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Removal of pharmaceuticals during river bank filtration

Elimination de produits pharmaceutiques par filtration sur berge de rivière

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Résumé

De plus en plus de micropolluants organiques sont détectés dans les rivières et comme leurs effets sur la santé sont encore mal connus, il est devenu primordial de les éliminer lors du procédé de traitement de l'eau. Le but du projet de recherche est d'étudier l'élimination de ces micropolluants durant la filtration sur berge de rivière et plus précisément de déterminer les rôles respectifs de la biodégradation et de l'adsorption durant le processus. L'idée générale serait d'utiliser cette méthode naturelle et peu coûteuse afin de filtrer toute une gamme de molécules qui ne sont pas éliminées par d'autres techniques de filtration. Le deuxième objectif de cette étude est de mettre en place un modèle prédictif concernant l'élimination des polluants en fonction de leurs propriétés physico-chimiques afin de pouvoir prévoir l'élimination de futurs composants. Ce rapport donne une rapide présentation du projet ainsi que les résultats de recherches personnelles et la description de l'expérience sur laquelle j'ai travaillé avec l'étudiante en thèse qui mène le projet.

Mots-clés : filtration sur berge de rivière, micropolluant organique, biodégradation, adsorption.

Abstract

The occurrence of organic micro pollutants in rivers is increasing and since their effect on health is not well known yet, it has become an important issue in water treatment. The aim of the research project is to investigate the removal of these micro pollutants during river bank filtration and more precisely to assess the respective roles of biodegradation and adsorption in the process. The idea would be to use this natural and cost effective technique as a barrier for a wide range of molecules which are not removed with other filtration techniques. The second aim of the project is to establish a predictive model for the removal of the pollutants according to their physical and chemical properties in order to be able to predict the effectiveness of the method for future compounds. This report provides a quick presentation of the project but also some personal research on the subject and a description of the experiment set-up which I worked on with the Ph.D. student leading the project.

Keywords : river bank filtration, organic micro pollutant, biodegradation, adsorption.

Synthèse du rapport en français

Le sujet de mon stage portait sur la filtration sur berge de rivière en tant que procédé naturel d'élimination de micropolluants de plus en plus présents dans les rivières. En effet, l'utilisation accrue de substances chimiques comme les produits pharmaceutiques ou les pesticides a pour conséquence une élévation de la concentration de micropolluants dans les eaux de surface ainsi que dans les nappes phréatiques. Comme leur effet sur la santé est encore mal connu, il est important pour les compagnies de traitement des eaux de les éliminer. Le procédé de filtration sur berge de rivière est bien connu pour être une barrière efficace contre les microorganismes ou les macromolécules, et est déjà utilisé comme technique de prétraitement des eaux de surface. La question qui se pose est donc de savoir dans quelle mesure cette technique est aussi efficace contre les micropolluants, ce qui permettrait aux compagnies de traitement des eaux d'utiliser cette méthode simple et peu coûteuse à la place d'une multitude de traitements spécifiques à chaque molécule. L'idée serait d'utiliser la filtration sur berge de rivière dans un procédé multi-barrière comprenant déjà la filtration sur charbon actif pour éliminer les molécules apolaires, et la nanofiltration à travers une membrane pour éliminer les molécules polaires les plus grandes. La filtration sur berge de rivière est supposée efficace contre les molécules polaires les plus petites.

L'étude des capacités barrière vis-à-vis des micropolluants de la filtration sur berge de rivière est le thème de recherche de Cheryl Bertelkamp, la doctorante avec qui j'ai travaillé pendant ces trois mois de stage. Son projet est intitulé ESTAB pour Emerging Substances: Towards an Absolute Barrier. Elle travaille en collaboration avec d'autres chercheurs afin de proposer à terme aux compagnies de production d'eau potable Néerlandaises une méthode de filtration de l'eau de rivière fiable, pratique et peu coûteuse.

Le deuxième objectif du projet ESTAB est de mettre en place une méthode permettant de prédire le comportement de futurs nouveaux micropolluants. En effet, comme de nouveaux produits chimiques et pharmaceutiques sont créés, consommés et rejetés chaque année, il est important que l'étude ne se borne pas aux seuls composants présents actuellement dans les eaux de surface. Ainsi, l'élaboration d'un modèle prédictif basé sur les propriétés physico-chimiques des molécules fait partie des principaux résultats attendus de cette recherche.

Le projet a commencé en Novembre 2010 et la soutenance de thèse est prévue pour Novembre 2014. Des expériences en laboratoire et sur le terrain seront menées. Cheryl Bertelkamp et son superviseur, Arne Verliefde, ont imaginé une première expérience en laboratoire utilisant des colonnes de sable simulant la berge de rivière.

J'ai commencé mon stage en lisant beaucoup d'articles et de publications sur le thème de la filtration sur berge de rivière pour découvrir et me familiariser avec le sujet mais aussi pour collecter des informations sur les différentes molécules étudiées afin d'en faire une synthèse. En effet, la diversité des études faites et des composants étudiés ne permet pas d'avoir une

vision globale du problème et il est toujours souhaitable de comparer les résultats d'une recherche avec ceux des travaux antérieurs. J'ai également lu le rapport de la stagiaire Italienne me précédant et effectué des recherches personnelles sur certains aspects théoriques nécessaires à la compréhension des mécanismes responsables de l'élimination des molécules comme la biodégradation ou l'adsorption, ou de certains aspects techniques de l'expérience.

Ma première partie expose ces aspects théoriques.

I-Aspects théoriques

Lors du passage dans le sol, les molécules organiques peuvent être éliminées de deux manières : par adsorption sur les particules minérales en suspension et par biodégradation.

Adsorption

Le phénomène d'adsorption est l'adhésion d'une molécule sur une surface solide. Elle se produit préférentiellement sur les particules minérales en suspension et résulte de forces physico chimiques comme les forces de Van der Waals. La capacité d'adsorption d'un milieu dépend de la nature du sol, notamment de la surface spécifique et donc de la teneur en argile. D'autre part, la nature des molécules joue également un rôle important : plus elles sont hydrophobes, plus elles auront tendance à s'adsorber sur la matière en suspension. L'hydrophobicité est mesurée par le coefficient de partage eau-Octanol (noté log K ou log D) et l'adsorption peut être quantifiée par le rapport frontal (R_f) de la vitesse du solvant sur la vitesse des molécules lors du passage à travers un milieu.

Biodégradation

La biodégradation correspond à l'utilisation de molécules organiques par des bactéries et autres microorganismes comme nutriment. Lors de la digestion, les molécules organiques sont cassées et transformées en sous-produits, comme le méthane et le dioxyde de carbone.

Toutes les molécules ne sont pas facilement biodégradables et il est parfois nécessaire d'utiliser le cométabolisme, qui consiste à forcer la bactérie à oxyder la molécule en question de manière « accidentelle » en même temps qu'un substrat primaire qu'elle utilise pour se nourrir. L'acétate de sodium peut être utilisé comme substrat primaire.

L'activité bactérienne peut être quantifiée par mesure de l'ATP (Adénosine Triphosphate) avec un luminomètre dans la matrice sol préalablement traitée dans un bain à ultrasons pour détacher la biomasse. L'ATP est une molécule essentielle pour la croissance des bactéries. Celle-ci dépend également de la nature du sol et particulièrement de sa porosité.

Voici ensuite la synthèse des différents articles et publications que j'ai lus sur le thème de la filtration sur berge de rivière.

II-Synthèse des précédents travaux de recherches

Ce travail m'a permis d'avoir un aperçu de ce qui a déjà été fait dans le domaine et de me familiariser avec les résultats déjà connus, les difficultés et questions encore en suspens.

Diversité des travaux

Les publications sur le sujet sont très diverses. Certaines traitent de la filtration sur berge de rivière en général, d'autres des conditions d'élimination de certaines molécules sur un site particulier, ou lors d'expériences en laboratoire. L'influence des conditions redox et de la température ont beaucoup été étudiés notamment. Globalement, les recherches sont plus ou moins fondées sur des observations du comportement de certaines molécules lors de leur passage dans le sol.

Molécules étudiées

Certaines recherches étudient une grande variété de molécules, principalement les micropolluants organiques les plus retrouvés dans les rivières, d'autres se concentrent sur certains groupes de produits chimiques comme les bêtabloquants ou les antibiotiques. Dans certains cas, la distinction est effectuée entre la matière organique globale « bulk organic matter » et certaines molécules à l'état de trace « trace organic compounds » en suspension.

Expériences menées

Une partie des études s'appuie sur des observations faites directement sur les berges de rivière ou dans les bassins de filtration des usines de traitement des eaux. L'autre partie s'appuie sur des expériences en vraie grandeur ou mises en place en laboratoire sous forme de colonnes de sol naturel ou reconstitué afin de comprendre plus en détail les mécanismes mis en jeu lors du processus. Les conditions redox et la présence ou non d'oxygène peuvent ainsi être contrôlées et les diverses mesures sont plus faciles dans ce cas. Les colonnes sont ensuite traversées par de l'eau naturelle ou artificielle enrichie des molécules étudiées.

Méthodes d'analyse

La matière organique globale est souvent quantifiée à partir de la mesure de la quantité de carbone totale (ou TOC pour Total Organic Carbon), ou de la quantité de carbone dissous (DOC pour Dissolved Organic Carbon). Des mesures d'absorbance à l'UV₂₅₄ permettent également de quantifier une grande partie de la matière organique, et l'activité de la biomasse est déterminée par des mesures d'ATP. Pour l'analyse des micropolluants, des mesures plus précises sont nécessaires comme la chromatographie ou la spectroscopie de masse, plus coûteuses. La capacité d'adsorption peut être analysée séparément dans des béchers (batch experiments) avec le calcul du rapport frontal.

Résultats

Les différentes observations et expériences montrent que la filtration sur berge de rivière permet d'éliminer un certain nombre de polluants, après un temps de résidence plus ou moins

long dans le sol. Certains composés sont cependant résistants et sont peu ou mal dégradés comme le Sulfaméthoxazole. Les résultats obtenus pour les différentes molécules, ainsi que les conditions favorisant leur élimination seront détaillés plus loin. Généralement, la richesse du sol en matières organiques et en oxygène dans les premières couches de la berge est un paramètre favorisant la biodégradation. L'influence de la température sur le caractère redox des sols en fait aussi un facteur déterminant.

Ces recherches préliminaires m'ont permis de mieux comprendre le projet mis en place par la doctorante et l'expérience qu'elle a choisi de mettre en œuvre.

III-Présentation de l'expérience

A mon arrivée, l'expérience avait déjà été imaginée par Cheryl Bertelkamp et la stagiaire qui me précédait avait déjà choisi et commandé le matériel nécessaire.

Objectif de l'expérience

Le but de cette expérience est d'observer pendant trois mois le comportement d'un certain nombre de composés chimiques lors de leur passage à travers le sol. La détermination des rôles respectifs de l'adsorption et de la biodégradation dans leur élimination et la comparaison avec les résultats d'études antérieures permettront ensuite d'élaborer un modèle prédictif : le « QSAR model » pour Quantitative Structure Activity Relationship.

Le montage expérimental

Le montage expérimental choisi par la doctorante consiste en 4 colonnes de 1m de hauteur de sable artificiel, 4 colonnes de pierre ponce et 4 faisceaux de capillaires de même surface spécifique que les colonnes de sable artificiel. Le temps de résidence qui est le temps caractéristique mis par le solvant pour traverser le système a été fixé à 1 journée et la température à 15 degrés pour bien reproduire les conditions naturelles.

Quatre solutions sont ensuite préparées pour être injectées grâce à une pompe dans chacun des trois milieux.

La première est un mélange d'eau du canal Schieweg à Delft et d'acétate de sodium à laquelle les micropolluants (OMP) sélectionnés pour l'expérience sont rajoutés. L'acétate de sodium est utilisé comme substrat primaire pour nourrir les bactéries tout en les forçant à dégrader de manière accidentelle les polluants. L'élimination des OMP est dans ce cas due à la fois à l'adsorption et la biodégradation.

La deuxième solution est de l'eau du canal et de l'acétate de sodium pendant 6 semaines puis de l'Azodure de sodium pour tuer les bactéries. Les OMP sont également rajoutés et leur élimination est cette fois due à l'adsorption sur le sable et sur le film composé de bactéries mortes.

La troisième solution est de l'eau du canal, des OMP et de l'Azodure de sodium tuant les bactéries déjà existantes et empêchant la création de tout film de bactéries. La dégradation des

OMP est alors due à l'adsorption sur le sable (ou pierre ponce ou paroi du tube) et dépend de la qualité de l'eau (adsorption possible sur les particules en suspension dans l'eau du canal).

La quatrième solution est enfin composée d'eau distillée et d'OMP afin de pouvoir évaluer l'adsorption due au type de milieu : sable, pierre ponce et tube.

Les mesures d'ATP pour déterminer l'activité bactérienne, et de DOC et d'UV₂₅₄ pour quantifier la matière organique dissoute dans l'eau en entrée et sortie des colonnes seront faites régulièrement. Les mesures plus spécifiques permettant de caractériser les différents composés seront faites de manière plus ponctuelle car plus coûteuses.

Si les résultats sont comparables pour le sable et les tubes, les expériences futures pourraient être faites simplement en utilisant des tubes.

Les expériences de traçage

Afin de déterminer la vitesse microscopique de l'eau à travers les colonnes, ainsi que le temps de résidence et la porosité, des traceurs comme NaCl sont injectés pendant un certain temps dans l'eau alimentant les colonnes. Leur mesure à la sortie des colonnes, permet ensuite de tracer une courbe représentant la concentration du traceur en fonction du temps. Cette courbe permet ensuite de calculer la vitesse de l'écoulement ainsi que d'autres grandeurs caractéristiques du milieu comme la porosité.

Voici donc l'expérience projetée, telle qu'elle m'a été présentée à mon arrivée. Une partie de mon travail a été d'aider Cheryl Bertelkamp à mettre en place le montage expérimental, et de nombreux changements ont été faits au fur et à mesure des problèmes rencontrés.

Afin de comparer les résultats de notre expérience avec ceux des études précédentes, j'ai fait une synthèse de ce que j'ai trouvé sur les molécules testées.

IV-Recherche sur les propriétés des molécules étudiées

Le deuxième objectif du projet étant d'élaborer un modèle prédictif basé sur les propriétés physiques et chimiques des micropolluants, il était nécessaire de rassembler les informations sur les différents produits étudiés.

Molécules étudiées

Le choix des 26 micropolluants étudiés a été fondé sur différents critères visant la plus grande diversité possible en ce qui concerne les propriétés physiques et chimiques tout en privilégiant les produits les plus souvent rencontrés dans les rivières aux Pays-Bas.

Comportements attendus lors de l'expérience

J'ai ici classé dans un tableau récapitulatif les comportements des molécules lors du passage à travers le sol, en détaillant la part d'adsorption et de biodégradation ainsi que les conditions expérimentales. Le problème est que les résultats obtenus dans les études passées en revue ne sont pas comparables car les conditions expérimentales sont toutes différentes, notamment en ce qui concerne la nature du sol qui influence énormément l'efficacité de la biodégradation et

de l'adsorption. Une étude générale concernant la plus grande diversité de molécules possible dans des conditions expérimentales identiques est donc nécessaire.

Comportement de trois molécules

Trois molécules sont très bien dégradées, et ce dans différentes conditions expérimentales. J'ai donc choisi d'exposer dans ce rapport le détail des résultats que j'ai obtenus à leur sujet dans plusieurs études afin d'essayer de comprendre les causes structurelles d'un tel comportement. Ces trois molécules sont : le Benzène, l'Ibuprofène et le Diclofénac.

Les résultats que j'ai rassemblés seront ensuite à comparer avec ceux de l'expérience, en essayant de prendre en compte les différences de conditions expérimentales et le type de sol.

Après cette partie théorique de compréhension du sujet et de recherche, mon travail a ensuite consisté à aider la doctorante à mettre en place le montage expérimental et à lancer l'expérience proprement dite.

V-Aspects pratiques de l'expérience

Tout le matériel nécessaire était déjà plus ou moins préparé par la précédente stagiaire et il nous suffisait normalement de monter l'expérience et de la lancer. Nous avons cependant rencontré certaines difficultés lors du montage ce qui a retardé le lancement de l'expérience de plusieurs semaines.

Mise en place du montage et lancement de l'expérience

Nous avons commencé par remplir les colonnes avec du sable et de la pierre ponce en grains préalablement pesés pour avoir à chaque fois la même hauteur de milieu poreux (50 cm). La porosité ayant été oubliée dans les calculs faits par la précédente stagiaire, la hauteur obtenue ne correspondait pas à ce qui était prévu et nous avons dû recommencer plusieurs fois le remplissage, sans compter la difficulté d'éviter les bulles d'air. Nous portions des gants et nous lavions le matériel avant chaque utilisation pour éviter toute contamination avec des molécules organiques ou des bactéries. Les colonnes doivent être constamment remplies d'eau ce qui nécessite une alimentation en continue et donc un changement régulier des jerrycans.

J'ai ensuite effectué des tests de traçage avec une solution de NaCl. La encore, il a fallu plusieurs essais avant de déterminer la bonne concentration, la bonne durée d'alimentation, et la bonne manière de remplir les colonnes pour obtenir des courbes correctes. Nous avons aussi remarqué que ces mesures peuvent perturber la vie bactérienne au sein des colonnes ; cela nécessitait donc deux colonnes supplémentaires réservées aux tests de traçage au cours de l'expérience. Cela nous a conduit à abandonner les colonnes de pierre ponce car la pompe n'avait pas assez de canaux.

Enfin, après avoir obtenu des courbes exploitables et effectué les mesures nécessaires et ajustements matériels, nous avons lancé l'expérience. Nous avons préparé les différentes solutions que nous avons ensuite utilisées pour alimenter les colonnes.

J'ai pu également assister aux premières mesures de DOC faites en entrée et en sortie des colonnes et tubes.

Analyse des tests de traçage

Les tests de traçage finaux m'ont permis de déterminer la vitesse microscopique de l'eau à travers chaque colonne, le temps de résidence et la porosité du milieu. Celle-ci est indispensable pour caractériser le milieu car c'est l'un des facteurs qui conditionne le développement des colonies de bactéries. Elle permet également de faire plusieurs calculs utiles à l'analyse des résultats comme le rapport frontal (R_f).

Mon stage s'est achevé juste après le lancement de l'expérience, mais Cheryl Bertelkamp m'a promis de m'envoyer les résultats.

VI-Résultats

A l'heure actuelle (début Septembre), l'expérience est lancée depuis un peu plus de deux mois. Les résultats ne sont pas pour l'instant très concluants car les colonies de bactéries ne se sont pas encore beaucoup développées dans les colonnes.

Conclusion

Travailler sur ce projet m'a permis d'acquérir des connaissances sur le thème de la filtration sur berge de rivière mais aussi sur le traitement de l'eau en général grâce aux lectures d'articles scientifiques que j'ai pu faire sur le sujet. Les recherches bibliographiques que j'ai faites sur les différentes molécules utilisées dans l'expérience, notamment concernant leur comportement lors de la filtration à travers le sol, et leur tendance à être adsorbées et/ou biodégradées vont permettre à Cheryl Bertelkamp de comparer ses résultats tout en tenant compte des différences de conditions expérimentales. J'ai ensuite pu l'aider pour le montage de son expérience sur des aspects pratiques comme le remplissage des colonnes, le réglage de la pompe ou les mesures. J'ai également pu l'aider lors de réflexions liées à l'amélioration du système de fermeture des tubes, ou à la manière de prendre les mesures de traçage pour avoir des résultats exploitables que j'ai ensuite pu analyser pour obtenir la porosité des colonnes.

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Introduction

Filtration of river water through aquifer sand is a well-known cleaning process which is often used as a pre-treatment technique for human use. Indeed, this method is efficient for the removal of macro pollutants, bacteria and viruses. Since we consume more and more chemical products such as pesticides or pharmaceuticals, the range of organic micro pollutants (OMPs) which end up in the rivers is widening and we don't know exactly the fate of these different chemicals during the river bank filtration (RBF) process. Even if these pollutants are found in very low concentrations, it is essential to investigate the conditions of their removal during RBF in order to provide cheap and safe drinking water.

This subject is of particular interest in the Netherlands where RBF provides only 5.6% of the produced drinking water.

A lot of water companies in the country are interested in this kind of research because it is cost effective and easy to operate compared to a series of specific treatments for each chemicals.

The aim of the ESTAB (Emerging Substances: Towards an Absolute Barrier) research project conducted by Cheryl Bertelkamp, the Ph.D. student I worked with, and Arne Verliefe, her supervisor, is to study the OMPs removal during river bank filtration. If it is found to be efficient, it could be the first step of a treatment process which would also include filtration on granular activated carbon (GAC) (to remove the non-polar molecules) and membrane filtration like nanofiltration (NF) (to remove the larger polar molecules). RBF is believed to be efficient for small and polar molecules.

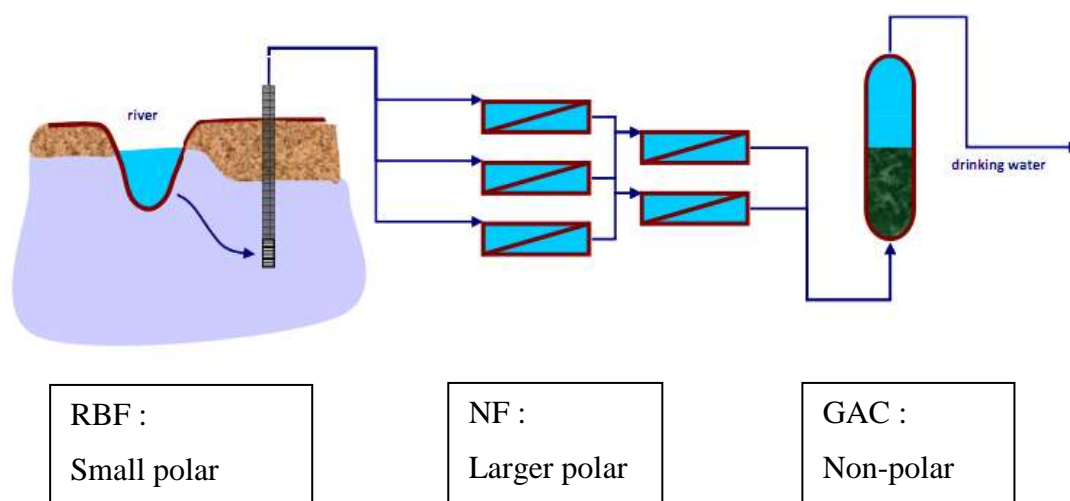


Figure 1 Scheme of the multi-barrier water filtration process

Since it is impossible to test every new OMP that is detected, the second aim of the research is to try to predict the removal of future pollutants by establishing a QSAR (Quantitative Structure Activity Relationship) model. This model would be able to predict the fate of a pollutant according to its physical and chemical properties such as charge, polarity, molecular

weight, chemical groups... and therefore to predict if it has to be removed by some additional barrier techniques.

The problem for the elaboration of this model is that all the previous studies have focused on the removal of some particular compounds or class of compounds in very different experimental conditions. In her study, Cheryl Bertelkamp wants to assess the respective roles of biodegradation and adsorption for a well representative panel of pollutants in an experimental set up and then to compare it with previous results.

The study consists in lab-scale and pilot-scale experiments. The project started in November 2010 and is expected to end in November 2014. When I arrived in April 2011, the theoretical part was mostly done and part of the lab set-up was already prepared. I was there to help Cheryl Bertelkamp prepare and start the lab-scale experiment. The pilot-scale experiments are scheduled for later.

In order to familiarize myself with the subject, I did some personal research and read some papers of which I will give an overview. Then, I will describe the experiment made up by Cheryl Bertelkamp and her supervisor as well as the research I did on the different chemicals tested in the experiment and their expected fate. I will then describe the practical aspects of the experiment set-up and the difficulties we encountered before giving the results.

Presentation of the host university and the supervisor

I did my internship in the water management department of the civil engineering faculty (CITG) at Delft University of Technology in the Netherlands. I worked with Cheryl Bertelkamp, a Ph.D. student from the sanitary engineering section. Her thesis work is about ESTAB (Emerging Substances: Towards an Absolute Barrier) and intends to investigate the possibility to create an absolute barrier for organic micro pollutants. She started in November 2010 and she expects to finish in November 2014. Her supervisor, Arne Verliefde is an assistant professor. He did his Ph.D. research on "Rejection of trace organic pollutants by high pressure membranes".

I- Theoretical background

1) Adsorption

Adsorption is the adhesion of molecules of gas, liquid or dissolved solids (the adsorbate) on the surface of a solid particle (the adsorbent). In the case of river bank filtration, the organic pollutants adsorb on ground particles or organic matter in suspension in the water.

As a consequence, the OMPs are retarded and move more slowly than the water through the ground. The process of adsorption can therefore be quantified by a retardation factor (R_f) which is the ratio between the velocity of the water and the velocity of the OMP.

$$R_f = \frac{V_{water}}{V_{OMP}}$$

This surface phenomenon is the result of different physical and chemical forces such as weak Van der Waals forces in the case of Physisorption, covalent bonding for Chemisorption, or electrostatic attraction.

Adsorption is different from absorption which corresponds to the uptake of the molecule into the physical structure of the adsorbent.

The most adsorbent molecules are the less soluble in water i.e. the most hydrophobic. The hydrophobicity of an organic compound can be quantified by the Octanol-Water partition coefficient (K_{ow} or P_{ow}). It ranges from -1.77 for Cefotaxime tartrate to more than 4.7 for Flunarizine at pH 7.4 (<http://www.cerep.fr>). The partition coefficient is the ratio between the amount of the neutral compound in the aqueous phase and the organic phase (Octanol).

$$\log P_{oct/wat} = \log \left(\frac{[solute]_{octanol}}{[solute]_{water}^{un-ionized}} \right)$$

The problem is that it does not describe the hydrophobicity of an ionized (charged) compound.

The distribution coefficient (D) is the ratio of the sum of the concentrations of all forms of the compound (whether charged or not) in the two solutions.

$$\log D_{oct/wat} = \log \left(\frac{[solute]_{octanol}}{[solute]_{water}^{ionized} + [solute]_{water}^{neutral}} \right)$$

The distribution coefficient is dependent on the pH. It is often tabulated at pH = 7.4 because it is the pH of blood serum. For neutral compounds, $\log K_{ow} = \log D$ at any pH. Since the pH affects the solubility of organic compounds, the adsorption rate can vary a lot with the acid-basic conditions.

The nature of the soil affects adsorption through its texture and particularly its specific surface which is the total surface area per unit of mass, area or volume of a solid. It can be calculated from a particle size distribution if the particle shape is simple. Clay is the soil compound that has the largest specific surface and it is also the most adsorbent. The ion exchange at its surface probably plays a role too in the adsorption process. Activated carbon is also a very good adsorbent.

The adsorption of OMP can be quantified by the sorption/distribution coefficient (K_d) which is the ratio between the adsorbed phase concentration and the solution phase concentration at equilibrium (when the water flow enables a sufficient contact between the adsorbent and the adsorbate). It is often given in ml/g.

$$K_d = \frac{\text{mass of adsorbate sorbed}}{\text{mass of adsorbate in solution}}$$

The retardation factor can therefore be calculated by:

$$R_f = \left(1 + \frac{p}{n}\right) \cdot K_d$$

Where: p = porous media bulk density (mass/length³)
n = effective porosity of the media at saturation

2) Biodegradation

Biodegradation is the use of organic pollutants dissolved in water by bacteria already present in the soil for the benefit of their own growth and metabolism. During the digestion, the bacteria break down biodegradable molecules and convert them into smaller molecules such as CH₄ and CO₂ in the case of anaerobic digestion.

In order to be able to oxidize the OMPs present at very low concentrations in the rivers, it is necessary to use co-metabolism which is the accidental oxidization of a substance (the secondary substrate) by bacteria while oxidizing a well-assimilated compound (the primary substrate). Sodium Acetate (CH₃COONa), which is a source of carbon for the bacteria, can be used as a primary substrate.

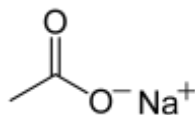


Figure 2 Sodium acetate

The bacterial activity can be quantified by ATP measurements. Adenosine Triphosphate is an essential molecule for bacteria: it provides energy for elementary biological functions such as adaptation to the environment, food consumption and reproduction functions. There is a good relationship between the ATP concentration and the number of bacteria.

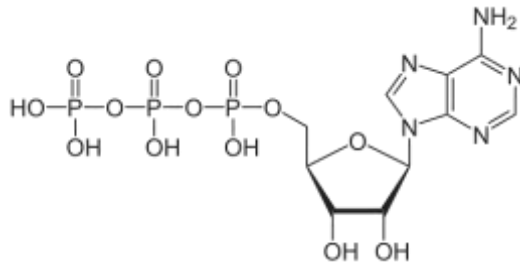


Figure 3 ATP

ATP is measured by taking wet sand samples of 1 to 4 g, and by sonication at a power of 40 W that detaches biomass. The biomass concentration is then detected with a luminometer. Indeed, ATP reacts with the enzyme luciferase naturally present in the living organisms and light is produced.

The development of the bacterial community depends on the quality of the water but also on the size of the canals of the porous environment.

The exact mechanisms in the biodegradation process are not well-known yet and we can't predict what types of bacteria will be more effective than others and on which molecules. On top of that we don't know exactly which products the decomposition of organic molecules can result in.

II- Overview of previous studies

As river bank filtration is not a new research topic, it seemed important to me to do some reading of previous studies in order to acquire a general understanding on the subject.

The detail of the overview is given in Appendix 1.

1) Subject of the studies

There is a large variety of studies on the theme of river bank filtration. Some describe the general results obtained for a broad range of pollutants; others focus on the elimination of a group of molecules during on-site or lab-scale experiments. Oxic or aerobic conditions and their influence on the removal efficiency have been investigated. For the most part, the research consisted of a series of observations on the molecules behavior during soil passage.

2) Investigated chemicals

Some works expose the results obtained for all OMPs found on the sites of the experiments, others focus on some groups of chemicals such as antibiotics, flame retardants, or pesticides. The distinction between bulk organic matter and trace organic compounds is done in some cases.

3) Experimental set-ups

Each study provides experimental results to confirm or contradict theoretical hypothesis and draw conclusions. Some experiments are done directly on the field and consist of a series of measurements at different places. Others consist of the study of lab-scale or pilot-scale sand columns reproducing the river bed. These artificial set-ups enable a wider range of measurements and tests while having the possibility to change redox, aerobic or temperature conditions in order to have a better understanding of the mechanisms responsible for the removal. The columns are often filled with artificial sand because it is easier to manipulate and more “universal” than some natural ground samples. Then the columns are fed with water spiked with the investigated compounds.

4) Analytical methods

Bulk organic matter is quantified with DOC (Dissolved Organic Carbon) or TOC (Total Organic Carbon) measurements. UV_{254} measurements can also quantify and characterize the organic content while ATP tests can assess the biological activity. More specific measurements such as chromatography and mass spectroscopy are needed to characterize the trace organic compounds. The adsorption capacity of the ground can be tested with batch experiments. Retardation factors can then be calculated.

5) Results

River bank filtration is a reliable cleaning process regarding organic micro pollutants as long as the residence time and travel path are long enough. However, some compounds such as Sulfamethoxazole are persistent and need other barriers to be totally eliminated. I gathered the

results obtained for the different molecules in a table. As for the conditions that favor the removal, the organic fraction of the soil, the presence of oxygen in the first layers of the river bed and the redox conditions which are influenced by the temperature are the most important parameters influencing the attenuation of the OMPs during soil passage.

III- Presentation of the experiment

1) Aim of the experiment

The aim of the experiment is to assess and compare the respective roles of adsorption (on the ground and the biofilm) and biodegradation in the elimination process during river bank filtration for a panel of pharmaceuticals. The results of this experiment will be analyzed and compared to previous results in order to find through experiments the chemical or physical properties responsible for the removal of the tested molecules. It could then lead to the elaboration of a predictive model: the QSAR model which would predict the degree of elimination of a compound according to its chemical and physical properties.

2) Experiment set-up

Here is the set-up as it was presented to me when I arrived. Since then, modifications have been done.

The Cheryl Bertelkamp decided to conduct column experiments instead of batch or on-site experiments. Batch experiments are really simple to perform but they are far from reality. On-site experiments are interesting in studies focusing on the removal of pollutants only present in situ. Column experiments, on the other hand, seemed to fit the purpose of the research because it has all the advantages of a lab experiment, such as the possibility to use a broad range of pharmaceuticals, or to perform various measurements, while keeping a constant flow of water.

As for the ground material, it was decided not to use natural ground because of the necessity to have the largest amount of information possible (size of the particles, density...) and also because of the difficulty to maintain the same oxic conditions during the transport of the samples from the site to the laboratory. But technical sand gives underestimation of OMPs removal capacity compared to aquifer sand. Sand and pumice were selected to fill the columns. Sand is the most common material found in ground, so the choice was obvious. Pumice, which is a volcanic rock, has the property to be a very bad adsorbent, so it would be interesting to compare it with the sand. Finally, tubes of the same specific surface than the filled columns were also chosen for the experiment because it would be a simpler way to conduct further experiments if they were to show similar results. The dimensions of the columns and tubes as well as the quantity of sand and pumice required were calculated so that the specific surface was the same in the different cases.

In order to match closely to natural conditions, the temperature was fixed at 15 degrees by installing the columns in a temperature room. In reality the seasonal variations play an important role but they were not taken into account in this experiment since it was meant to last three months.

The retention time of the water in the columns and the tubes was set to 1 day and the velocity of the pump was calculated accordingly (42.5 round per minute).

It was then established that four different solutions would feed the columns in order to get detailed results from the experiment.

First solution: canal water + OMPs + sodium acetate

Canal water is taken from the Schieweg canal in Delft and is supposed to already contain micro pollutants and bacteria. Sodium acetate is used as a primary substrate, to make the bacteria grow and metabolize the OMPs. ATP measurements will be conducted in order to determine when the number of bacteria is stable at its higher level. Then, UV and DOC measurements will be useful to determine the OMPs removal. In this case, the removal is due to both adsorption and biodegradation.

Second solution: canal water + OMPs + sodium acetate during 6 weeks then sodium azide

Sodium azide is expected to kill the bacteria. Then, only the dead biofilm remains and the DOC and UV decrease will only be due to adsorption on the sand AND on the biofilm. Biodegradation will no longer play a role since all the bacteria will be dead.

Third solution: Canal water + OMPs + sodium azide

In this third case, sodium azide will kill the pre-existent bacteria from the canal water and will prevent the growth of new bacteria in the columns. The OMP removal will then only be due to adsorption on the sand, pumice or tube and dependent of the water quality. Indeed, the adsorption of OMP is affected by the water properties such as hardness, alkalinity or presence of salt.

Fourth solution: demi water + OMPs

Finally, the fourth column will be filled with demineralized water in order to evaluate the adsorption only due to the adsorbent material. The comparison between the sand and pumice, and the tubes will be particularly interesting because in the three cases, the specific surface is the same.

To summarize, the experiment will be able to assess the contributions of adsorption and biodegradation.

Table 1 Synthetic table of the experiment

	Biodeg.	Ads. biofilm	Ads. Canal water	Ads. sand	Ads. pumice	Ads. tube
Sand 1	Yes	Yes	Yes	Yes		
Sand 2		Yes	Yes	Yes		
Sand 3			Yes	Yes		
Sand 4				Yes		
Pumice 1	Yes	Yes	Yes		Yes	
Pumice 2		Yes	Yes		Yes	
Pumice 3			Yes		Yes	
Pumice 4					Yes	
Tube 1	Yes	Yes	Yes			Yes
Tube 2		Yes	Yes			Yes
Tube 3			Yes			Yes
Tube 4						Yes

For example, the part of biodegradation can be deduced from experiments 1 and 2.

The measurements of DOC and UV₂₅₄ for bulk organic matter quantification will be performed on a regular basis when the ATP measurements show a regular trend indicating that the bacterial growth is stable. The specific measurements relative to the different compounds which are more expensive will be less frequent and performed in Australia where it is cheaper.

3) Tracer tests

Artificial tracers are often used in column experiments to characterize the porosity of the ground, the residence time or the real flow.

In the case of constant-rate release, a soluble, non conservative tracer such as NaCl is released in the influent stream until its concentration in the effluent reaches a constant value. The tracer needs to be chemically neutral. Indeed, sorption on the ground used or mass losses during the passage should be avoided in order to obtain good results.

Rhodamine, NaCl or Iodine are examples of tracers.

Then, the shape of the breakthrough curve, which is the concentration of the tracer in the effluent relative to the time, enables to characterize the solute residence time distribution. We can also get information on the ground properties such as the porosity.

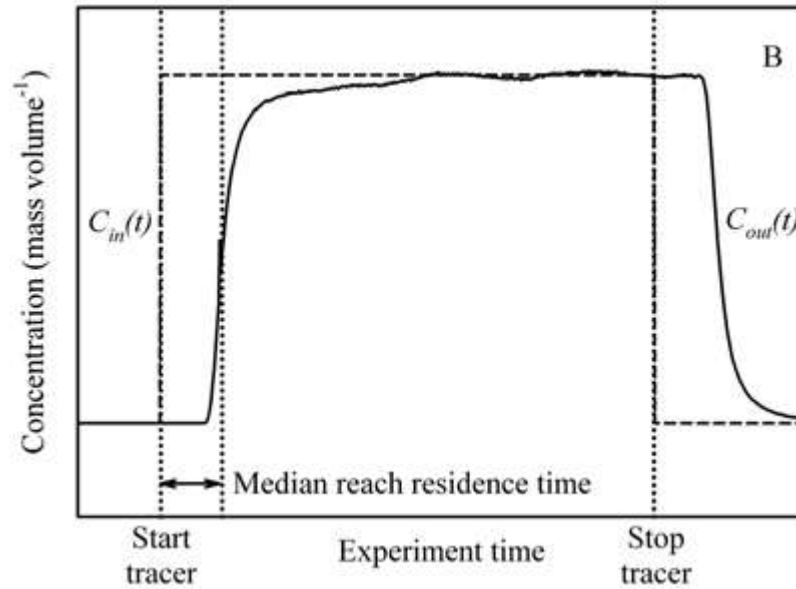


Figure 4 Tracer test graph (Payn et al. 2008)

In this graph the residence time is calculated from the first part of the curve. The mean breakthrough time $t_{1/2}$ is the time that the tracer concentration takes to reach half the input concentration. It is also called the contact time and lead to the filtration velocity v :

$$v = \frac{d}{t_{\frac{1}{2}}}$$

d is the length of the column.

Then, the pore volume PV is the mean breakthrough time multiplied by the flow Q :

$$PV = t_{\frac{1}{2}} \cdot Q$$

Finally, the porosity ε is the pore volume divided by the total volume V of the column:

$$\varepsilon = \frac{PV}{V}$$

IV- Investigation on the chemical properties

1) Investigated chemicals

The aim of the experiment is to try and develop a predictive model for the removal of all kinds of OMPs during RBF: The Quantitative Structure-Acticity Relationship (QSAR) model. The list of chemicals tested was based on:

1. Physico-chemical properties such as Molecular Weight, $\log K_{ow}$, Log D or charge. The chemicals tested have to represent all possible cases.
2. Research literature in order to be able to compare the results with previous studies.
3. Occurrence of OMPs in Dutch rivers.
4. The molecular weight which should not be higher than 300 Da because of the desired membrane (MWCO of about 300 Da).
5. The diversity of the nature of OMP which should represent pharmaceuticals, industrial waste products, pesticides, etc...

The list of the 26 OMPs investigated in the ESTAB project is given in appendix 2.

I found interesting to investigate the different molecules and to do an overview of what had already been done in previous studies in order to be able to compare the results with the ones of the experiment.

Here is the synthesis of what I found concerning the removal of the molecules.

2) Expected fate during the experiment

It is important to understand why a molecule is well degraded or not if we want to predict the removal of future compounds according to their chemical or physical properties. If the process of adsorption is rather well understood, the mechanisms of biodegradation are still not well explained. I gathered in a table (appendix 3) the empirical results obtained in previous experimental studies for each compound then tried to find a correlation between the results and some chemical and physical properties such as the partition coefficient ($\log K_{ow}$), the distribution coefficient ($\log D$) which are relevant for adsorption, or the molecular weight and the charge. I also detailed the characteristics of the soil to be able to compare the results from the different experiments more accurately. Indeed, the porosity and the organic content of the soil seem to favor bacterial growth responsible for biodegradation, and high clay content can explain good adsorption results.

Only 1-4 dioxane, Carbamazepine, TCEP, Norfluoxetine and clofibric acid seemed to be resistant to both adsorption and biodegradation, and were still present in the ground water after a few months.

NDMA and Dichlorprop are biodegradable but do not adsorb on soils.

Benzene, Ibuprofen and Diclofenac could be removed by both adsorption and biodegradation.

When results were available, I found that the other compounds were generally more or less biodegraded.

The problem is that since the studies are done in very different conditions, we cannot quantify the removal of the OMPs and compare the results of the studies. The retardation factor, for instance, which is the ratio between the velocity of the water and the velocity of the OMP, takes different values in the different studies. Only results obtained in the same conditions can be compared. That is the reason why it is essential to elaborate a general study for all kinds of compounds.

3) Fate of 3 specific chemicals

Here are the results I found concerning Benzene, Ibuprofen and Diclofenac which seem to be the three less persistent compounds. Indeed, it would be interesting to understand the physical, chemical or structural reasons for their non resistance to both adsorption and biodegradation.

a) Benzene

Formula: C₆H₆

Molecular weight: 78.11 g/mol

Log K_{ow}: 1.99

Log D_{pH 7.4}: 2.177

Charge at pH 7: 0

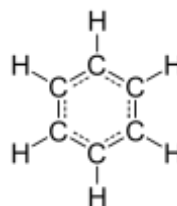


Figure 5 Benzene

Benzene is often used as an organic solvent, or as a precursor to other chemicals like drugs and polymers. It is also a constituent of crude oil. It is carcinogenic.

[Choi et al. \(2005\)](#) reported that Benzene was retarded 1.10 and 1.20 times relative to a conservative tracer (flow of 28 ml/min). The mass recovery they conducted showed a significant reduction of benzene mass during transport through the soil passage. They concluded that it was due to volatilization and/or irreversible sorption. These retardation factors increased over retention time and distance. [Priddle and Jackson \(1991\)](#) found a retardation factor of 14.3 with different conditions (flow of 1.25ml/min, porosity of 30%). In our case, the flow is 0.7 ml/min and the porosity is about 30-40%.

According to Wikipedia (I haven't been able to find the references); benzene can be oxidized by bacteria. The aromaticity is lost by dioxygenase enzyme that can add an oxygen atom to benzene ring making it unstable. It is immediately reduced by NADH to a non aromatic diol. The diol is then reduced by NADH to catechol which is finally metabolized to acetyl CoA and succinyl CoA. These two compounds are metabolized by bacteria for energy production.

b) Ibuprofen

Formula: C₁₃H₁₈O₂

Molecular weight: 206,29 g/mol

Log K_{ow}: 4.00

Log D_{pH 7.4}: 0.8

Charge at pH 7: -1

pKa: 4.47

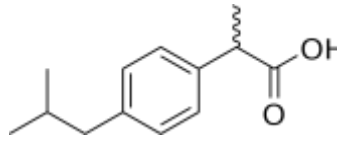


Figure 6 Ibuprofen

Ibuprofen is a non-steroidal anti-inflammatory drug (NSAID). It is used as an analgesic. It works by inhibiting the enzyme cyclooxygenase, which converts arachidonic acid to prostaglandin.

[DiaCruz et al. \(2008\)](#) found a significant removal of Ibuprofen due to both adsorption and biodegradation processes. These results were similar to those of [Heberer et al. \(2001\)](#), [Verstraeten et al. \(2002\)](#), [Heberer and Adam \(2004\)](#), [Ternes et al. \(2007\)](#).

[Preuss et al. \(2002\)](#) found a 60–80% elimination and added that mechanisms, such as hydrogen bonding, would be related to the removal of more polar organic micro pollutants.

[Rauch-Williams et al \(2010\)](#) found a retardation factor of 94.2 for Ibuprofen, a sorption coefficient of 0.03 mL/g, and a Mass recovery of 92.7 %. (1meter Plexiglas columns in series filled with aquifer material ($d_{50}= 0.8\text{mm}$, $f_{oc}= 0.003\%$), with a flow of 0.065 m/d (1m/d for us) under saturated and anoxic conditions.)

[Scheytt et al. \(2006\)](#) also reported a good removal of Ibuprofen (54%) with a retardation factor of 3.00 (The sediment was sampled from a depth of 1.0–2.5 m below ground surface in the Berlin area. It was composed of fine-grained alluvial sands with a low content of organic carbon (fraction of organic carbon: 0.13%, clay: 0%, silt (2-63 μm): 0.7%, fine sand (63-200 μm): 42.05%, medium sand (200-630 μm): 56.46%, coarse sand (200-2000 μm): 0.8%, gravel (>2 mm): 0.2% and the flow was $1.30 \cdot 10^{-4} \text{ m}^3 \cdot \text{h}^{-1}$ i.e. 130 ml/h (42.4 ml/h for us)). And this retardation factor was the same for saturated and unsaturated conditions. Their experiment also showed the role of biodegradation in the removal: “In our experiment, it seems as if the elimination has a lag of approximately 5 exchanged pore volumes. Concentrations of ibuprofen decrease after 5 pore volumes, even before the end of spiking of the test water. This could be an indication of biodegradation in the sand column with an adaptation time for microorganisms.”

[Xu et al. \(2009\)](#) found retardation factors of 3, 3, 4 and 13 in different types of soil during batch experiments.

Table 2 different types of soil properties (Xu et al. 2009)

Soil	Clay (%)	Sand (%)	Silt (%)	OM (%)	Bulk density: rhob	Porosity: theta
HLS	3.6	95.6	0.8	0.58	1.60	0.38
ASL	12.5	70.9	16.6	1.93	1.55	0.40
ISC	42.5	10.8	46.7	2.46	1.33	0.48
PSL	18.1	32.2	49.7	5.45	1.42	0.43

Retardation factors: HLS: 3 / ASL: 3 / ISC: 4 / PSL: 13

The role of biodegradation was highlighted: “Degradation rate of ibuprofen in non sterile soil was 34.5-fold faster than in the sterilized HLS soil. The inhibition by sterilization suggested that microbial transformations contributed to the overall degradation of PPCPs in the agricultural soils.”

c) Diclofenac

Formula: $C_{14}H_{11}Cl_2NO_2$

Molecular Weight: 296,148 g/mol.

Log K_{ow} : 4.02

Log $D_{pH 7.4}$: 1.437

Charge at pH 7: -1

pKa: 4.15

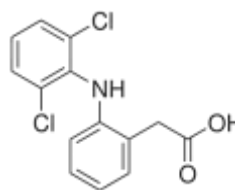


Figure 7 Diclofenac

Diclofenac is a non-steroidal anti-inflammatory drug (NSAID). It is used as an analgesic and to reduce inflammation. The exact mechanism of action is not yet well known but it seems that it also works by inhibiting cyclooxygenase which provokes the inhibition of prostaglandin synthesis. It also has bacteriostatic effects by inhibiting bacterial DNA synthesis.

[DiaCruz et al. \(2008\)](#) reported a significant removal. As for Ibuprofen, [Preuss et al. \(2002\)](#) found 60-80% elimination.

[Hoppe Jones et al \(2010\)](#) found that biodegradability for a travel time of 10 days and more was 50 to 90%.

[Rauch-Williams et al. \(2010\)](#) found a retardation factor of 1.41, a sorption coefficient of 0.01 ml/g and a mass recovery of 93.6% after reporting several research results concerning diclofenac: “For diclofenac, a popular analgesic drug, low removal due to biodegradation or adsorption was reported ([Buser et al., 1998](#); [Mořhle et al., 1999](#)) unless soils contain high organic carbon content ([Drillia et al., 2003](#)). Several studies report a faster degradation of diclofenac under anoxic conditions as compared to aerobic conditions ([Zwiener and Frimmel, 2003](#); [Hua et al., 2003](#)). Opposing results were reported by [Schmidt et al. \(2004\)](#) in that

diclofenac was almost completely removed during aerobic bank filtration but recalcitrant during anaerobic recharge.”

[Scheytt et al. \(2006\)](#) found a retardation factor of 4.80 and 35% elimination and reported that both retardation and elimination were higher under unsaturated conditions than under saturated conditions. They explained that “Elimination of diclofenac under unsaturated conditions might be due in part to photochemical biodegradation as has been reported by [Buser et al. \(1998\)](#).”

[Barber et al. \(2009\)](#) also found a significant retardation of diclofenac in a 0–5 cm soil sample. Under the experimental conditions (pH of 7.5–7.8), diclofenac is negatively charged but is more hydrophobic than Naproxen, another molecule negatively charged which was less affected by the interactions with the soil organic matter. Contrary to the study of [Scheytt et al. \(2006\)](#), biotic degradation was prevented in the experiment by using NaN_3 and “diclofenac recovery values with the 5–15 and 15–25 cm soil samples were all >96%. For the experiments with the 0–5 cm sample, diclofenac recovery values were 36 and 68% with freshwater and STWW (secondary treated waste water) respectively.” They also believe that the significant retardation of diclofenac observed in the 0–5 cm soil sample “was mainly due to interactions (sorption) with the SOM and/or formation of non-extractable residues of diclofenac in the soil similar to carbamazepine”. The higher the level of SOM was, the more diclofenac was removed: they indeed found retardation factors of 2.2 and 2 in the 5–15 cm sample and 1.3 and 1.4 for the 15–25 cm sample with STWW and freshwater, respectively.

[Xu et al. \(2009\)](#) found retardation factors of 6, 14, 9 and 60 for Dichlofenac in different types of soil during batch experiments.

Retardation factors: HLS: 6 / ASL: 14 / ISC: 9 / PSL: 60. (The composition of the soils are given for Ibuprofen).

Diclofenac was more degraded in nonsterile conditions than in sterile conditions (only 33% removal) with a degradation rate 22.8 faster than in sterile conditions. They concluded that “The inhibition by sterilization suggested that microbial transformations contributed to the overall degradation of PPCPs in the agricultural soils.”

V-The experiment : practical aspects

1) Different steps of the set-up

The experiment was already designed by Cheryl Bertelkamp and her supervisor and a previous trainee had prepared the required equipment and material needed like the pump, the sand and the columns. She also had calculated the different sizes and diameters of the tubes in order to have the right flow velocities and retention times. I was given her report when I arrived with all the results and data.

The aim of my internship was to help Cheryl Bertelkamp prepare and start the experiment and then to manage the different measurements and water supply.

First step: preparation of the set up:

We first connected the pump, the tubes and the columns, and then we filled some columns with sand and others with pumice in grains. The set-up is presented in Appendix 5.

Problems: We had to make sure the columns were filled without air bubbles coming in to avoid preferential path for the water flow in the columns. We also had some difficulties with the pumice because it floated.

The set up also had to be free from organic molecules so we had to wear gloves, wash every buckets, jerrycans, and connectors with acid/base solution before using them. The sand and pumice also had to be washed and dried before being weighted.

We found out that instead of filling half a column (50 cm), the sand filled about $\frac{3}{4}$ of it. This was due to the fact that the porosity had not been taken into account in the calculation of the required weight.

Second step: tracer experiments:

Once the columns were filled, we did some tracer tests with a NaCl solution in order to calculate the real retention time, velocity, and porosity of the columns.

Problems: We had to find the optimal NaCl concentration and the duration of the tracer spiking: the effluent concentration has to reach the one of the influent and a step has to be observed. In the meantime, the concentration has to be high enough to be detected by the conductivity meter but not too high to avoid changes in the viscosity of the water or disturb the bacterial activity too much. We found out a spiking duration of 7 hours and a concentration of 5g/L. We decided that we needed 2 more columns for both sand and pumice in order to do the tracer experiments without disturbing the bacteria. But unfortunately the pump didn't have enough channels. Cheryl Bertelkamp and her supervisor decided to do the experiment without the pumice.

Tracer tests: I performed one tracer test per day. In the morning, I switched the influent from demi water to NaCl solution, and then I waited about 7 hours to switch again to demi water.

In the mean time the conductivity was measured in the effluent with a conductivity meter. I collected the measurements the next morning.

Example of a tracer test:

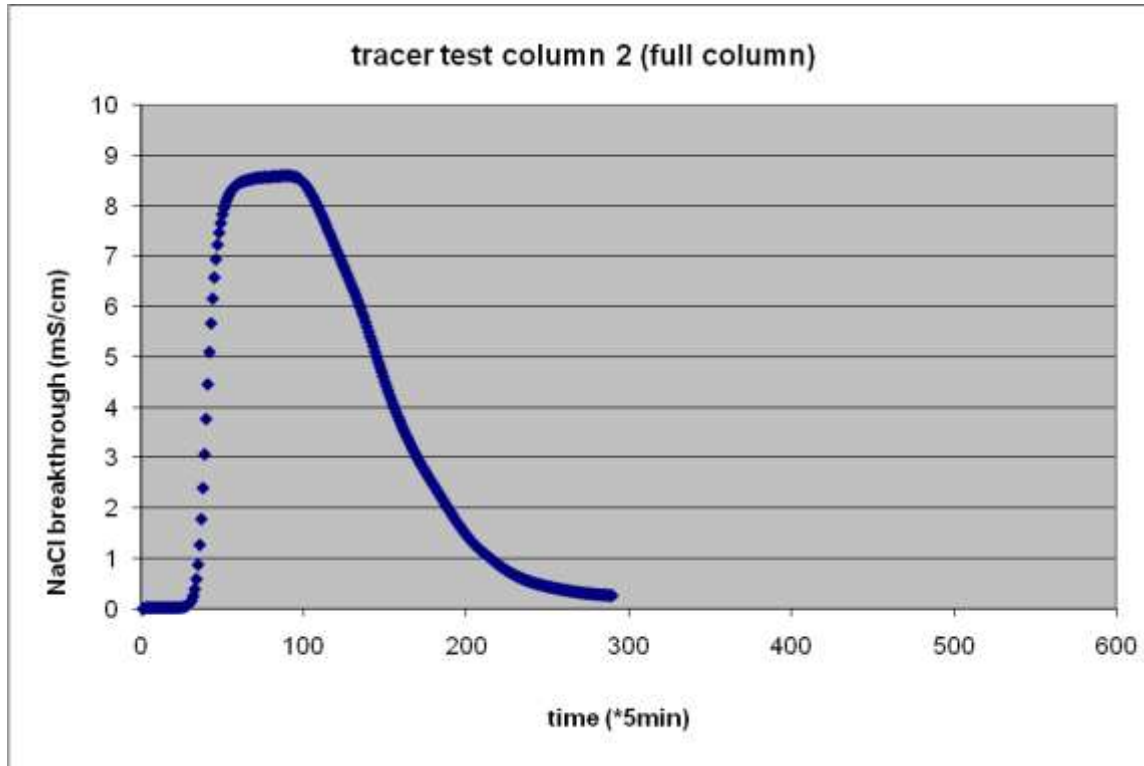


Figure 8 Tracer curve for column 2

At first, the columns were not filled entirely and the tracer curves were not symmetrical. We deduced that it was caused by the diffusion of the tracer in the layer of water above the surface of the sand. We decided to fill the whole columns with sand.

The final calculations for the columns and tubes are the following:

Table 3 Experiment data

Column data	<i>m</i>	<i>cm</i>	<i>m</i> ²	<i>m</i> ³	<i>dm</i> ³ = <i>l</i>
D diameter	0,036	3,6			
L length	1	100			
S base surface			0,001018		
V volum				0,0010179	1,017876

Sand data	m^2	m^3	m^{-1}	kg	m^2/kg	kg/m^3
SS (sieve analysis)			3325,48			
ρ density						2600
M sand mass in the column				1,614		
V volum of sand		0,000621				
SSA					1,2790308	
SSC	2,0643557					

Tube data	m	mm	m^2
Inner surface			2,064356
Lt*Dt			0,657105
Dt inner diameter	0,007	7	
Lt length	93,872117		
St base surface			3,85E-05

The specific surface of one column full of sand (1.614 kg of sand) is about 2.06 m^2 and is equivalent to the inner surface of a 93.87 m long tube.

We found that there was no mass loss of the tracer in the columns because the effluent concentration reached the influent one. It means that NaCl doesn't adsorb or react with the sand which is what we expected.

We also measured the pressure loss in the columns. This measurement will be used during the experiment to detect the presence of the biofilm (which should increase the pressure in the column).

Final step: starting the experiment

After all the tracer tests were performed correctly, and the porosity and real flow calculated, we started the real experiment. We prepared the sodium azide and sodium hydroxide solutions, washed the jerrycans with acid/base solutions, filled them with demi / canal water.

Problems: Since the diameter of the smaller tubes is 0.5 mm we had to sieve the canal water. We observed air bubbles in the columns about 3 weeks after the filling. But air bubbles might also be present in the first meter of the river bed. Cheryl Bertelkamp decided to go on with the experiment.

We measured the temperature, the O_2 and the pH in all the affluent and effluents. The pH was about 6-7 and the O_2 concentration between 5 and 9 mg/L which confirmed the aerobic conditions. We also made the first DOC measurements in the affluent and effluent of the columns.

2) Analysis of the tracer experiments

Here is one of the final tracer tests results I got from the columns. The others are in appendix 4. I normalized the NaCl concentration so that we can see the influent concentration is reached in the effluent.

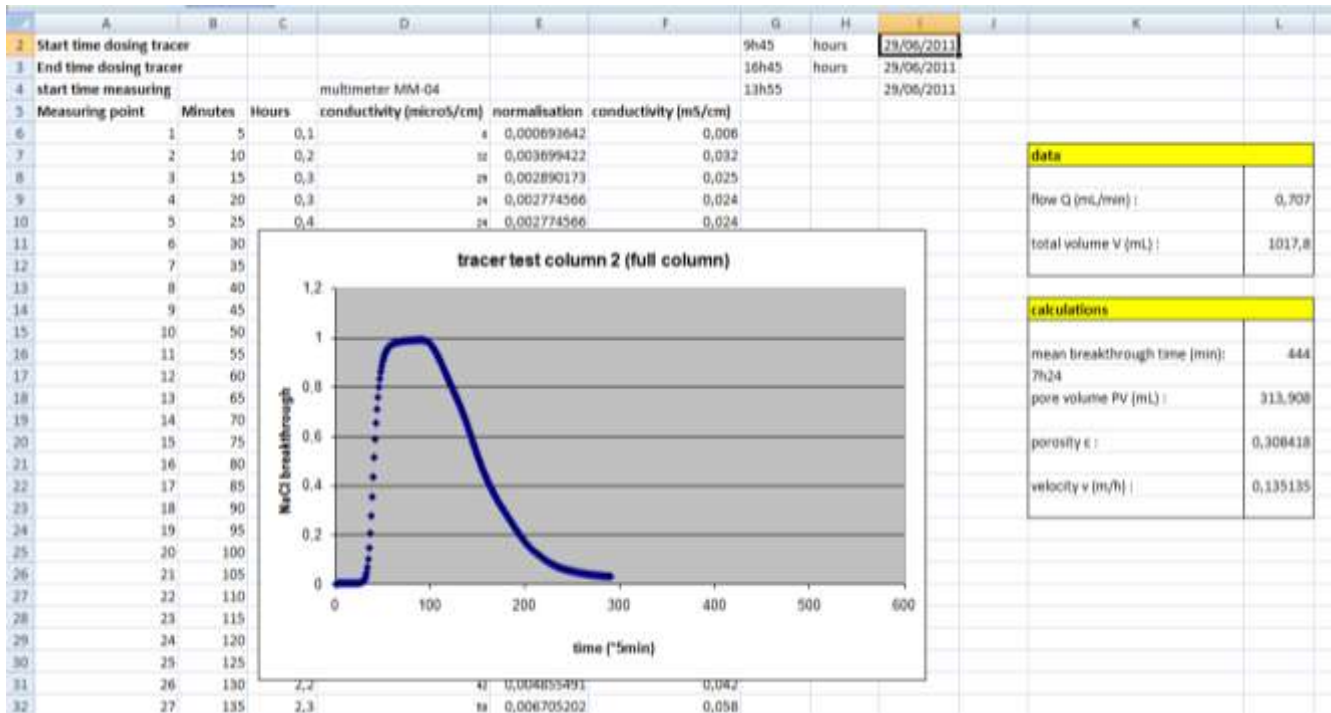


Figure 9 Tracer curve and calculations for column 2

I used these curves to calculate the filtration velocity in the columns and the porosity which is a useful data for further calculations (calculation of the retardation factor for example).

Table 4 Columns data

data	
flow Q (mL/min) :	0,707
total volume V (mL) :	1017,8

The flow of 0,707 mL/min corresponds to 42.58 rpm for the pump.

The total volume V is the volume of the tube without the sand.

Table 5 Columns calculations

calculations column 1	
mean breakthrough time (min): 10h03	603
pore volume PV (mL) :	426,321
porosity ε :	0,418865
velocity v (m/h) :	0,099502

calculations column 2	
mean breakthrough time (min): 7h24	444
pore volume PV (mL) :	313,908
porosity ε :	0,308418
velocity v (m/h) :	0,135135

calculations column 3	
mean breakthrough time (min): 8h11	491
pore volume PV (mL) :	347,137
porosity ε :	0,341066
velocity v (m/h) :	0,1222

calculations column 4	
mean breakthrough time (min): 8h35	515
pore volume PV (mL) :	364,105
porosity ε :	0,357737
velocity v (m/h) :	0,116505

calculations column 5	
mean breakthrough time (min): 9h42	582
pore volume PV (mL) :	411,474
porosity ε :	0,404278
velocity v (m/h) :	0,103093

calculations column 6	
mean breakthrough time (min): 7h42	462
pore volume PV (mL) :	326,634
porosity ε :	0,320922
velocity v (m/h) :	0,12987

The detail of the calculation of the pore volume and the porosity is given in III.3.

The porosity ranges from 0.308 to 0.418 which means that the soil conditions are not exactly the same in the different columns. It is a little surprising since the exact same mass of sand was poured into each column in order to have the same specific surface in the columns and the tubes.

These differences are a problem because the dimensions of the soil canals influence the development of the biofilm. Besides, the specific surface is not exactly the same in the different columns so adsorption should not be the same either.

Cheryl Bertelkamp decided to go on with the experiment because of the schedule she was submitted to. We decided to use columns 5 and 6 respectively for the tracer experiments of columns 1 and 2 because the porosity is similar in both cases. We can assume that the same bacterial activity will develop.

VI- Results

The experiment has been running for two month, but unfortunately the results haven't been satisfying so far because the bacteria didn't grow well in the columns.

Conclusion

This internship was a real opportunity for me to discover a subject I had only heard of before and to improve my scientific knowledge of it. Indeed, the first part of my traineeship was about reading articles on river bank filtration and water management in general. I could then understand the importance of water cleaning and river bank filtration as a new alternative to conventional cleaning methods, given the difficulties encountered by water companies to get rid of all these new pollutants. My job was then to understand and analyze the research project of Cheryl Bertelkamp and help her with the set-up of her experiment. I helped her with the practical aspects of the set-up such as finding the right way to fill the columns or optimize the tubes closing system. I was also asked to do some tests, the tracer tests in particular which took me some time because I had to find the right way to do it, calculate the spiking duration, the solution right concentration etc...The tracer tests were useful for the calculation of some essential parameters such as the porosity of the sand in the columns. In the meantime, I did some research on the investigated chemicals and tried to gather information on the behavior of these chemicals during river bank filtration in the previous studies. I gave my research results to Cheryl so that she could compare them with the ones from her own experiment.

My feedback

This traineeship in the water management department of the civil engineering faculty of TU Delft was the opportunity for me to discover a very interesting and important research field related to civil engineering, health and environmental issues. Indeed, working on the removal of pharmaceuticals through river bank filtration requires basic geology knowledge in order to be able to calculate the porosity of a soil by analyzing a tracer graph for example. A theoretical and experimental chemical knowledge is also essential to understand and analyze the properties of the complex organic molecules studied but also to be able to perform a dosage or a dilution in the chemistry laboratory. I was glad to use the knowledge I acquired on the subject in preparatory classes and do some practice. My personal research on the molecules properties was the opportunity to learn more about some pharmaceuticals: the way they act on the body cells, their side effects or environmental contamination hazards. The obvious link of this research to environmental conservation and sanitary safety was also a good motivation for me. I genuinely think that this project could lead to an efficient, sustainable and cost effective way to process river water into potable water. And I'm not the only one to think so; Cheryl Bertelkamp's project has been selected in order to be presented during the Water Quality and Technology Conference and Exposition (WQTC) in the US this September. She had to give a small presentation of her research in a paper and she stated me as a coauthor.

I didn't really use the knowledge I got from my first year classes at école des Ponts but I was thrilled to broaden my scientific knowledge to other fields. The research aspect was totally new to me and even if I don't plan to do more research in a near future, I was happy to see how things work for a Ph.D. or master student in an international university such as TU Delft.

I chose this research traineeship because the subject seemed, and was, very interesting to me and also because I wanted to go abroad in a big university for these 3 months and have the opportunity to improve my English. The consistency with my choice of doing Industrial management (Génie Industriel) next year is not obvious. However I acquired some knowledge about pharmaceuticals which may be useful if I want to work in the pharmaceutical industry.

Bibliography

Articles

Micòl Mastrocicco, Nicolò Colombani, Alberto Cavazzini, Luisa Pasti, 2009. *A green and fast chromatographic method for determining organic compound mobility in soils*. Journal of Chromatography A, 1216, 6802–6809.

Fadi Al Housari, Patrick Höhener, Serge Chiron, 2011. *Factors responsible for rapid dissipation of acidic herbicides in the coastal lagoons of the Camargue (Rhône River Delta, France)*. Science of the Total Environment 409, 582–587.

B. von Oepen, W. Kordel and W. Klein, 1991. *Sorption of Nonpolar Compounds to Soils: Processes, Measurements and Experience with the Applicability of the modified OECD-Guideline 106*. Chemosphere, Vol. 22, 285-304.

Larry B. Barbier, Stephanie H. Keefe, Denis R. Leblanc, Paul M. Bradley, Francis H. Chapelle, Michael T. Meyer, Keith A. Loftin, Dana W. Koplín, and Fernando Rubio, 2009. *Fate of Sulfamethoxazole, 4-Nonylphenol, and 17 β -Estradiol in Groundwater Contaminated by Wastewater Treatment Plant Effluent*. Environ. Sci. Technol., 43, 4843–4850.

Benny Chefetz, Tamar Mualem, Julius Ben-Ari, 2008. *Sorption and mobility of pharmaceutical compounds in soil irrigated with reclaimed wastewater*. Chemosphere 73, 1335–1343.

Jae-Woo Choi, Heon-Cheol Ha, Song-Bae Kim and Dong-Ju Kim, 2005. *Analysis of benzene transport in a two-dimensional aquifer model*. Hydrol. Process. 19, 2481–2489.

M. Silvia Diaz-Cruz, Damia Barcelo, 2008. *Trace organic chemicals contamination in ground water recharge*. Chemosphere 72, 333–342.

S. Grunheid, U. Huebner and M. Jekel, 2008. *Impact of temperature on biodegradation of bulk and trace organics during soil passage in an indirect reuse system*. Water Science & Technology—WST 57.7, 987-994.

Steffen Grunheid, Gary Amy, Martin Jekel, 2005. *Removal of bulk dissolved organic carbon (DOC) and trace organic compounds by bank filtration and artificial recharge*. Water Research 39, 3219–3228.

Thomas Heberer, Gudrun Massmann, Britta Fanck, Thomas Taute, Uwe Dünnebier, 2008. *Behaviour and redox sensitivity of antimicrobial residues during bank filtration*. Chemosphere 73, 451–460.

K.M. Hiscock, T. Grischek, 2002. *Attenuation of groundwater pollution by bank filtration*. Journal of Hydrology 266, 139–144.

Lionel Ho, Charlotte Grasset, Daniel Hoefel, Mike B. Dixon, Frederic D.L. Leusch, Gayle Newcombe, Christopher P. Saint, Justin D. Brookes, 2011. *Assessing granular media filtration for the removal of chemical contaminants from wastewater*. *Water Research* 45, 3461–3472.

Christiane Hoppe-Jones, Gretchen Oldham, Jorg E. Drewes, 2010. *Attenuation of total organic carbon and unregulated trace organic chemicals in U.S. riverbank filtration systems*. *Water Research* 44, 4643 – 4659.

M. Jekel and S. Gruenheid, 2005. *Bank filtration and groundwater recharge for treatment of polluted surface waters*. *Water Science and Technology: Water Supply* Vol 5 No 5 pp 57–66.

N.T. Litz, A. Weigert, B. Krause, S. Heise, G. Grützmacher, 2011. *Comparative studies on the retardation and reduction of glyphosate during subsurface passage*. *Water Research* 45, 3047 – 3054.

S. K. Maeng, S. K. Sharma, A. Magic-Knezev and G. Amy, 2008. *Fate of effluent organic matter (EfOM) and natural organic matter (NOM) through riverbank filtration*. *Water Science & Technology—WST* 57.12, 1999-2007.

Gudrun Massmann, Uwe Dünbier, Thomas Heberer, Thomas Taute, 2008. *Behaviour and redox sensitivity of pharmaceutical residues during bank filtration – Investigation of residues of phenazone-type analgesics*. *Chemosphere* 71, 1476–1485.

Traugott J. Scheytt, Petra Mersmann, Thomas Heberer, 2006. *Mobility of pharmaceuticals carbamazepine, diclofenac, ibuprofen, and propyphenazone in miscible-displacement experiments*. *Journal of Contaminant Hydrology* 83, 53– 69.

Oranuj Lorphensri, David A. Sabatini, Tohren C.G. Kibbey, Khemarath Osathaphan, Chintana Saiwan, 2007. *Sorption and transport of acetaminophen, 17 α -ethynyl estradiol, nalidixic acid with low organic content aquifer sand*. *Water Research* 41, 2180 – 2188.

M. W. Priddle and R.E Jackson, 1991. *Laboratory column measurements of VOC retardation factors and comparison with field values*. *Ground Water* Vol. 29, No. 2, 260-266.

Maria Ramil, Tarek El Aref, Guido Fink, Marco Scheurer, Thomas A. Ternes, 2010. *Fate of Beta Blockers in Aquatic-Sediment Systems: Sorption and Biotransformation*. *Environ. Sci. Technol.* 44, 962–970.

T. Rauch-Williams, C. Hoppe-Jones, J.E. Drewes, 2010. *The role of organic matter in the removal of emerging trace organic chemicals during managed aquifer recharge*. *Water Research* 44, 449-460.

Clare H. Redshaw & Martin P. Cooke & Helen M. Talbot & Steve McGrath & Steven J. Rowland, 2008. *Low biodegradability of fluoxetine HCl, diazepam and their human metabolites in sewage sludge-amended soil*. J Soils Sediments 8, 217–230.

Thorsten Reemtsma, Ulf Mieke, Uwe Duennbier, Martin Jekel, 2010. *Polar pollutants in municipal wastewater and the water cycle: Occurrence and removal of benzotriazoles*. Water research 44, 596-604.

M. Rocio Estrella, Mark Brusseau, Robert S. Maier, Ian L. Pepper, Peter J. Wierenga, Raina M. Miller, 1993. *Biodegradation, Sorption, and Transport of 2,4-Dichlorophenoxyacetic Acid in Saturated and Unsaturated Soils*. Applied and environmental microbiology, Vol. 59, No. 12, 4266-4273.

Nina Tuxen, Peter L. Tuchsén, Kirsten Rügge, Hans-Jürgen Albrechtsen, Poul L. Bjerg, 2000. *Fate of seven pesticides in an aerobic aquifer studied in column experiments*. Chemosphere 41, 1485-1494.

Michael J. Watts, Karl G. Linden, 2008. *Photooxidation and subsequent biodegradability of recalcitrant tri-alkyl phosphates TCEP and TBP in water*. Water research 42, 4949 – 4954.

Jian Xu, Laosheng Wu, Andrew C. Chang, 2009. *Degradation and adsorption of selected pharmaceuticals and personal care products (PPCPs) in agricultural soils*. Chemosphere 77, 1299–1305.

Quanlin Zhou, Sally McCraven, Julio Garcia, Monica Gasca, Theodore A. Johnson, William E. Motzer, 2009. *Field evidence of biodegradation of N-Nitrosodimethylamine (NDMA) in groundwater with incidental and active recycled water recharge*. Water research 43, 793 – 805.

Robert A. Payn, Michael N. Gooseff, David A. Benson, Olaf A. Cirpka, Jay P. Zarnetske, W. Breck Bowden, James P. McNamara, and John H. Bradford, 2008. *Comparison of instantaneous and constant-rate stream tracer experiments through non-parametric analysis of residence time distributions*. Water resources research, vol. 44, W06404.

Books

C.A.J. Appelo & D. Postma. Chapter 3: Flow and transport. In *Geochemistry, groundwater and pollution, 2nd edition*. Amsterdam: A A Balkema Publishers, 2005, 672 p.

Others

OECD guideline for the testing of chemicals, 106. Adopted: January, 21 2000.

Appendixes

Appendix 1 : overview of previous studies

1) Subject of the studies

[Mastrocicco et al. \(2009\)](#) Determination of organic compounds mobility in soils with a new chromatographic method.

[Scheytt et al. \(2006\)](#) Investigation on the mobility of four pharmaceuticals in transport experiments.

[Ramil et al. \(2010\)](#) Sorption and Biodegradation of beta blockers in aquatic-sediment systems.

[Chefetz et al. \(2008\)](#) Sorption and mobility of pharmaceuticals in soil irrigated with reclaimed wastewater.

[Rauch-Williams et al. \(2010\)](#) Investigation on the role of soil organic matter in the removal of trace organic chemicals during managed aquifer recharge.

[Hoppe-Jones et al. \(2010\)](#) Conditions favoring the attenuation of total organic carbon and trace organic chemicals in riverbank filtration.

[Diaz Cruz and Barcelo \(2008\)](#) Overview of the trace organic chemicals the most responsible for ground water recharge contamination, and the conditions of their fate and removal.

[Heberer et al. \(2008\)](#) Behaviour and redox sensitivity of antimicrobial residues during bank filtration in a field site.

[Hiscock and Grischek \(2002\)](#) A general presentation of riverbank filtration and its ability to reduce groundwater pollution.

[Gruenheid et al. \(2008\)](#) Influence of temperature on the biodegradation of bulk and trace organic compounds during soil passage in indirect reuse systems.

[Gruenheid et al. \(2005\)](#) Factors of influence in the removal of bulk dissolved organic carbon and trace organic compounds by bank filtration and artificial recharge.

[Ho et al. \(2011\)](#) Removal of pollutants by granular media filtration.

[Jekel and Gruenheid \(2005\)](#) Behavior of different organic compounds during bank filtration and groundwater recharge.

Maeng et al. (2008) Characterisation of Bulk organic matter which is composed of effluent organic matter (EfOM) and natural organic matter (NOM) during riverbank filtration.

Xu et al. (2009) Degradation and adsorption of selected pharmaceuticals and personal care products (PPCPs) in agricultural soils.

2) Investigated chemicals

Mastrocicco et al. (2009) Aniline, Aniside, Cresol, Hydroquinone, p-Nitroaniline, Phenol, Phenylenediamine, Piridine, Sulfanilamide, Sulfathiazole, Sulfamethoxazole, Metolachlor and Toluene.

Scheytt et al. (2006) Carbamazepine, Diclofenac, Ibuprofen and Propyphenazone.

Ramil et al. (2010) Atenolol, Acebutolol, Bisoprolol, Celiprolol, Metoprolol, Nadolol, Pindolol, Propranolol and Sotalol.

Chefetz et al. (2008) Carbamazepine, Naproxen and Diclofenac.

Rauch-Williams et al. (2010) Small and hydrophilic organic chemicals (MW from 180 to 360 Dalton and $\log D_{\text{pH}=7}$ of less than 2.6) were tested in this experiment. They were expected to badly adsorb on the porous media and move easily in ground water. Carbamazepine, diclofenac, Gemfibrozil, Ibuprofen, Ketoprofen, Naproxen, Phenacetine, Primidone, Propyphenazone and TCEP.

Hoppe-Jones et al. (2010) Water soluble, polar contaminants commonly found in rivers. Bisphenol A, Carbamazepine, Clofibric acid, Dichlorptop, Diclofenac, Fenofibrate, Gemfibrozil, Ibuprofen, Ketoprofen, Mecoprop, Naproxen, Primidons, TCEP, TCPP and TDCPP.

Diaz Cruz and Barcelo (2008) A wide range of pharmaceuticals (Diclofenac, Clofibric acid, Propyphenazone, AMDOPH, Carbamazepine, Primidone, Indometazine, Bezafibrate, Iopromide, Sulfamethoxazole), pesticides (Bentazone, Mecoprop, ...) and industrial chemicals (1,5, 1,7, 2,7 – naphtalenesulfonic acid, ...)

Heberer et al. (2008) Residues of 19 antibiotic drugs (Tetracycline, Clindamycin, Sulfamethoxazole, Erythromycin, ...)

Gruenheid et al. (2008) Bulk organics (polysaccharides, humics, low molecular acids, ...) and trace organics (1,5 NDSA and its isomers (1,7 and 2,7), Iopromide, Sulfamethoxazole, ...)

Gruenheid et al. (2005) Bulk dissolved organic compounds (BDOC), adsorbable organic halogens (AOX), trace organics (Iopromide, Sulfamethoxazole, naphthalenesulfonic acids,...)

Ho et al. (2011) atrazine, estrone (E1), 17 α -ethynylestradiol (EE2), N-nitrosodimethylamine (NDMA), N-nitrosomorpholine (NMOR) and N-nitrosodiethylamine (NDSEA).

Jekel and Gruenheid (2005) Bulk organics (polysaccharides, ...), adsorbable organic halogens (AOI, AOB_r) and three groups of trace compounds: X-ray contrast media (Iopromide); bacteriostatics (Sulfamethoxazole) and the industrial chemicals naphthalenedisulfonates (1,5-NSA; 1,7-NSA; 2,7-NSA).

Maeng et al. (2008) Bulk and trace organics naturally present in Delft canal water and in the effluents from a wastewater treatment plant (Hoek van Holland, The Netherlands).

Xu et al. (2009) Six selected PPCPs (clofibric acid, ibuprofen, naproxen, triclosan, diclofenac and bisphenol A).

3) Experimental set-ups

Mastrocicco et al. (2009) Small columns (0.39cm×10cm) with different types of soils (alluvial sediment, coarse sand and standard Eurosoil mixed with quartz).

Scheytt et al. (2006) Small (13 cm) sand column experiments under unsaturated conditions filled with artificial sewage effluent. The pharmaceuticals (one for each experiment) were spiked with the tracer LiCl. The flow was 0.22 m/d (1m/d in our experiment).

Ramil et al. (2010) Samples of different compositions were taken from the sediment surface of streams and rivers. They differed in total organic carbon content (TOC) and size distribution. The experiment was performed in aerobic conditions in test vessels. Sorption/Desorption Batch Experiments were also conducted on the samples.

Chefetz et al. (2008) Soil layers were sampled from a land irrigated with secondary treated wastewater (STWW) and used for column experiments fed with both fresh water and STWW at a flow of 2ml/h (0.7ml/h in our experiment).

Rauch-Williams et al. (2010) Four biologically active columns (1 m) under aerobic and anoxic recharge conditions were set in series and filled with aquifer material (d_{50} = 0.8mm, foc (organic carbon content) = 0.003%). The flow was 0.065 m/d. Different waste water effluents were used to feed the columns in order to have different soil biomass growth in the columns.

[Hoppe-Jones et al. \(2010\)](#) Three full-scale RBF facilities in the United States. One in Colorado (mostly sand, $f_{oc} = 0.05\%$), one in Cedar River (sandy aquifer, $f_{oc} = 0.01\%$), and one in Ohio river (glacial sand and gravel aquifer).

[Heberer et al. \(2008\)](#) Samples of bank filtrate taken in wells from a field site in Berlin, where bank-filtered water is used for the production of drinking water. The travel times were 1 to 4 months long. The redox conditions were different in the different wells and varied with the seasons.

[Gruenheid et al. \(2008\)](#) Temperature controlled soil columns (5°C, 15°C, 25°C, 50 x 14 cm) representing the conditions of an artificial recharge facility at different times of the year. They were filled with technical sand (0.7-1.2 mm) and coarse sand (5 mm) at the extremities. They were fed with filtered river water at a flow of 18ml/h. The chemicals were continuously spiked at a concentration 10 times higher than in the river.

[Gruenheid et al. \(2005\)](#) The analyses were directly conducted on bank filtration and artificial recharge sites during more than one year.

[Ho et al. \(2011\)](#) Laboratory scale sand and granular activated carbon (GAC) filters were used to fill columns (30 cm) filled with tertiary treated effluent (TTE) at a flow of 4.5 ml/h. Pilot-scale column experiments were also conducted at the wastewater treatment plant.

[Jekel and Gruenheid \(2005\)](#) On site measurements near Lake Tegel in Germany and long retention soil column experiments were conducted during more than two years. The lake sediments were mostly composed of sand with a rich DOC composition (7.5 mg/l). The column system was 30 m long with a retention time of 30 days, under first oxic then anoxic conditions. The compounds were spiked at a concentration 10 times higher than in the river.

[Maeng et al. \(2008\)](#) Wastewater effluent-derived surface water and surface water were used as source waters in experiments with soil columns (2.5 m x 10 cm). The columns were filled with silica sand sized between 0.8 and 1.25 mm. They were first fed with wastewater to enhance biomass accumulation on sand then one was fed with wastewater and Delft canal water and the other only with Delft canal water.

[Xu et al. \(2009\)](#) Samples from four US agricultural soils associated with reclaimed wastewater reuse were investigated. Degradation studies were conducted in centrifuge tubes, and batch adsorption studies were conducted with sterilized soil.

4) Analytical methods

[Mastrocicco et al. \(2009\)](#) Soil leaching column chromatography (SLCC) employing totally aqueous mobile phases were used to analyse the chemicals. Retardation factors and adsorption isotherm of Metolachlor were determined.

[Scheytt et al. \(2006\)](#) Solid phase extraction, derivatization and detection with GC-MS (gas chromatography mass spectrometry).

[Ramil et al. \(2010\)](#) LC-ESI-tandem MS (mass spectrometer) detection were used to determine the beta blockers in sediments. Biotransformation studies and sorption isotherms were also conducted.

[Chefetz et al. \(2008\)](#) batch sorption/desorption studies with mass balance analyses.

[Rauch-Williams et al. \(2010\)](#) gas chromatography coupled with mass spectrometry (GC/MS) and high performance liquid chromatography (HPLC) combined with a UV diode array detector (DAD) for TO_rC analyses. A Total Organic Carbon Analyzer was used for DOC measurements. Soil biomass was determined using phospholipid extraction (PLE).

[Hoppe-Jones et al. \(2010\)](#) TOC analyzer for determining bulk organic carbon and specific UV absorbance (SUVA) analyses to determine the aromaticity of organic matter. TO_rC were extracted and analysed by gas chromatographs and mass spectrometers.

[Heberer et al. \(2008\)](#) After solid-phase extraction (SPE), the antibiotic residues were analysed by electrospray ionization tandem mass spectrometry (ESI-HPLC–MS/MS) with selected reaction monitoring (SRM).

[Gruenheid et al. \(2008\)](#) DOC, UVA₂₅₄ and LC-OCD (liquid chromatography with organic carbon detection) measurements to quantify the bulk organics and assess the changes of composition.

[Gruenheid et al. \(2005\)](#) Analyses were conducted monthly. They consisted of dissolved organic carbon (DOC) measurements, UV absorbance (UVA₂₅₄), liquid chromatography with organic carbon detection (LC-OCD), differentiated adsorbable organic halogens (AOX) analysis and single organic compound analysis of a few model compounds.

[Ho et al. \(2011\)](#) Batch degradation experiments were conducted to assess the nature and the kinetics of the removal. Atrazine was analysed using a gas chromatography-nitrogen phosphorus detector method. E1 and EE2 were analysed using a gas chromatography-mass spectrometry (GCMS) method. Nitrosamines were analysed using a GCMS system. Atrazine degradation was analysed by a qualitative polymerase chain reaction which detects the first gene involved in its degradation.

[Jekel and Gruenheid \(2005\)](#) DOC and UVA measurements, LC-OCD measurements to assess the changes in character of DOC during soil passage, AOX analysis and solid phase extraction (SPE)/ HPLC-analysis of the three groups of trace compounds.

[Maeng et al. \(2008\)](#) Soil biomass was determined by adenosine triphosphate (ATP) concentrations and heterotrophic plate counts. The concentration of bulk organic matter was determined as DOC by a total organic carbon analyzer. Its characteristics were analysed by fluorescence excitation—emission matrix (F-EEM), liquid chromatography with an on-line organic carbon detector and an organic nitrogen detector (LC-OCD/OND) and specific ultraviolet absorbance (SUVA).

[Xu et al. \(2009\)](#) solid phase extraction (SPE) then Gas chromatography (GC) and mass spectrometry were used to analyze the chemicals.

5) Results

[Mastrocicco et al. \(2009\)](#) Small column experiments are an interesting alternative to large columns or batch experiments providing good results concerning the mobility of a wide range of organic micro pollutants.

[Scheytt et al. \(2006\)](#) Ibuprofen, Propyphenazone and Diclofenac were significantly removed as in saturated conditions whereas Carbamazepine was not eliminated in these unsaturated conditions.

[Ramil et al. \(2010\)](#) Pindolol and Atenolol were significantly removed while Sotalol, Propanolol and Celiprolol had a low elimination. Beta blockers sorption correlation to the Freundlich model varied according to the different sediments.

[Chefetz et al. \(2008\)](#) Carbamazepine and Diclofenac were well retarded in the first layers of the soil sample rich in soil organic matter (SOM). Diclofenac was more retarded in freshwater than in STWW. The presence of SOM favors the sorption process in the first layers of soil.

[Rauch-Williams et al. \(2010\)](#) The degradable TO_{RC} were generally better or equally removed under aerobic conditions. The presence of soil organic carbon in the first layers of soil enhanced the degradation of the pollutants. Indeed, it is used as a co-substrate in their metabolism and degradation by bacteria. High degradation rates were also found in areas with lower BDOC concentrations. It was probably due to a certain type of microbial organisms.

[Hoppe-Jones et al. \(2010\)](#) RBF was a good barrier for TOC, nitrogen and some TO_{RC}. However, the seasonal temperature variations influenced the efficiency of the removal.

[Diaz Cruz and Barcelo \(2008\)](#) Artificial recharge of pre-treated reclaimed waste water could be a viable solution to provide potable water in high quantities. Filtration through the ground is an efficient way to remove trace organic micro pollutants but depends on various conditions. It is sometimes not sufficient for some very persistent compounds.

[Heberer et al. \(2008\)](#) Most macrolides were well removed after a residence time of a few months. Sulfamethoxazole was the most persistent but its concentration was under the safety level. Redox sensibility was also found for some compounds which were more degraded under oxic or anoxic conditions.

[Hiscock and Grischek \(2002\)](#) The removal of pollutants is highly due to the microbial activity in the colmation layer within the river bed. This activity is influenced by a lot of parameters such as the aquifer composition, the redox conditions or the level of oxygen and nitrates in the water.

[Gruenheid et al. \(2008\)](#) The degradation of the degradable pollutants in the first few centimeters of the columns was effective and not temperature dependant. Then, since temperature has an influence on bioactivity, higher temperatures enhanced the degradation of the organic pollutants.

[Gruenheid et al. \(2005\)](#) The most important factors influencing the DOC, AOX and trace compounds degradation were redox conditions (temperature dependant) and travel time.

[Ho et al. \(2011\)](#) In general, contrary to GAC filtration, sand was not enough to remove the pollutants from tertiary treated wastewater. The exceptions were E1 and EE2 which were biodegraded.

[Jekel and Gruenheid \(2005\)](#) Redox conditions influenced DOC degradation rates but not necessarily the residual concentrations. The change in character of most DOC were similar under aerobic and anaerobic conditions. However, Redox conditions had an influence on the degradation of some trace chemicals (better removal under anoxic conditions for Sulfamethoxazole, no dehalogenation under oxic conditions for Iopromide,...)

[Maeng et al. \(2008\)](#) Non-humic substances like biopolymers were well removed from wastewater effluent-derived surface water and most bulk organic matter was removed after 5 m soil passage in the column experiments. Half of the DOC removal was observed in the first 50 cm of the column where biomass was present.

[Xu et al. \(2009\)](#) The adsorption of all 6 chemicals in soils could be described with the Freundlich equation. Their degradation generally followed first-order exponential decay kinetics and was influenced by the nature of the soil (SOM and clay fraction), and the microbial activity. This activity was inhibited when the concentration of chemicals was too high.

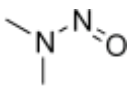
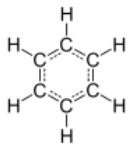
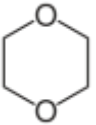
Appendix 2: List of 26 OMPs investigated in the ESTAB project

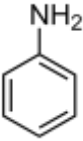
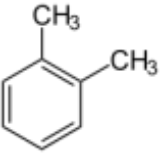
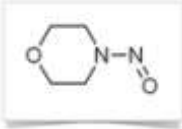
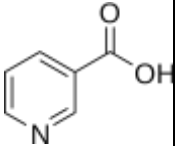
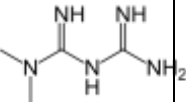
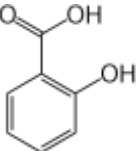
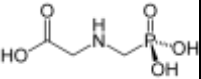
Table 6 Physical properties of the OMP investigated

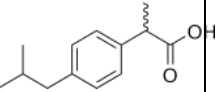
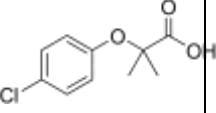
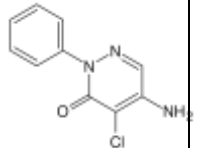
Compound	MW	Log K _{ow}	Log D _{pH} 7.4	Charge at pH 7	pKa
NDMA	74.1	-0.64	0	0	-
Benzene	78.1	1.99	2.177	0	-
1,4-dioxane	88.1	-0.32	0	0	-
Aniline	93.1	1.08	1.135	0	-(?)
1,2-dimethylbenzeen (o-xyleen)	106.2	3.09	3.178	0	-
NMOR	116.1	-0.43	-0.2	0	-(?)
Niacin (vitamin B3, nicotinezuur)	123.1	0.40	-2.9	-1	2.8, 4.2
Metformin	129.0	-2.64	-3.8	1	12.3
Salicylzuur	138.1	2.26	-1.1	-1	2.8, 13.3
Glyfosaat	169.1	-4.47	-6.75	-1	<2, 2.6, 5.6, 10.6
Ibuprofen	206.3	4.00	0.8	-1	4.47
Clofibrac acid	214.0	2.57	-0.9	-1	3.4
Chloridazon	221.6	0.76	1.06	0	-(?)
Terbutaline	225.3	0.90	-1.4	1	8.9
Bisphenol A	228.3	3.64	4	0	-
Dichlorprop	235.1	3.03	-0.15	0	-
Carbamazepine	236.3	2.25	1.895	0	-
Pindolol	248.3	2.00	0.1	1	9.2
Sulfamethoxazole	253.3	0.48	-0.2	-1	-
Ketoprofen	254.3	3.10	-0.3	-1	4.29
Propranolol	259.3	3.50	1.3	1	9.6
Metoprolol	267.4	1.69	-0.06	1	9.49
Sotalol	272.4	0.37	-1.56	1	9.44
TCEP (tris(2-chloroethyl)-phosphate)	285.5	1.63	2.0	0	-(?)
Fluoxetine metabolite: Norfluoxetine	295.3	4.20	2.7	1	9.8
Diclofenac	296.1	4.02	1.437	-1	4.15

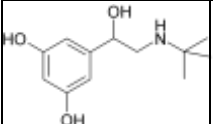
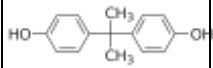
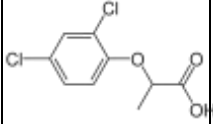
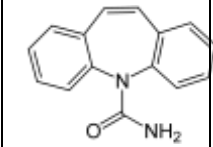
Appendix 3: Expected behavior of investigated chemicals

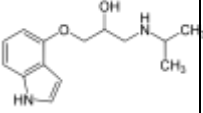
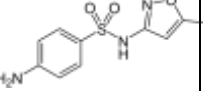
Table 7 Overview of the reported behavior of the different OMP during RBF

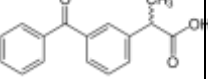
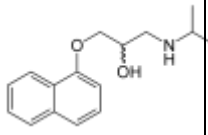
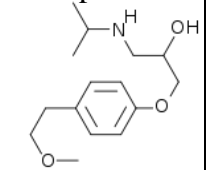
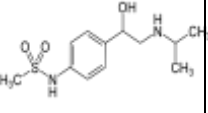
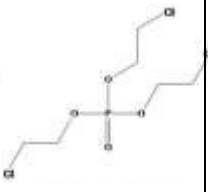
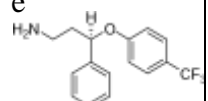
Compound	Source	Retardation factor	adsorption	biodegradation	Type of soil
NDMA 	(Ho et al., 2011)		no	yes	Sand effective size of 0.95 mm with a uniformity coefficient of 1.3.
Benzene 	(Choi et al., 2005) Priddle and Jackson (1991)	1.10, 1.20 14.3 (decreases with flow velocity)	Yes (+ volatilization)	yes	Aquifer materials. Porosity: 0, 40. Dry bulk density: 1,66 g/cm ³ . Aquifer material obtained from a core sample at depth of 14.9 to 15.8 m below ground surface. $f_{oc}=0.00077$. Grain size distribution: >10mm: 7.7%, 0.5-1.0mm: 6.4%, 0.25-0.5mm: 28.0%, 0.124-0.25mm: 37.4%, <0.125mm: 20.5%. Bulk density of sediments: 1.78 g/cm ³ . Calculated pore volume: 200 cm ³ .
1,4-dioxane 	Priddle and Jackson (1991)	1.1	no	no	Aquifer materials. Porosity: 0, 40. Dry bulk density: 1,66 g/cm ³ . Aquifer material obtained from a core sample at depth of 14.9 to 15.8 m below ground surface. $f_{oc}=0.00077$. Grain size distribution: >10mm: 7.7%, 0.5-1.0mm: 6.4%, 0.25-0.5mm: 28.0%, 0.124-0.25mm: 37.4%, <0.125mm: 20.5%. Bulk density of sediments: 1.78 g/cm ³ . Calculated pore volume: 200 cm ³ .
Aniline	(Mastrocicco et al., 2009)	1.04 1.37 (tabulat			Sandy loam soil collected from an agricultural field located in alluvial sediments. Bulk density: 1.71 g/cm ³ , volumetric

		ed value)			water content of the column: $\theta = 0.39\%$, $f_{oc} = 0.34\%$, cation exchange capacity (CEC) = 0.11 meq/g. Composition: sand (200-630 μm): 7.8%, sand (63- 200 μm): 65.2%, silt (2-63 μm): 21.9%, clay (<2 μm): 5.1%)
1,2-dimethylbenz een (o- xyleen) 					
NMOR 	(Ho et al., 2011)		Little		Sand effective size of 0.95 mm with a uniformity coefficient of 1.3.
Niacin 					
Metformin 					
Salicylic acid 					
Glyphosate 	(Litz et al., 2011)	1.4 2.2 5 14 31	slow	Yes (+ in saturated con., + in oxic cond.)	Sandy substrate: in average 2% fine sand (0.1-0.2 mm), 43% medium sand (>0.2-0.5 mm), 49% coarse sand (>0.5-2.0 mm) and 6% fine gravel (>2 mm), no clay or silt with only traces of organic matter and an effective

					porosity of 0.38-0.4%.
<p>Ibuprofen</p> 	<p>(Rauch-Williams et al., 2010)</p> <p>(Scheytt et al., 2006)</p> <p>(Xu et al., 2009)</p>	<p>94.2</p> <p>3</p> <p>HLS: 3</p> <p>ASL: 3</p> <p>ISC: 4</p> <p>PSL: 13</p>	<p>yes</p>	<p>yes</p>	<p>aquifer material (d50= 0.8mm, foc=0.003%)</p> <p>f_{oc}= 0.0013, clay: 0%, Silt (2-63 μm): 1.7%, fine sand (63-200 μm): 42.05%, medium sand (200-630 μm): 56.46%, coarse sand (200-2000 μm): 0.8%, gravel (>2mm): 0.2%.</p> <p>HLS (clay: 3.6%, sand: 95.6%, silt: 0.8%, OM: 0.58%, bulk density: 1.60, porosity: 0.38.)</p> <p>ASL (clay: 12.5%, sand: 70.9%, silt: 16.6%, OM: 1.93%, bulk density: 1.55, porosity: 0.40.)</p> <p>ISC (clay: 42.5%, sand: 10.8%, silt: 46.7%, OM: 2.46%, bulk density: 1.33, porosity: 0.48.)</p> <p>PSL (clay: 18.1%, sand: 32.2%, silt: 49.7%, OM: 5.45%, bulk density: 1.42, porosity: 0.43.)</p>
<p>Clofibric acid</p> 	<p>(DiaCruz et al., 2008)</p> <p>(Xu et al., 2009)</p>	<p>HLS: 24</p> <p>ASL: 19</p> <p>ISC: 557</p> <p>PSL: 12</p>	<p>No</p> <p>Yes>ibuprofen</p>	<p>Low</p> <p>Yes (faster in nonsterile soils.>ibuprofen and bisphenol)</p>	
<p>Chloridazon</p> 					
<p>Terbutaline</p>					

					
<p>Bisphenol A</p> 	<p>(Hoppe Jones et al., 2010)</p> <p>(Xu et al., 2009)</p>	<p>HLS: 73</p> <p>ASL: 109</p> <p>ISC: 45</p> <p>PSL: 140</p>	<p>Yes<clof ibric>ibu profen</p>	<p>Yes</p> <p>Yes<clof ibric</p>	<p>Sandy aquifers ($f_{oc}=0.01-0.05$)</p>
<p>Dichlorprop</p> 	<p>(Hoppe Jones et al., 2010)</p> <p>(Tuxen et al., 2000)</p>		<p>Slightly. Kd (l/kg): 0.04 (I) / 0 (II)</p>	<p>Yes degradation rate constant: k_0 ($\mu\text{g/l/day}$): 1.6 / 2.0</p>	<p>Sediment I: Org carbon: 0.02% / gravel (2-4mm): 2.10% / sand (0.063-2mm): 97.31% / silt+clay (<0.063mm): 0.59 / microbial density (104 colony forming units/g wet sediment): 106</p> <p>Sediment II: Org carbon: 0.02% / gravel (2-4mm): 13.03% / sand (0.063-2mm): 85.66% / silt+clay (<0.063mm): 1.31 / microbial density (104 colony forming units/g wet sediment): 58</p>
<p>Carbamazepine</p> 	<p>(DiaCruz et al., 2008)</p> <p>(Hoppe Jones et al., 2010)</p> <p>(Rauch-Williams et al., 2010)</p> <p>(Scheytt et</p>	<p>1.90</p> <p>1.84</p>	<p>No</p> <p>no (+ in</p>	<p>No</p> <p>Insensitive to red-ox cond.</p> <p>no</p>	<p>aquifer material ($d_{50}= 0.8\text{mm}$, $f_{oc}=0.003\%$)</p> <p>$f_{oc}= 0.0013$, clay: 0%, Silt (2-63microm): 1.7%, fine sand (63-</p>

	al., 2006) (Barber et al., 2009) Mersmann et al. (2002)	5.8, 5.3, 3.3, 2.3, 1.6	saturated cond.) No (+ in unsaturated cond.)	(+ in saturated cond.) Yes in the 0–5 cm soil sample No (+ in unsaturated cond.)	200microm): 42.05%, medium sand (200-630 microm): 56.46%, coarse sand (200-2000 microm): 0.8%, gravel (>2mm): 0.2%. sediment containing 0.2% organic carbon
Pindolol 	(Ramil et al., 2010)			yes	TOC 0.74%, clay/silt 10% and TOC 4.36%, clay/silt 47%
Sulfamethoxazole 	(Heberer et al., 2008) (Grunheid et al., 2005) Gruenheid et al. (2008) (Jekel et al., 2005) (Mastroicco	1.09 1.92		Yes (+ in anoxic cond.) Yes (bank filtration site > artificial recharge site) Yes (+ with Ta) Yes (+ in oxic cond. in the columns contrary to the field)	Natural sandy aquifer technical sand (0.7-1.2 mm) and coarse sand (5 mm) at the extremities Sand with a rich DOC composition (7.5 mg/l). sand (200-630 microm) : 7.8%, sand (63- 200 microm) : 65.2%, silt (2-63microm) : 21.9%, clay (<2

	et al., 2009) (Barber et al., 2009)	(tabulated value) 0.9 1.0 0.8 1.0			microm) : 5.1%) quartz, feldspars (+ glauconite, biotite, amphiboles, pyroxenes, hematite, magnetite, and traces of clay minerals). Sediment organic carbon (SOC) ranges from <0.001-1%. Dissolved oxygen is near saturation.
Ketoprofen 	(Hoppe Jones et al., 2010) (Rauch-Williams et al., 2010)			Yes (+ in Aerobic cond.)	aquifer material (d50= 0.8mm, foc=0.003%)
Propranolol 	(Ramil et al., 2010)			yes	TOC 0.74%, clay/silt 10% and TOC 4.36%, clay/silt 47%
Metoprolol 	(Ramil et al., 2010)			yes	TOC 0.74%, clay/silt 10% and TOC 4.36%, clay/silt 47%
Sotalol 	(Ramil et al., 2010)			yes	TOC 0.74%, clay/silt 10% and TOC 4.36%, clay/silt 47%
TCEP 	(Watts et al., 2008)		no	No (but oxidation products are possible carbon source for bacterial growth)	
Norfluoxetin 	(Watts et al., 2008)		no	no	

Appendix 4 : Final tracer experiments

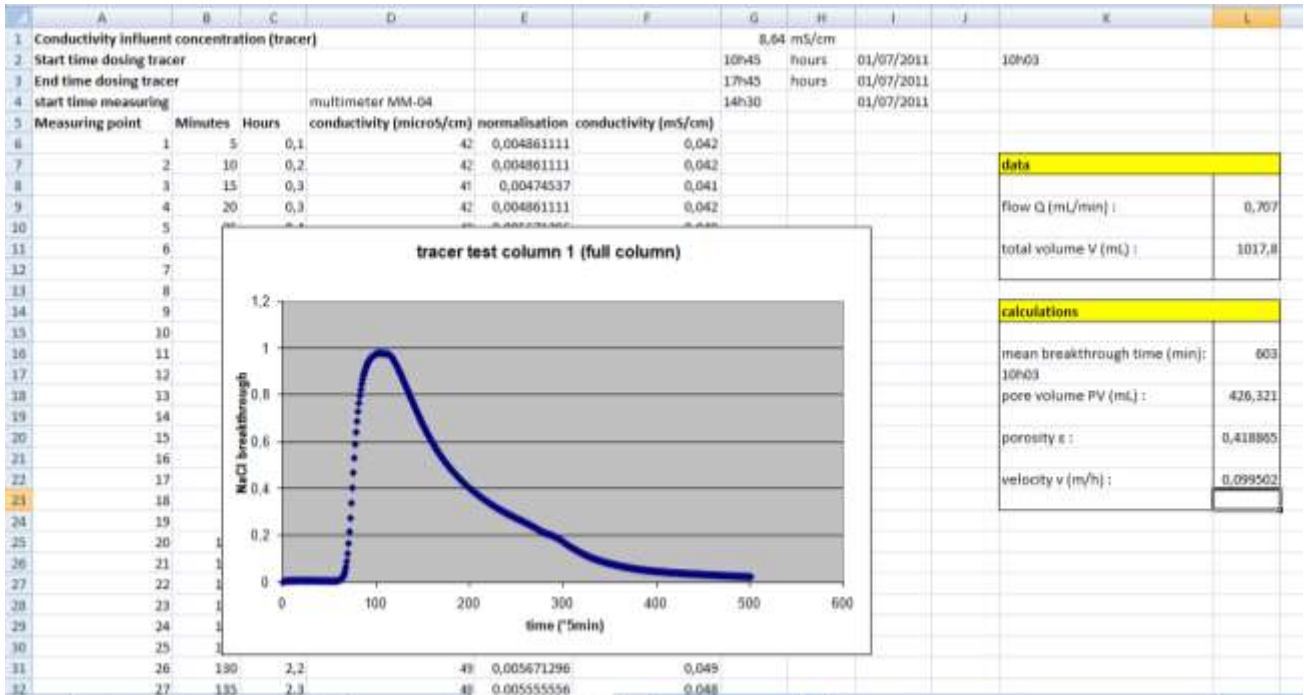


Figure 10 Tracer test column 1

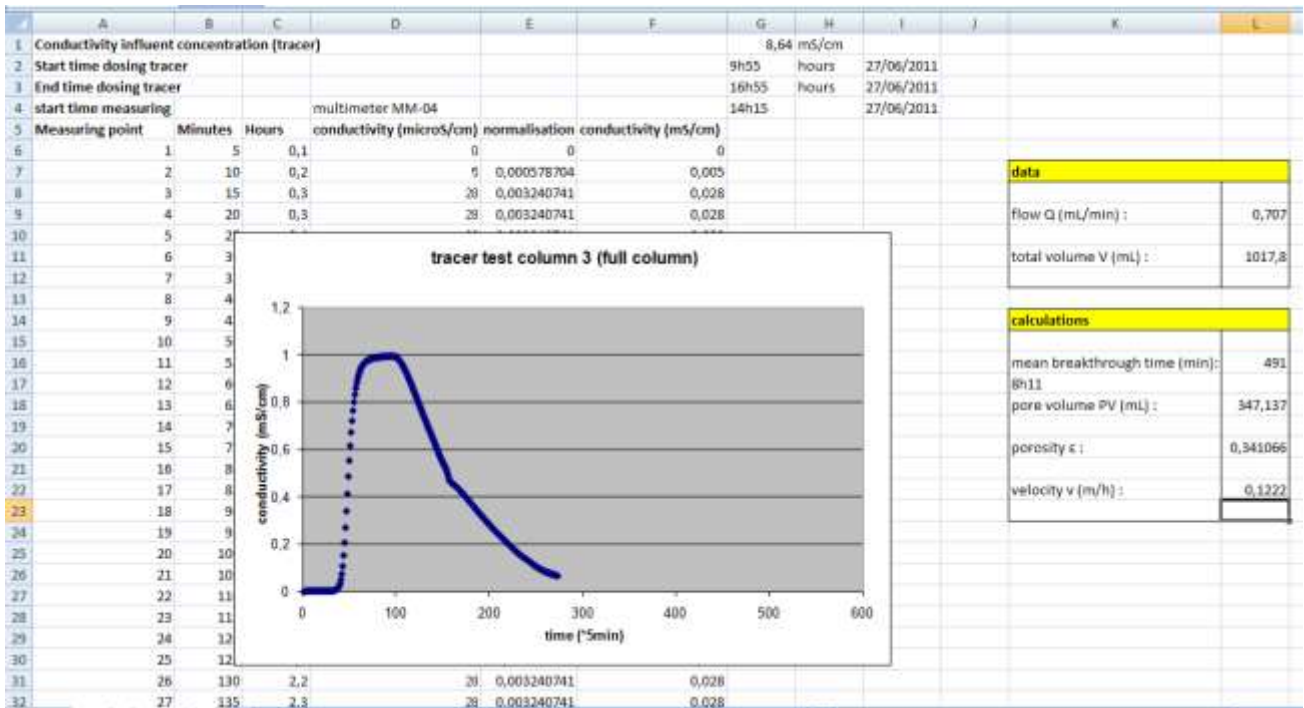


Figure 11 Tracer test column 3

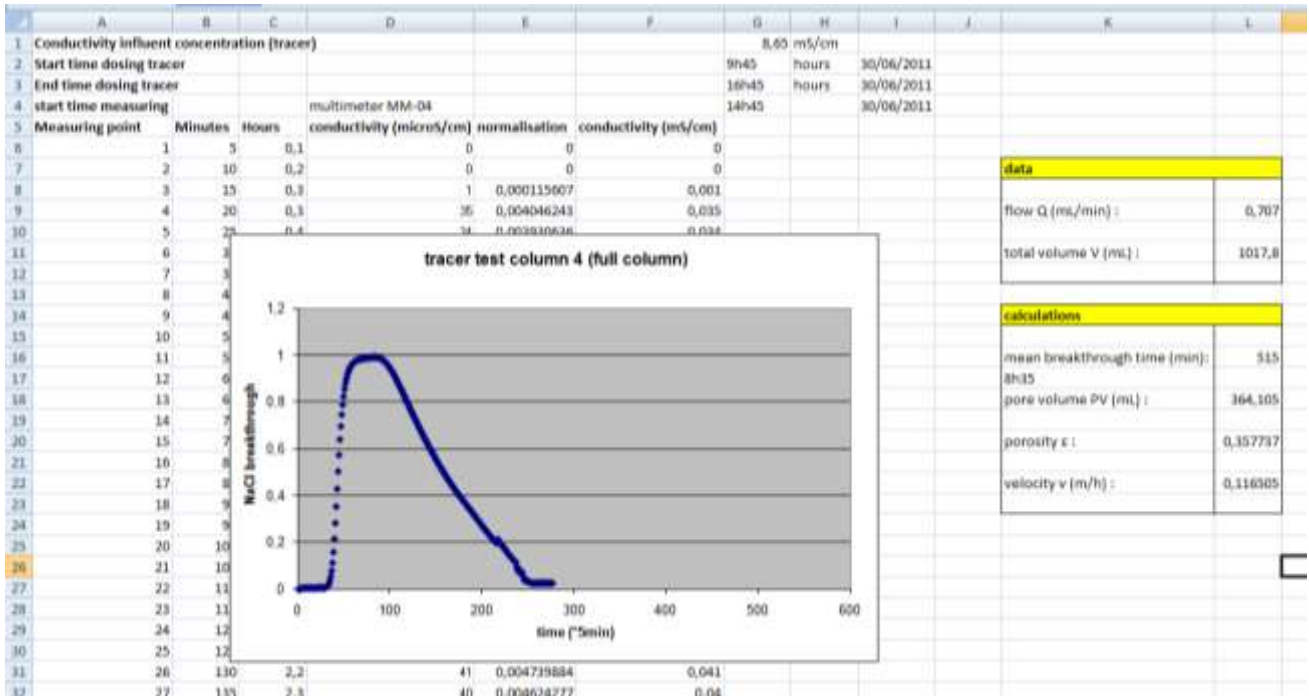


Figure 12 Tracer test column 4

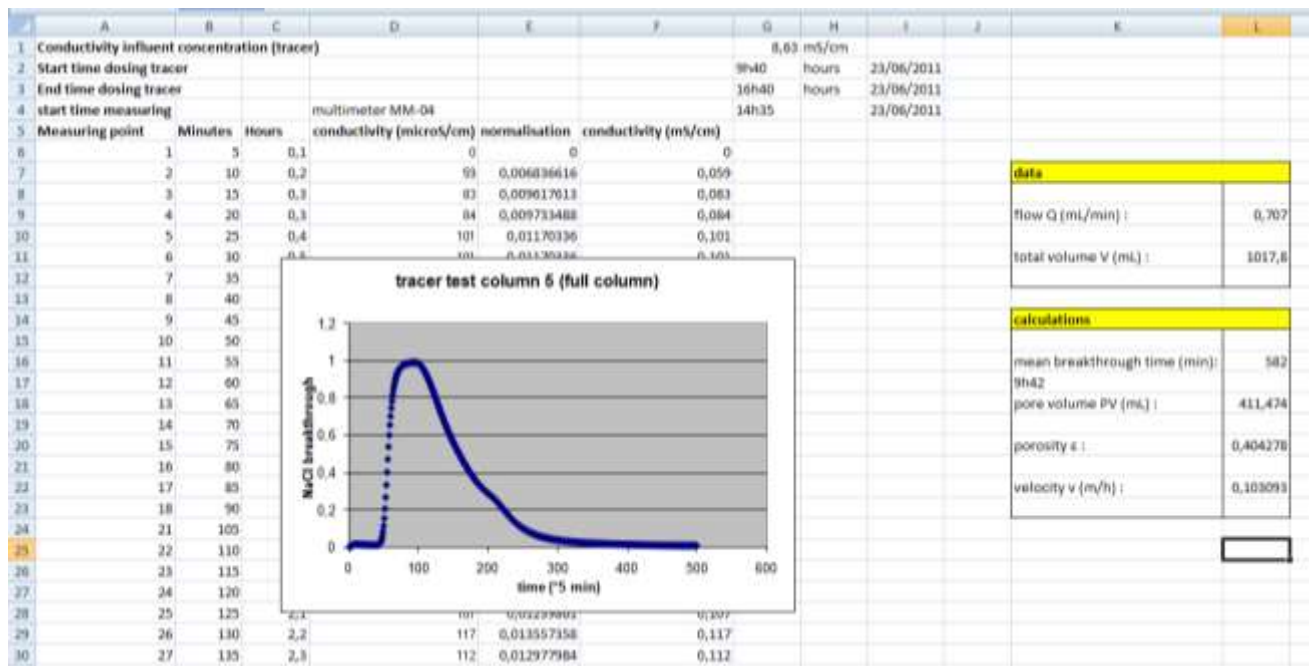


Figure 13 Tracer test column 5

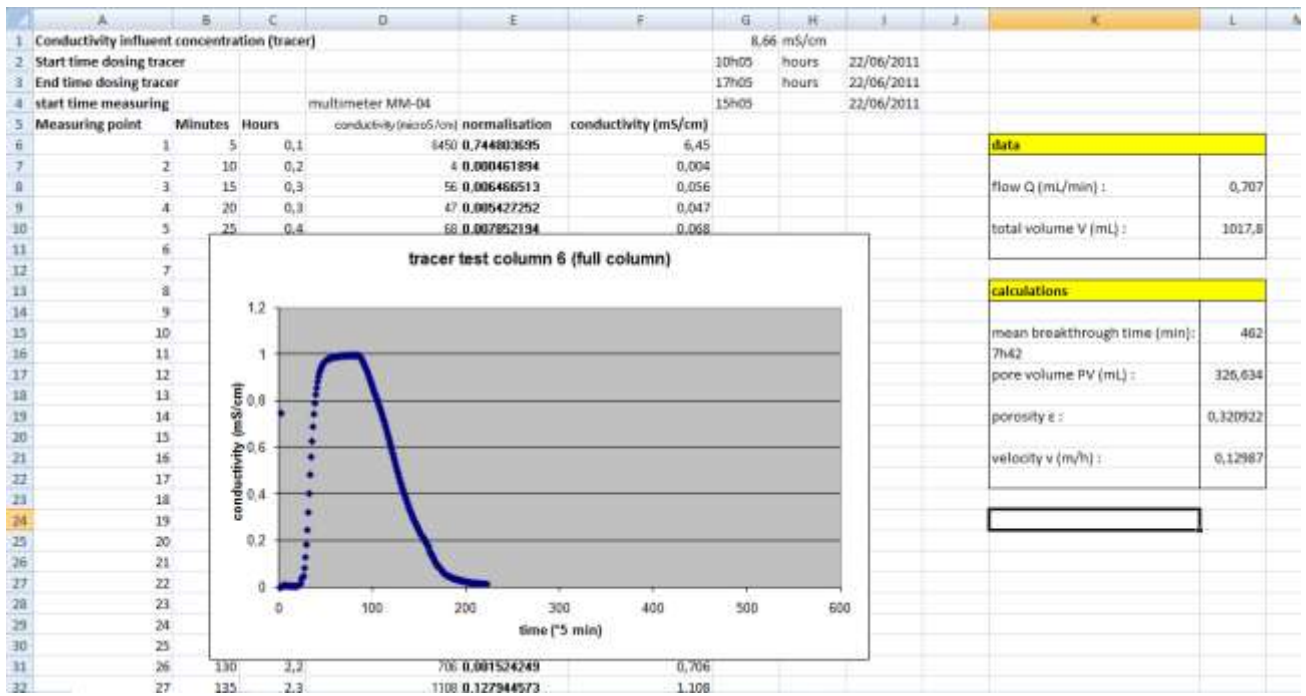


Figure 14 Tracer test column 6

Appendix 5: Pictures of the set-up



Figure 15 Experiment set-up



Figure 16 Conductivity meter and measuring cell



Figure 17 Pump