogeneous surface, and the amount that is adsorbed increases infinitely with an increase in concentration (Freundlich 1906). In liquid phase, this isotherm is given by

$$q_e = K_F C_e^{\frac{1}{nF}}$$

where K_F is the Freundlich constant (a common error is noted in K_F unit, i.e., $\text{mg}^{1-c} \text{L}^c/\text{g}$, where $c = 1/nF$) and $1/nF$ is the heterogeneity factor. This isotherm attempts to incorporate the role of adsorbate–adsorbate interactions on the surface.

3.3 Solute transport modeling

3.3.1 Transport of a non-reactive solute

3.3.1.1 Convection-dispersion equation

Le mouvement d'un soluté dans un milieu poreux est la résultante de deux mécanismes principaux, le premier est la convection et le second est la dispersion hydrodynamique. Le processus de convection implique que chaque molécule d'un traceur non réactif se déplace à la vitesse moyenne du mouvement de l'eau (transport passif d'un soluté avec le liquide). La dispersion quant à elle, tend à propager les molécules aussi bien dans le sens longitudinal de l'écoulement que dans des directions transversales (Zheng et Bennett, 1995). Il en résulte que les molécules s'écartent du parcours moyen du fluide. D'autre part, lorsqu'on prend en compte le processus d'adsorption équilibrée, un facteur de retard est introduit et l'équation de convection-dispersion (Bear, 1979 ; Freeze et Cherry, 1979 ; de Marsily, 1986) générale élaborée en termes de directions longitudinale X_L (dans la direction du flux) et transversale X_T (perpendiculaire à la direction du flux) pour un écoulement permanent s'écrit telle que :

$$\theta \frac{\partial C}{\partial t} = \theta D_L \frac{\partial^2 C}{\partial X_L^2} + \theta D_T \frac{\partial^2 C}{\partial X_T^2} - J_w \frac{\partial C}{\partial X_L}$$

En divisant par θ , on obtient :

$$\frac{\partial C}{\partial t} = D_L \frac{\partial^2 C}{\partial X_L^2} + D_T \frac{\partial^2 C}{\partial X_T^2} - V_L \frac{\partial C}{\partial X_L} \quad \text{avec} \quad V_L = J_w / \theta$$

Avec, C , la concentration du soluté dans la phase liquide sous la forme d'une fonction de deux dimensions spatiales et d'une durée t (ML^{-3}) ; $\partial C / \partial t$, la dérivée temporelle ; D_L , le coefficient de dispersion dans la direction longitudinale (L^2T^{-1}) ; D_T , le coefficient de dispersion dans la direction transversale (L^2T^{-1}) ; V_L , la vitesse du soluté dans la direction longitudinale (LT^{-1}) ; R , le facteur de retard (-) ; J_w , la vitesse de Darcy (LT^{-1}) ; θ , la teneur en eau volumique du milieu (L^3L^{-3}).

La dispersion transversale est beaucoup plus petite que la dispersion longitudinale d'environ un à deux ordres de grandeur (Bear, 1972). Elle est généralement fixée à une valeur de 1/10 de la valeur de la dispersion longitudinale (Domenico et Schwartz, 1990 ; Appelo et Postma, 1996 ; Anguela, 2004).

Dans le cas d'un écoulement unidimensionnel vertical l'équation devient :

$$\frac{\partial C}{\partial t} = D_L \frac{\partial^2 C}{\partial X_L^2} - V_L \frac{\partial C}{\partial X_L}$$

3.3.1.2 Longitudinal dispersion coefficient and longitudinal dispersivity

La dispersivité est un paramètre qui détermine la dispersion d'un soluté à travers un milieu poreux et qui est défini en unités de longueur. La valeur de la dispersivité affecte la forme de la courbe de percée, mais pas la localisation du pic de concentration affectée par le facteur de retard. La dispersivité longitudinale λ_L est liée au coefficient de dispersion longitudinale par l'équation suivante :

$$D_L = \lambda_L * V_L$$

Avec, D_L , le coefficient de dispersion longitudinale (L^2T^{-1}) ; λ_L , la dispersivité longitudinale (L) ; V_L , la vitesse du soluté dans la direction longitudinale (LT^{-1}).

Bear (1972), Burns (1996) et Roth et Hammel (1996) considèrent la dispersivité comme une valeur caractéristique du milieu poreux étudié et de sa taille. En effet, la dispersion est un processus dépendant de l'échelle, des valeurs de dispersivité plus importantes étant observées à des échelles spatiales plus grandes (Gelhar et al., 1992). À l'échelle de la colonne, une dispersivité typique peut être de l'ordre du centimètre alors qu'à l'échelle du champ, les dispersivités apparentes peuvent varier de 10 à 1000 m (Gelhar, 1986). De plus, Bromly et al. (2007) ont montré qu'à l'échelle du laboratoire les effets d'échelle semblent être significatifs pour des colonnes de matériaux homogènes tassées, avec des diamètres de colonne $\geq 7,59$ cm entraînant des dispersivités mesurées plus grandes. D'autre part, les colonnes de longueur inférieure à 10 cm ont généralement donné lieu à des dispersivités plus importantes que les colonnes plus longues.

Bear (1972) a établi pour les matériaux granulaires la dispersivité est dépendante du diamètre de grain moyen. Une large gamme de distribution de la taille des pores entraîne une plus grande dispersion du front de soluté. Néanmoins, en essayant de relier la dispersivité aux paramètres physiques du matériau étudié (teneur en sable, limon et argile, densité apparente, teneur en eau), Bromly et al. (2007) a conclu que cela n'est possible qu'en tenant compte des conditions (vitesse de l'eau interstitielle) et des conceptions expérimentales, incluant la géométrie de la colonne (longueur et diamètre), qui entraîne un effet d'échelle à la fois latéralement et verticalement, et le tassement du matériau.

3.3.2 Transformations/degradation of solutes

De nombreux contaminants tels que les micropolluants et les nutriments tels que les nitrates subissent d'importantes transformations microbiennes dans les sols par exemple. Tous ces processus peuvent être représentés comme des processus de transformation de premier ordre. Dans chaque cas, le taux de transformation est proportionnel à la masse de produit chimique présent :

$$\frac{\partial(\theta C)}{\partial t} = -\mu\theta C$$

Avec, θ , la teneur en eau volumique du milieu (L^3L^{-3}) ; C , la concentration du soluté dans la phase liquide (ML^{-3}) ; μ , la constante de vitesse de transformation de premier ordre (T^{-1}). La multiplication de C par θ convertit la concentration en masse par unité de volume de sol. Les unités pour cette équation sont le taux de perte de masse par volume de sol ($ML^{-3}T^{-1}$).

L'équation montre que seule la phase en solution du soluté subit une décroissance. En ajoutant ce terme de transformation comme terme source/puits au processus de transport pour un écoulement permanent on obtient :

$$\frac{\partial C}{\partial t} = D_L \frac{\partial^2 C}{\partial X_L^2} - V_L \frac{\partial C}{\partial X_L} - \mu C$$

Avec, C , la concentration du soluté dans la phase liquide (ML^{-3}) ; D_L , le coefficient de dispersion dans la direction longitudinale X_L (L^2T^{-1}) ; V_L , la vitesse du soluté dans la direction longitudinale (LT^{-1}) ; μ , la constante de vitesse de transformation de premier ordre (T^{-1}).

3.3.3 Reactive transport of solutes with adsorption on the substrate

Dans le cas où le soluté interagit avec le substrat, du fait notamment de processus d'adsorption ou de désorption, le transport de soluté n'est pas équilibré et ne peut pas être décrit de façon adéquate par l'équation de convection-dispersion (CDE) précédente. L'équation qui gouverne le transport réactif d'un soluté dans un substrat adsorbant résulte d'un bilan de masse sur l'espèce chimique considérée, en incluant à la fois la quantité présente en phase dissoute (décrite par la concentration C), et la quantité adsorbée sur la matrice solide (décrit par la concentration en phase solide q_t) :

$$\frac{\partial C}{\partial t} + \frac{\partial}{\partial t}(\rho \theta q_t) = D_L \frac{\partial^2 C}{\partial X_L^2} - V_L \frac{\partial C}{\partial X_L} - \mu C$$

La quantité q_t adsorbée sur le substrat est par ailleurs reliée à la concentration C par les lois de cinétique et d'isotherme d'adsorption présentées en 3.2. Pour certaines molécules l'adsorption s'effectue de façon instantanée, et q_t est en équilibre avec C : $q_t = q_e = f(C)$. Pour d'autres, l'adsorption est dépendante du temps, $q_t = f(q_e, t) = f(C, t)$, le modèle chimique est non équilibré.

Le modèle chimique non équilibré le plus simple est le modèle chimique non équilibré à un site de sorption. Il suppose que l'adsorption suit une cinétique de pseudo premier ordre (voir 3.2.1.1) et que l'isotherme d'adsorption est linéaire (voir 3.2.2.2). Dans ce cas, la relation entre q_t et C peut être décrite par l'équation :

$$\frac{\partial q_t}{\partial t} = k_1(K_d C - q_t)$$

Avec, S , la concentration du soluté adsorbée (ML^{-3}) ; k_1 , la constante de vitesse cinétique (T^{-1}) ; $q_e = K_d C$, la concentration du soluté adsorbée finale à l'équilibre (ML^{-3}).

4 ADSORPTION STUDIES IN THE LAB

4.1 Experimental methods

4.1.1 General principles

4.1.1.1 Type of tests

Two types of lab experiments were implemented:

- Batch experiments: they mainly consisted in equilibrium adsorption measurements and kinetic studies. A leaching test was also performed to assess the potential risk of a new adsorbent material to release organic and inorganic contaminants. The objective of the batch experiment is to give a first assessment of the parameters of kinetic and isotherms laws, for the different material present in the LifeAdsorb biofilter prototype, and for the best of our knowledge, to scale adsorption columns experiments.
- Column test: these tests aimed at assessing the longitudinal dispersion parameters of the sand and the Rainclean material, and assessing in conditions close to field condition the adsorption behaviour of the Rainclean material.

4.1.1.2 Sorbents

The sorbents tested are the different materials that constitute the filtration layers of the LifeAdsorb reed-bed filter:

- the commercial adsorbent Rainclean®, which is a technical mixture manufactured by Funke,
- the sand used as filtration layer in the reed-bed filter,
- sediments collected from the surface of the red-bed filter close to the water entry.



Figure 4 : tested sorbents – from left to right: sediment, Rainclean®, sand

Rainclean® and sand samples were new materials collected during the construction of the facility. Sediment was collected on-site in summer 2022. Physical characteristics of sorbents are shown below in Table 5.

All sorbents were oven dried at 60°C. Sediments were crushed and sieved at 2 mm. Rainclean was unaltered, and implemented without crushing or sieving, in order not to modified it's contact conditions with the solution. Note that Rainclean is a very heterogeneous material. Due to its wide granulometry and pulverulent nature, it is difficult to ensure totally replicable subsamples.

Table 5 : physical properties of the tested sorbents (manufacturer data, *field data*)

Filter material	Composition	Bulk density Porosity, Permeability	Grain size distribution
RainClean®	Porous minerals, Zeolites, Iron hydroxide, Organic matrix, Activated carbon, Calcareous mineral (lime admixtures)	600 ± 125 g/L 500 ± 100 g/L 0.6 m ³ /m ³ 7.72 *10 ⁻³ m/s	0.06 to 8 mm D50 = 2 mm; D10 = 0.5 mm D60/D10 = 3.76
Sand	Silicate (>86%)	1590 ± 45 g/L 0.4 m ³ /m ³ 10 ⁻³ m/s	0 to 4 mm D50 = 1 mm; D10=0.27 mm D60/D10 = 4.1
Sediments	Mixture of SS from the runoff and vegetation debris	-	-

4.1.1.3 Sorbates

Lab experiments were performed for a selection of micropollutants among those targeted in the LifeAdsorb project. They were performed separately for tracers, for trace metals and for organic micropollutants. Only the dissolved phase of these compounds was considered, in both batch and columns tests.

A range of trace metals was considered: arsenic (As), cadmium (Cd), copper (Cu), chromium (Cr), nickel (Ni), lead (Pb), vanadium (V) and zinc (Zn). Cu, Zn, Pb, Ni, Cr were selected as they are documented for their recurrent presence in road runoff and are emblematic of traffic emissions. Arsenate (As) is less specific to road runoff but has been documented in some regions where it is found in the geologic background.

Among the micropollutant families studied in the LifeAdsorb project, lab experiments focused on those which can be found at significant concentrations in the dissolved form, thus PAH were not considered. The organic micropollutants tested were: bisphenol (BPA), nonylphenol (NP) and 4-tert-octylphenol (OP). DEHP was initially considered, as the most significant representative of the phthalate's family. Its lab testing was however abandoned after the first set of batch tests due to the excessive adsorption of the compound onto lab glassware which rendered the results unusable.

Tracer compounds were also including in the lab testing. NaCl was used as non reactive tracer in column studies. Rhodamine B (RhB), Fluorescein (F) and Acid Amino G (AAG) were tested for their adsorption behaviour in batch studies, and for AAG also in column studies. RhB, F and AAG were considered as potential surrogates to the behavior of micropollutants with different affinities for adsorption.

4.1.2 Batch tests

4.1.2.1 Experimental Setup

Batch tests were all conducted in duplicate, in closed 2 L PEHD bottles and metals, and in closed 2 L glass bottles for organic micropollutants and for tracers. The solid over liquid ratio of the batches was set to S/L = 10 g.L⁻¹, which a relatively standard value in the literature. Considering the heterogeneous nature of Rainclean®, the choice was made to use the largest possible sample size, in order to maximise their representativeness. The important volume of the batches (2L) allowed for subsamples of sorbent of 20 g. Tests were performed at room temperature (22±1°C), under continuous stirring with an overhead

shaker at approximately 5rpm. For organic micropollutants, the experiments were performed in the dark to avoid photodegradation.

pH was not adjusted, to fit the natural pH that would be reaches on-site or in column tests. pH and EC of each sample were monitored at $t=0\text{min}$ and at $t=24\text{h}$ (and $t=72\text{h}$ for tracers).

Adsorption kinetics were measured over 72h for tracers and 24h for micropollutants, for Rainclean and sediment. For tracers and metals, 10 mL sub samples were taken in the same batch after different times. For organic micropollutants, the important volume of solution needed for chemical analysis of these pollutants (250 mL) did not allow for successive sampling over time from a same batch. Thus 9 bottles were prepared from the same stock solution and sampled at different times. The sampling time for adsorption kinetics were the following:

- tracers: 0, 15 mn, 30 mn, 1 h, 2 h, 3 h, 4 h, 5 h, 6h, 7 h, 9 h, 12 h, 24 h, 48h, 72h.
- metals : 0, 15 mn, 30 mn, 1 h, 2 h, 4 h, 7 h, 12 h, 24 h.
- organic micropollutants: 0, 15 mn, 1 h, 2 h, 4 h, 6 h, 9 h, 11h, 24 h.

For equilibrium tests, performed in order to establish adsorption isotherms, a 24 h hour time of contact was set. These batch were implemented with 6 different initial concentration levels for metals, and 5 for organic micropolluants.

For each concentration level of equilibrium batch tests, a control batch was set up in duplicate: bottle containing the same adsorbate solution but without sorbent material, subject to the same manipulations as the batches with sorbent.

In parallel with the equilibrium adsorption tests, lixiviation tests were also done in duplicate: a 2 L bottle (glass or PEHD depending on the considered pollutants) was filled MilliQ water and 20 g of sorbent (Rainclean®, sand or sediment), and stirred for 24h. This aimed to assess potential leaching of the considered micropollutants by the considered sorbent.



Figure 5 : Experimental set-up for batch tests

Samples were immediately filtered with a cellulose nitrate filter ($0.45\text{ }\mu\text{m}$) for metals and tracers, and with whatman GFF glass fiber filter for organic micropollutants, to separate the dissolved and solid phases and to later evaluate the residual dissolved concentration. The metal aliquots were acidified at 1% with HNO_3 (Merck) and refrigerated until metals measurement. Sample for organic micropollutant

were brought to the analysis laboratory on the same day for immediate extraction or have been frozen until their transfer and analysis.

4.1.2.2 Stock solutions and initial concentrations

Tracers.

Stock solutions of 1 g.L⁻¹ of Rhodamine B (RB), Fluorescein (F) and Acid Amino G (AAG) were prepared by dissolving a mass of RB, F and AAG respectively in miliQ water.

The initial concentrations targeted range between 0.05 to 10 mg.L⁻¹ for the Rbh solution, 0.25 to 8 mg.L⁻¹ for the F solution and 0.1 to 10 mg.L⁻¹ for the AAG solution. These concentrations ranges were chosen based on concentration level used in the literature for on-site tracer experiments for the max value, and based on preliminary test to check the minimum quantifiable values for the min value. The solutions were stored in the fridge at 4°C.

Metals.

All batch experiments were performed on multi-elementary metal solutions, where the 8 considered trace elements were present in mixture, with different concentrations ranges depending to their relative prevalence in the runoff and to their adsorption capacity. MilliQ water was used for the preparation of all batch solutions.

To prepare the metallic solutions, stock solutions were first prepared for each metal, at the following concentrations: As 0.3 g.L⁻¹, Cd 0.12 g.L⁻¹, Cr 0.6 g.L⁻¹, Cu 3 g.L⁻¹, Ni 0.6 g.L⁻¹, Pb 0.3 g.L⁻¹, V 0.6 g.L⁻¹ and Zn 3 g.L⁻¹. These solutions were prepared by dissolving in miliQ water (electric conductivity of <1 µS/cm) the following metallic salts in ultra-pure water: sodium arsenate dibasic heptahydrate ≥ 98%, cadmium sulfate ≥ 99%, copper (II) sulfate ≥ 99%, potassium dichromate ≥ 99%, nickel (II) sulfate 99,99%, lead (II) nitrate ≥ 99%, vanadium (V) oxide ≥ 98% and zinc chloride ≥ 98% (Sigma-Aldrich). The stock solutions were further used to prepare the needed volume of solution mixing the different metals at the targeted initial concentration levels, for each batch test.

For the kinetic experiments, 2 different solutions were used, a mixed solution of metals without Cr and the other without Pb, because with the presence of both in the solution they can precipitate as lead chromate (PbCrO₄). While for the study of the isotherms which were done first, the solution mixed with both was used.

Initial concentrations were based K_d values that had been estimated in 2017 based on preliminary tests of Rainclean material and on concentration levels of dissolved metals observed in road runoff (Table 1). The objective was to reach equilibrium solution concentrations that fit with the levels found in road runoff. This objective could not be completely met, probably because of an evolution of the composition of Rainclean between the material tested in 2017 and the one implemented in the LifeAdsorb prototype in 2019. Initial concentrations in the different batch experiments, as well as final equilibrium concentrations that were reached, are presented in Table 6 and compared to maximum values reported for dissolved metals in the road runoff.

Table 6: Initial and final concentrations of batch studies for trace metals ($\mu\text{g.L}^{-1}$)

		As	Cd	Cu	Cr	Ni	Pb	V	Zn
Equilibrium study (isotherms)	Target Ci range	250-5000	100-2000	2500-50000	500-10000	500-10000	250-5000	500-10000	2500-50000
	Ci range M1-M6 Rainclean, sand	260-4094	105-1954	2526-48511	473-10483	537-9862	52-713	219-4528	2407-46591
	Ci range M'1-M'4 sediment	10-100	10-100	500-5000	-	25-250	10-100	25-250	500-5000
	C _f range, Rainclean	5-153	1-1221	23-3330	458-6446	5-7786	0-10	84-336	22-30604
	C _f range, sand	166-3838	72-1917	1205-45705	475-9812	160-9470	8-63	191-3840	2464-44480
	C _f range, sediment								
Kinetic study with Pb/with Cr	Target Ci	750	500	7500	1500	1500	-	1500	7500
	Ci Rainclean	580/706	469/472	7439/7261	-/1494	1581/1602	47/-	1468/1510	7549/7431
	Ci sediment	677/793	460/510	7052/8094	-/1614	1492/1754	160/-	1132/1698	7136/8428
	C _f Rainclean	101/171	10/11	57/60	-/1343	252/264	1/-	672/771	101/102
	C _f sediment	219/249	7/6	441/562	-/1362	171/114	20/-	541/612	291/345
Max measured in road runoff		7	0.2	251	11	13	4	58	362

Organic pollutants

Stock solutions were prepared using the first a mixture of nonylphenol (NP) (Sigma-Aldrich), 4-tert-octylphenol (OP) (Dr. Ehrenstorfer) and bisphenol A (BPA) (Brand) both of 1g L^{-1} , all dissolved in methanol (MOH) (Brand). Batch solutions were prepared with MilliQ water.

Here again, initial concentrations to be targeted for batch tests were at first estimated based on the 2017 preliminary work. However, a first set of batches based on these estimations led to final concentrations that were too low for Rainclean and could thus not be accurately quantified. A second set of batches had to be performed for the Rainclean with higher initial concentrations. Initial and equilibrium concentrations of this second set are presented in Table 7.

Table 7: Initial and final concentrations of batch studies for organic micropollutants ($\mu\text{g.L}^{-1}$)

		BPA	NP	OP
Equilibrium study (isotherms)	Ci range Rainclean and sand	24-571	27-260	14-377
		1-13*	1-12*	1-11*
	Ci range sediment	10-100		
	C _f range, Rainclean	0.11-38	0.09-22	0.10-23
	C _f range, sand	0.9-458	0.7-241	0.6-232
Kinetic study	C _f range, sediment			
	Ci Rainclean	24	27	14
	Ci sediment	33	39	19
	C _f Rainclean	0.11	0.09	0.10
	C _f sediment	12.06	0.50	2.56
Max measured in road runoff		4.63	4.49	1.01

* = first set of batchs, results used for sand only, not usable for Rainclean

4.1.2.3 Measured pH and EC values

pH values were not fixed but were measured at time $t = 0$, 1h, 12h, 24 h during kinetic batch studies and at time $t = 0$ and $t = 24$ h during equilibrium batch studies.

The Rainclean material has an alkaline pH. When put in contact with the non spiked ultrapure water (pH 6.0 to 6.5), pH quickly increases over the first hour and stabilises after 24 h at values in the range 8.1 to 9.5 (see Figure 6 “non spiked water” and Figure 7, M0 and C0 concentration levels). The variability in these equilibrium pH values probably reflects the heterogeneity of the Rainclean material and thus difficulty to have replicable Rainclean sub-samples during the batch tests. Electric conductivity (EC) also increases rapidly over the first hour when Rainclean is in contact with the non spiked ultrapure water, and reaches values between 152 and 186 $\mu\text{S/cm}$ after 24h (see Figure 6 and Figure 8). In the case of the sediment, the increase of pH and electric conductivity is also observed during lixiviation with non spiked ultrapure water but remains more limited. pH reaches 7.6 to 7.8 and EC 67 to 96 $\mu\text{S/cm}$ after 24h. Sand lixiviation in ultrapure water does not induce any variation in pH or EC.

Spiking with metal salts induces a reduction in pH of the sorbate solutions and an increase of EC, especially for the higher spiking levels M4 to M6. For the lower spiking levels M1 to M3 and for the kinetic study, this is compensated for pH by the buffer effect of Rainclean, and the final pH of the batches is close to neutrality, in the range 6.8 to 7.6, with one batch at 8.5. For M4 to M6 levels, the equilibrium pHs are slightly acidic, in the range 6.1 to 6.5, with one batch at 5.6. In the case of sand, equilibrium pHs remain close to those of the control batchs without adsorbent and are slightly acidic (6 to 6.5) for M1 – M3 levels and acidic (4.9 to 5.1) for M4-M6 level. These differences of pH could have induced differences in adsorption behaviour between batches M1-M3 and M4-M6. For the sediment, spiking levels (M'1 to M'4) were all in the lower range compared to Rainclean/sand batchs and the equilibrium pH of batchs is close to neutral, in the range 6.8 – 7.8.

Spiking with organic micropollutants (ie with very small volumes of methanol containing the targeted micropollutants) does not modify the EC of the sorbate (EC of controls without sorbent close to 0) but leads to an increased pH compared to metal batches. The equilibrium pH of organic test batches is in the range 7.8 to 8.6 for sand and 8.7 to 9.4 for Rainclean.

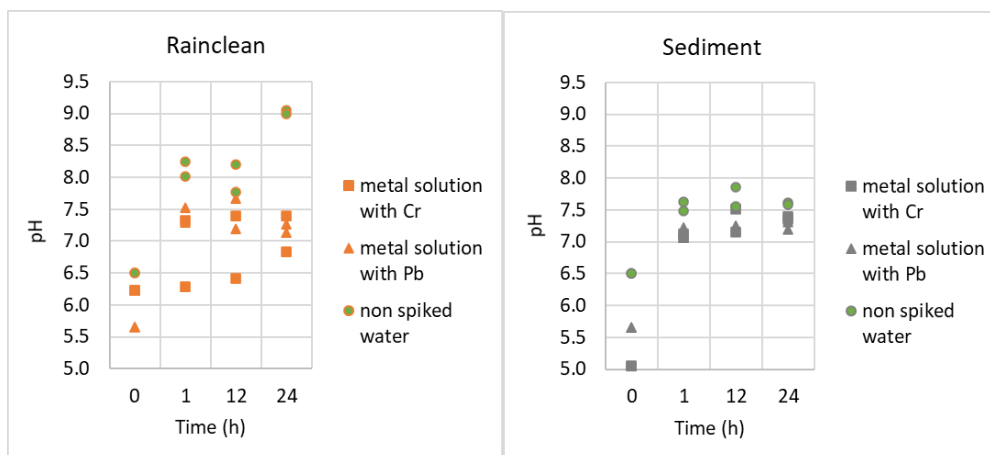


Figure 6 : evolution of pH values during kinetic experiments, for Rainclean and sediment batches

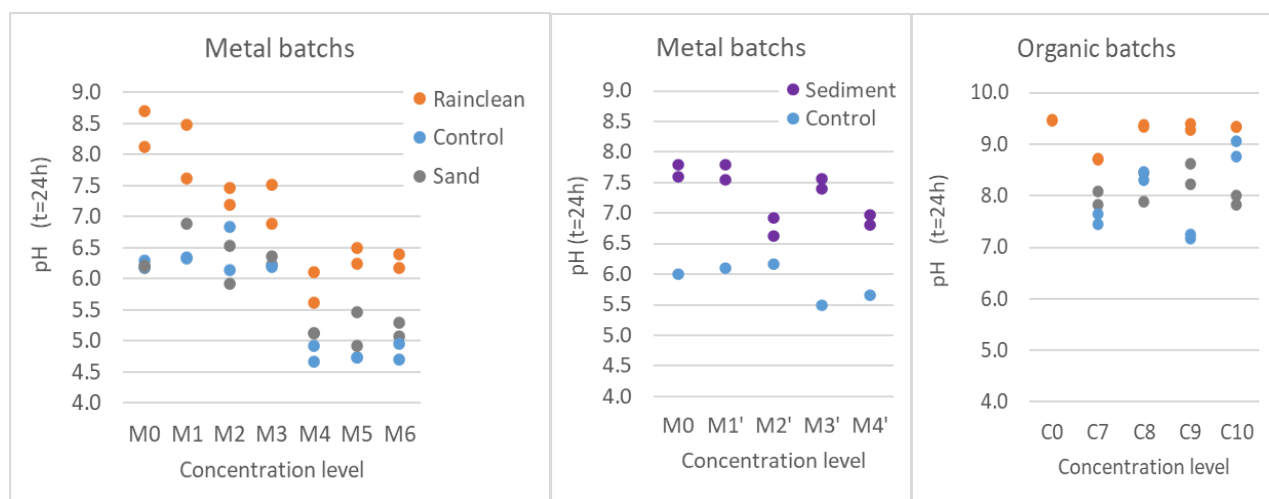


Figure 7 : pH values at t=24h for the different adsorption equilibrium batches

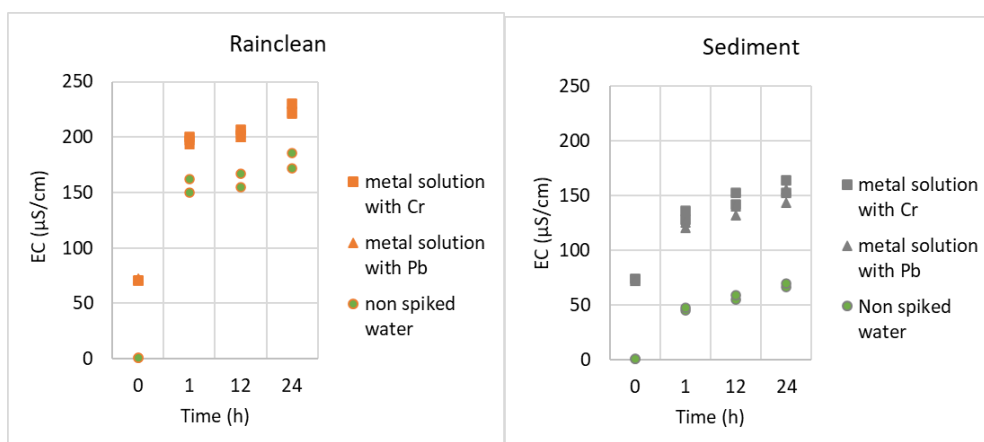


Figure 8 : evolution of electric conductivity (EC) during kinetic experiments, for Rainclean and sediment batches

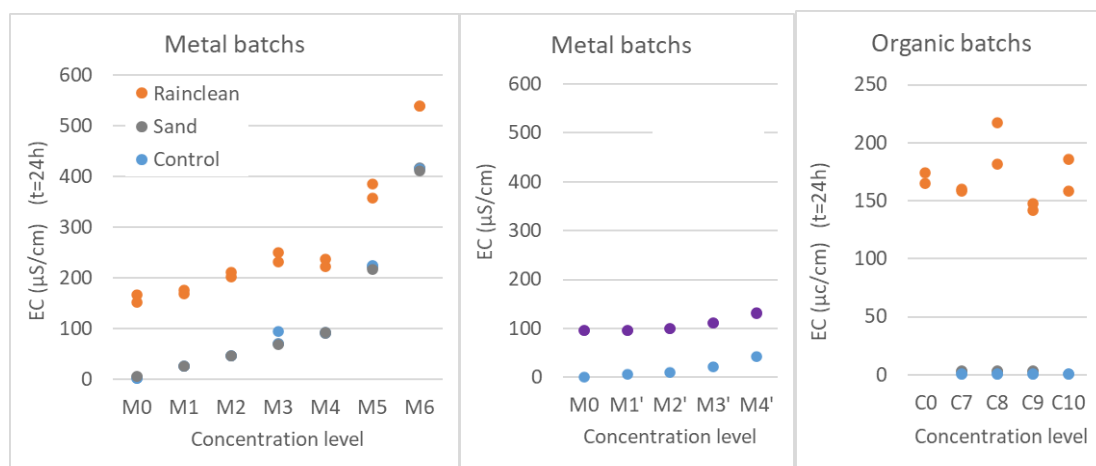


Figure 9 : electric conductivity (EC) values at t=24h for the different adsorption equilibrium batches

4.1.3 Column tests

4.1.3.1 Design of column tests

Column tests were conducted in order to simulated long term evolution of micropollutants (metals, BPA and alkylphenols) adsorption/transport and final breakthrough, in an accelerated way, but under flow conditions as close as possible to the real field conditions.

Column test were also performed with two tracer components NaCl and AAG (aminoG acid). NaCl was used to assess the hydrodynamics of the column flow and evaluate the non-reactive advection/dispersion parameters. AAG is often used in field studies to assess the hydrodynamics of red bed filters, and was also used in Bugeaud. However, while AAG does not adsorb on the sand this might not be the case for Rainclean, and column tests were used to assess this potential adsorption.

In order to meet real field conditions, but with accelerated loading, the following choices were made:

- Column depth: The depth as the Rainclean layer present in the LifeAdsorb prototype is of 20 cm. Thus, possible depths of 5 to 20 cm of Rainclean were considered when designing the column system.
- Flow conditions: The columns are fed from the top, and works with downstream flow. A 5 cm water head is maintained at the top of the column. The flow is limited by a valve at the outlet of the column. Column were fed continuously (7/7days, 24/24h) at a (relatively) constant flow rate and concentration.
- Effluent used: in order to have a water matrix composition as close as possible to real case for micropollutant experiments, clear water was collected on site, at the outlet of filter n°2 (sand filter without Rainclean layer) of the LifeAdsorb red bed prototype. This water was then spiked with solutions of dissolved micropollutants to reach the targeted inlet concentrations. In the case of tracer experiments deionised water was used and spiked with the tracer.
- Flow rate and inlet concentrations: in order to accelerate the saturation of the column and reach breakthrough within a reasonable number of days, flow rates and inlet concentrations had to be increased compared to field data. It was however decided not increase them more then by a factor 5 to 10.

To design column operation conditions, breakthrough times, and associated adsorbate volumes, were roughly estimated based on batch experiment results (for isotherm laws), and on data from a field survey conducted in 2016 by the municipality of Paris (for the range of field inlet concentrations). This calculation was carried out for metallic (Zn, Cu) and organic micropollutants (BPA, OP, NP).

The estimated time t_p and adsorbate volume V_e needed to saturate the column were calculated as : $t_p =$

$$\frac{V_e}{Q} = \frac{q_e \times M_s}{C_e \times Q} = \frac{q_e}{C_e} \times \frac{L\rho}{V_D} \quad \text{and} \quad V_e = \frac{q_e}{C_e} \times \frac{L\pi d^2}{4} \rho$$

with : V_e volume of adsorbate, Q adsorbate inflow rate to the column, V_D specific inflow rate (Darcy velocity), M_s mass of Rainclean substrate, L depth of Rainclean, d internal diameter of the column, ρ bulk density of Rainclean, C_e targeted inflow concentration, q_e the adsorbed particulate load at saturation (given by batch isotherms).

Different scenarios were considered combining different values of parameter. The different values tested and the ones chosen are summarised in Table 8. For heavy metals, it was assessed on this basis that at least 17 days and 500 L of adsorbate per column would be needed. For organic micropollutants, the initial assessment based on isotherm data from preliminary tests conducted in 2017 indicated relatively quick breakthrough in a few days. However, batch tests performed in 2022, with the Rainclean material implemented in Bugeaud prototype (new formulation compared to the 20017 material) lead to much higher adsorption capacity for alkylphenols, and time before breakthrough was assess to more than 100 days. As this was not feasible, a different test procedure, with a phase of highly accelerated loading, was implemented (see section xxx).

Table 8 : tested design parameters for column systems and chosen values

	Tested values	Chosen target value
d (cm)	5; 8	5
L (cm)	5; 10; 20	5+20
V_D (m/s)	V_D field (3.3×10^{-5} m/s) x1; x2; x5; x10	V_D field x5 (1.65×10^{-4} m/s)
C_e (µg/L)	$C_{\text{dissolved field}}$ x1; x5; x10	$C_{\text{dissolved field}}$ x5 (metals); x10 (organics)

4.1.3.2 Construction and operation of column systems

Six columns were built, three in plastic and three in glass. The plastic columns were used to study the behavior of metals and tracer substances, glass columns were used for the removal of organic micropollutants. For each series of tests, 2 columns were used for duplicate test on the Rainclean material, 1 column was used as a blank reference (column without Rainclean fed with the same adsorbate inflow to check for possible contaminations or losses by adsorption on the column).

Then a system was set up as shown in figure 1. In the fluid direction the system was composed of: feed tank (1), feed pipes (2), peristaltic pump (3), UV lamp (4), inlet pipes to the columns (5), glass columns (6) and plastic columns (7), effluent outlet valve (8), effluent storage tank (9).



Figure 10 : column system

Porosity measurements. To determine the porosity (ϵ), a simple volumetric method was used where a known volume of water was placed in a graduated cylinder and a determined volume of the material in a beaker. Then water was added until the volume of the substrate was covered and the amount of liquid used was checked. Finally, the percentage occupied by this volume was calculated, which provided an approximation of the porosity of the material used. It should be noted that the experiment was carried out in triplicate. Porosity was assessed to $\epsilon_s = 0.37$ for sand and $\epsilon_R = 0.56$ for Rainclean.

4.1.3.3 Tracer experiments

The objective of performing the tracer experiences was to analyze the advection / dispersion in the columns. Therefore, a known and measurable concentration is added to the inlet of the column system and then its value is also evaluated in the column effluent. The tracer can be applied continuously or instantaneously. In the first, the solution is applied in a very short period of time, $1/30$ of the theoretical residence time (t_t). While in continuous dosing, the tracer enters the column with a continuous concentration for a time greater than 3 times the t_t . In this work a continuous dosing was used and the residence time t_t was calculated as in the following equation, where d is the diameter de la columns, L the bed length, ϵ the bed porosity and Q the flow through the column.

$$t_t = \frac{\frac{\pi d^2}{4} \epsilon L}{Q} \quad (14)$$

Column tests were performed with 2 different tracers in order to study the dispersion and adsorption process. For the first a solution of sodium chloride (NaCl) was used and for the other the AAG (described before). The last was used as a tracer as it was considered by the teams in the Life-Adsorb project for tracing in the Bugeaud prototype. It was also previously reported in the literature with very good results as tracer.

NaCl tests.

Three sets of column test were carried out for NaCl tracer (Figure 11):

- Test 1 : bed = 20 cm of a Rainclean (237 g),
- Test 2 : bed =20 cm of sand (660.5 g)

- Test 3 : bed = 10 cm sand (330.3 g) + 20 cm of Rainclean (196 g) + 10 cm of sand (330.3 g). This “sandwich” bed is similar to the structure of the filtration bed in the Bugeaud reed bed prototype. In all cases, a 2 cm layer of inert gravel was placed on the bottom and top of the Rainclean or sand bed.

All experiments were carried out in duplicate, continuously and at room temperature ($20\text{ }^{\circ}\text{C} \pm 2$). Initially, demineralized water was circulated until constant EC was obtained (approximately 24 hours). Subsequently, the concentrated NaCl solution (0.55 g L^{-1}) began to flow with a known initial EC of $9160 \pm (20)\text{ }\mu\text{S cm}^{-1}$ and average flow rate of $18 \pm (1)\text{ mL min}^{-1}$. In all experiments, EC determinations in the column effluent were performed every 5 minutes. A total of 1.5 L of NaCl solution, corresponding to 4 to 10 times the pore volume (depending on the test) was injected in each column.

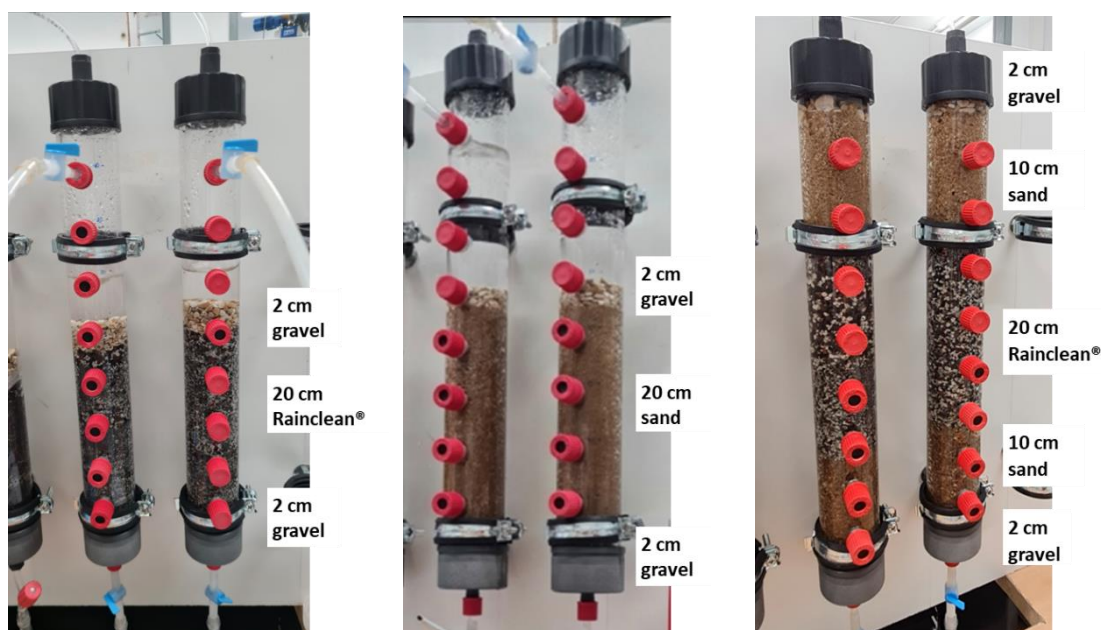


Figure 11 : Configuration of the columns for NaCl tests. a) Column of Rainclean b) Column of Sand c) Column of Sand and Rainclean.

AAG tests

The three following sets of column tests were carried out for AAG tracer (Figure 11):

Test 1 : bed = 20 cm of Rainclean® (225 g),

Test 2 : bed = 20 cm of sand (660 g)

Test 3 : bed = 10 cm of Rainclean® (127 g)

Experiments were carried out in duplicate, continuously and at room temperature ($20\text{ }^{\circ}\text{C} \pm 2$). Columns were fed at a constant flow rate of $17.7 (\pm 0.6)\text{ mL min}^{-1}$, 10 mL of sample were taken every 10 minutes to be subsequently analyzed in the UV fluorimeter. The inlet AAG concentration (1 mg L^{-1}) was taken identical to the one used to perform the in-situ tracing in the Bugeaud biofilter. Based on the results from batch studies showing AAG adsorption on Rainclean®, the total volume of AAG solution fed to each column was set to 7.5 L for tests 1 and 2 (ie 34 pore volumes), and extended to respectively 27 L (245 pore volumes) and 63 L (572 pore volumes) for the first and second replicate of test 3, in order to try to saturate the material used in the column.

In all the experiments, the tracer's accumulated mass in the influent and effluent of the columns was calculated as $m_{a_n} = C_i Q t_n + m_{a_{(n-1)}}$

4.1.3.4 Micropollutant experiments

Metals

The column study for metallic micropollutants was conducted over a period of two months (04/04/2022 to 07/06/2022), including 2 days of initial conditioning of the column, 39 days of feeding with the metal solution and 7 days of washout with clear water.

The column setup was similar to Test 1 of tracer experiments: 20 cm of Rainclean (253.6 g), with 2 cm of inert gravel at the bottom and on the top, and a water of approximately 5 cm maintained on top of the Rainclean layer. Two of the three columns were filled with the Rainclean material to be studied, while the third column was left empty and used as a control with only the metal solution circulating in it.

At the beginning of the experiment, it was necessary to purge the air trapped in the columns filled with Rainclean. This phenomenon also occurred during the NaCl test. All the columns were covered with aluminium foil to reduce the formation of microbiological colonies.

Clear water was pumped from the outlet of filter N°2 (sand filter) of the LifeAdsorb biofilter prototype into a 1 m³ tank, transferred to the lab, where it was stored in 3 plastic tanks of 270 L each in the cold room (4 °C). Three series of clear water (~800 L each time) were needed for the whole column experiments on metals. The content of the 270 L tanks was spiked with a mix of the previously created metal stock solutions (As, Cd, Cr, Cu, Ni, Pb, V and Zn) to produce batches of metal solutions at the targeted concentrations. Table 9 summarises the dissolved metal concentrations in the clear water and in the spiked water. Dissolved metal concentrations of the clear water appear to be very low. Also, for the metal solution, comparison between column inflow and outflow from the control column indicated that the experimental setup does not introduce any modification in the metal concentrations (no contamination or metal loss on the column material).

Table 9 : Dissolved metal concentrations (µg L⁻¹) in the column inflow and control column outflow - average ± standard deviation

	As	Cd	Cr	Cu	Ni	Pb	V	Zn
Clear water collected	0.5	<0.02	0.4	<0.1	0.6	0.02	0.9	5.4
Spiked water – inflow	27±1	10±1	53±3	279±32	12±3	4±1	51±4	134±6
Spiked water – control column outflow	27±2	10±1	53±4	277±37	13±3	4±1	51±5	135±11

First, the clear water was passed through the column for 48 hours and a sample was taken to determine the initial conditions of the system. The metal solution was then circulated. During the metal loading phase, samples were taken each time at the inlet of the system, at 5 cm, and 20 cm depth of the Rainclean bed in each column. Sampling was performed at 1, 2, 24 and 48 hours initially. Then, every 48 hours and in the last 20 days the samples were taken every 72 hours, all in duplicate. They were always filtered, acidified at 1% with HNO₃ and then refrigerated until analysis. Effluent at the outlet of each column was collected continuously in a container and every 24 hours the collected volume was weighted, an aliquot of 10 mL of sample (filtered and acidified) was taken, and the container emptied. The sample aliquots were accumulated to later determine the total mass of micropollutants in the cumulated outflow from each column. Likewise, each time samples were taken to determine metals, inlet sampling was also

performed before and after the pump and outlet sampling at 20 cm from each column to analyze dissolved organic carbon (DOC) and major ions. Throughout the experience, pH and EC were monitored, as well as the inlet and outlet flow rates, and if needed the outlet valve as reajusted. As it can be seen from Table 10, pH, EC and DOC were relatively stable throughout the column experiment and did not vary significantly between the inlet and the outlet of the columns. pH of the clear water collected of the sand reed bed, and spiked with metals, was already close to 8 – which is in the range of pH value measured for runoff in Paris region. One can note a very slight decrease of EC and DOC at the outlet of Rainclean® columns, compared to inlet of control column. Flow data is summarised in Table 11 and show slight fluctuation over the period of the experiment. Average flow is however similar between the columns, with a difference of total volume between the two Rainclean® columns around 10%.

Table 10 : Range of pH, electric conductivity (EC) and dissolved organic carbon (DOC) in the inflows and outflows of columns during metal loadings

		pH	EC	DOC (mg.L ⁻¹)
Batch of water 1	Inflow	8.0 ± 0.2	639 ± 2	1.48 ± 0.04
	Control column	8.2 ± 0.1	639 ± 2	1.49 ± 0.17
	Outflow Rainclean columns	8.0 ± 0.2	585 ± 21	1.35 ± 0.17
Batch of water 2	Inflow	7.6 ± 0.2	611 ± 3	2.66 ± 0.24
	Control column	8.0 ± 0.1	609 ± 4	2.59 ± 0.27
	Outflow Rainclean columns	7.9 ± 0.2	605 ± 5	2.55 ± 0.19

Table 11 : Range of flow through the three columns during metal loadings and total volume of solution added to each column

	Rainclean column S1	Rainclean column S2	Control column S3
Flow (mL.mn ⁻¹)	12.9 ± 1.3	13.3 ± 1.1	13.2 ± 1.6
Specific flow (m.s ⁻¹)	1.10x10 ⁻⁴	1.13 x10 ⁻⁴	1.12 x10 ⁻⁴
Total outflow of metal solution (L)	577	647	609

Organics

The column study for organic micropollutants (BPA, NP, OP) was conducted over a period of three weeks (20/06/2022 to 08/07/2022), including 1 day of initial conditioning of the column (P0 period), 13 days of feeding with the micropollutant solution (P1-P3) and 2 days of washout with non-spiked water (P4). The period of continuous loading with micropollutant solution were divided in three sub-periods, with different inlet concentration and flow as presented in Table 12. The P2 period with high concentration and increased inflow was intended to accelerate the breakthrough of micropollutants, while P1 and P3 are closer to real-life conditions. P0 and P4 correspond to periods of feeding with non-spiked water (collected at the outlet of the conventional sand reed bed filter). However, inlet concentrations monitored during these periods showed already high concentrations of micropollutants even without spiking, they will thus be included in the adsorption phase during data analysis.

Note that for BPA, inlet concentrations showed erratic variations with some unexpectedly high measurements. This might indicate BPA contaminations in the feeding system, or possibly contaminations during analyses, which makes it difficult to analyse the column results.

Table 12 : characteristics of the three loading periods

		P0	P1	P2	P3	P4
Time		0 to 24h	24 to 120h	120h to 264h	264h to 336h	336h to 364h
Flow (mL.mn ⁻¹)		12.6 ± 1.8		20.9 ± 3.4	13.0 ± 2.6	
Target inflow concentration (µg.L ⁻¹)		0	0.5	9	0.5	0
Actual inflow concentration (µg.L ⁻¹)	BPA	1.4	1.1± 1.1	12.6± 8.7	5.6± 4.5	7.1
	OP	0.04	0.6± 0.1	7.8± 1.4	1.8± 0.8	0.6
	NP	0.6	0.7± 0.2	7.6± 1.3	1.5± 0.1	0.8

Column set up was similar to metal tests, but with a depth of Rainclean bed limited to 10 cm (86 g). In these experiments, glass columns were used, 2 of which were loaded with Rainclean and one through which only the liquid circulated.

As with the metal solution, clear water was collected on-site at the outlet of filter n°2 from the LifeAdsorb prototype. It was collected and stored in 50 L stainless steel containers, and spiked with known concentrations of organic micropollutants before use.

250 mL samples were collected in the feed flow and at the outflow of each column after 1h, 2h, 24h and than every 48 hours (approximately). They were filtered and subsequently frozen prior to analysis.

4.2 Experimental results

4.2.1 Lixiviation of adsorbent materials

Results from leaching tests are synthetised in Table 13.

For sand no significant leaching is observed for either of any of the studied micropollutants.

For Rainclean however, an important leaching of dissolved nonylphenol is measured: approximately 1 µg/L, which is in the upper range of dissolved concentrations measured in the runoff. Leaching of octylphenol of 0.3 µg/L is also important compared to runoff concentrations. The only trace metal leached at a significant concentration of 4 µg/L is vanadium.

In the case of sediment, very high leaching compared to concentrations in the dissolved phase of runoff is observed for copper (164 µg/L), BPA (1 µg/L), Pb (0.9 µg/l) and As (1.5 µg/l), as well as moderate leaching of zinc (17 µg/L).

Table 13: micropollutant leaching from adsorbents – concentrations measured after 24h lixiviation at S/L = 10 g/L

µg/l	As	Cd	Cr	Cu	Ni	Pb	V	Zn	BPA	OP	NP
Sand	0.59	< LQ	< LQ	0.55	0.32	0.25	0.66	0.35	NA	NA	NA
Rainclean	0.67	< LQ	< LQ	0.40	0.16	0.25	4.35	0.40	0.03	0.30	0.99
Sediment	1.5	0.02	0.67	164	3.6	0.91	1.9	17	1.0	0.01	0.08

4.2.2 Batch kinetics

Kinetic experiments show rapid decrease of concentration over time for most pollutants, a relatively stable concentration is reached in most cases at t=12h. This is illustrated in Figure 12 for trace metals. The only exception is AAG, for which the adsorption rate is much slower and concentrations decrease the solution till 72h. Thus, the choice of 24h for the adsorption equilibrium studies is validated for all studied micropollutants, as well as for fluorescein and rhodamine. For AAG, equilibrium experiment will be conducted over 72h.

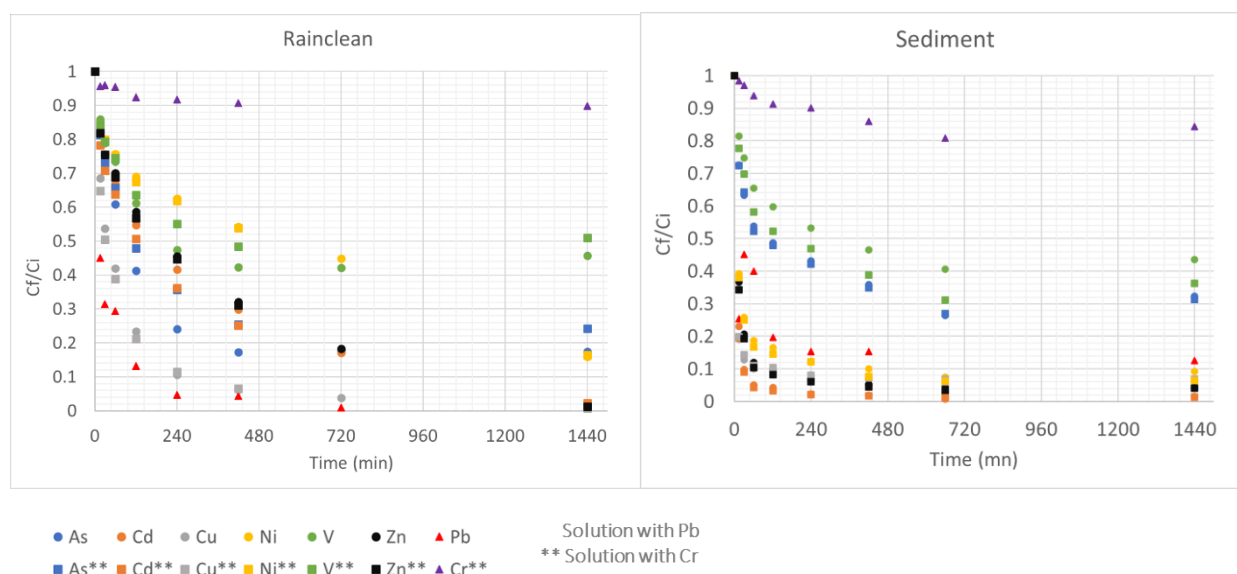


Figure 12 : evolution of metal concentrations over time during kinetic study

Kinetic batch experiments highlight however a diversity of behaviours depending on the considered pollutant or sorbent. Strong differences are noticed in the speed of the adsorption processes as well as in the adsorption efficiency (removal rate).

Table 14 : parameters of pseudo first order (PFO) and pseudo second order (PSO) kinetic models fitted on batch data for Rainclean®

	PFO model			PSO model			
	qe (mg/g)	k ₁ (mn ⁻¹)	R ²	qe (mg/g)	k ₂	qe*k ₂ (mn ⁻¹)	R ²
AAG	0.51	1.27E-03	0.992	0.62	2.06E-03	1.28E-03	0.997
Rd	0.44	2.45E-02	0.985	0.47	7.37E-02	3.48E-02	0.993
Fl	0.46	1.24E+00	0.963	0.46	3.61E+00	1.66E+00	0.963
	qe (µg/g)	k ₁ (mn ⁻¹)	R ²	qe (µg/g)	k ₂	qe*k ₂ (mn ⁻¹)	R ²
NP	2.62	1.58E-01	0.997	2.65	2.27E-01	6.02E-01	0.999
OP	1.30	9.12E-02	0.982	1.35	1.40E-01	1.89E-01	0.992
BPA	2.28	8.03E-02	0.981	2.37	6.68E-02	1.58E-01	0.998
As	49.6	1.16E-02	0.99	55.3	2.74E-04	1.52E-02	0.99
Cd	40.4	6.96E-03	0.96	46	1.92E-04	8.83E-03	0.98
Cu	683	2.03E-02	0.99	744	3.82E-05	2.84E-02	0.998
Cr	13.7	1.66E-02	0.89	15	1.58E-03	2.37E-02	0.936
Ni	122	3.11E-03	0.924	136	3.18E-05	4.32E-03	0.947
Pb	4.39	4.49E-02	0.943	4.65	1.52E-02	7.07E-02	0.985
V	78.7	1.25E-02	0.986	86.3	2.02E-04	1.74E-02	0.989
Zn	673	4.76E-03	0.967	770	7.91E-06	6.09E-03	0.984

Table 15 : parameters of pseudo first order (PFO) and pseudo second order (PSO) kinetic models fitted on batch data for the sediment

	PFO model			PSO model			
	qe (µg/g)	k ₁ (mn ⁻¹)	R ²	qe (µg/g)	k ₂	qe*k ₂ (mn ⁻¹)	R ²
NP	3,81	8,39E-02	0,997	3,93	4,64E-02	1,82E-01	0,997
OP	1,54	2,79E-02	0,973	1,66	2,26E-02	3,76E-02	0,963
BPA	1,64	4,77E-02	0,857	1,75	4,22E-02	7,37E-02	0,907
As	44.9	2.94E-02	0.965	48.9	8.18E-04	4.00E-02	0.979
Cd	46.7	1.10E-01	0.997	47.8	6.13E-03	2.93E-01	0.997
Cu	686	1.41E-01	0.992	699	6.56E-04	4.59E-01	0.993
Cr	24.2	6.29E-03	0.961	27.6	2.84E-04	7.84E-03	0.974
Ni	141	7.45E-02	0.99	147	9.72E-04	1.43E-01	0.991
Pb	13.5	2.74E-02	0.947	14.4	3.21E-03	4.62E-02	0.957
V	76	2.30E-02	0.922	82.7	3.78E-04	3.13E-02	0.989
Zn	718	7.56E-02	0.992	745	2.04E-04	1.52E-01	0.992

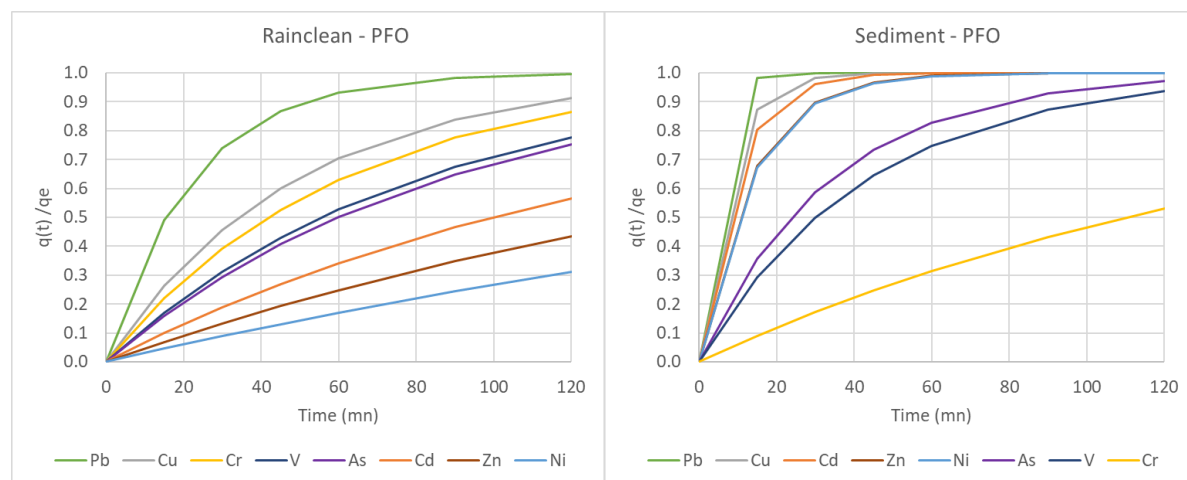
Based on these measurements, $q_e = f(t)$ data was calculated, and pseudo first order (PFO) and pseudo second order (PSO) kinetic models were adjusted with a least square method. For metal kinetic studies two multi-elementary solutions were tested, one containing Pb and no Cr and another containing Cr and no Pb (this to avoid possible precipitation of lead chromate), along with six other metals (As, Cd, Cu, Ni, V, Zn). No difference was observed in the As, Cd, Cu, Ni, V and Zn kinetics between both solutions in the case of the Rainclean material. Small differences were observed mainly for vanadium in the sediment. Thus results from both solutions were used together to fit a single kinetic law for each metal on each sorbent.

Parameters of the fitted laws are given in Table 14 for Rainclean and Table 15 for sediment. Both PFO and PSO models show very good fits. Values of the decrease rate parameter, which is k_1 for PFO and $q_e \cdot k_2$ for PSO, are consistent between the two models. For Rainclean, they range from 0.003 (Ni) to 0.16 mn^{-1} depending on the considered micropollutants. The three tracers considered cover a similarly wide range of kinetics, with decreasing rates from 0.001 mn^{-1} for AAG to 1.2 mn^{-1} for FL.

The shape of the PFO kinetic laws, over the first 2 hours, is illustrated in Figure 13. The PFO model was used to assess the times $t_{50\%}$ and $t_{80\%}$ needed, for each adsorbate and each sorbent, to reach respectively 50% and 80% of the equilibrium value. These characteristic times are compared in Table 16 for all studied micropollutants between Rainclean and sediment. K_d values, calculated from the concentrations reached at the end of the kinetic ($t=24\text{h}$) are also given to assess adsorption efficiency.

Strong differences in the adsorption properties of the Rainclean and the sediment are highlighted. Micropollutants can be classified as follows based on their adsorption velocity:

- Rainclean : NP, OP, BPA > Pb > Cu, Cr > V, As > Cd, Zn > Ni
- Sediment : Cu, Cd, NP, Ni, Zn > BPA > As, OP, Pb, V > Cr



The fastest adsorption is observed in the case of Rainclean for organic micropollutants (NP, OP, BPA) and in the case of the sediment for Cu, Cd, NP, Ni and Zn : less than 10 minutes are needed to reach 50% of equilibrium. Cd, Zn and Ni, which show fast adsorption on the sediment present much slower adsorption kinetics for Rainclean : their $t_{50\%}$ values for Rainclean range from 100 to 223 mn. Similarly low adsorption rate is only observed for Cr in the case of the sediment.

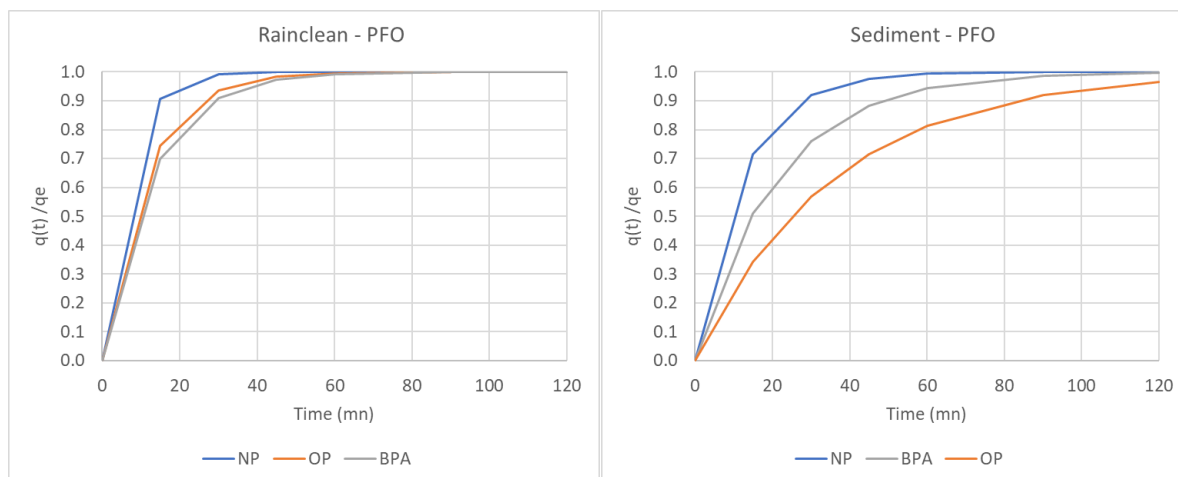


Figure 13 : adsorption dynamics for the different micropollutants studied, on Rainclean and on sediment

It has to be noted that adsorption velocity is not necessarily in line with adsorption efficiency, ie there is no correlation between the kinetic rate and the K_d values. Based on their K_d values, evaluated at the end of the kinetic experiment, the pollutants can be ordered as follows:

- Rainclean : NP, BPA > OP, Cu, Pb, Zn > Cd >> Ni, As > V >> Cr
- Sediment : NP, Cd >> Zn, Cu, Ni > Pb, OP > As, BPA, V >> Cr

Table 16 : equilibrium concentration, K_d value of the kinetic experiment and time needed to reach respectively 50% and 80% of the equilibrium condition – comparison between Rainclean and sediment

	Ce (µg/L)		Kd kinetic (L/kg)		t _{50%} (mn)		t _{80%} (mn)	
	Rainclean	Sediment	Rainclean	Sediment	Rainclean	Sediment	Rainclean	Sediment
AAG	2120		253		545		1267	
Rd	60		8033		28		66	
Fl	840		733		1		1	
NP	0.09	0.5	29922	7831	4	8	10	19
OP	0.10	2.56	13382	657	8	25	18	58
BPA	0.11	12.1	21977	173	9	15	20	34
As	136	234	372	214	60	24	139	55
Cd	10	7	4406	7209	100	6	231	15
Cu	57	502	12713	1409	34	5	79	11
Cr	1343	1362	11	19	42	110	97	256
Ni	258	126	517	1191	223	9	518	22
Pb	0.6	20	8319	694	15	25	36	59
V	721	555	106	155	55	30	129	70
Zn	102	318	7273	2345	146	9	338	21

4.2.3 Batch equilibrium studies – isotherm models

4.2.3.1 Pollutant removal rates

Figure 14, Figure 15 and Figure 16 present the removal rates of micropollutants, as a function of the initial concentration of batches, for the different micropollutants studied, in the case of Rainclean, sand and sediment.

Note that no data is available for equilibrium batch studies for Pb in the case of Rainclean and sand, as experimental results were not consistent for this metal, possibly due to precipitation in the multi-elementary solution. In the case of sediment, no Cr was introduced in the batches to avoid this phenomenon and results are thus provided for Pb but not Cr.

As expected, pollutant removal by adsorption on sand is very low, and most removal rates drop below 20% with increasing solution concentration.

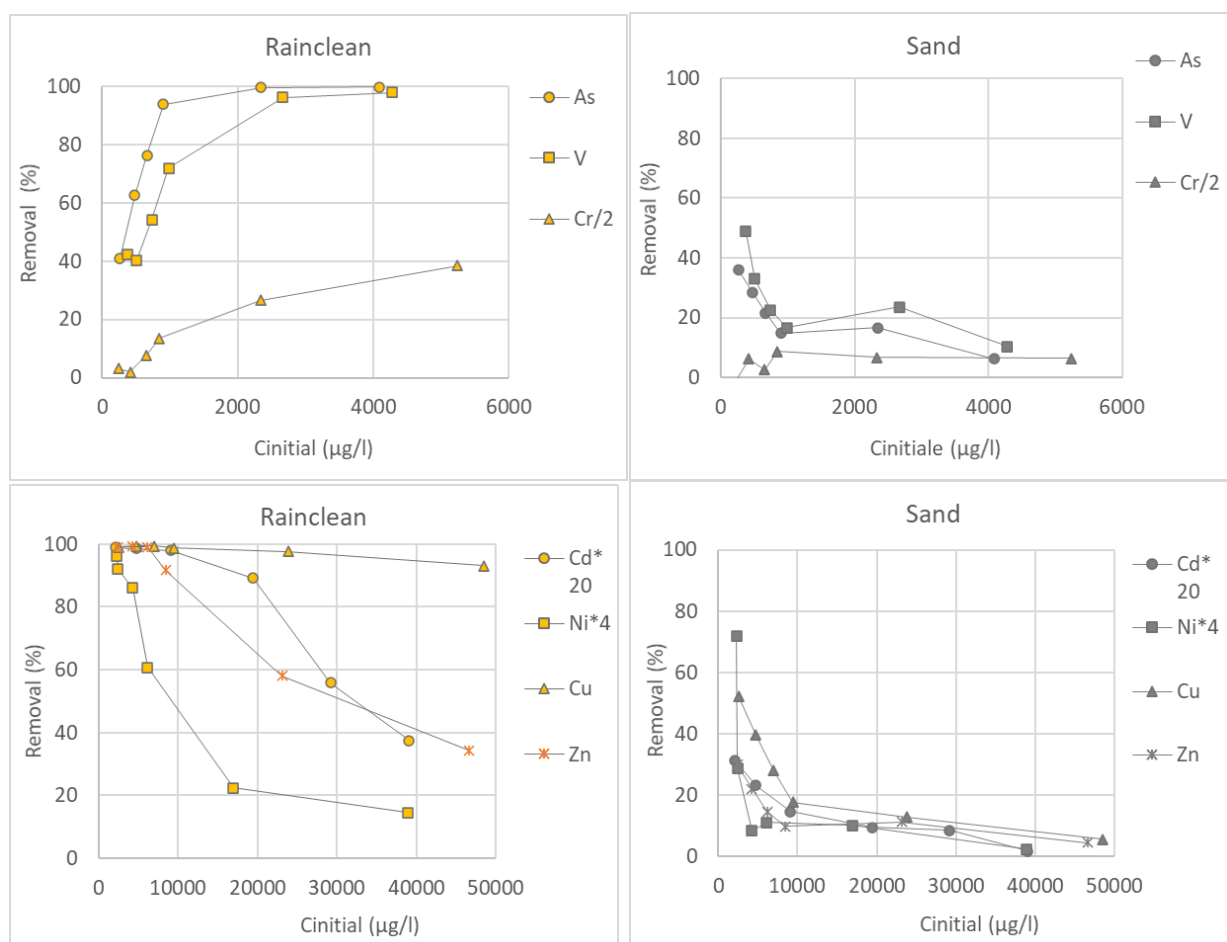


Figure 14 : Rainclean and sand removal rates of trace metal at adsorption equilibrium as a function of the initial concentration of the batch

In the case of Rainclean, micropollutants can be divided in three groups:

- NP, OP, BPA, Cu present removal rates superior to 90% for all tested concentrations levels;
- Cd, Ni, Zn present decreasing removal rates with increasing solution concentration, which is consistent with progressive saturation of the sorbent. The drop of removal rate is very quick for Ni;

- As, V and Cr present increases in the removal rate with increasing solution concentration. This is unexpected for adsorption processes and probably corresponds to precipitation occurring at higher concentration levels. Removal rates of Cr remain however low.

In the case of sediment, removal rates superior to 80% are observed for most pollutants, except As and BPA which show lower removal efficiency. The lower removal rates observed for the lowest initial concentration have to be related to the observed leaching of some contaminants from the sediment, and especially Cu, BPA, Pb, As during lixiviation experiments.

Equilibrium concentrations reached in the solutions were compared to the concentration ranges expected for dissolved micropollutants in road runoff. A number of batches present equilibrium concentrations that are far superior to these target concentrations and are thus not representative of the use intended for the adsorbent. These batches were discarded for further analyses, and only equilibrium concentrations in the same order of magnitude than the runoff to be treated were considered for isotherm calculations.

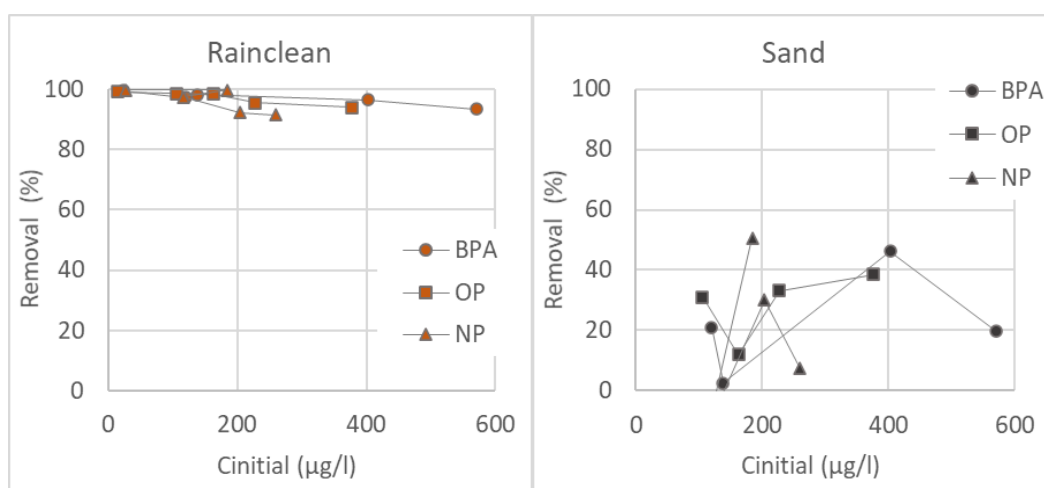


Figure 15 : Rainclean and sand removal rates of organic micropollutants at adsorption equilibrium as a function of the initial concentration of the batch

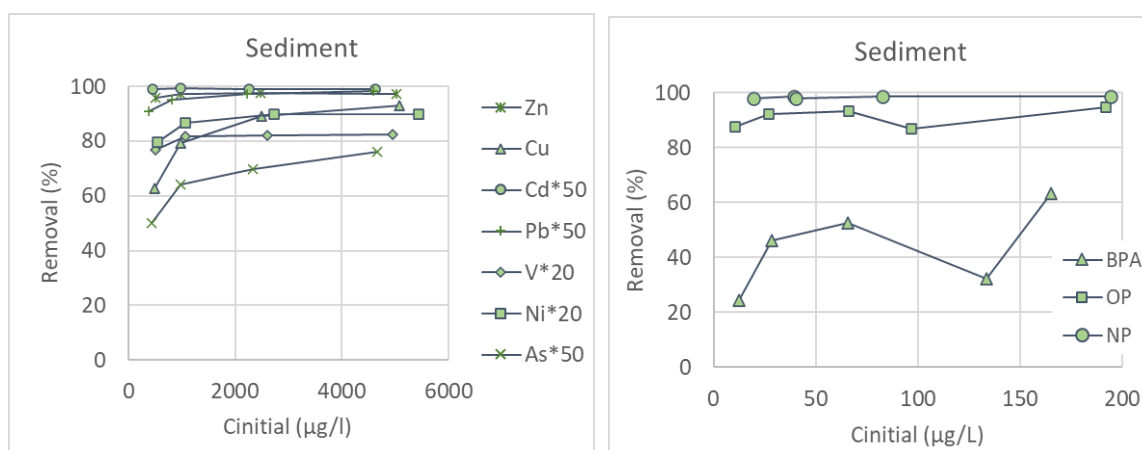


Figure 16 : sediment removal rates of trace metals and organic micropollutants at adsorption equilibrium as a function of the initial concentration of the batch

4.2.3.2 Isotherm laws

Based on batch concentration the mass of pollutant adsorbed per unit mass of sorbent q_e ($\mu\text{g/g}$) was calculated and represented as a function of the equilibrium concentration C_e ($\mu\text{g/l}$).

Three types of isotherm laws $q_e = f(C_e)$ were tested: linear, Langmuir and Freundlich. Then were fitted using a least square method on the experimental results for batches with equilibrium concentration in the same order of magnitude then targeted runoff concentrations.

In the case of sand, where adsorption was usually very low, this analysis was limited to the estimation of a K_d value ($K_d = q_e/C_e$), based on the batches with the lowest concentration levels. This was also the case for Cr with the Rainclean sorbent, as even the batch with the lowest concentration presented a C_e value much superior to runoff concentration for this metal.

No isotherm law could be fitted for Rainclean in the case of As: for this compound the $q_e = f(C_e)$ law present a decreasing slope with is not consistent with any of the tested adsorption model.

Parameter of the fitted isotherm law for Rainclean and for sediment, with the C_e concentration range for which they were fitted, are given in Table 17 for tracers, Table 18 for trace metals and Table 19 for organic micropollutants. K_d values for sand are also indicated. The shape of the isotherms, over the range C_e concentrations of relevant for road runoff, is present in Figure 17, Figure 18 and Figure 19.

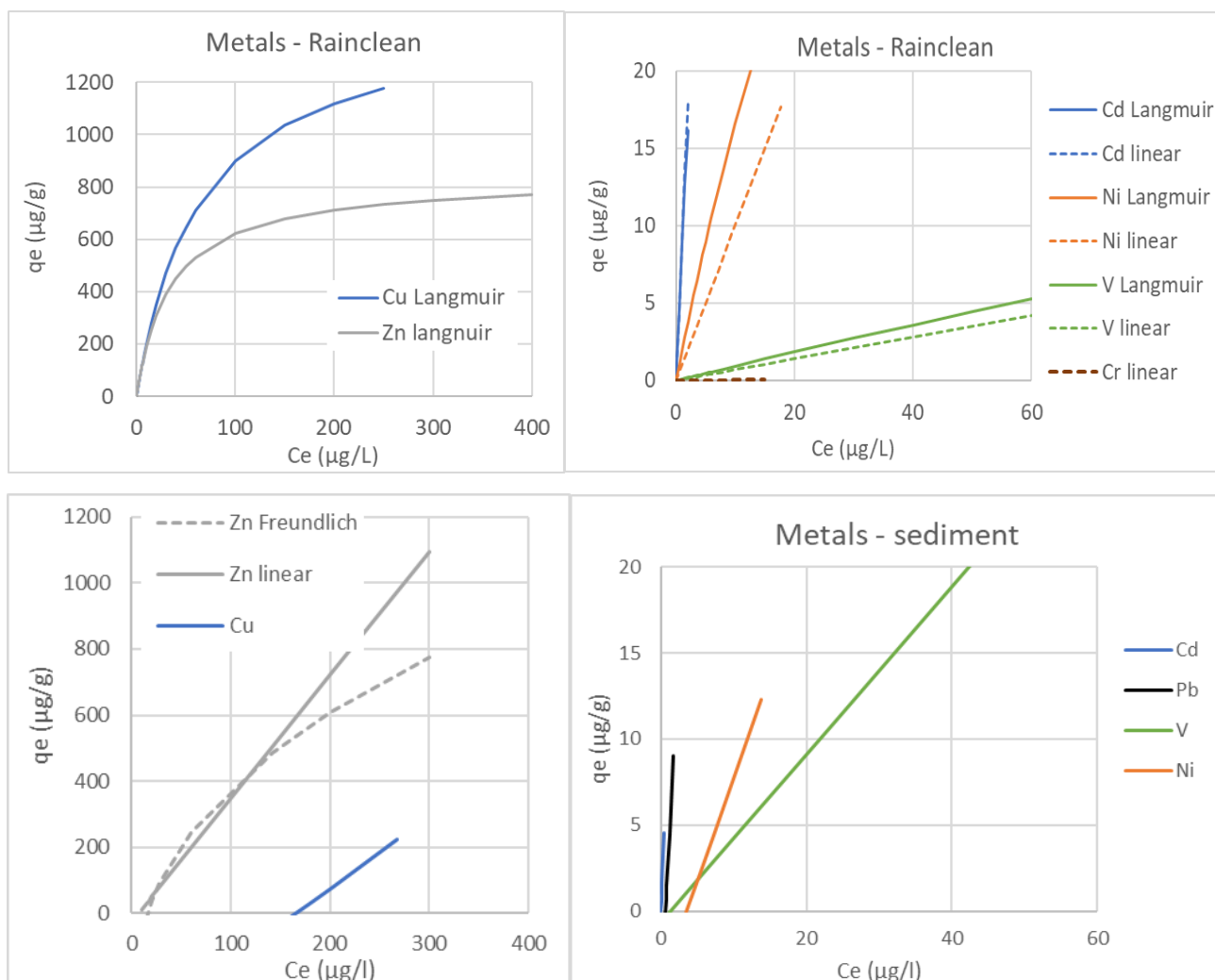


Figure 17 : adsorption isotherms of metals for Rainclean®

For Rainclean and in the case of trace metals, the Langmuir model gave the best fit, along with the linear model for some compounds. Cu and Zn, which have the largest range of target C_e range, clearly show a non linear Langmuir isotherm. Adsorption capacity for these two metals is very good. Maximum q_e , over the targeted C_e range, is of 1200 $\mu\text{g/g}$ for Cu and 800 $\mu\text{g/g}$ for Zn. For Cd, Ni and V, the Langmuir and the linear isotherm are very close over the smaller range of the target C_e concentrations and the isotherm can be approximated by a simple K_d model. Adsorption capacity on Rainclean is very low for Cr and for V (K_d respectively of 3 and 70 L/kg), similar to that of sand (K_d respectively of 7 and 95 L/kg).

For organic compounds with Rainclean, be it tracers or organic micropollutants, both Langmuir and Freundlich offer a good fit, except for OP for which Freundlich seems less appropriate. Even so slight differences appear between the fitted models, the limited number of calibration points available does not allow to choose between them. The three studied organic micropollutants show a strong adsorption onto the Rainclean. Maximal adsorbed load, over the targeted C_e ranges, are of 16 $\mu\text{g/g}$ for NP, 18 $\mu\text{g/g}$ for BPA and 10 $\mu\text{g/g}$ for OP. For OP and BPA, the simpler linear model offers a good alternative to Langmuir over the range of targeted C_e values. OP and BPA present high K_d value in the Rainclean (K_d respectively 8458 and 4156 L/kg), similar to that of Cd (9041). In comparison the K_d value for sand are between 13 and 46 L/kg.

For sediment, the linear adsorption model is well fitted for all micropollutants. Freundlich might be a alternative for Zn however the range of measurement points available for the fitting does not allow to discriminate between them. Note that in the case of sediment, and for those micropollutants for which leaching has been noticed during the lixiviation test, the isotherm does not go to the origin and a parameter Q_0 had to be added so that $q_e(C_e) = C_e \cdot K_d - Q_0$. The adsorption capacity of the sediment is higher than that of the Rainclean for V and Cd, similar to the Rainclean for Zn, for Ni and for NP but much lower for Cu, OP and BPA.

Concerning the tracer compounds, the highest adsorption on Rainclean is observed for rhodamine (Rd). Adsorption capacity is the lowest for fluorescein (Fl). Batch studies show that AAG cannot be considered as a non-reactive tracer in the case of Rainclean and presents an adsorption capacity on Rainclean superior to Fl. In the case of sand the adsorption of AAG and Fl is almost zero and adsorption of Rd is very limited ($K_d = 12$ L/kg).

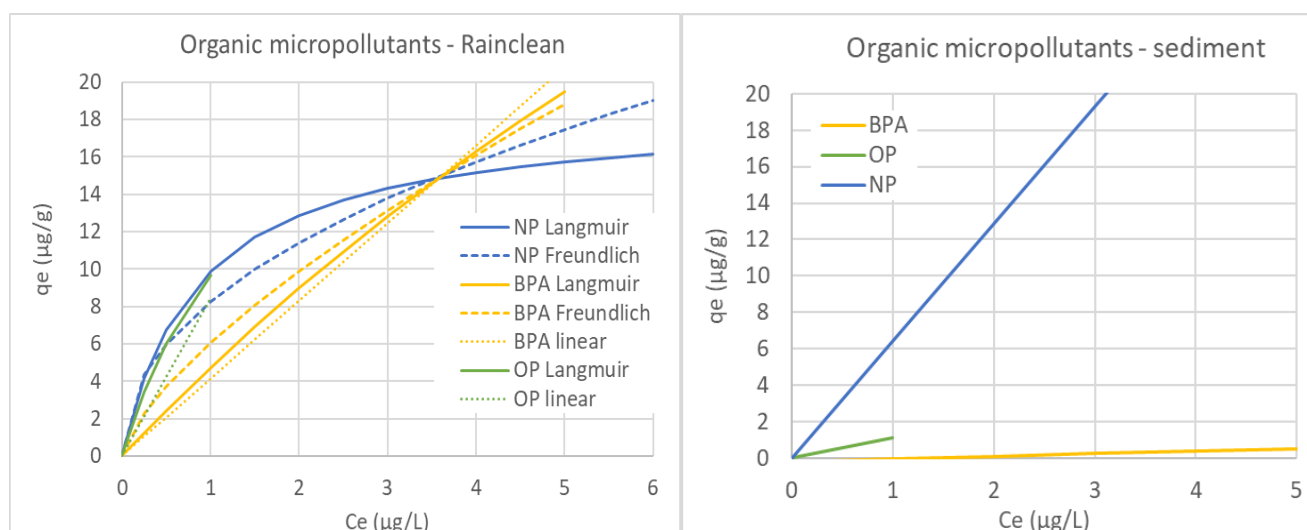


Figure 18 : adsorption isotherms of organic micropollutants and tracer compounds for Rainclean®

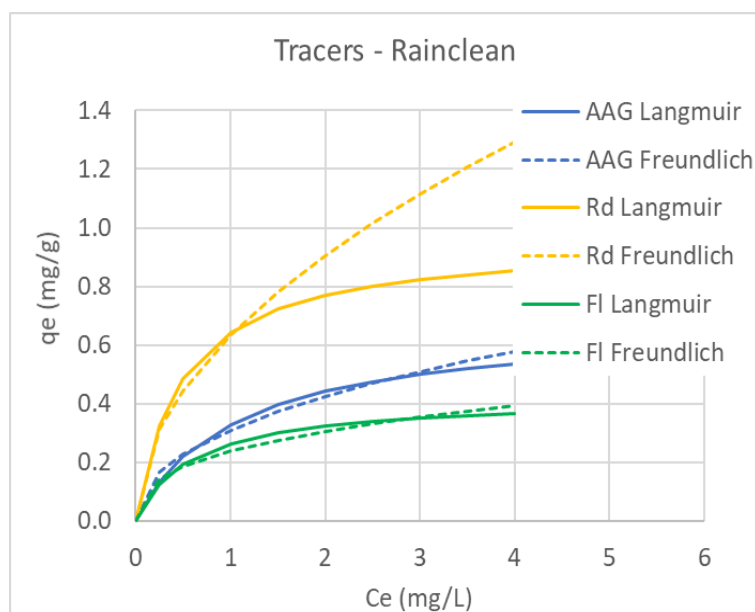


Figure 19 : adsorption isotherms of tracer compounds for Rainclean®

Table 17 : parameters of adsorption isotherm laws for tracers

	Ce fitting range (mg/L)	Rainclean				Sand
		Langmuir		Freundlich		
		qm (mg/g)	K_L (L/mg)	n	K_F	Kd (L/kg)
AAG	0.1 - 4.5	0.7	1.0	2.22	0.31	~ 0
Rd	0 - 1.4	1.0	2.1	1.94	0.63	12
Fl	0.01 - 3.8	0.4	1.7	2.79	0.24	~ 0

Table 18 : parameters of adsorption isotherm laws for trace metals

	Target Ce in runoff ($\mu\text{g/L}$)	Rainclean – Langmuir isotherm			Rainclean – linear isotherm		Sediment – linear isotherm		Sand
		Ce fitting range	qm ($\mu\text{g/g}$)	K_L (L/ μg)	Ce fitting range	Kd (L/kg)	Kd (L/kg)	Qo ($\mu\text{g/g}$)	Kd (L/kg)
As	<7	na	na	na	na	na	286	1	57
Cd	<1	1 - 9	85.1	1.17e-1	1	9041	12318	0	46
Cr	<11	na	na	na	450	3	Na	na	7
Ni	<13	5 - 130	114.7	1.69e-2	<45	1178	1201	4	256
V	<60	215-300	72.3	1.31e-3	215-300	70	489	1	95
Cu	<250	23-120	1481	1.55e-2	na	na	2169	359	110
Zn	<400	22-700	835	2.93e-2	na	na	3502	0	43
Pb	<4	na	na	na	na	na	8344	5	na

Table 19 : parameters of adsorption isotherm laws for organic micropollutants

	Target Ce in runoff ($\mu\text{g/L}$)	Ce fitting range ($\mu\text{g/L}$)	Rainclean						Sediment	Sand
			Langmuir		Freundlich		Linear		Linear	
			qm ($\mu\text{g/g}$)	K_L ($\text{L}/\mu\text{g}$)	n	K_F	Ce fitting range	K_d (L/kg)	K_d (L/kg)	K_d (L/kg)
NP	<6	0.1 - 4	18.5	1.15	2.15	8.27	na	Na	6424	70
OP	<1	0.1-11	24.9	0.634	2.69	9.53	< 2	8458	1115	42
BPA	<5	0.1-14	87.9	0.057	1.42	6.07	< 3.5	4156	143 ($q_0=0.2 \mu\text{g/g}$)	13

4.2.3.3 Comparison with data from the preliminary study conducted on Rainclean in 2017

Adsorption capacity established based on the batch studies in 2022 on the Rainclean material that has been implemented in 2020 in the LifeAdsorb red bed filter prototype are here compared to the results from the preliminary study conducted in 2017. Note that, as confirmed by Funke who produces and sells the adsorbent, the formulation of the Rainclean material has been subject to some changes in the meantime.

Isotherms laws fitted in 2017 and in 2022 are compared in Figure 20 for trace metals and in Figure 21 for organic micropollutants. In the case of Pb, as no equilibrium studies are available for 2022, the K_d calculated during the kinetic study was used for the comparison.

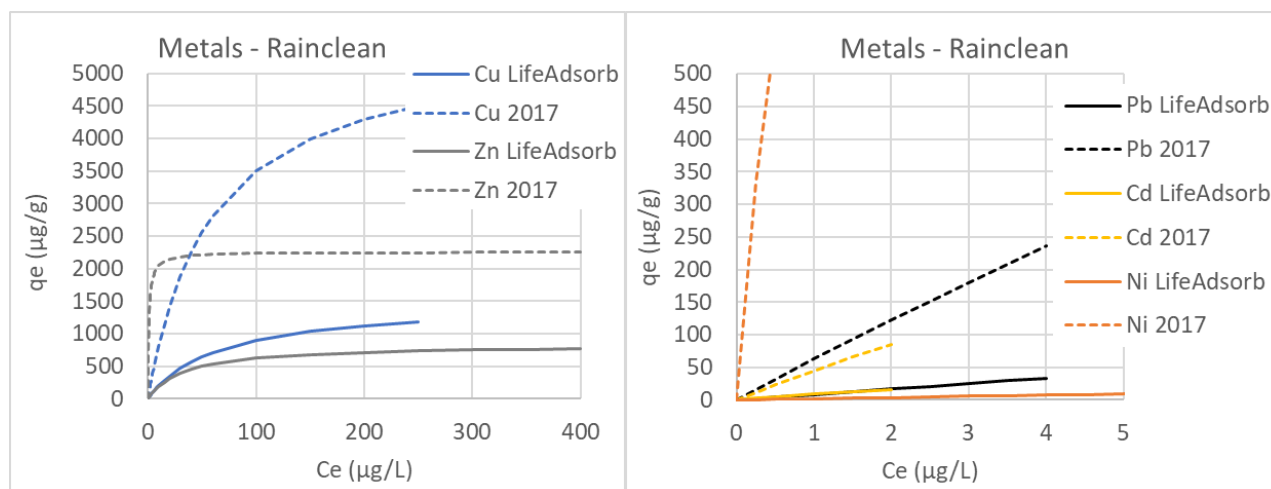


Figure 20: comparison of trace metals adsorption isotherms for the Rainclean tested in 2017 and the Rainclean implemented in the LifeAdsorb prototype

It appears that the Rainclean implemented in the LifeAdsorb prototype has much lower adsorption capacity for trace metals than what was expected based on the 2017 tests. For a same C_e value, q_e values are 3 to 7 times lower, and even more in the case of Ni. While preliminary experiments conducted in 2017 are not very precise, with a very limited measurements that fitted in the targeted C_e range, this comparison still shows that the modification of the material formulation probably impaired the efficiency for trace metals.

In the case of the studied organic micropollutants however, the new Rainclean formulation tested in 2022 shows much better adsorption performance (Figure 21). The adsorbed mass q_e , for the maximum targeted C_e concentration, is 3 times superior for BPA, 6 times for OP and 14 times for NP.

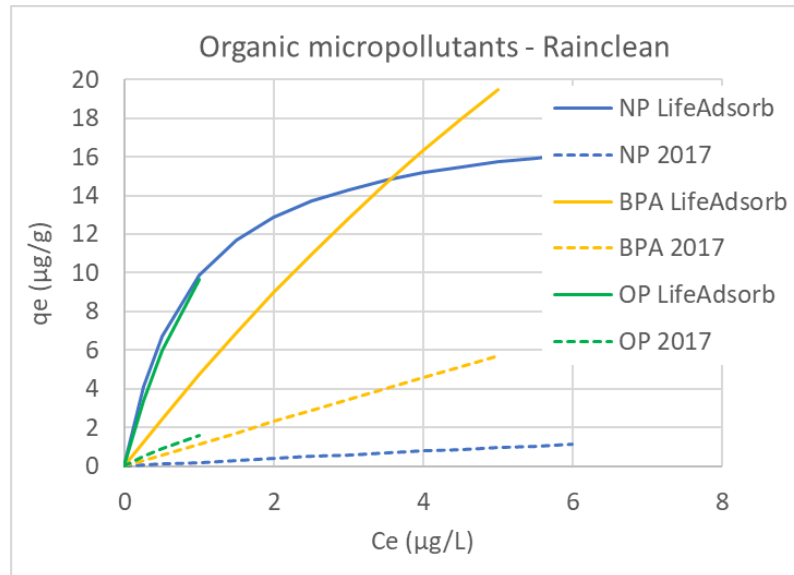


Figure 21: comparison of organic micropollutants adsorption isotherms for the Rainclean tested in 2017 and the Rainclean implemented in the LifeAdsorb prototype

4.2.4 Column studies

4.2.4.1 Non-reactive and low reactive tracers – column experiment

Results from breakthrough experiments with NaCl, a non-reactive tracer which should not adsorb on the substrate but only undergo advection/dispersion transport processes are presented in Figure 22 (zoom on the breakthrough phases). The breakthrough was assessed based on the evolution of the electrical conductivity. Data are normalized to the pore volume of the column (V_p) and to the inflow electrical conductivity EC_0 .

For the 20 cm column, similar behaviour is observed for Rainclean and sand: 80% breakthrough is reached for 3 and 3.6 pore volumes, respectively, and 100% breakthrough for respectively 6 and 9 pore volumes. For the sandwich system however, the breakthrough appears much quicker: 1.6 pore volumes for 80% breakthrough and 4 pore volumes for 100% breakthrough.

During the operation of the “sandwich” column, which reproduces the sand/Rainclean/sand layering system in the Bugeaud filter prototype, pockets of air trapped in the Rainclean layer were observed. The filling of the column was repeated, with the lateral valves open to allow for the air to exit the column, however it was impossible to completely prevent air bubbles in the Rainclean. This phenomenon seems to be linked to the much higher permeability of the Rainclean, in a filling procedure where the water arrives from the top while the column fills up from the bottom due to the limited outflow rate. This feeding and filling mode is similar to the real operation conditions of the Bugeaud prototype. Thus, air trapping in the Rainclean layer could also happen in the reed bed prototype. This phenomenon might limit the contact between the effluent to be treated and the Rainclean adsorbent and thus reduce adsorption efficiency.

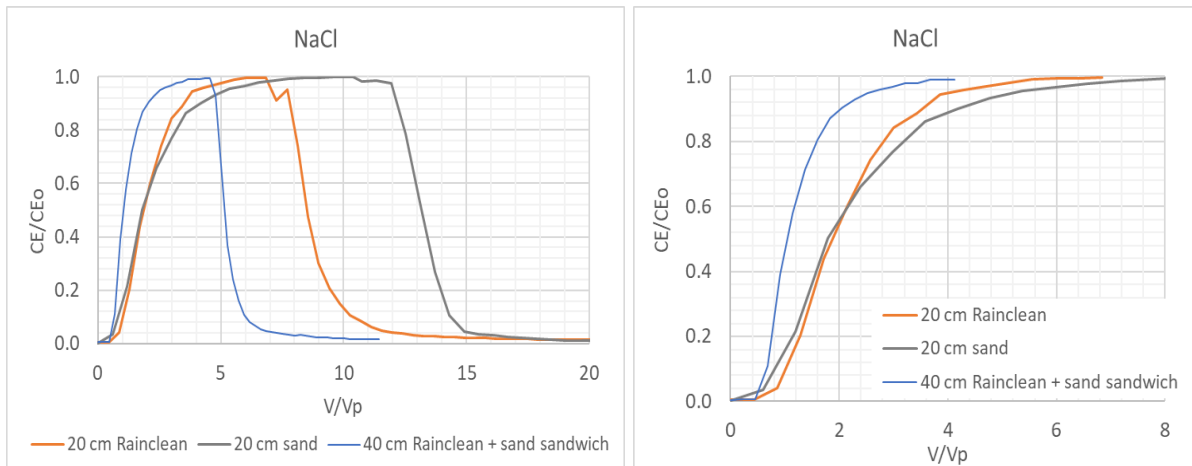


Figure 22 : non-reactive tracer breakthrough curve for columns with 20 cm sand, 20 cm Rainclean and a sandwich of 10cm sand+20cm Rainclean+10 cm sand (CE/CE_o = electrical conductivity of the outflow normalised by the electrical conductivity of the inflow, V/V_p = cumulated outflow volume normalized by the pore volume of the column)

The breakthrough curves of the AAG tracer – which is the reference tracer usually used for the hydrodynamic monitoring for reed bed filter – are presented in Figure 23 and Figure 24. This tracer is supposed to have only very limited adsorption of the filter material. For sand, 80% breakthrough was reached in 3 pore volumes, which is similar to NaCl. Maximum breakthrough reached 97%, which shows only very limited AAG losses in the system.

For Rainclean however, adsorption of a fraction of the tracer is observed: the breakthrough is only of less than 50% at 4 pore volumes (compared to 95% for NaCl), and maximum breakthrough did not exceed 80 to 90% for 10 cm column and 60% for 20 cm columns. The adsorption of AAG on the Rainclean material documented by these experiments means that this tracer cannot be considered as a completely non-reactive tracer for tracer experiments on the filter prototype containing Rainclean material.

Thus, the hydrodynamic parameters (advection/dispersion parameters) needed for the Bugeaud prototype modelling will be established by inverse modelling with STANMOD based on NaCl for the three types of column experiments (20cm sand, 20 cm Rainclean and 40 cm sand/Rainclean/sand) in part 2 of this report.

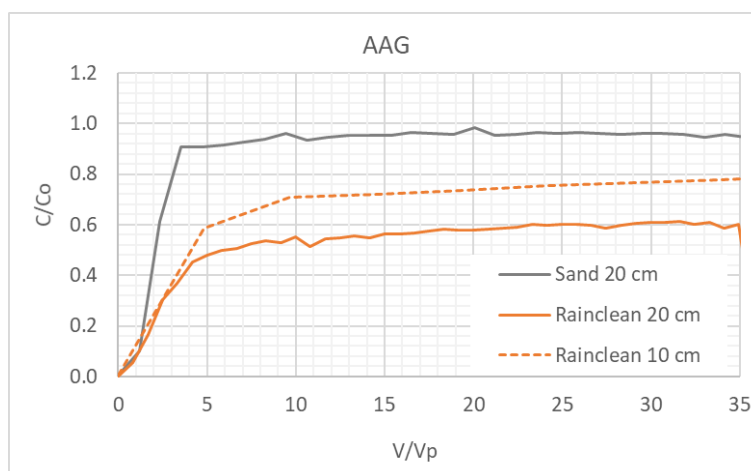


Figure 23 : comparison of the breakthrough curves of AAG tracer in sand and Rainclean columns

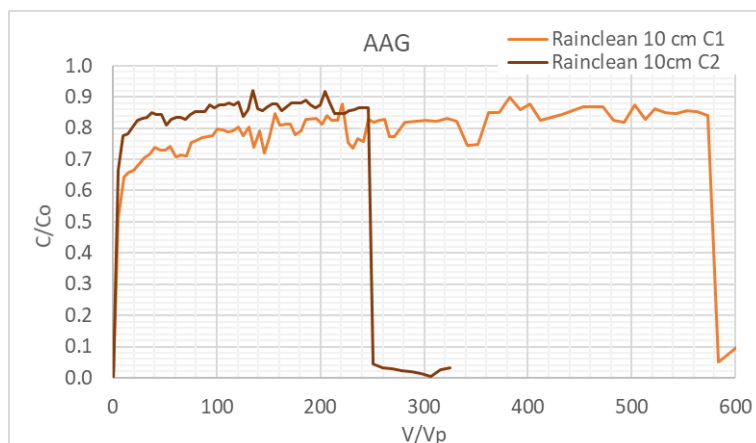


Figure 24: extension of AAG breakthrough experiment over 600 volumes of pores

4.2.5 Trace metals – column experiment

Adsorption performance assessment

Normalized trace metals breakthrough curves obtained for a 5 cm depth Rainclean layer are presented in Figure 25.

Three groups of trace elements can be distinguished. As, Cr and V do not show any significant adsorption on the Rainclean material column experiments with 80% breakthrough obtained within less than 30 pore volumes. This is consistent with the very low K_d values evaluated for these elements during batch studies. Ni shows limited adsorption with relatively quick breakthrough: 80% breakthrough is exceeded after 2000 pore volumes. Zn, Cu and Cd show stronger adsorption. Outflow concentrations increase progressively over the column experiment and reach 80% breakthrough towards the end of the test for 10000 pore volumes. Pb shows very strong adsorption of the Rainclean material, with a breakthrough that does not exceed 50% of the inlet concentration at the end of the column test.

The pore volume of the 20 cm deep layer of Rainclean implemented in the Bugeaud reed bed prototype represents 112 mm of water, and the annual loading of the LifeAdsorb prototype is around 150 m/year for each of the two compartments of the filter. Thus, based on the column tests, 80% breakthrough would occur within 1 or 2 years for Ni and 8 years for Cu, Zn and Cd for this prototype. Yet it is usually recommended a maximum of 100 m/year for the loading rates for reed bed filters. Under this recommendation, the life time can be estimated to 2 to 3 years for Ni and 12 years for Cu, Zn and Cd.

Moreover, due to the progressive increase of outflow concentrations, the average dissolved metal removal efficiency over the whole period of functioning till 80% breakthrough is relatively low: only 40 to 44% for Zn and Cd, and 34 to 38% for Cu.

We have to note however that column tests were conducted with a flow velocity 5 times superior to real prototype conditions. Thus, better treatment performance, with lower outlet concentrations and possibly longer lifetime of the adsorbent material, can be expected under real operation. This will have to be tested by modelling within part B2-2 of the project.

Column protocol assessment and comparison with batch isotherms

Figure 26 compares the normalized breakthrough curves obtained with a 5 cm depth Rainclean layer and a 20 cm depth layer. This comparison is only possible for V/V_p within the range 0 to 3000 which is the common interval between both experiments and corresponds to 336 m of water loading applied to the columns. If flow and adsorption processes are homogeneous in the columns, the normalized curve shouldn't depend on the considered adsorbent depth.

Here, normalized results obtained for 5 cm and 20 cm are relatively consistent. However, the 20 cm show a progressive and relatively smooth increase of outlet concentrations, while the 5 cm curves show more erratic shapes, with a quick concentration increase in the yearly stage of column feeding ($V/V_p < 500$) followed by a relatively flat part of the curve ($500 < V/V_p < 2200$). This could be linked to more important shortcut effects with some rapid flow pass ways when the considered layer is very thin, as well as local disturbances of the flow in the column due to the tapping sampling system at 5 cm. We thus recommend for future experiments to use an adsorbent layer depth of at least 10 cm and collect the water at the outlet of the column rather than with a side water intake.

For those metals for which more than 80% breakthrough was reached at the end of the column experiment (Ni, V, Cd, Cu, Zn), the total mass adsorbed to the Rainclean was calculated based on an inlet/outlet mass balance, and compared to equilibrium adsorption loads given by the batch isotherms. As it can be seen from Table 20, results are relatively consistent between column and batch adsorption loads. For V, Cd and Zn, the loads are almost similar with both methods, for Ni they are 20% lower in the column study and for Cu the difference is more significant with values 40% lower in the column study.

Table 20 : comparison of metal loads adsorbed on the Rainclean at equilibrium between column and batch experiments

	Inflow concentration C_e ($\mu\text{g/l}$)	Mass adsorbed on the Rainclean at equilibrium - q_e (mg/g)	
		Columns	Batch isotherms
Ni	13	12	15.5
V	47	3	3.3
Cd	10	40	46
Cu	300	980	1200-1600
Zn	125	550	660



Figure 25 : normalized trace metals breakthrough curves (C = outflow concentration, C_0 = inflow concentration, V = cumulated volume, V_p = pore volume of the column)

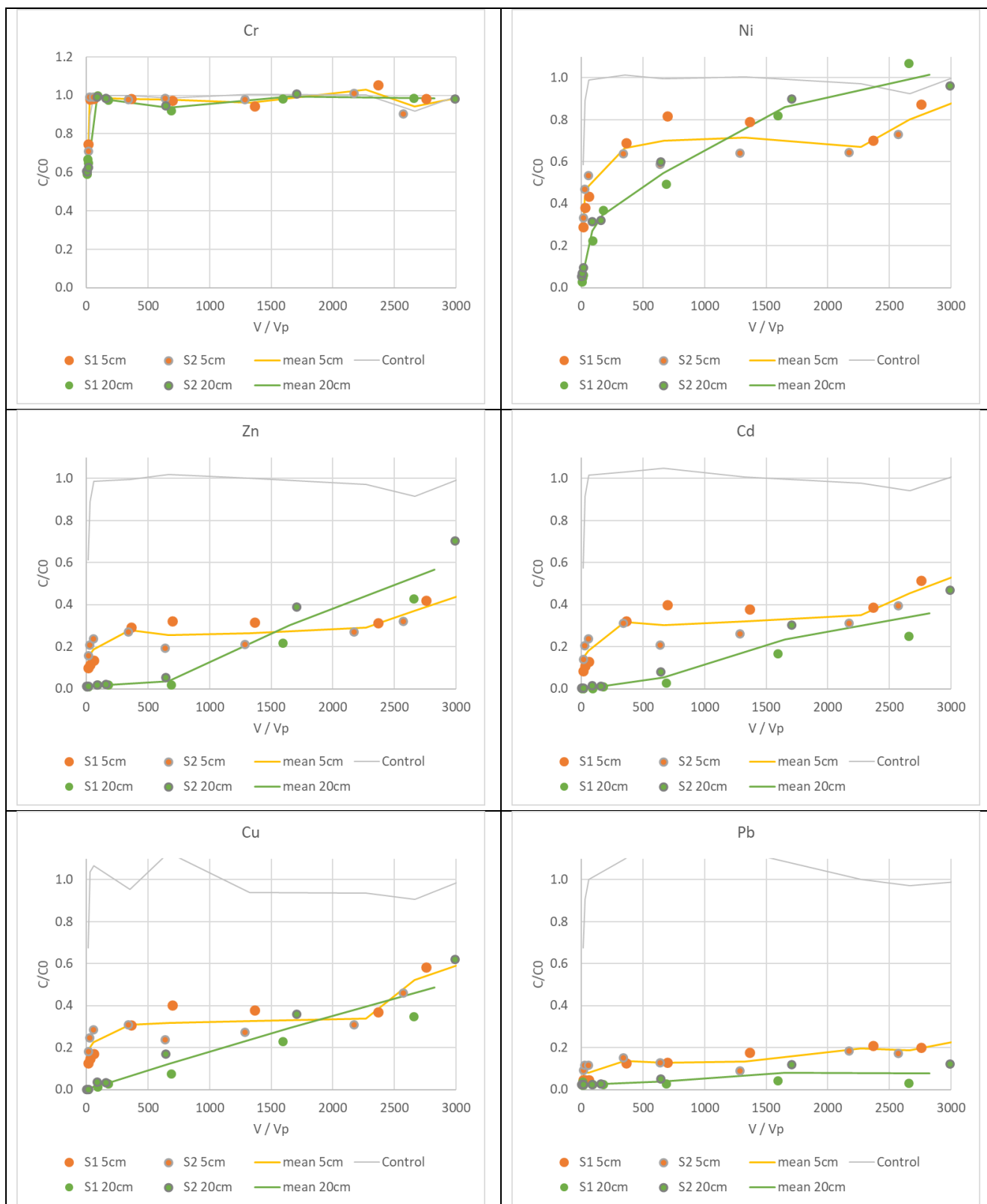


Figure 26: Comparison of normalized trace metal breakthrough curves measured for 5 cm and 20 cm of Rainclean depth

4.2.6 Organic micropollutants – column experiment

Column test results for organic micropollutants are presented in Figure 27.

For BPA, inflow concentrations showed some unexpected variations, with a very high inflow pic of 22.5 µg/l within period P2 as well as higher concentrations as expected in periods P3 and P4. These concentrations are confirmed by the control column measurements. For the outflow, the dynamic of concentrations also shows unexpected behaviours: breakthrough is high in the first part of the experiment ($V/V_p < 1500$) with outflow concentrations reaching 80% of the inflow, indicating very low adsorption of BPA. But the % of breakthrough decreases for $V/V_p > 2000$, down to 20%. For this last part of the experiment (P3 and P4 periods) the batch of water collected at the sand filter prototype outlet, and used with or without spiking with micropollutants, had an unusual aspect (yellowish color and evidence of colloids). Adsorption or complexation on colloids or dissolved organic matter present in the water for this part of the experiment may have interfered with the adsorption on the Rainclean material. However, this behavior was not observed for the other two organic micropollutants, OP and NP, so it might also be linked to contaminations or analytical issues.

For octylphenol (OP), adsorption is not very efficient from the start of the experiment. 60% breakthrough is reached at the end of the P1 loading period for $V/V_p = 750$, and no adsorption is observed anymore after the start of P2 loading period, ie for $V > 1000 V_p$. Equilibrium conditions seem to be reached at the end of the column experiment.

For nonylphenol (NP), the breakthrough is more progressive, showing a slightly better treatment potential than OP. 80% breakthrough is however reached at the end of P2 loading period, ie for $V > 2500 V_p$. As for OP, equilibrium conditions seem to be reached towards the end of the column experiment.

The mass of OP and NP adsorbed on the Rainclean at the end of the column experiments are significantly lower than what could have been expected based on batch isotherm results. Based on an inlet / outlet mass balance calculation, the total mass accumulated in the Rainclean column at the end of the experience is around 1.4 µg/g for OP and 4.5 µg/g for NP. From the batch isotherms, the mass adsorbed at equilibrium for an OP inlet concentration of 0.65 µg/l (final inlet value in the column test) should be in the range 5.5 to 8 µg/g, and for an NP inlet concentration in the range 0.8-1.8 µg/L it should be in the range 7.5-11 µg/g.

Adsorption of the tested organic micropollutants appears much less efficient than for trace metals, and breakthrough and saturation of the Rainclean material is expected to happen within a few years of functioning of the reed bed filter.

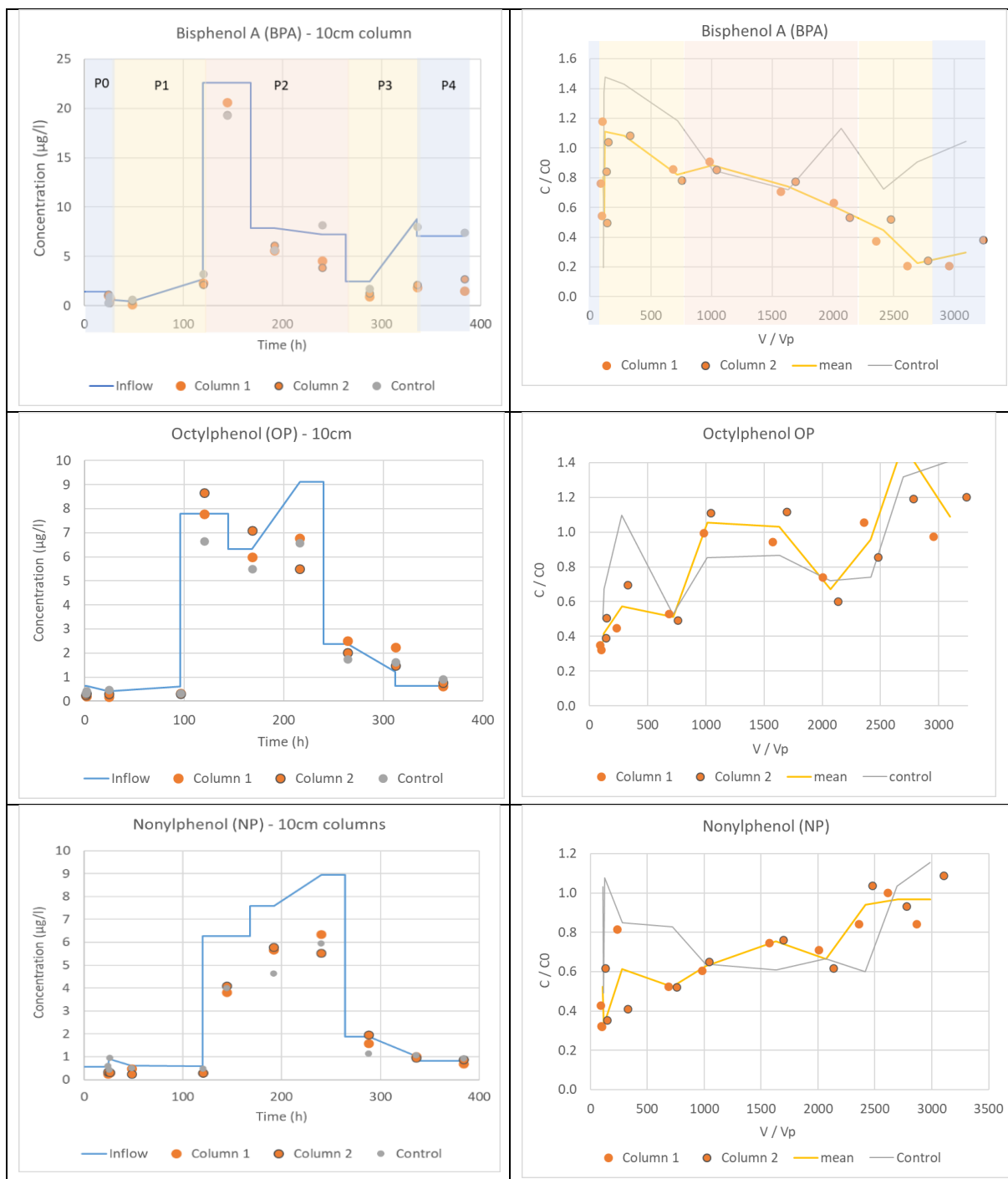


Figure 27: column experiment results for organic micropollutants. Left : temporal evolution of inflow and outflow concentrations. Right : normalized breakthrough curves (C = outflow concentration, C_0 = inflow concentration, V = cumulated volume, V_p = pore volume of the column)

5 MODELLING OF SOLUTE TRANSPORT AND CALIBRATION OF PARAMETERS

5.1 Establishment of longitudinal dispersion and dispersivity coefficients

Les traçages sont l'une des méthodes courantes utilisées pour étudier l'écoulement des eaux en milieu poreux et les propriétés des systèmes poreux, telles que la porosité et la dispersivité (Ptak et al., 2004). Les traçages peuvent être effectués à la fois sur le terrain et en laboratoire en mesurant la concentration d'espèces déjà présentes ou qui sont introduites délibérément dans le système. Les colorants fluorescents sont souvent utilisés à cette fin. Dans la présente étude, le comportement du sel et de l'acide amino-G dans des colonnes remplies de sable et de Rainclean® (identiques à ceux mis en place dans les filtres de Bugeaud) a été étudié. Les traçages au sel sur les colonnes de sable et de Rainclean® ont pour but de déterminer la valeur du coefficient de dispersion longitudinale pour chaque matériau. Les traçages à l'acide amino-G sur les mêmes colonnes de sable ont pour objectif de valider ou invalider la valeur précédemment déterminée. En cas de résultat positif, les coefficients déterminés avec les colonnes de sable et de Rainclean® sera ensuite utilisé pour la modélisation du transport d'acide amino-G et de micropolluants dans les colonnes remplies de Rainclean® d'une part, et pour la modélisation du transport de micropolluants dans les filtres de Bugeaud (tâche B2-2) d'autre part.

5.1.1 Rappel de la méthodologie et des résultats de traçage au sel (NaCl)

Des traçages hydrauliques réalisés avec du sel (NaCl) ont été réalisés sur trois colonnes différentes en duplicat : deux colonnes contenant 20 cm de sable, deux colonnes contenant 20 cm de Rainclean® et deux colonnes contenant des couches successives de 10 cm de sable - 20 cm de Rainclean® - 10 cm de sable. Les matériaux vierges utilisés, sable et Rainclean®, sont les mêmes matériaux que ceux mis en place sur les filtres de Bugeaud. Les colonnes ont toutes un diamètre de 5 cm et sont saturées en eau distillée avant le lancement des traçages. Les porosités mesurées sont de 0,37 pour le sable et 0,56 pour le Rainclean® (porosités mesurées au laboratoire dans un bécher en saturant un volume connu de matériau). Le volume poral est de 0,14 L, 0,22 L et 0,36 L pour la colonne de sable seul, pour la colonne de Rainclean® seul et pour la colonne de sable-Rainclean®-sable, respectivement.

Chaque traçage s'est effectué avec une alimentation en continue et le type d'injection du traceur est une injection de type « créneau ». Pour l'injection de type créneau, l'apport de traceur, ici le sel, d'une concentration ou ici d'une conductivité électrique donnée c_0 , est appliqué au temps zéro, t_0 . Il est précédé et suivi par l'injection d'une solution sans traceur (eau distillée). L'injection du traceur a été réalisée en continue dès le démarrage du traçage (t_0) puis s'est arrêtée au bout d'un certain temps (environ 85 minutes pour les six colonnes). En sortie des colonnes les volumes sortants ainsi que les conductivités électriques sont mesurées à chaque pas de temps (5 minutes).

Le Tableau 1 présente les conditions expérimentales dans lesquels les traçages ont été réalisés avec le sel. Les Figure 28, Figure 29, Figure 30 présentent les résultats obtenus pour les six colonnes (colonne de sable seul x2, colonne de Rainclean® x2, colonne de sable-Rainclean®-sable x2). Les résultats sont présentés sous la forme de conductivité électrique relative pour chaque type de colonne, c'est-à-dire de l'évolution du rapport de la conductivité électrique mesurée en sortie à chaque pas de temps (5 minutes) et de la conductivité électrique en entrée des colonnes. Le créneau d'injection du sel ainsi que le temps de séjour hydraulique théorique sont indiqués pour chaque type de colonne.

Pour les trois matériaux on constate que l'allure globale des courbes est la même, une augmentation graduelle du rapport des conductivités électriques jusqu'à ce que ce rapport atteigne un plateau à la valeur de 1, c'est-à-dire lorsque la conductivité électrique mesurée en sortie est égale à la conductivité électrique de la solution salée injectée en entrée. On peut donc dire qu'**il n'y a pas d'adsorption du sel sur les matériaux**. Les différences notables entre les trois matériaux constituant les colonnes sont le temps à partir duquel l'augmentation de la conductivité électrique mesurée en sortie est observée (5-10 minutes pour les colonnes de sable seul, 10-15 minutes pour les colonnes de Rainclean® seul, 15 minutes pour les colonnes de sable-Rainclean®-sable) et le temps pour lequel le plateau est atteint (70 minutes pour les colonnes de sable et Rainclean® seuls, 90 minutes pour les colonnes de sable-Rainclean®-sable).

Tableau 1 : Conditions expérimentales des tracages réalisés au sel

	Colonnes de sable seul (20 cm)	Colonnes de Rainclean® seul (20 cm)	Colonnes de sable-Rainclean®-sable (40 cm)
Conductivités électriques du traceur en entrée ($\mu\text{S}/\text{cm}$)	$CE_0 = 9170 - 9150$	$CE_0 = 9140 - 9140$	$CE_0 = 9170 - 9180$
Débits d'alimentation moyens (mL/min)	17,2	18,8	18,2
Temps de séjour hydraulique théorique (min)	8,7	11,7	20,0
Durée du traçage (min)	235	250	250

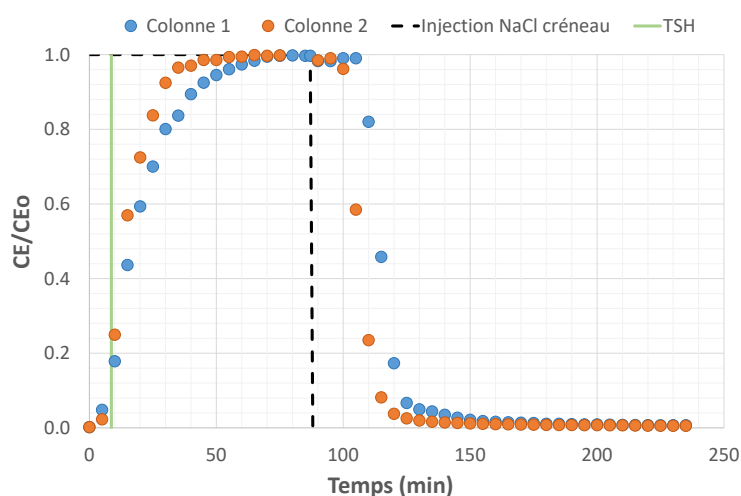


Figure 28 : Évolution de la conductivité électrique relative des colonnes de sable seul

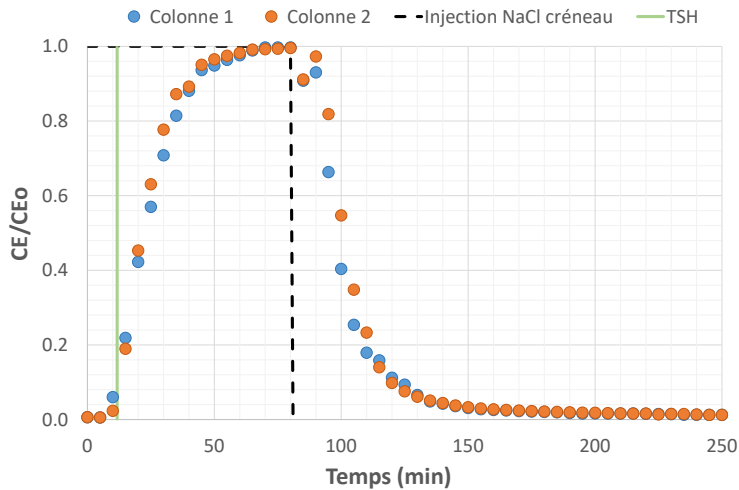


Figure 29 : Évolution de la conductivité électrique relative des colonnes de Rainclean® seul

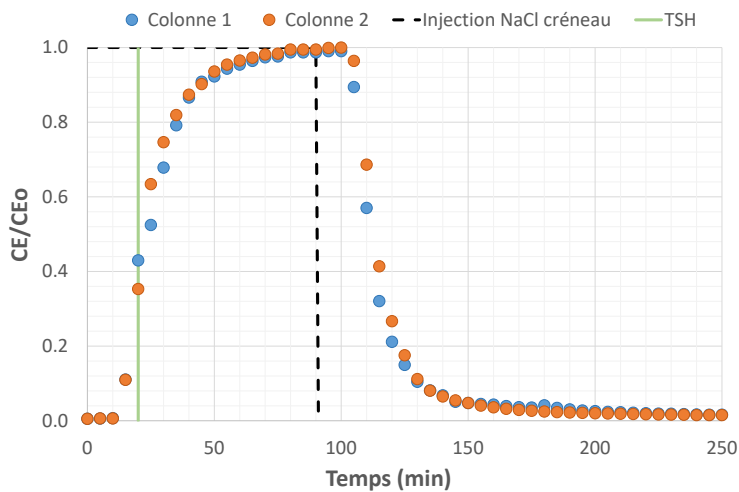


Figure 30 : Évolution de la conductivité électrique relative des colonnes de sable-Rainclean®-sable

Dans le cas d'une injection de type créneau d'un traceur avec une alimentation continue, le temps réponse du traceur en sortie d'une colonne (i) correspond au temps de séjour hydraulique théorique pour un écoulement piston idéal, (ii) est plus faible que le temps de séjour hydraulique théorique pour un écoulement avec court-circuit, (iii) est constitué de plusieurs temps pour lesquels le traceur sort de la colonne pour un écoulement avec zone(s) morte(s) (Figure 31). Pour les colonnes de sable et Rainclean® seuls, les temps de sortie du sel sont très similaires aux temps de séjours hydrauliques théoriques correspondants (Tableau 1). Pour la colonne de sable-Rainclean®-sable le temps de sortie du sel (15 min) est légèrement plus faible que le temps de séjour théorique (20 min). On peut donc en déduire que **l'écoulement dans les colonnes de sable et Rainclean® seuls est un écoulement piston alors que des petits court-circuit (négligeables) sont présents dans la colonne de sable-Rainclean®-sable.**

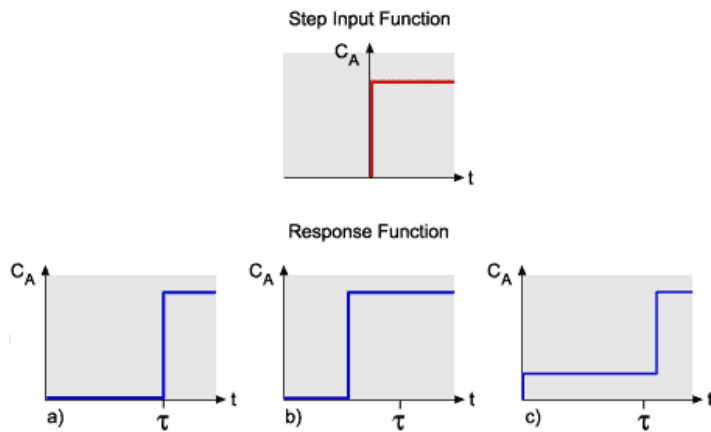


Figure 31 : Fonction de réponse à une entrée en créneau pour un réacteur à écoulement piston idéal (a), avec court-circuit (b), avec zone morte (c). τ = temps de séjour hydraulique théorique

5.1.2 The STANMOD software and CXTFIT 2.1 program

Le logiciel STANMOD (Šimůnek et al., 1999) et notamment le programme CXTFIT (Parker et van Genuchten, 1984 ; Toride et al., 1995) a été utilisé pour simuler les traçages au sel réalisés sur les six colonnes.

5.1.2.1 Le logiciel STANMOD

Le logiciel STANMOD (Studio of ANalytical MODEls, Šimůnek et al., 1999) est un logiciel public fonctionnant sous Windows pour évaluer le transport de solutés uni-, bi- ou multidimensionnels dans les sols et les eaux souterraines à l'aide de solutions analytiques de l'équation de CDE. Il contient sept codes pour les applications unidimensionnelles (CFITM, CFITIM, CXTFIT, CHAIN, SCREEN) ou multidimensionnelles (3DADE, N3DADE). Tous les modèles peuvent être exécutés pour des problèmes directs et plusieurs (CFITM, CXTFIT, 3DADE) également pour des problèmes inverses.

5.1.2.2 Le programme CXTFIT 2.1

Ce programme peut être utilisé pour le **problème direct de prédiction des distributions de solutés** en fonction du temps et/ou de l'espace pour des paramètres de modèle spécifiés. CXTFIT 2.1 peut aussi être utilisé pour résoudre des **problèmes inverses**, c'est-à-dire estimer les paramètres de modèles analytiques pour le transport de solutés pour un écoulement unidimensionnel régulier en adaptant les solutions analytiques des modèles aux données de transport de solutés observées en laboratoire ou sur le terrain. Le problème inverse est résolu en minimisant une fonction objective qui consiste en la somme des différences au carré entre les concentrations observées et ajustées. La fonction objectif est minimisée en utilisant une méthode d'inversion non linéaire des moindres carrés selon Marquardt (1963).

CXTFIT 2.1, utilise l'équation de CDE, mais avec un plus grand nombre de solutions analytiques se rapportant à divers problèmes de valeurs initiales, limites et de production.

5.1.3 Simulations avec le logiciel STANMOD/CXTFIT 2.1

5.1.3.1 Méthodologie

Dans le cas des traçages avec le sel, aucune adsorption n'a été observée quel que soit le matériau étudié ni aucun flux préférentiel pour les colonnes de sable et Rainclean® seuls (Figure 28, Figure 29, Figure

30). De plus, les petits court-circuits observés pour les colonnes de sable-Rainclean®-sable sont considérés comme négligeables. Par conséquent le modèle de transport sélectionné est la **CDE conventionnelle (transport équilibré)**. Les paramètres pouvant être déterminés (modélisation inverse) ou être utilisés (modélisation directe) sont v (V_L : pore-water velocity in the longitudinal direction), D (D_L : longitudinal dispersion coefficient) et R (retardation factor).

La valeur du facteur de rétention est imposée à $R = 1$ et la vitesse de l'eau interstitielle (v) est connue (Tableau 1). Par conséquent, **seul le coefficient de dispersion longitudinale (D) est estimé par modélisation inverse** par le programme CXTFIT dans le logiciel STANMOD à partir des résultats des traçages au sel réalisés sur chaque colonne de sable seul, Rainclean® seul, sable-Rainclean®-sable.

Pour chaque simulation (pour chaque colonne) :

- La valeur initiale du coefficient de dispersion longitudinale indiquée dans le programme CXTFIT est de $1 \text{ cm}^2/\text{min}$ et les bornes indiquées pour la modélisation inverse sont $0,1 \text{ cm}^2/\text{min}$ pour la valeur minimale et $50 \text{ cm}^2/\text{min}$ pour la valeur maximale.
- La condition à la limite en entrée est une injection de type créneau durant un temps T (environ 85 minutes pour les six colonnes) d'une « concentration » de 1. Cette « concentration » correspond à la valeur de la conductivité électrique relative des colonnes une fois le régime permanent atteint.
- La « concentration » (conductivité) initiale dans les colonnes est nulle.
- Le coefficient de dispersion longitudinale est estimé à partir des mesures des courbes de percée réalisées à 20 cm ou 40 cm (hauteur de matériaux dans les colonnes de sable et Rainclean® seuls et dans la colonne sable-Rainclean®-sable, respectivement).
- Les données nécessaires pour la modélisation inverse sont entrées sous la forme d'un tableau à deux colonnes, une colonne correspondant au temps où chaque ligne correspond à un pas de temps et une colonne correspondant à la « concentration » c'est-à-dire à la conductivité électrique relative des colonnes (valeurs tracées sur les Figure 28, Figure 29, Figure 30).
- Les durées de simulations sont les durées de chaque traçage (235 minutes pour la colonne de sable seul et 250 minutes pour la colonne de Rainclean® seul et pour la colonne de sable-Rainclean®-sable).

Une fois toutes les informations demandées entrées dans le logiciel STANMOD la modélisation inverse est réalisée pour chaque colonne.

Pour chaque colonne, la dispersivité longitudinale λ est ensuite calculée à partir de la vitesse interstitielle v et du coefficient de dispersion longitudinale D , telle que : $\lambda = D/v$.

5.1.3.2 Résultats

Le logiciel STANMOD fournit les résultats de la modélisation inverse sous forme :

- D'un graphique présentant les points expérimentaux et les valeurs prédites. La Figure 32, présente des exemples pour une colonne de sable seul, Rainclean® seul, sable-Rainclean®-sable
- D'une fenêtre résumant la description du modèle choisit, les valeurs initiales du paramètre D , les conditions initiales et aux limites, le nombre d'itérations réalisées lors de l'optimisation, le coefficient de détermination r^2 , le carré moyen des erreurs MSE (Mean Squared Error), les résultats de l'estimation du paramètre D (valeur estimée, valeurs basse et haute de l'intervalle de confiance à 95%) ainsi que les valeurs ayant permis de produire le graphique résultant de l'optimisation (points expérimentaux et points prédits, Figure 32 et annexe). Les coefficients de détermination (r^2) ainsi que les carrés moyens des erreurs (MSE) associés à chaque optimisation sont indiqués sur la Figure 32 et en annexe.

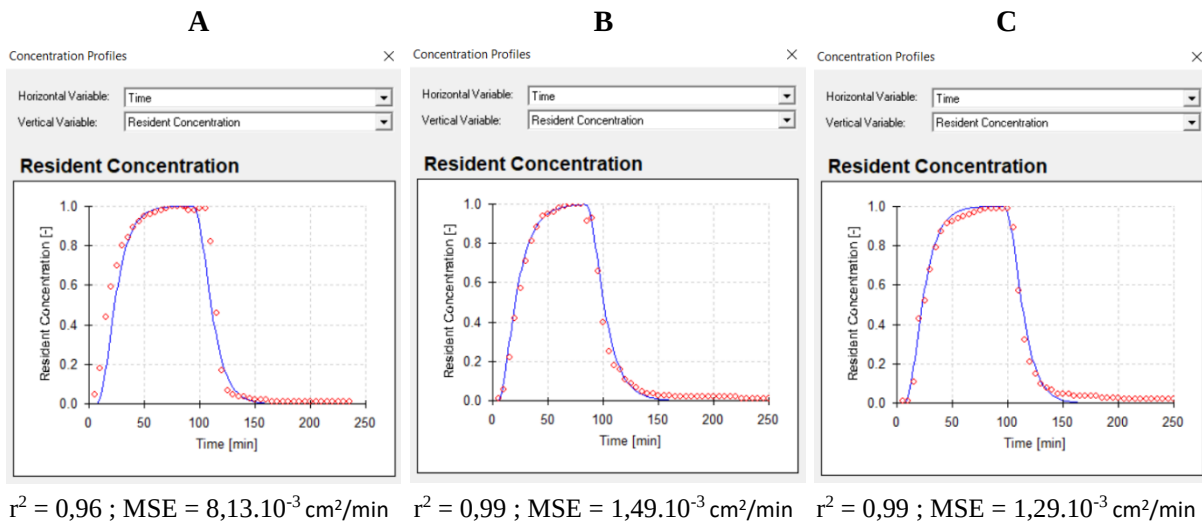


Figure 32 : Valeurs mesurées (cercles rouges) et prédites (ligne bleue) de la conductivité électrique relative d'une des deux colonnes de sable seul (A), Rainclean® seul (B), sable-Rainclean®-sable (C). r^2 = coefficient de détermination, MSE = Mean Squared Error

Pour les trois matériaux le transport équilibré optimisé (ligne continue bleue) s'ajuste très bien aux données mesurées (cercles rouges). Les coefficients de détermination pour l'ajustement du modèle aux données sont très élevés pour toutes les colonnes des trois matériaux ($r^2 > 0,96$, annexe). Ainsi, il est possible de se servir des valeurs des paramètres estimées pour la suite des simulations des traçages réalisés en colonne au laboratoire.

Le Tableau 2 présente les valeurs du coefficient de dispersion longitudinale D estimé par modélisation inverse et de la dispersivité λ calculé à partir de D et v , pour les colonnes de sable seul, Rainclean® seul, sable-Rainclean®-sable.

Tableau 2 : Valeurs du coefficient de dispersion longitudinale D estimé par modélisation inverse et de la dispersivité longitudinale λ pour les colonnes de sable seul, Rainclean® seul, sable-Rainclean®-sable

	Colonne 1	Colonne 2	Valeurs moyennes
SABLE SEUL (20 cm)			
Coefficient de dispersion longitudinale D (cm^2/min)	2,02	1,27	1,65
Dispersivité longitudinale λ (cm)	6,03	3,81	4,92
RAINCLEAN® SEUL (20 cm)			
Coefficient de dispersion longitudinale D (cm^2/min)	3,16	2,38	2,77
Dispersivité longitudinale λ (cm)	5,88	4,42	5,12
SABLE-RAINCLEAN®-SABLE (40 cm)			
Coefficient de dispersion longitudinale D (cm^2/min)	8,28	6,88	7,56
Dispersivité longitudinale λ (cm)	10,07	8,36	9,19

5.2 Validation of longitudinal dispersion and dispersivity coefficients based on AAG tracer column experiments

L'objectif ici est de voir si les paramètres de dispersion précédemment déterminés pour le sable et le Rainclean® avec le sel (modélisation inverse) peuvent être utilisés lors des simulations du transport de l'acide amino-G dans les mêmes colonnes (modélisation directe) et par conséquent être validé.

5.2.1 Rappel de la méthodologie et des résultats de traçage à l'AAG

Des traçages hydrauliques réalisés à l'acide amino-G ont été réalisés sur trois colonnes différentes en duplicat : deux colonnes contenant 20 cm de sable, deux colonnes contenant 10 cm de Rainclean® et deux colonnes contenant 20 cm de Rainclean®. Les matériaux vierges utilisés, sable et Rainclean®, sont les mêmes matériaux que ceux mis en place sur les filtres de Bugeaud. Les caractéristiques des colonnes et des matériaux ainsi que les conditions dans lesquelles les traçages ont été réalisés sont identiques aux traçages au sel (diamètre de 5 cm, porosités de 0,37 pour le sable et 0,56 pour le Rainclean®, saturation en eau distillée des colonnes préalable aux traçages).

Comme pour les traçages au sel, chaque traçage s'est effectué avec une alimentation en continue et l'injection du traceur est de type créneau. En sortie des colonnes les volumes sortants ainsi que les concentrations en acide amino-G sont mesurées à chaque pas de temps (10 minutes pour les colonnes de 20 cm de sable et 20 cm de Rainclean®, 30 minutes pour les colonnes de 10 cm de Rainclean®).

Le Tableau 3 présente les conditions expérimentales dans lesquels les traçages ont été réalisés avec l'acide amino-G.

Tableau 3 : Conditions expérimentales des traçages réalisés à l'acide amino-G

	Colonnes de 20 cm de sable	Colonnes de 10 cm de Rainclean®	Colonnes de 20 cm de Rainclean®
Concentrations du traceur en entrée (mg/L)	$C_0 = 0,98 - 0,96$	$C_0 = 0,97 - 0,96$	$C_0 = 1,03 - 1,03$
Débits d'alimentation moyens (mL/min)	17,1	18,4 - 17,7	18,3
Temps de séjour hydraulique théorique (min)	8,5	6,0 - 6,2	12,0
Durée du traçage (min)	630	3600 - 2100	670
Durée d'injection du traceur (min)	440	3420 - 1590	410
Durée d'injection de l'eau distillée (min)	190	180 - 510	260

Les Figure 33, Figure 34, Figure 35 présentent les résultats obtenus pour les six colonnes (colonne de 20 cm de sable x2, colonne de 10 cm de Rainclean® x2, colonne de 20 cm de Rainclean® x2). Les résultats sont présentés sous la forme de concentration en acide amino-G relative pour chaque type de colonne, c'est-à-dire du rapport de la concentration en acide amino-G mesurée en sortie à chaque pas de temps (10 minutes) et de la concentration en acide amino-G en entrée des colonnes. Le créneau d'injection de l'acide amino-G ainsi que le temps de séjour hydraulique théorique sont indiqués pour chaque type de colonne.

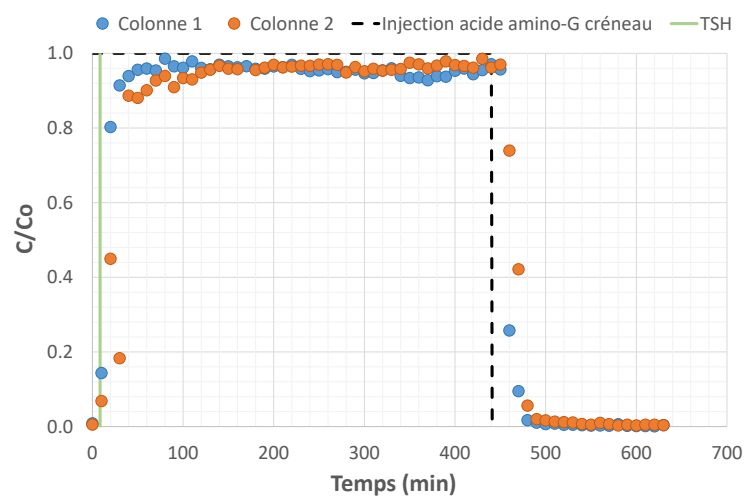


Figure 33 : Évolution de la concentration en acide amino-G relative des colonnes de 20 cm de sable

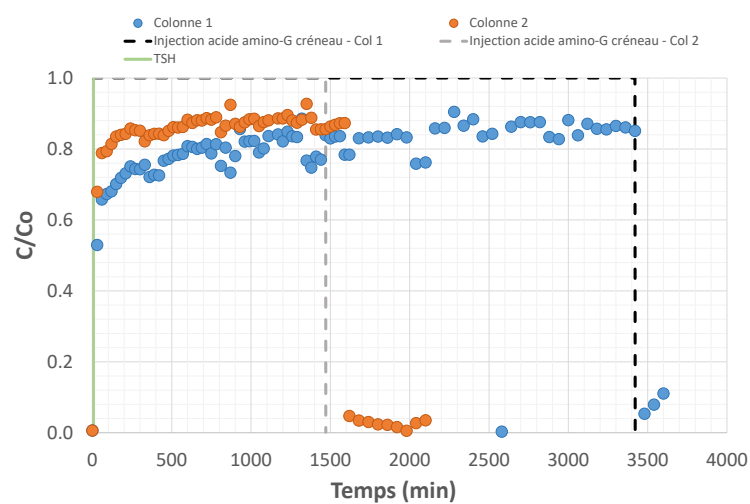


Figure 34 : Évolution de la concentration en acide amino-G relative des colonnes de 10 cm de Rainclean®

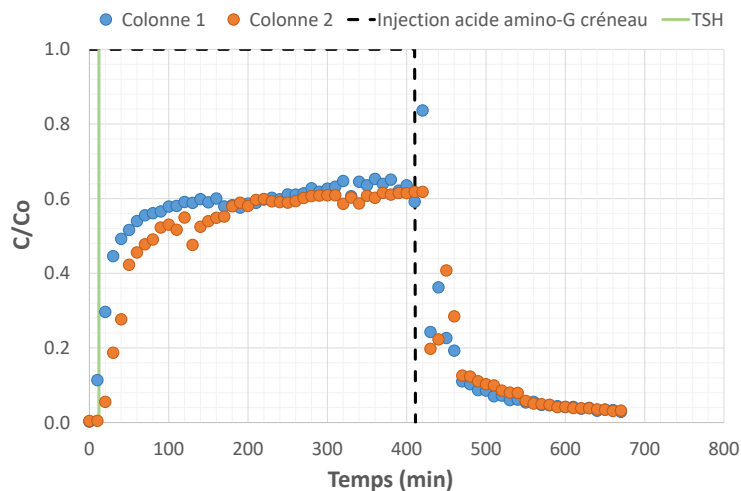


Figure 35 : Évolution de la concentration en acide amino-G relative des colonnes de 20 cm de Rainclean®

Pour les trois matériaux on constate que l'allure globale des courbes est la même, une augmentation du rapport des concentrations en acide amino-G jusqu'à ce que ce rapport atteigne un plateau. La valeur du plateau atteint est différente pour chaque colonne. Le plateau atteint la valeur de 0,97 pour les colonnes de 20 cm de sable. Ainsi, pour le sable la concentration en acide amino-G mesurée en sortie est quasiment égale à la concentration de la solution injectée en entrée. On peut donc dire qu'**il n'y a pas d'adsorption de l'acide amino-G sur le sable**. D'autre part, on note que le plateau du rapport des concentrations en acide amino-G pour les colonnes de sable est atteint environ 1 heure après le début du traçage et reste stable jusqu'à la fin de l'injection du traceur.

En revanche, le plateau atteint des valeurs de 0,86 et 0,88 pour les colonnes de 10 cm de Rainclean® et 0,63 pour les colonnes de 20 cm de Rainclean®. Ces valeurs inférieures à 1 indiquent que **l'acide amino-G s'adsorbe sur le Rainclean®**. On note aussi, pour les deux hauteurs de Rainclean®, une **augmentation graduelle du rapport des concentrations en acide amino-G jusqu'au plateau**, augmentation beaucoup moins rapide que celle observée pour le sable. Le plateau est atteint au bout de 2340 minutes et 600 minutes pour les colonnes de 10 cm de Rainclean® et au bout de 350 minutes pour les colonnes de 20 cm de Rainclean®. Ainsi, on peut dire que **l'acide amino-G subi une adsorption cinétique sur le Rainclean®**.

5.2.2 Simulations avec le logiciel STANMOD

5.2.2.1 Méthodologie

Dans le cas des traçages avec l'acide amino-G, aucune adsorption n'est observée sur le sable (Figure 33), par conséquent le modèle de transport sélectionné pour réaliser la modélisation directe est la **CDE conventionnelle (transport équilibré)**. La valeur du facteur de rétention est imposée à $R = 1$ et la vitesse de l'eau interstitielle (v) est connue (17,1 mL/min, Tableau 3). Pour simuler les concentrations d'acide amino-G en sortie des deux colonnes de 20 cm de sable, la **valeur du coefficient de dispersion longitudinale (D) estimée pour chaque colonne de sable lors des traçages au sel est utilisée** (Colonne 1 : 2,02 cm²/min et Colonne 2 : 1,27 cm²/min, Tableau 2) **pour la modélisation directe du comportement de l'acide amino-G avec le sable**.

En revanche, une adsorption cinétique est observée sur le Rainclean® (Figure 34, Figure 35). Par conséquent, il ne sera pas possible d'isoler et de valider le coefficient de dispersion longitudinale seul si au moins un autre phénomène entre en jeu. Si la valeur du coefficient de dispersion longitudinale estimée pour chaque colonne de sable est validée, alors la valeur du coefficient de dispersion longitudinale estimée pour chaque colonne de Rainclean® avec le sel et les colonnes de sable sera considérée comme étant validée.

Pour chaque simulation par modélisation directe (pour chaque colonne de sable) :

- La condition à la limite en entrée est une injection de type créneau durant un temps T d'une concentration en acide amino-G présentée dans le Tableau 3.
- La concentration initiale dans les colonnes est nulle.
- Les durées de simulations sont les durées de chaque traçage (630 minutes).

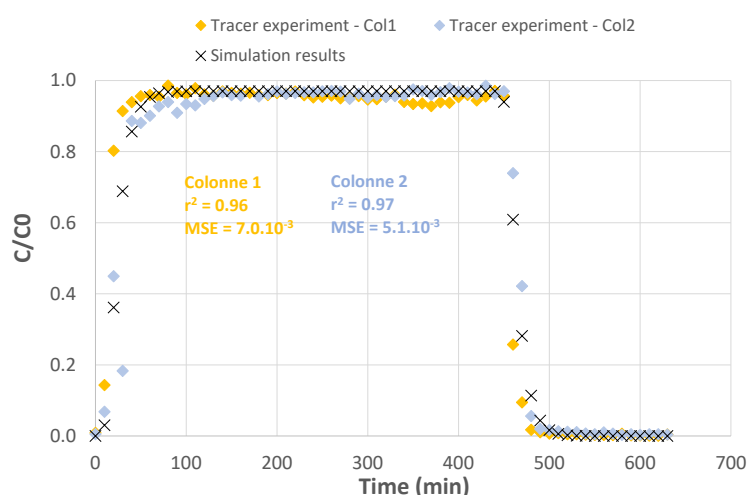
Une fois toutes les informations demandées entrées dans le programme CXTFIT du logiciel STANMOD les modélisations directes sont réalisées pour chaque colonne de sable.

5.2.2.2 Résultats – Colonnes de sable

Le Tableau 4 présente les jeux de paramètres utilisés dans STANMOD pour les simulations directes (transport équilibré) des traçages à l'acide amino-G réalisés sur les colonnes de 20 cm sable. Les coefficients de détermination (r^2) ainsi que les carrés moyens des erreurs (MSE) sont indiqués pour chaque résultat de simulation pour chaque colonne.

Tableau 4 : Jeux de paramètres utilisés pour les simulations directes des traçages à l'acide amino-G réalisés sur les colonnes de 20 cm de sable

	v	D	R	r²	MSE
	cm/min	cm ² /min	-		cm ² /min
SABLE 20 cm					
Colonne 1	0,87	2,02	1	0,96	7,0.10 ⁻³
Colonne 2	0,91	1,27	1	0,97	5,1.10 ⁻³



La Figure 36 présente les valeurs mesurées (losanges) et prédites avec le modèle de transport équilibré (croix) de la concentration en acide amino-G en sortie des colonnes de 20 cm sable.

L'évolution du rapport des concentrations en acide amino-G prédit avec le modèle à l'équilibre s'ajuste très bien aux données mesurées avec un coefficient de détermination de 0,96 et un MSE de $7,0 \cdot 10^{-3}$ cm²/min pour la colonne 1 et 0,97 et $5,1 \cdot 10^{-3}$ cm²/min pour la colonne 2 (Tableau 4). Ainsi ce **modèle est adéquat pour simuler le transport de solutés non réactifs à travers le sable et la valeur du coefficient de dispersion longitudinale estimée pour chaque colonne de sable avec le sel (Tableau 2) est considérée comme étant validée et utilisable pour la suite (D = 2,02, 1,27, 1,65 cm²/min pour les colonnes 1, 2 et valeur moyenne, respectivement).**

Ainsi, comme la valeur du coefficient de dispersion longitudinale estimée pour chaque colonne de sable est validée, alors **la valeur du coefficient de dispersion longitudinale estimée pour chaque colonne de Rainclean® avec le sel (Tableau 2) est considérée comme étant validée et utilisable pour la suite (D = 3,16, 2,38, 2,77 cm²/min pour les colonnes 1, 2 et valeur moyenne, respectivement).**

5.3 Modelling reactive transport of AAG (longitudinal dispersion + adsorption) in Rainclean® columns

5.3.1 Direct modelling with Hydrus-1D

Comme une adsorption cinétique est observée pour l'acide amino-G sur le Rainclean®, l'objectif est de reproduire le comportement de l'acide amino-G dans les colonnes de Rainclean® lors des traçages (Figure 34 et Figure 35) par simulation afin de valider ou invalider les valeurs des paramètres d'adsorption obtenues en laboratoire.

5.3.1.1 Méthodologie

Des simulations ont été réalisées avec le logiciel Hydrus-1D (Šimůnek et van Genuchten, 2008), supposant un apport homogène de l'eau en surface. Les colonnes de Rainclean® utilisées lors des traçages (10 et 20 cm de hauteur) ont été reproduites en 1D dans le logiciel.

Plusieurs modèles hydrauliques sont disponibles dans ce logiciel tel que, par exemple le modèle conceptuel à deux régions (encore appelé modèle double-porosités, van Genuchten et Wierenga, 1976) représentant des zones mortes ou des écoulements préférentiels. Dans cette étude, assumant un écoulement homogène au sein de toutes les colonnes, le modèle hydraulique choisi pour y décrire les écoulements est le modèle de Richards, tenant compte des équations de Van Genuchten et Mualem. Le modèle de transport est le modèle CDE non-équilibré prenant en compte la dispersivité et une adsorption (isothermes de Langmuir ou Freundlich) cinétique (pseudo-premier ordre).

Les conditions expérimentales prises en compte pour simuler les traçages à l'acide amino-G étaient celles présentées dans le Tableau 3, avec, pour les paramètres de transport, la valeur de la dispersivité estimée pour chaque colonne lors des traçages au sel (5,88 et 4,42 cm pour la colonne 1 et colonne 2, respectivement, Tableau 2) et les valeurs des paramètres d'adsorption pour l'acide amino-G obtenues avec le Rainclean® lors des expérimentations en batch (isothermes de Langmuir ou Freundlich et cinétique de pseudo-premier ordre, Tableau 5). Toutes les combinaisons de cinétique de pseudo-premier ordre et d'isothermes de Langmuir et de Freundlich (2 simulations/colonne/hauteur du matériau) ont été réalisées.

Tableau 5 : Valeurs des paramètres d'adsorption pour l'acide amino-G sur le Rainclean® obtenues lors des expérimentations en batch (cinétique à gauche, isothermes à droite)

Kinetics		Isotherms			
Pseudo-first order		Langmuir		Freundlich	
q _e (mg/g)	k ₁ (mn ⁻¹)	q _m (mg/g)	K _L (L/mg)	n	K _F
0.51	1.27E-03	0.7	1.0	2.22	0.31

Pour chaque simulation (pour chaque colonne) :

- La condition à la limite en entrée et en sortie pour le modèle hydraulique est une vitesse constante (vitesse d'alimentation) et une pression constante, respectivement.
- La condition à la limite en entrée pour le modèle de transport est une injection de type créneau durant un temps T d'une concentration présentée dans le Tableau 3.
- La concentration initiale en acide amino-G dans les colonnes de Rainclean® est nulle.
- Les durées de simulations sont les durées de chaque traçage (Tableau 3).

Les données obtenues à la fin de chaque simulation sont comparées aux données expérimentales obtenues lors des traçages hydrauliques réalisées avec l'acide amino-G pour les colonnes de 10 cm et 20 cm de Rainclean®.

5.3.1.2 Résultats

La Figure 37 présente les valeurs de la concentration en acide amino-G mesurées (ronds) et prédites (lignes) en sortie des colonnes de 10 et 20 cm de Rainclean® avec le modèle de transport avec dispersion et adsorption cinétique dans Hydrus-1D.

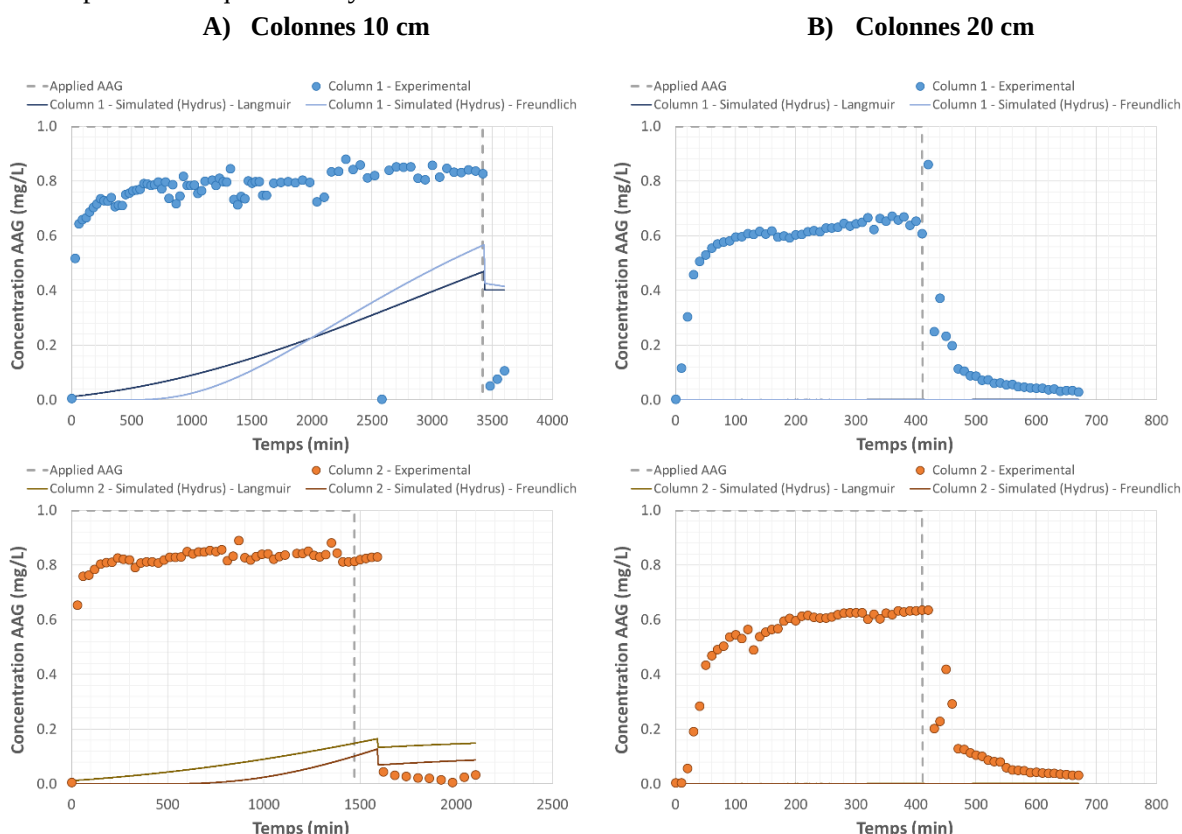


Figure 37 : Valeurs de la concentration en AAG (ronds) en sortie des colonnes de 10 cm (A) et de 20 cm (B) et prédites (lignes) en sortie des colonnes par modélisation directe des données des traçages par le modèle de transport avec dispersion et adsorption cinétique dans Hydrus-1D

Les valeurs de concentration en acide amino-G prédites par le modèle, quelles que soient l'isotherme et la hauteur de Rainclean® simulées, ne correspondent pas aux valeurs mesurées lors des traçages. En effet, les valeurs obtenues avec les simulations sont très en-dessous des valeurs mesurées, la différence s'amplifiant lorsque la hauteur de Rainclean® augmente. Les valeurs des isothermes et de la cinétique mesurées en batch surestiment l'adsorption mesurées dans les colonnes.

Ainsi, **il n'est pas possible d'appliquer directement les valeurs de la cinétique et des isothermes obtenues par batch pour représenter les concentrations mesurées à la sortie des colonnes ainsi que dans le filtre de Bugeaud contenant du Rainclean®.**

5.3.2 Inverse modelling of AAG transport parameters in Rainclean columns with Hydrus-1D

Pour pouvoir simuler au mieux le comportement des espèces dans le filtre de Bugeaud contenant du Rainclean®, une modélisation inverse a été réalisée afin de déterminer les valeurs des paramètres d'adsorption (cinétique et isothermes).

5.3.2.1 Methodology

Cette modélisation inverse a été conduite à l'aide du module d'optimisation de Hydrus-1D afin de déterminer les paramètres d'adsorption de l'acide amino-G à partir de données expérimentales issues des traçages en colonne. Le domaine était le même que pour les simulations directes pour représenter les colonnes de 10 et 20 cm de hauteur. Les paramètres hydrauliques, la dispersivité ainsi que les conditions opératoires étaient les mêmes que pour les simulations directes (Tableau 2 et Tableau 3), tandis que les paramètres d'adsorption ont été ajustés par optimisation. Pour chaque colonne, l'optimisation a été réalisée sur toute la durée du traçage (ajout d'acide amino-G puis ajout d'eau distillée). La fonction objectif correspondait à la minimisation de la somme des carrés des écarts entre les concentrations mesurées et les concentrations simulées aux temps de prélèvements expérimentaux. Le modèle d'adsorption (isothermes de Langmuir ou Freundlich) cinétique (pseudo-premier ordre) a été considéré. Les bornes des paramètres à ajuster ont été définies en s'appuyant sur les valeurs des paramètres d'adsorption estimées avec les batch (Tableau 5). L'algorithme d'optimisation utilisé est celui de Levenberg-Marquardt, intégré dans Hydrus-1D et particulièrement adapté à l'ajustement de modèles non-linéaires.

L'estimation de tous les paramètres (cinétique/isothermes) a été réalisée simultanément pour chaque colonne et hauteur de matériau. Le r^2 et le RMSE sont calculés et fournis par Hydrus-1D.

5.3.2.2 Results

La Figure 38 présente les valeurs de la concentration en acide amino-G mesurées (ronds) et prédites (lignes) par modélisation inverse en sortie des colonnes de 10 et 20 cm de Rainclean® avec le modèle de transport avec dispersion et adsorption cinétique dans Hydrus-1D. Le coefficient de détermination r^2 et le RMSE sont aussi indiqués pour chaque colonne.

L'optimisation inverse a permis de reproduire le comportement de l'acide amino-G dans les colonnes de Rainclean® : les valeurs de concentration prédites par le modèle, quelles que soient l'isotherme et la hauteur de Rainclean® simulées, correspondent aux valeurs mesurées lors des traçages ($r^2 > 0,72$ et RMSE correspondant à 1.5 à 7.2% de l'ordre de grandeur des concentrations mesurées). Ainsi, les résultats de la **modélisation inverse ont permis de déterminer les valeurs optimales des paramètres**

d'adsorption reproduisant le plus fidèlement les cinétiques expérimentales de percée de l'acide amino-G.

La modélisation inverse à partir des résultats en colonnes et initialisée à partir des valeurs obtenues par batch est une stratégie adaptée pour estimer les valeurs des paramètres d'adsorption et caractériser un matériau adsorbant lorsque les résultats par la modélisation directe sont très éloignés des valeurs mesurées.

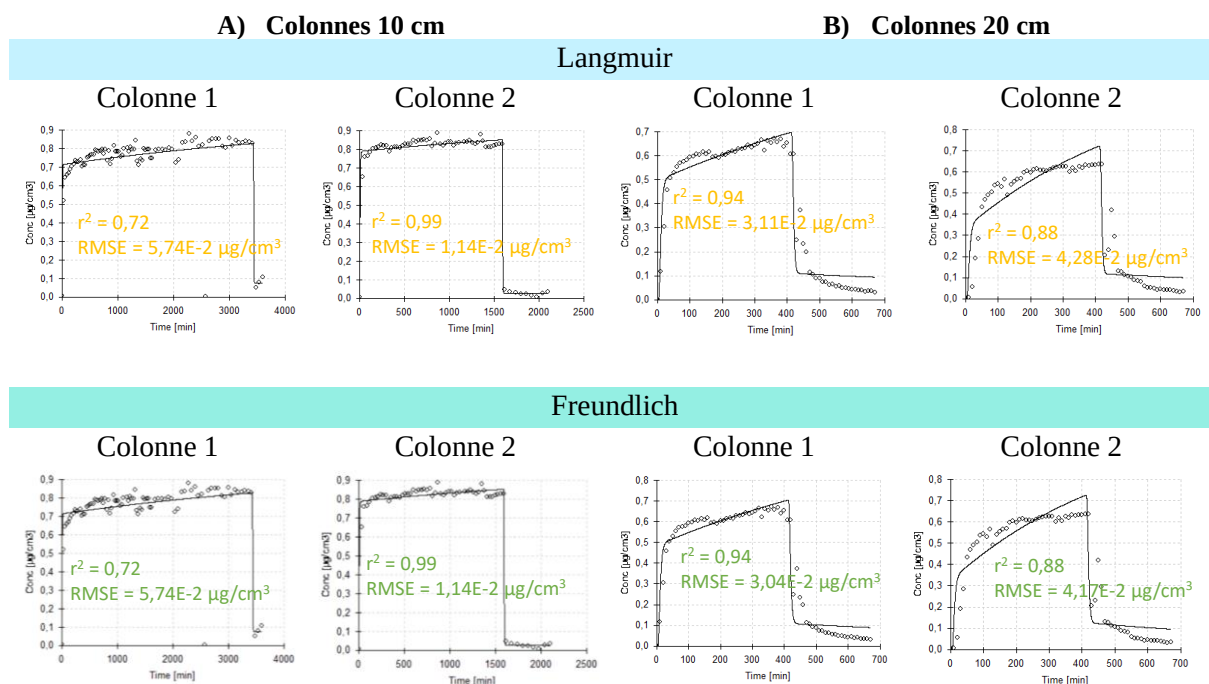


Figure 38 : Valeurs de la concentration en acide amino-G mesurées (ronds) en sortie des colonnes de 10 cm (A) et des colonnes de 20 cm (B) et prédites (lignes) par modélisation inverse des données des traçages avec le modèle de transport avec dispersion et adsorption cinétique dans Hydrus-1D. r^2 = coefficient de détermination, RMSE = Root Mean Squared Error

5.4 Modeling reactive transport of micropollutants in Rainclean® columns – calibration of adsorption isotherm and adsorption kinetic parameters

Les objectifs ici sont de (i) déterminer si les résultats obtenus en batch (valeurs des paramètres d'adsorption) pour les micropolluants avec le Rainclean® sont représentatifs de leur comportement en colonne, ou si, comme pour l'acide amino-G, il est nécessaire de réaliser une modélisation inverse pour obtenir la valeur des paramètres d'adsorption, et (ii) d'obtenir les valeurs des paramètres d'adsorption (isotherme et cinétique) pour la modélisation du filtre de Bugeaud contenant du Rainclean®.

5.4.1 Direct modeling with Hydrus-1D

Comme une adsorption cinétique sur le Rainclean® est observée pour les micropolluants métalliques (As, Cd, Cr, Cu, Ni, Pb, V et Zn) et organiques (BPA, OP, NP) étudiés, l'objectif est de reproduire leur comportement dans les colonnes de Rainclean® lors des essais en colonne par simulation afin de valider ou invalider les valeurs des paramètres d'adsorption obtenues en laboratoire.

5.4.1.1 Methodology

Des simulations ont été réalisées avec le logiciel Hydrus-1D (Šimůnek et van Genuchten, 2008), supposant un apport homogène de l'eau en surface. Les colonnes de Rainclean® utilisées lors des traçages ont été reproduites en 1D dans le logiciel : 20 cm avec des points d'observation 5 et 10 cm de hauteur pour les micropolluants métalliques et organiques, respectivement, permettant d'obtenir les concentrations à ces hauteurs.

Le modèle hydraulique choisit pour y décrire les écoulements est le modèle de Richards, tenant compte des équations de Van Genuchten et Mualem. Le modèle de transport est le modèle CDE non-équilibré prenant en compte la dispersivité et une adsorption (selon une isotherme propre à chaque micropolluant) cinétique (pseudo-premier ordre).

Les conditions expérimentales prises en compte pour simuler les essais en colonnes étaient celles présentées en 4.2.5, avec, pour les paramètres de transport, la valeur de la dispersivité estimée pour chaque colonne lors des traçages au sel (5,88 et 4,42 cm pour la colonne 1 et colonne 2, respectivement, Tableau 2) et les valeurs des paramètres d'adsorption pour chaque micropolluant obtenues avec le Rainclean® lors des expérimentations en batch.

Pour chaque simulation (pour chaque colonne et chaque micropolluant) :

- La condition à la limite en entrée et en sortie pour le modèle hydraulique est une vitesse constante (vitesse d'alimentation) et une pression constante, respectivement.
- La condition à la limite en entrée pour le modèle de transport est une injection de type créneau durant un temps T d'une concentration présentée en 4.2.5 .
- La concentration initiale en micropolluant dans les colonnes de Rainclean® est nulle.
- Les durées de simulations sont les durées de chaque traçage (Tableau 3).

Les données obtenues à la fin de chaque simulation sont comparées aux données expérimentales obtenues en colonnes.

5.4.1.2 Results

La Figure 39 présente les valeurs des concentrations en micropolluants métalliques mesurées (ronds) et prédites (lignes) à 5 cm des colonnes de Rainclean® avec le modèle de transport avec dispersion et adsorption cinétique dans Hydrus-1D. La Figure 40 présente les valeurs des concentrations en micropolluants organiques mesurées (ronds) et prédites (lignes) à 10 cm des colonnes de Rainclean® avec le modèle de transport avec dispersion et adsorption cinétique dans Hydrus-1D.

Parmi les micropolluants métalliques, les valeurs des concentrations prédites par le modèle concordent aux valeurs mesurées à 5 cm des colonnes pour As, Cr, Ni, Pb et V. Les valeurs des isothermes et de la cinétique mesurées en batch permettent de reproduire l'adsorption mesurées dans les colonnes. Ainsi, **il est possible, pour ces espèces, d'appliquer directement les valeurs de la cinétique et des isothermes obtenues par batch pour représenter leur comportement dans le filtre de Bugeaud contenant du Rainclean®.**

En revanche, pour Cd, Cu, Zn et les trois micropolluants organiques étudiés, BPA, OP et NP, les valeurs des concentrations prédites par le modèle ne correspondent pas aux valeurs mesurées à 5 cm et 10 cm des colonnes, respectivement. En effet, les valeurs obtenues avec les simulations sont en-dessous des valeurs mesurées. Les valeurs des isothermes et de la cinétique mesurées en batch surestiment l'adsorption mesurées dans les colonnes. Ainsi, **il n'est pas possible, pour ces espèces, d'appliquer directement les valeurs de la cinétique et des isothermes obtenues par batch pour représenter leur comportement dans le filtre de Bugeaud contenant du Rainclean®.**

Micropolluants métalliques



Figure 39 : Valeurs de la concentration en micropolluants métalliques mesurées (ronds) en entrée et à 5 cm des colonnes de Rainclean® et prédites (lignes) à 5 cm par modélisation directe par le modèle de transport avec dispersion et adsorption cinétique dans Hydrus-1D

Micropolluants organiques

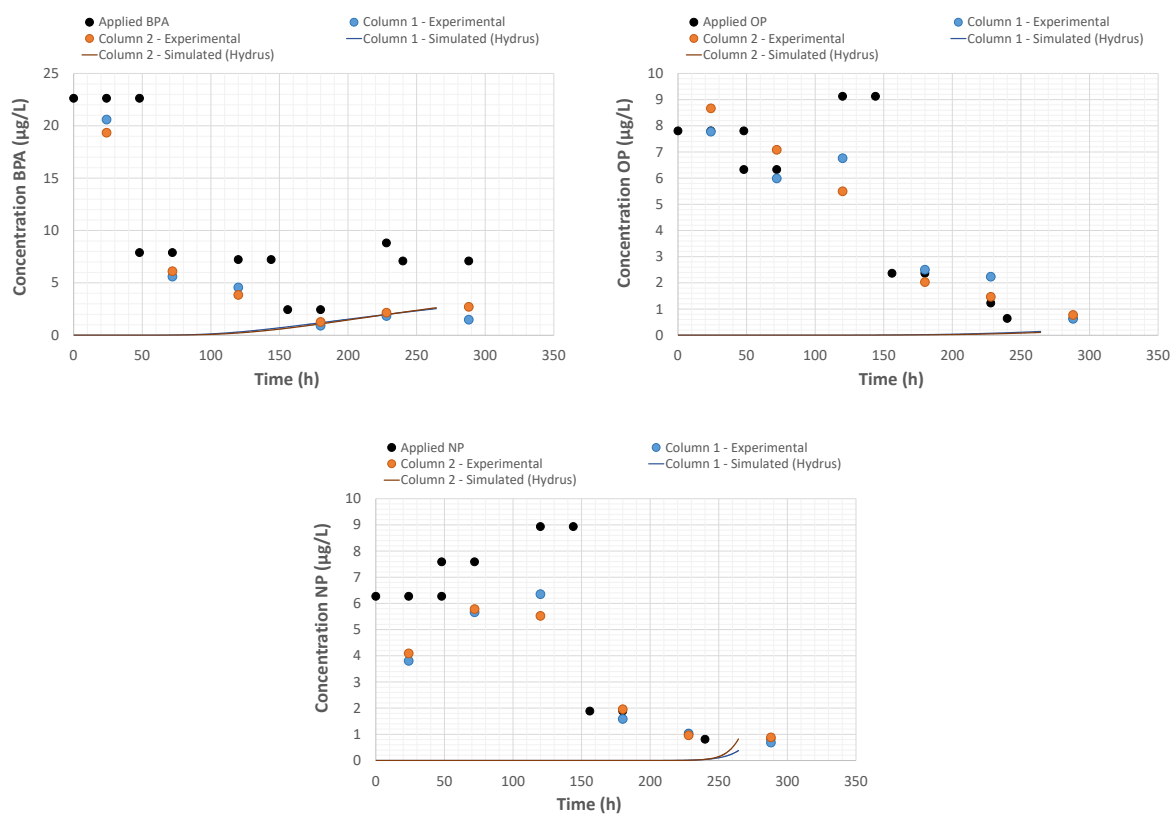


Figure 40 : Valeurs de la concentration en micropolluants organiques mesurées (ronds) en entrée et à 10 cm des colonnes de Rainclean® et prédites (lignes) à 10 cm par modélisation directe par le modèle de transport avec dispersion et adsorption cinétique dans Hydrus-1D

Ainsi, pour les micropolluants avec une bonne adsorption sur le Rainclean®, Cd, Cu, Zn, NP, OP et BPA, les valeurs des paramètres d'adsorption déterminées en batch ne permettent pas de reproduire les valeurs obtenues en colonnes, sauf pour Pb. Pour les micropolluants avec une mauvaise adsorption sur le Rainclean®, As, Cr, Ni et V, les valeurs des paramètres d'adsorption déterminées en batch permettent de reproduire les valeurs obtenues en colonnes.

5.5 Calibration of micropollutant adsorption parameters through inverse modelling with Hydrus-1D

Pour pouvoir simuler au mieux le comportement des espèces dans le filtre de Bugeaud contenant du Rainclean®, une modélisation inverse a été réalisée pour les micropolluants pour lesquels les valeurs des paramètres d'adsorption déterminées en batch ne permettent pas de reproduire les valeurs obtenues en colonnes, afin de déterminer les valeurs des paramètres d'adsorption (cinétique et isothermes).

5.5.1 Methodology

Cette modélisation inverse a été conduite à l'aide du module d'optimisation de Hydrus-1D afin de déterminer les paramètres d'adsorption des micropolluants Cd, Cu, Zn, NP, OP et BPA à partir de données expérimentales issues des essais en colonnes. Le domaine était le même que pour les simulations directes pour représenter les colonnes de 5 et 10 cm de hauteur pour les micropolluants métalliques et organiques concernés, respectivement. Les paramètres hydrauliques, la dispersivité ainsi que les conditions opératoires étaient les mêmes que pour les simulations directes tandis que les paramètres d'adsorption ont été ajustés par optimisation. Pour chaque colonne, l'optimisation a été réalisée seulement sur la durée de l'essai où l'ajout de micropolluant était réalisée (durée d'injection de l'eau distillée non prise en compte). La fonction objectif correspondait à la minimisation de la somme des carrés des écarts entre les concentrations mesurées et les concentrations simulées aux temps de prélèvements expérimentaux. Le modèle d'adsorption (isothermes linéaire ou Langmuir) cinétique (pseudo-premier ordre) a été considéré. Les bornes des paramètres à ajuster ont été définies en s'appuyant sur les valeurs des paramètres d'adsorption estimées avec les batch. L'algorithme d'optimisation utilisé est celui de Levenberg-Marquardt, intégré dans Hydrus-1D et particulièrement adapté à l'ajustement de modèles non-linéaires. L'estimation de tous les paramètres (cinétique/isothermes) a été réalisée simultanément pour chaque colonne et hauteur de matériau. Le r^2 et le RMSE sont calculés et fournis par Hydrus-1D.

5.5.2 Results

La Figure 41 présente les valeurs de la concentration en micropolluants métalliques Cd, Cu et Zn mesurées (ronds) et prédites (lignes) par modélisation inverse à 5 cm des colonnes de Rainclean® avec le modèle de transport avec dispersion et adsorption cinétique dans Hydrus-1D. La Figure 42 présente les valeurs des concentrations en micropolluants organiques mesurées (ronds) et prédites (lignes) par modélisation inverse à 10 cm des colonnes de Rainclean® avec le modèle de transport avec dispersion et adsorption cinétique dans Hydrus-1D. Le coefficient de détermination r^2 et le RMSE sont indiqués pour chaque colonne.

L'optimisation inverse a permis de reproduire le comportement des trois micropolluants métalliques dans les colonnes de Rainclean® : les valeurs de concentration prédites par le modèle correspondent globalement aux valeurs mesurées à 5 cm ($r^2 > 0,43$ et RMSE correspondant à 0.1 à 2.9% de l'ordre de grandeur des concentrations mesurées). Ainsi, les résultats de la **modélisation inverse ont permis de déterminer les valeurs optimales des paramètres d'adsorption** reproduisant le plus fidèlement les cinétiques expérimentales de percée de Cd, Cu et Zn.

En revanche, hormis pour le **OP pour lequel l'optimisation inverse a permis de globalement reproduire son comportement dans les colonnes de Rainclean®** ($r^2 > 0,74$ et RMSE correspondant à 3.3 à 4.2% de l'ordre de grandeur des concentrations mesurées), pour le **BPA et le NP, la modélisation inverse n'a pas permis de reproduire les cinétiques expérimentales** (r^2 entre 0.07 et 0.25 et RMSE

correspondant à 8 à 151% de l'ordre de grandeur des concentrations mesurées). Cela vient du fait que très peu de données de concentrations à optimiser sont disponibles et la possibilité de la présence de court-circuit ou de passages préférentiels, notamment pour le BPA, révélée quand la valeur de concentration est très importante au début des essais puis que ces valeurs diminuent par la suite.

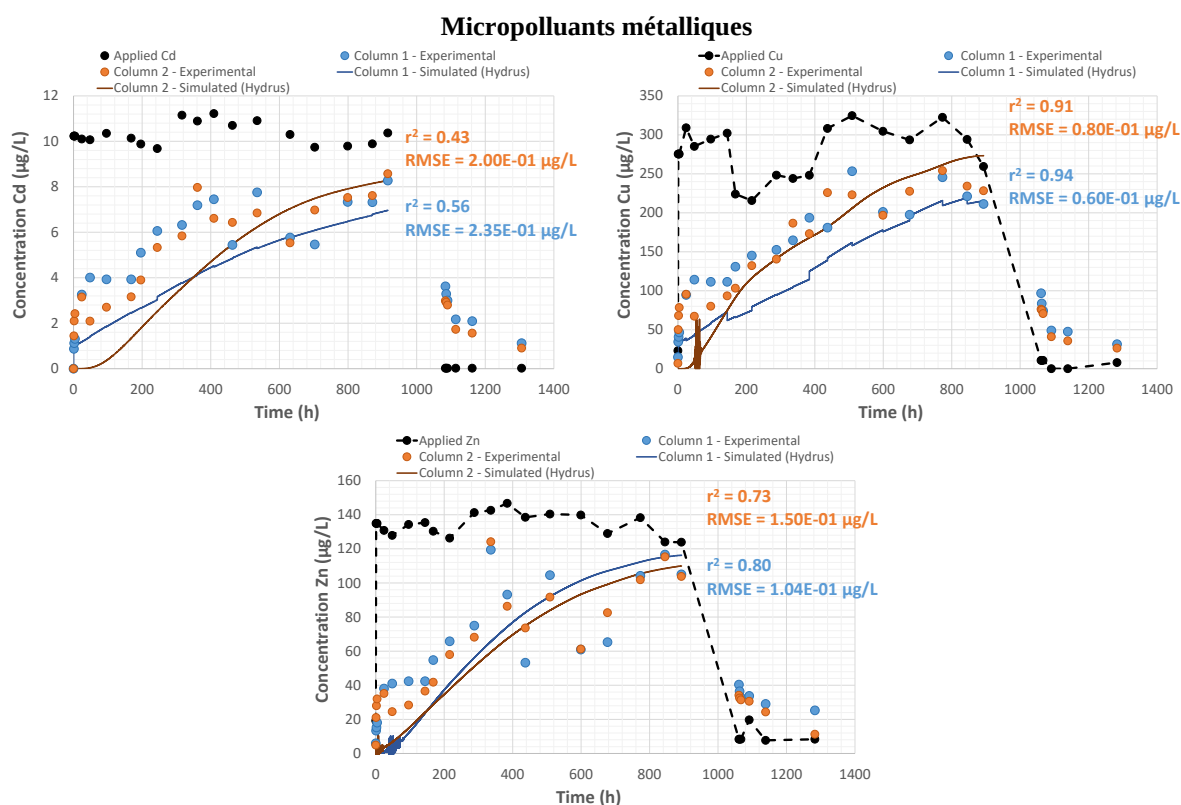


Figure 41 : Valeurs de la concentration en micropolluants métalliques Cd, Cu, Zn, mesurées (ronds) en entrée et à 5 cm des colonnes de Rainclean® et prédites (lignes) à 5 cm par modélisation inverse par le modèle de transport avec dispersion et adsorption cinétique dans Hydrus-1D. r^2 = coefficient de détermination, RMSE = Root Mean Squared Error

Micropolluants organiques

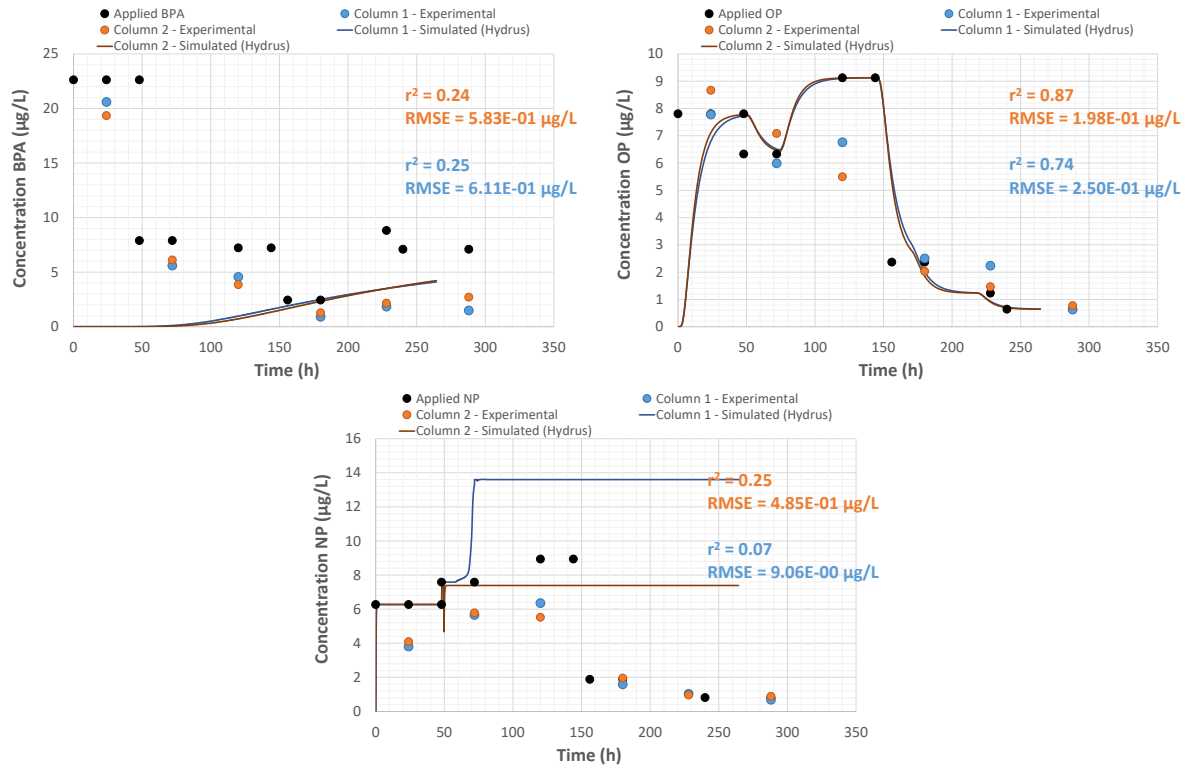


Figure 42 : Valeurs de la concentration en micropolluants organiques mesurées (ronds) en entrée et à 10 cm des colonnes de Rainclean® et prédites (lignes) à 10 cm par modélisation directe par le modèle de transport avec dispersion et adsorption cinétique dans Hydrus-1D. r^2 = coefficient de détermination, RMSE = Root Mean Squared Error

5.6 Validation of calibrated adsorption parameter values

Une validation finale des valeurs des paramètres d'adsorption pour les micropolluants métalliques, obtenues en batch ou par modélisation inverse, a été réalisée afin de vérifier si ces valeurs déterminées pour les 5 premiers centimètres étaient aussi valides pour reproduire les concentrations mesurées en sortie des colonnes à 20 cm. Cette validation n'a pas été réalisée pour les micropolluants organiques car seules les mesures réalisées à 10 cm ont été réalisées et utilisées pour l'optimisation.

5.6.1 Methodology

Pour les micropolluants métalliques dont les valeurs des paramètres d'adsorption obtenues en batch permettent de représenter leur comportement à 5 cm, As, Cr, Ni, Pb et V, les simulations directes ont déjà été réalisées. Pour les autres micropolluants métalliques, Cd, Cu, Zn, des simulations ont été réalisées (Hydrus-1D), dans des conditions identiques aux simulations directes réalisées précédemment, avec pour seule différence les valeurs des paramètres d'adsorption (isothermes et cinétique) égales aux valeurs optimisées par modélisation inverse.

Les données obtenues à la fin de chaque simulation sont comparées aux données expérimentales obtenues en colonnes à 20 cm.

5.6.2 Results

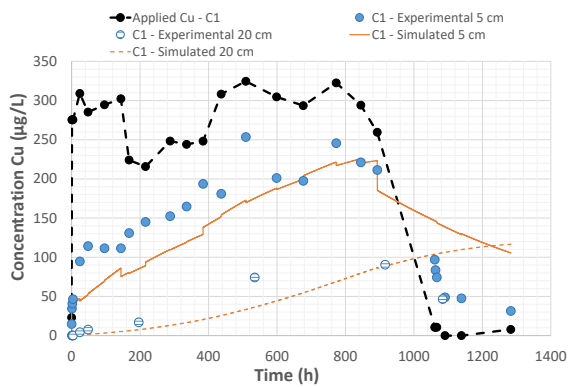
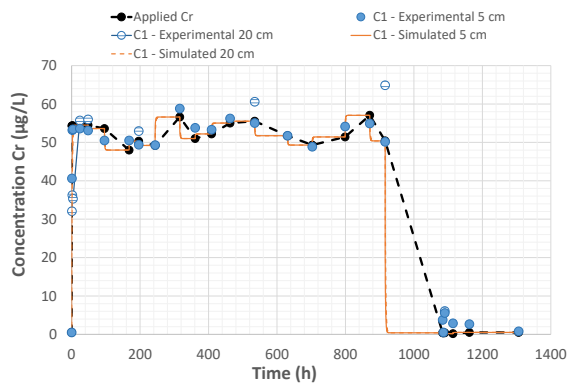
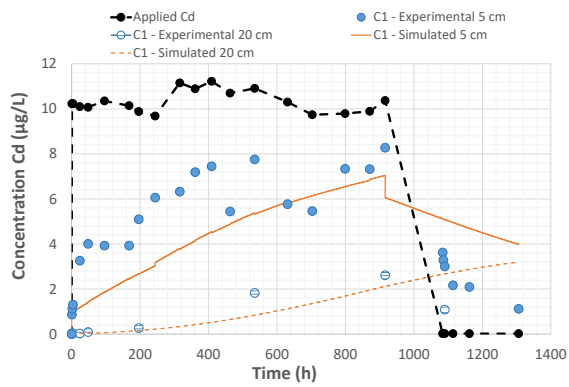
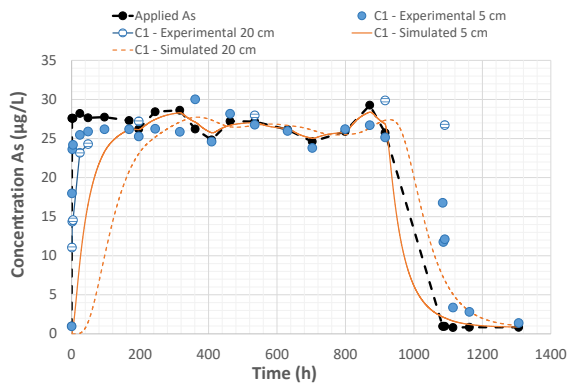
La Figure 43 présente les valeurs des concentrations de tous les micropolluants métalliques mesurées (ronds) et prédites (lignes) à 5 et 20 cm des colonnes de Rainclean® avec le modèle de transport avec dispersion et adsorption cinétique (avec les valeurs des paramètres obtenues soit par batch pour As, Cr, Ni, Pb et V, soit par optimisation inverse pour Cd, Cu et Zn) dans Hydrus-1D.

Parmi les micropolluants métalliques, les valeurs des concentrations prédites par le modèle concordent aux valeurs mesurées à 20 cm pour Cd, Cr, Cu, Pb et V (pour au moins une des deux colonnes). Pour As et Ni, l'allure générale des valeurs de concentrations prédites en sortie des colonnes concorde avec celle des concentrations mesurées sauf au début des essais où les concentrations simulées sont inférieures à celles mesurées. Pour le Zn, les paramètres d'adsorption ne permettent pas de reproduire les concentrations mesurées à 20 cm et surestiment l'adsorption du Zn sur le Rainclean®, avec des concentrations prédites nettement inférieures à celles mesurées.

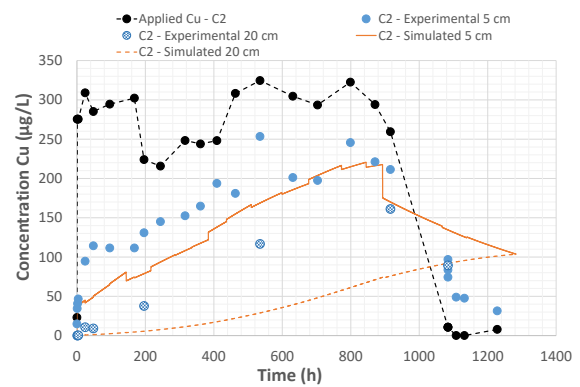
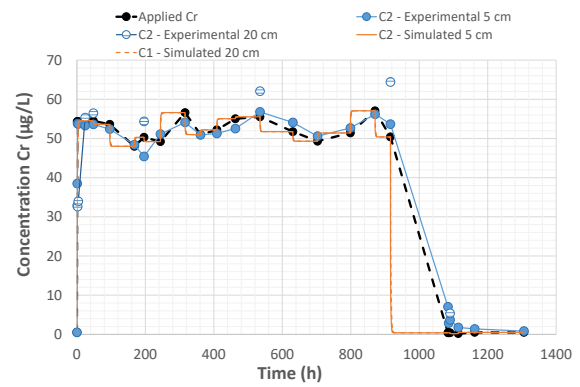
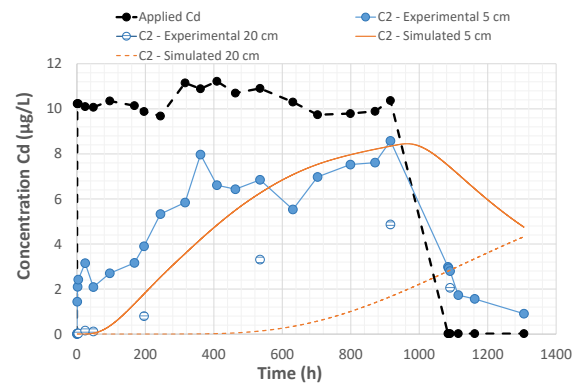
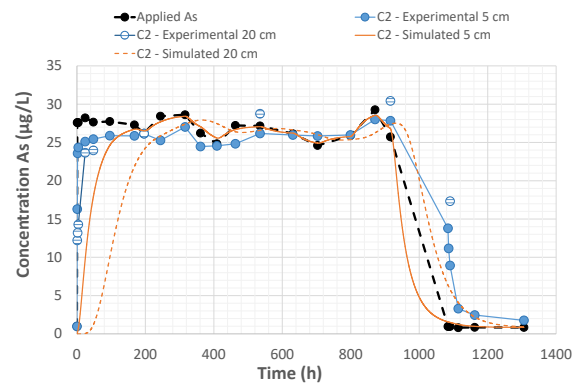
Ainsi, pour les micropolluants avec une mauvaise adsorption sur le Rainclean®, As, Cr, Ni et V, les valeurs des paramètres d'adsorption déterminées en batch sont validées. Pour les micropolluants métalliques avec une bonne adsorption sur le Rainclean®, Cd et Cu, les valeurs des paramètres d'adsorption déterminées par optimisation inverse sont validées. Pour le Zn, même si les valeurs des paramètres d'adsorption n'ont pas permis de reproduire les concentrations mesurées à 20 cm, comme celles à 5 cm étaient correctement prédites, les valeurs des paramètres d'adsorption déterminées par optimisation inverse seront prises en compte pour la modélisation du Zn dans le filtre de Bugeaud contenant du Rainclean®.

Micropolluants métalliques

Colonne 1



Colonne 2



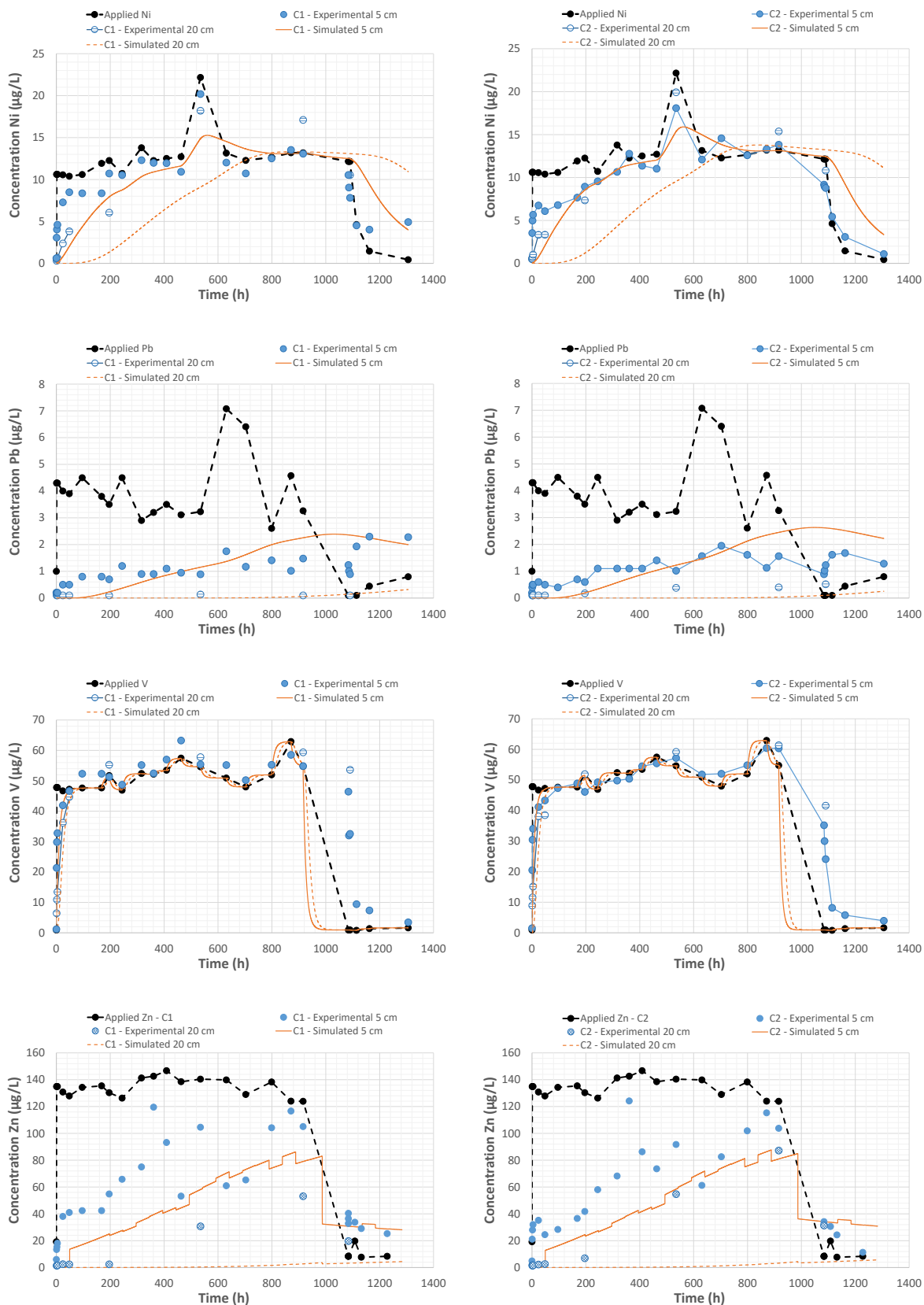


Figure 43 : Valeurs de la concentration en micropolluants métalliques mesurées (ronds) en entrée, à 5 et 20 cm des colonnes de Rainclean® et prédites (lignes) à 5 et 20 cm par modélisation directe par le modèle de transport avec dispersion et adsorption cinétique dans Hydrus-1D ; paramètres batch : As, Cr, Ni, Pb, V - paramètres optimisés : Cd, Cu, Zn

Le Tableau 6 récapitule les valeurs des paramètres des isothermes et cinétique d'adsorption sur le Rainclean® pour chaque micropolluant métallique et organique étudié.

Tableau 6 : Valeurs des paramètres des isothermes et cinétique d'adsorption sur le Rainclean® pour chaque micropolluant métallique et organique

			As	Cd	Cr	Ni	Pb	V	BPA	OP
			Batch	Inversion	Batch	Batch	Batch	Batch	Inversion	Inversion
Isotherme	Linéaire	Kd [L/kg]	372	5099	3	1178	8319	70	3146	100
Cinétique	Pseudo-premier ordre	k _i [min ⁻¹]	1.16E-02	4.02E-03	1.66E-02	3.11E-03	4.49E-02	1.25E-02	8.03E-02	9.12E-02

			Cu	Zn	NP
			Inversion	Inversion	Inversion
Isotherme	Langmuir	q _m [µg/g]	4733	603	6.2
		KL [L/µg]	7.50E-04	4.24E-02	3.7
Cinétique	Pseudo-premier ordre	k _i [min ⁻¹]	1.10E-04	3.97E-05	1.58E-01

6 CONCLUSIONS ON RAINCLEAN® ADSORPTION PROPERTIES

The adsorption capacity of the different substrates which are present in the LifeAdsorb reed bed filter prototype was assessed in the lab for a range of trace metals (As, Cd, Cr, Cu, Ni, Pb, V, Zn) and organic micropollutants (BPA, OP, NP).

Leaching test in deionised water showed significant leaching concentrations of NP and to a lesser extent OP from the new Rainclean material, compared to concentration found in the dissolved phase in urban runoff. The sediment was characterized by high leaching levels of Cu as well as BPA.

Simple batch tests, where the adsorbent is put in contact with the adsorbate at different concentration levels and for different durations, were carried out for a first assessment of the adsorption kinetic (i.e. adsorption speed as a function of substrate concentration) and the adsorption isotherm (i.e. equilibrium conditions between concentration in the water and in the substrate) laws. These batch experiment confirmed the expected inefficiency of sand to adsorb micropollutants. Rainclean as well as sediment (collected from the top of the filter, close to the inlet) showed variable adsorption capacities for the different micropollutants. Micropollutants can be classified as follows based on their adsorption velocity Rainclean : NP, OP, BPA > Pb > Cu, Cr > V, As > Cd, Zn > Ni, Sediment : Cu, Cd, NP, Ni, Zn > BPA > As, OP, Pb, V > Cr.

Based on the batch studies, Rainclean shows good adsorption capacity for Cd, Cu and Zn, as well as BPA, NP and OP but very limited or no adsorption for V, Ni, Cr and As. The adsorption capacity of the sediment is higher than that of the Rainclean for V and Cd, similar to the Rainclean for Zn, Ni and NP but much lower for Cu, OP and BPA.

Column studies were carried on for further assessment of the Rainclean under dynamic conditions and at micropollutant concentrations levels more representative of field conditions. Three groups of trace elements can be distinguished. **As, Cr and V do not show any significant adsorption on the Rainclean material. Zn, Cu and Cd show stronger adsorption. Pb shows very strong adsorption of the Rainclean material.** For a loading rate of 100 m/year of the reed bed filters, and under the flow conditions of the column (5 times higher than the field velocity) **the life time of the Rainclean material before saturation can be estimated to 2 to 3 years for Ni and 12 years for Cu, Zn and Cd.** However, the **average dissolved metal removal efficiency over this period is limited: only 40 to 44% for Zn and Cd, and 34 to 38% for Cu.** This efficiency will be recalculated in task B2 with the filter model calibrated based on these column studies and for real operation conditions. **Adsorption of the tested organic micropollutants appears much less efficient** than for trace metals, and **breakthrough and saturation of the Rainclean material is expected to happen within a few years** of functioning of the reed bed filter.

Column tests carried out with tracers (NaCl and aminoG acid AAG) were successfully used to calibrate and validate the longitudinal dispersion coefficient of the Rainclean and sand materials.

The reactive transport of micropollutants under column test conditions was modelled with the Hydrus1D software. First, kinetic and isotherm adsorption parameters established during batch tests were used in a direct modelling approach. Inverse modelling was used to recalibrate these parameters based on the column data for those pollutant where results from direct modelling were not consistent with experimental results. **For those trace metals with very limited adsorption on Rainclean®, As, Cr, Ni and V, batch parameter values were validated with the dynamic model.** For trace metals with good adsorption on Rainclean®, Cd et Cu, batch parameters did not fit with column study results

but the **adsorption parameters were successfully calibrated with the inverse modelling** approach and validated. For Zn, even if the values of the adsorption parameters calibrated on the 5 cm column depth did not allow to reproduce the concentrations measured at 20 cm, as those at 5 cm were correctly predicted, the values of the adsorption parameters determined by inverse optimization will be taken into account for the modeling of Zn in the Bugeaud filter containing Rainclean®.

For organic micropollutants, the limited number of data available in the column experiments coupled to important experimental uncertainty did not allow successful modelling of the column tests.

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8 APPENDICES

Résultats obtenus lors de la modélisation inverse des traçages au sel réalisés sur les six colonnes (sable seul x2, Rainclean® x2, sable-Rainclean®-sable x2)

La Figure 44 présente les résultats sous forme de graphique fournis par STANMOD lors de l'optimisation par modélisation inverse du paramètre de dispersion longitudinale D pour chaque colonne pour lesquelles les traçages au sel ont été réalisés (sable seul x2, Rainclean® x2, sable-Rainclean®-sable x2). Les coefficients de détermination (r^2) ainsi que les carrés moyens des erreurs (MSE) sont indiqués pour chaque optimisation.

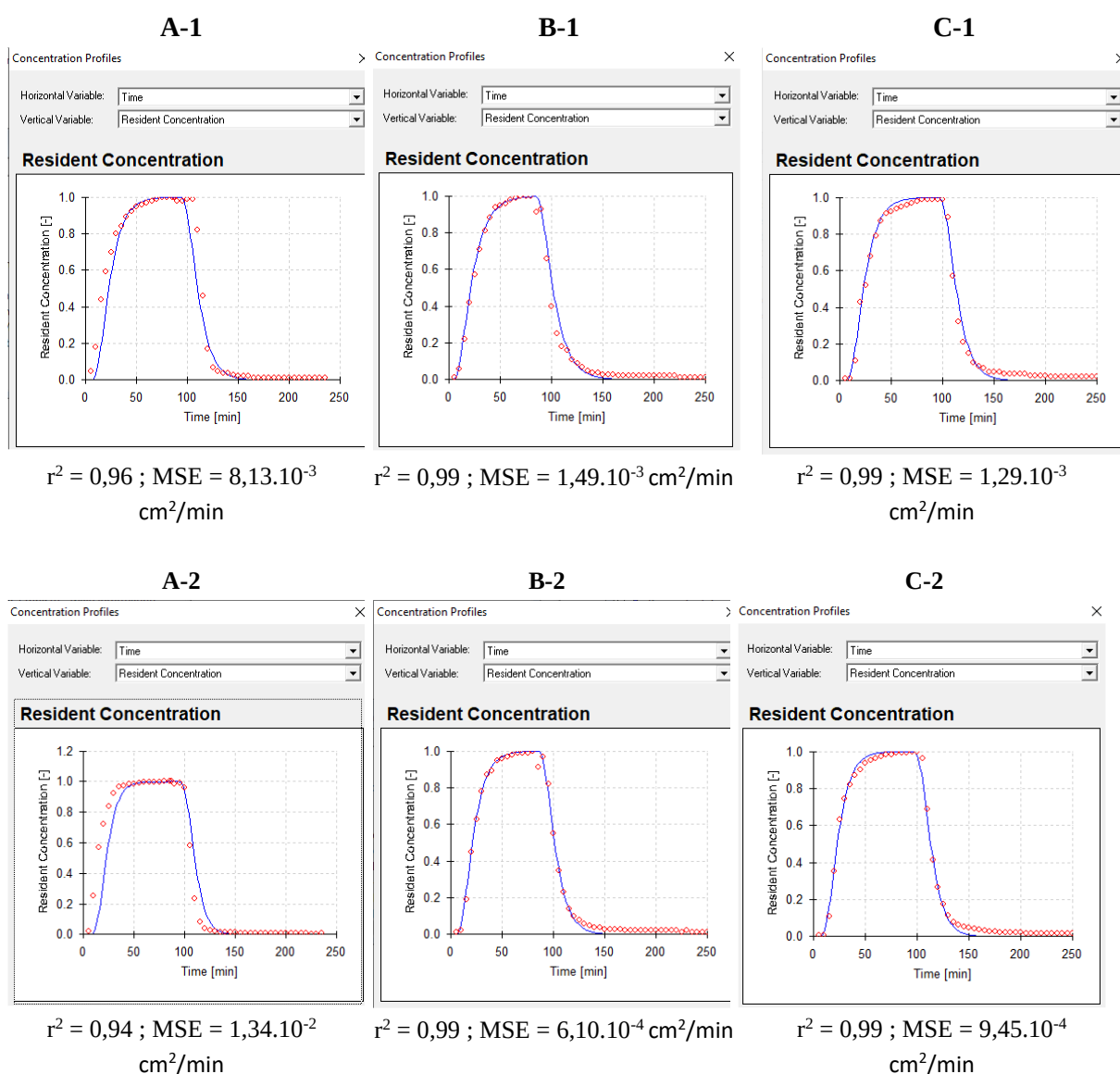


Figure 44 : Valeurs mesurées (cercles rouges) et prédites (ligne bleue) de la conductivité électrique relative des deux colonnes de sable seul (A), Rainclean® seul (B), sable-Rainclean®-sable (C). r^2 = coefficient de détermination, MSE = Mean Squared Error