

Guidelining protocol for soil-column experiments assessing fate and transport of trace organics





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Summary

Generally, the complexity of natural systems and the multitude of factors influencing removal processes on field scale make it highly unlikely to link certain effects observed in the field to one well-founded parameter. Laboratory studies are preferred for this purpose because experimental conditions can be much better controlled. However, lab studies may result in erroneous or irrelevant results if designed or operated inappropriately. The apparent simplicity of constructing soil-columns conceals a number of technical issues which can seriously affect the outcome of an experiment, such as the presence or absence of macropores, artificial preferential flow paths, non-ideal infiltrate injection and unrealistic moisture regimes. This guidelines review the literature to provide practical recommendations. Common design challenges are discussed and best practices and solutions are presented. The information in this review will assist soil scientists, hydrogeologists and environmental professionals in optimising the construction and operation of soil-column experiments to assess the behaviour of emerging organic micropollutants (EOCs) in order to achieve their objectives, while avoiding serious design flaws which can compromise the integrity of their results.

1. Introduction

Fate and transport of emerging organic contaminants (EOCs) in Managed Aquifer Recharge (MAR) systems are often studied in soil-column experiments, since this type of experiment can easily be carried out under controlled conditions. Column tests essentially consist in the percolation of a feed solution through a cylindrical column filled with soil under conditions that are aimed to be representative of the MAR field site. The advantages of soil-column experiments as proxies to field scale studies include improved control over the operation, monitoring and sample collection in ways that would be impractical on site.

Soil-column experiments have the inherent disadvantage of fairly artificial boundary conditions, which might differ significantly from real field conditions for a number of crucial parameters and groundwater constituents, such as flow rate fluctuations, redox conditions, temperature, dissolved oxygen content, among others. They must thus be regarded at best only as an ex-situ representation of a small section of the natural system.

For all this, column experiment must be appropriately designed and operated to reproduce conditions that are prevalent in the MAR system of study by setting correspondingly the adjustable parameters of the column system. Otherwise the column experiment might result in erroneous or irrelevant results not directly applicable to the MAR systems of study.

Definition of soil column: For the purpose of this guideline, a soil column is defined as a discrete block of soil located either outdoor or in a laboratory, which allows control and measurement of the infiltration and which incorporates equipment for the total recovery of the effluent. This is usually achieved by encasing the soil column in a rigid and impermeable shell material, both for structural reasons and to prevent fluid loss.

The report is divided in 4 technical sections (section 4: *column design and setup*; Section 5: *operation*; Section 6: *sampling and monitoring*; Section 7: *Interpretation of results using numerical models*). Following scheme summarises the mind-map of the report and its contents. Each section has been prepared taking into account the phase of the column experiment, from the initial design of the experiment, selection of materials, sampling and sample conservation and interpretation of results using the most advanced numerical modelling. The readers can also be deeper in detail using the references listed at the end of the report.

Preliminary design is the key to the success of the column experiment, and will define the reliability of the obtained results. It is hardly recommended to think about the specific objectives of the experiment, as some of the initial decisions, as the size of the column, the packaging of the material and the start-up and acclimation will be later on discussed jointly with the results of the elimination of organic micropollutants.



Mind-Map of report contents:

How can be simulated field conditions in a column experiment?



2. Objective

The purpose of this document is to review the practical aspects of design, operation and monitoring of a column experiment for the simulation of a MAR system, focusing on the behaviour of EOCs. The review has been done by compiling information from up-to-date published articles from the on-line database Web of Science. The selected peer-reviewed articles have been limited to those exclusively focusing on soil-column experiments assessing the fate of EOCs in MAR systems. Given the novelty of this type of contaminants in such in-situ treatment systems, the number of identified articles focused exclusively on this topics is 20, mostly dating back only from the last 10 years (and mostly from the last 5 years).

With this insight into the present-day practices for the construction of soil columns simulating a MAR system, this review ultimately aims provide soil scientists practical guidance to avoid design flaws and to meet their experimental needs.

Authors remark: This document considers aspects to be taken into account for column design and methodologies oriented to simulate MAR systems where both processes of sorption and biodegradation may occur, as both processes are acknowledged to play their role in the transport (and removal) of EOCs through typical MAR systems. Therefore, only studies with soil-column experiments considering both processes have been compiled and compared. Studies focused on sorption (or leaching) of EOCs on (or from) soils (i.e. considering only abiotic processes) have not been included, because such studies pursuit other objectives than simulating all processes potentially occurring in the subsurface of a MAR site.

While it is true that some aspects of the set-up for both types of experiments may be essentially the same, differences in their design such column size and operation (flow rate, residence time, experiment duration, need for prior acclimatization of microorganisms...) make abiotic-based experiments different enough not to be included in the present review. Moreover, leaching tests have already well-established standard test methods (e.g. ASTM D-4874, NEN 7343).



3. Preliminary considerations before designing a soil-column experiment

Before revising the practical aspects when designing a soil-column experiment, it may be helpful to give an insight into the factors acknowledged to influence the fate of EOCs crossing a MAR system, so that they can somewhat be taken into consideration in the design and operation of the column.

It is well known that EOCs crossing a MAR system suffer from a variety of processes: advection, sorption, biodegradation which in turn depend upon a plethora of factors, including physicochemical properties of the EOCs themselves, their concentration in water, the amount and type of organic carbon source present in the aqueous matrix, pH, the lithology of the soil and its hydraulic and textural properties as well as the load of soil organic matter, saturation conditions, redox state, temperature, microbial environment. The difficulty in interpreting the performance of a MAR system is even increased if, as it often happens, these factors are not only interdependent but also highly transient.

Taken this in mind, it appears clear that reproducing field conditions in a column is not a trivial or easy task and that a reasonable compromise between field-like conditions and practicability (in terms of time, costs, existing knowledge) has to be found so that the obtained results are as reliable and realistic as possible.

In the following, the main considerations that need to be taken into account when designing a column experiment that aim to mimic a MAR system are discussed. These considerations try to answer questions that arise when designing a column experiment, such as:

- How big should the column be?
- Which materials are recommended to minimise bias of observed findings?
- How can the soil be packed into the column?
- How can preferential flow be minimised?
- How can anaerobic or aerobic conditions be reproduced into the column to best mimic the conditions of the MAR of study?
- Should microbial populations within the column be acclimatized prior to the injection of the feed water?
- If so, how long should this acclimatization last?
- How should collected samples be preserved?
- Which parameters are often monitored in the study of EOCs removal through soil passage?
- Which numerical modelling tools are available to experiment results simulation and calibration?

For presentation purposes only, the above considerations have been arranged in four sections, namely: 1) column design and set-up, 2) operation, 3) monitoring and sampling and 4) interpretation of results using numerical models. As aspects described in the different sections may be interrelated, they should not be read or interpreted in a hierarchical or sequential order but concurrently. The published articles reviewed for this document are listed and summarised in the appendix.

4. Column design and set-up

A soil column is characterized as a discrete block of soil encased in a rigid and impermeable shell material through which the feed solution is percolated. Caution must be paid on how this column should be mounted.

Prior to start: Since the behaviour of EOCs in a given MAR system is very site-specific, any simulation with column experiment should start with the gathering of as much as possible information from the site at the proposed location of the MAR system. This information should include data on lithology, climatology, temperature, properties of the aquifer, infiltration/discharge rates, composition of the water to be recharged, type and concentration of the EOC to be removed, autochthonous microbial communities ... This information will be used when deciding practical aspects such as selection of filling material, column dimensions, flow rate, temperature or composition of feed water.

4.1 Selection of column material

For the assembling of soil-column experiments, the recommendation given by OECD (2004) talk about "use suitably inert material (e.g. glass, stainless steel, aluminum, Teflon, PVC, etc.)" for testing chemicals. Despite this general consideration, not all the materials listed are really inert to the EOCs. At least, the material used for constructing the outer shell of the column should fulfil certain physical and chemical requirements. The selected material should be:

- **Rigid**, to ensure that the column offers the structural strength at the desired column size and wall thickness. Among the commercially available candidate materials, stainless steel, galvanized steel and concrete (all available in a wide variety of outer diameters) are often used. Plastics may be another reasonable choice, although their greater flexibility may limit their applications to shorter lengths and/or thicker walls of the column compared to the former materials. Among the plastics most used are PTFE, PE, acrylics and polycarbonates, all commercially available in a variety of outer diameters. Heavy glass tubes have also been used by some researchers.
- Inert, to avoid any chemical interference with any solute and particularly with any EOC. Glass exhibits the least adsorptive or reactive effect with EOCs and its use is preferable. Other commonly used candidate materials are stainless steel and PVC. Plastic materials should be used with caution, as it is known that some EOCs may interact with and be sorbed onto some of them. The most suitable plastics (i.e. exhibiting sorption at lowest degree) are (in descending order): PTFE, HDPE and PP. The use of Pharmed©, silicone, NBR70, Tygon© and LDPE should be avoided. The convenience of one or another material may also depend on the prevalent ionic form for a given EOC of interest and the K_{ow} (characterising the polar character of the molecules). For further details the reader is addressed to Hebig *et al.* (2014).
- Transparent, in order to facilitate visual observations of events occurring within it. In cases where
 a dye tracer is used, it may be desirable that the column shell be constructed of a transparent
 material. If this is the case, choices are limited to glass, polycarbonates (Lexan[™]) and acrylic
 (Plexiglas[™]).
- Impermeable.
- **Compatible** with the installation of instrumentation and/or sampling devices (see section 3.4).

• Resistant to corrosion.

The review of the literature indicates that the four most common materials used for the construction of a column are stainless steel (58% of the experimental setups which were reviewed), PVC (18%), glass (12%), and acrylic (12%).

4.2 Selection of the material for the accessory tubing (sampling bottles and filters)

The requirement of inertity not only applies to the material of the column but also to any other exposed surface of any other material in contact with the solution such as tubes, fittings, connections, filters... These are in most studies made of polytetrafluoroethylene (PTFE). Because PTFE is too stiff to be used through a peristaltic pump, other materials that are more flexible (silicone, Pharmed©, Tygon©) are commonly used.

Due to the diversity of chemical properties among EOCs some of them may interact with materials commonly used in field and laboratory studies like tubes, filters, or sample bottles. Many experimental studies are not aware of this problem and therefore, details about their laboratory materials are often not known or published. In soil-column experiments it is even impossible to conduct blank tests for excluding material – solute interactions. Most critical is that commonly compound loss is solely related to the tested substrate. An addition mass loss of the compounds of interest to the materials used in the setup of such studies is rarely considered. To minimise these errors, some recommendations are given regarding for the type of materials used in the assembling of the column experiment and during the sampling procedure.

Generally, a mass loss > 20% is defined as significant and therefore unacceptable for quantitative investigations. Hillebrand *et al.* 2013 and Hebig *et al.* 2014) conducted a recent study with the aim of the evaluation of: tubing, sampling bottles and filters materials. Regarding their conclusions, the selection of the materials should take into account the following criteria:

- Avoid flexible materials like silicone tubes and Pharmed[©] and Tygon[©] tubes.
- Use if possible amber glass materials
- Discard first fraction filtered (the highest mass loss occurs in the first fraction and the recoveries improve in the following fraction)

Table 1lists the type of materials recommended and not recommended for tubing and sampling soilcolumn experiments assessing EOC behaviour. For fuller details on material compatibility with EOC see Hebig *et al.* (2014). Optionally, and as reported by some of the reviewed studies, tubing, fittings, connections, sampling devices... are sterilized prior to use. This sterilization is carried via either autoclaving or by contacting with a sterilizing agent (ethylene oxide gas, chlorine bleach) for a period of time followed by thoroughly rinsing with sterile water.



Table 1:Recommended and discarded materials for tubing and sampling bottles
Source: Hebit *et al.* (2014). Modified

	Acryl glass	Bold States
	PTFE Polytetrafluoroethylene	
Recommended materials	HDPE High-density polyethylene (HDPE) or polyethylene high- density (PEHD)	
	PP Polypropylene or polypropene	
	Silicone	
	Pharmed©	
Discarded materials	NBR70 Nitrile O ring	
	Tygon©	
	LDPE Low Density Polyethylene	

4.3 Filling materials: characterisation and packing within the column

The soil used for the filling of the column plays a key role in the performance of a lab-scale simulated MAR. Issues related to the material include not only to its nature but also to how it is packed into the column.

With regards to the nature of the soil, it is usual that the soil characterization includes, but is not limited to, texture (% sand, % silt, % clay according to FAO or USDA classification system), porosity, hydraulic conductivity, pH, cation exchange capacity (CEC), organic carbon content, bulk density and water holding capacity. Additional information such as specific surface area, microbial biomass may be helpful for interpreting the results. Original soil from the MAR site of study (optionally sieved (<2 mm) and homogenized) is often preferable because of better representativeness. For simplification purposes, in some studies sand is used to ensure that the flow is evenly distributed as water flows through the column.

With regards to how the soil is transferred and packed into the column, this can be categorized into two types:

4.3.1 Packed (soil disturbed) columns

Packed columns are built using soils generally collected on-site by excavation, optionally screened and homogenized, and finally backfilled and compacted into the column (hence also called "disturbed" columns) ideally with a bulk density similar to that observed in the MAR system of study. A basic assumption of suck packing method is that soil is homogenously packed in a continuum, with no stratifying layers and hence all particles are exposed equally to the water solution. Hence, the distribution of the solution is uniform and preferential flow pathways are avoided. A major advantage of packed soil columns is that their lack of heterogeneities and macropores allows a better reproducibility of bulk densities and dispersivities.

The two main packing methods are:

- Dry packing, which consists in pouring (e.g. with a spoon) discrete soil portions into the column and then mechanically pressing them either by hand or with some type of ram or plunger. The soil portions are thus deposited in small lifts (commonly in the order of a few cm). Lightly scarifying the soil surface after compaction and before addition of another lift is recommended in order to ensure hydraulic connectivity between the lifts. Gentle column vibration can simultaneous be applied to help soil being more uniformly deposited. This procedure is repeated several times until the top of the soil column is reached.
- Wet packing, which consists in either saturating first the soil with an excess of water, and then letting the prepared slurry settle at the bottom of the column or proceeding with a dry packing as described above while the column is flooded from the bottom to avoid air entrapment. As in dry packing, gentle vibration can be applied to help compact the deposited soil. A significant downside to this method is the potential loss of aqueous solutes during the filling process.

A useful measurement for the level of packing is the estimation of the packing rate:

$$n = \rho_b / \rho_s$$

Where ρ_s is the particle mass density, which is the oven-dried mass, divided by the volume of the solid particles, as determined by a water displacement test. Unless great accuracy is required, $\rho_s = 2.65$ g/cm³ is an appropriate estimate for most mineral soils. Following table provide information on common ranges for the two values, which should assist in determining whether a packed soil column has been sufficiently compacted.

Common ranges of porosity and bulk density expected in columns packed with different textured-soils are given in the following Table 2 (Lewis and Sjöstrom, 2010):

Type of soils	Porosity range (%)	Bulk density range (g/cm ³)
Coarse gravel	24 - 36	2.0-1.7
Fine gravel	25 - 38	2.0 - 1.6
Coarse sand	31 - 46	1.8 - 1.4
Fine Sand	26 - 53	2.0 - 1.2
Silt	34 - 61	1.7 - 1.0
Clay	34 - 60	1.7 - 1.0

Table 2:Average range of bulk densities and porosities of typical unconsolidated soils
Source: Lewis & Sjöstrom (2010)

4.3.2 Monolithic (undisturbed) columns

Monolithic columns are built using monoliths extracted whole and intact from the subsurface of the MAR site of study and wholly introduced into the column ideally keeping the native structure and stratigraphy (hence also called "undisturbed" columns). In such a packing method the soil can be tested under conditions as close to actual field conditions as possible.

A large number of techniques for obtaining undisturbed soil monoliths have been reported. These can be divided into two broad groups: drive samplers and rotary samplers. Drive samplers are samplers which are pushed or driven into the soil without rotation, displacing the soil as they penetrate. The volume of soil corresponding to the thickness of the sampler wall is displaced into the surrounding soil, which is either compacted or compressed. This type of samplers generally has a sharp cutting edge at their base to facilitate their penetration into the soil. In contrast, rotary samplers have a relatively thick and blunt cutting surface, which has hard inclusions of tungsten or diamond set into it. The sampler is rotated and pushed (relatively) gently downwards, cutting and grinding the soil away beneath it. More details on how undisturbed soils samples are collected can be found in Lewis and Sjöstrom (2010) and references therein.

Packed columns and monolithic columns have each advantages and disadvantages. Packed columns (which are typically much more homogenous) offer a better reproducibility at the expense of realism, whereas monolithic columns (which are much more heterogeneous) may better reproduce field conditions at the possible expense of reproducibility. Thus, the first type of columns may be useful for assessing and comparing the behaviour of different EOCs under simplified operational conditions, which is often the aim of most studies, regardless the effect that macropores (worm holes, cracks, channels...) may have on this behaviour. With respect to undisturbed columns, however, it must also be taken into account that there is no guarantee that heterogeneities within the monolith sampled are always representative of the whole site. Another significant disadvantage to monoliths is that depending on their size, extracting them can be prohibitively difficult. For more details on column packing techniques and their advantages and disadvantages, the reader is addressed to Lewis and Sjöstrom (2010) and references therein.

Although the repacking of soil columns significantly influences the resulting EOCs behaviour and fate within the column, it has received relatively little attention, and details on it are rarely explicitly reported or explained in published studies. Of the examined studies, only eight of them document the type of soil packing, with all except one running a packed column.



4.4 Column dimensions

An issue that obviously appears first when designing a column experiment is the dimensions of the column. Of course, if a small soil column is used, the representativeness of the column to field applications may be questioned. On the other hand, if a large column is used, the obtained results may be more reliable but the operation of the column can be unpractical at lab-scale. Thus, a reasonable compromise must be found between field-like conditions and practicability in lab-scale conditions.

Ratio of column diameter to mean sediment grain diameter: The column diameter is related with the grain diameters, according the rule of thumb for the "representative elementary volume" (REV), where a REV has the same volume, shape and orientation, regardless of location within the column. REV can be 40 – 100 grain diameters, with experiments for chemistry and microbiology requiring smaller REVs than flow experiments (Mioska, 2006). Therefore, the calculation of the column diameter, required to accurately represent the porous media, is as follows:

G_s = grain size diameter REV = 40 (for a chemical experiment) Column diameter = G_s x REV

Ratio of column length to column diameter: Ratio of column length (L) to column diameter (D) has been reported to be at least 4 (Fand and Thinakaran, 1990; Bergström, 2000).

Reasons that can modify these recommendations are lengthening the column to provide long residence time within the column to better simulate the MAR site of study, or enlarging the column diameter and/or length to facilitate the collection of adequate water sample volumes if required by the analysis of the EOCs of interest (see section 6) without compromising the hydraulics of the column.

The literature review shows that column dimensions usually were in the range of 1.5-2.5 m and 0.1-0.2 m for the respective height and diameter.

4.5 Inflow distribution

It is well known that when feed water enters and exits the column through an orifice with a radius less than the column radius, a potential issue of transversal dispersion might result from the inlet and outlet point, giving a non-uniform profile front. The length of the column affected by this non-uniform profile front can be on the order of the column radius. Hence, influent must be somehow distributed uniformly over the column section.

This is commonly achieved by placing a layer of an inert and highly permeable material immediately after the inlet point. This highly permeable layer acts as a buffer zone allowing the influent to move laterally from the inlet point and saturate the entire width of the soil column. The most common materials used for this purpose are gravel, sand and glass or stainless steel beads.

The inflow distribution in columns using treated wastewater (typical MAR application) may be complicated since water often contains particular organic compounds (depending on pre-treatment processes) blocking pores. In addition, biofilm may grow and block the inflow system. As a consequence, the inflow system has to be accessible for cleaning. In this context, it may be good to point out, that tubes and equipment of the inflow and outflow should be arranged to remove them easily for cleaning – if required. Depending on the experimental runtime a removal of biofilm from the topsoil might be needed, too. Tubes should be also

covered in order to reduce algae growth. In this specific context, a layer of inert material may be also problematic as this layer can react as a filter media which is not part of the natural system and may lead to a transfer of reactive processes from top soil to the inert material.

4.6 Soil confinement within the column

The filling material of a column (the soil plus the gravel layer if added) needs to be hold by a rigid material, which also prevents fine particles escaping or flushing from the column and eventually migrating into the influent and effluent tubing. This structure often consists in a coarse and/or fine-mesh screen or net made up of nylon or stainless steel. Perforated plates and acrylic wool are alternatives also commonly used for this purpose. To avoid accumulation of sediment in the lower part of the column it is recommended to adapt flow velocity slowly from very low to higher rates in order to stabilize the sediment.

4.7 Preferential flow paths and its minimisation

Avoiding preferential flow paths in packed columns (or unnatural preferential flow paths in monolith columns) is a key design issue associated with soil columns. The existence of preferential flow paths leads to a portion of the influent water traveling more quickly through the column (resulting in a lower residence time) and therefore significantly biasing any experimental result.

Preferential flow paths can be originated from:

- **Sidewall flow**, which refers to the preferential flow occurring in the proximity to the rigid edge of the column. Increases in the velocity of the flow adjacent to the wall of up to 1.11 and 1.45 times higher than that of the flow in the center of the column has been observed (Sentenac *et al.*, 2001).
- **Macropore flow**, which refers to any preferential flow due to heterogeneities within the porous medium, including cracks, root holes, wormholes and macropores. While this type of heterogeneities is expected, in more or less extent, in monolith-type columns, they may also be present in apparently homogeneous packed soil columns.
- **Fingering**, which refers to the preferential flow taking place as a result of the wetting front instability. It may occur for a number of reasons, including changes in hydraulic conductivity with depth and compression of air ahead of the wetting front. Fingering is most likely to occur in soils that are predominantly sand and that are initially extremely dry.

Various strategies have been applied in previous studies to minimise sidewall flow, including:

- Ensuring a column diameter-soil grain diameter ratio greater than 40 (Fand and Thinakaran, 1990; Bergström, 2000) (see section 4.4).
- Roughening the sidewall, for instance by:
 - Embossing relief rings or installing annular rings on the inner side of the column wall.
 - Gluing sand to the inner side of the column wall.

4.8 Prevention of disturbances from environmental light

After filling, the transparent parts of the setup (including the column if it is made up of a transparent material) are usually wrapped with an opaque material (commonly aluminum foil) to simulate light conditions encountered in the subsurface and prevent the growth of photolithotrophic microorganisms and photodegradation of EOC resulting from exposure to light.

5. Operation

5.1. Saturated/unsaturated conditions

Soil-column experiments fall in two broad categories: saturated and unsaturated conditions.

5.1.1. Saturated conditions

Soil columns operating under saturated conditions have their pores entirely filled with water (i.e. they do not contain any air) at a pressure greater than atmospheric. Saturated conditions can easily be implemented experimentally in both up and down flow modes. In downflow mode, water moves downwards, usually draining through the column by gravity. In upflow mode water moves upwards, generally by pumping it with a (variable speed peristaltic) pump or by placing the feed tank above the platforms on which the column is fixed.

In both operation modes, saturation is achieved by ensuring an overlying layer of water above the surface of the bed soil maintained using a constant head reservoir (e.g. allowing the overlying water to overflow into a drainage system). An advantage of the upflow mode is that as long as water moves from the bottom to the top it displaces the air in the soil pores by water and hence saturation conditions are better achieved. A vacuum can additionally be applied to the top of the column to facilitate this displacement of air through the top of the column and prevent the entrapment of air bubbles within the soil bed. Alternatively, the bed soil can be pre-saturated with a highly water soluble gas (e.g. CO_2) other than air allowing the subsequent water solution to fill all the soil pores avoiding thus undesirable bubbles of air (see also how to achieve anaerobic conditions below). For fuller accounts on saturation methods the reader is addressed to Lewis and Sjöstrom (2010) and Shackelford *et al.* (1991).

It would be good if you could point out that rain simulator devices are usually used for column experiments,

5.1.2. Unsaturated conditions

Soil columns operating under unsaturated conditions are characterized by containing both air and water in their pore spaces. This type of operation may thus better mimic MAR systems implemented in unsaturated vadose zones, however, it does not mimic most MAR systems such as ponds or flooding planes. To mimic MAR systems such as infiltration ponds or pitches top soil should be completely covered with water in order to prevent gas exchange in the top soil (unlike sprinkler systems).

Unsaturated conditions are usually applied in down-flow modes by applying the feed solution continuously to the head of the column, using a sprinkler, to specified water contents by modifying flow rates at the top of the column and/or by applying a constant suction at the bottom end of the column.

Another approach of running a column under unsaturated conditions consists in applying repeated wetting and drying cycles over a long period of time. Such flow-no flow-flow sequence can be achieved by means of a "rain simulator device" to deliver the feed solution at the desired flow.

Because running a column under saturated conditions is easier from a practical point of view than under unsaturated conditions, soil-column experiments carried out to investigate the EOCs behaviour through a simulated-MAR system are mostly run under saturated soils (82% of the reviewed literature).

5.2. Flow rate and residence time

A crucial property to study in a soil column is water residence time. Residence time is the average time that the feed solution spends in crossing the whole column, and it essentially depends upon the volume of the soil bed, its porosity and flow rate of the solution. The importance of residence time relies on the fact that the extent of most processes occurring in a filling medium such as the subsoil (sorption, biodegradation...) depend on the time given for the process to evolve.

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Residence time in the soil column should be selected to mimic that of the MAR site of study. This implies that, for given column dimensions, flow rate through the column during the experiment should be specified so as to match the average residence time at the MAR site as much as possible.

Residence time can be determined by measuring the breakthrough curve of an injected conservative tracer and using the equilibrium convective-dispersive equation assuming one-dimensional, steady-state flow in a homogeneous soil. The tracer is usually mixed in a small volume of injectate and injected as rapidly as possible (a spike of tracer) to simplify test analysis. It is assumed that the tracer is a nonreactive species and, as such, it does not sorb onto soil particles or column walls nor suffers from any type of degradation or transformation, and therefore it is useful to confirm the hydrodynamic properties of the soil column. This assumption implies that the mass of tracer injected equals the mass recovered by integration of the concentrations over the test duration. Tracer recovery should ideally approach 100%. If the residence time does not approach the desired value, then the experimental conditions should be changed prior to the start of the experiment, for instance by increasing the average linear velocity of the infiltrating fluid or by modifying the column dimensions (i.e. lengthening/shortening the height/diameter of the soil column). The most common tracers used are Cl⁻ and Br⁻.

5.3. Redox conditions

Together with residence time, redox conditions also play a key role in the biodegradation within a MAR system. It has been reported, for instance, that sulfamethoxazole (SMX) is well degraded in long-term soil-column experiments under aerobic conditions (with half-life between 1-9 days), but less under anaerobic conditions (half-life around 16 days) (Muller *et al.*, 2013).

It is thus of paramount importance to identify the MAR of study as to be aerobic or anaerobic and to translate these conditions into the column experiment. It is generally understood that aerobic (or oxic) environments are characterized by redox potentials above +200 mV, anoxic environments by redox potentials between -200 and +200 mV, and anaerobic environments by redox potentials below -200 mV (Maeng *et al.*, 2010).

Redox conditions are tightly related to the degree of saturation discussed in section 5.1. In the saturated zone of an aquifer, dissolved oxygen tends to be limited and thus anoxic-anaerobic conditions usually prevail. This is the case where there is a hydraulic continuity between the recharge point and the aquifer. On the contrary, the unsaturated zone is characterized by the intrusion of air and thus the existence of aerobic processes.

5.3.1. How to achieve anaerobic conditions

Achieving anaerobic conditions within a column first implies that the column is fully saturated (i.e. that no bubbles of air are entrapped within the pores of the soil bed) (see subsection 2.1.1). A series of measures can be undertaken to this end:



- 1) As already described in the achievement of saturated conditions, carrying out an initial saturation of the column under an upflow mode (i.e. from the bottom to the top of the column) help ensuring total saturation of the system. Upflow favours the displacement of air bubbles in the soil pores as long as feed water moves from the bottom to the top of the column. A vacuum can additionally be applied to the top of the column to facilitate this displacement of air through the top of the column and prevent the entrapment of air bubbles within the soil bed.
- 2) Once the column is saturated, maintaining flow circulation for a period of time is desired, as this will kelp any entrapped air dissolve and disperse in the pore liquids.
- 3) Alternatively, flushing the soil-column with a highly water soluble gas (e.g. CO₂) prior to saturation will also help achieve anaerobic conditions, as the high solubility of CO₂ in water (several orders of magnitude higher than that of the O₂ present in air) allows the subsequent water solution to fill all the pores in the column avoiding thus undesirable bubbles to accumulate in the pore space.
- 4) Keeping the feed solution in anoxic conditions will help maintaining anaerobic conditions within the column. This can be achieved by sparging the feed water tank with high-purity Ar or N₂ to remove any dissolved O₂, or by placing the feed water in a sterile gas-impermeable and collapsible bag to prevent headspace as the bag empties out.
- 5) Lengthening the column may also be an easy way to help create anaerobic conditions, as it is thus more difficult for O_2 to penetrate the whole soil bed. Modifying the column dimensions needs however to take into account the effect on residence time (see section 5.2).
- 6) If an active heterotrophic biomass is found in the column, applying an organic carbon source will also promote reducing conditions. This organic source can be applied either as a dissolved compound in the feed water or as a solid as part of the initial filling material of the column. The main disadvantage of this approach is that applying a carbon source may alter the composition of the feed water.
- 7) A second measure based on the use of an external reactive material consists in installing a preliminary column filled with a (reductive) reactive material to remove any O₂ from the feed water. Fe⁰ grains have been used for this purpose in studies focused on other treatment scenarios different from MAR simulations. In this case it is recommended to disperse the Fe⁰ grains with sand to avoid permeability losses due to the precipitation of the corrosion products (basically iron oxyhydroxides). Analogously with the addition of an organic source, a main disadvantage of this approach is that contacting the feed water with Fe⁰ may alter its composition.
- 8) A last, and costly, method to help achieve anaerobic conditions is to place (at least temporally) the column set-up within an anaerobic glovebox under inert gas headspace at slight overpressure.

5.3.2. How to achieve aerobic conditions

Achieving aerobic conditions within a column implies that somehow dissolved oxygen is present within the column. This is commonly accomplished by the continuous aeration of the feed solution tank with compressed air to maintain high levels of dissolved oxygen (DO) in the feed water.

5.4. Spiking feed water with EOCs

EOCs present in the water used in MAR systems are usually detected at very low concentration (at the ng/L level). Feeding soil-column experiments with such water poses an evident analytical challenge concerning on how to reliably analyse such low concentrations.

This problem can be overcome by collecting large volumes of aqueous samples for further preconcentration prior to analysis. This practice however faces two problematic issues: on one hand preconcentration of samples is often a potential further error source, and on the other hand collection of large volumes is not always possible without strongly altering hydrodynamics within the column.

A common practice to overcome drawback consists in spiking the feed water with the studied EOCs to the μ g/L or mg/L level. In this way, more significant and directly measurable concentrations for the analysis are assured and also sample volumes are reduced.

The practice of spiking, however, is not free either from drawbacks. It has been observed that EOCs at concentrations different than those encountered in natural systems may alter their removal. For instance, Baumgarten *et al.* (2011) reported that increasing sulfamethoxazole (SMX) concentration in the influent by one order of magnitude resulted in a significantly improved removal.

Dosing higher EOCs concentrations than present in the environment could significantly overestimate the biodegradation rates. Therefore, dosing should be avoided or, if applied, minimised as much as possible to better mimic MAR site conditions.

5.5. Temperature control

Temperature also plays an important role in the behaviour and fate of EOCs through a porous medium. Its effects on the EOCs occurrence are manifold:

- 1) It alters the kinetics of reactions, as higher temperatures deliver more energy into the system accelerating the reaction rates.
- 2) It may change redox conditions, as oxygen solubility increases at lower temperatures. In turn, the developed redox conditions may modify the behaviour of the EOCs present in the system.
- 3) It can stimulate (or hinder) microbial populations and biological processes, favouring or retarding the biodegradation of certain EOCs.

It must be beared in mind that temperature may vary not only from one site to another but even in a given site at different moments of a day. Some column-based experiments are run outdoors where air temperatures fluctuates similarly to the MAR system (with maximum temperature gradients between night and midday), while others are run indoors in the laboratory at temperatures oscillating in a narrower range. Fewer columns are operated at controlled temperatures. In these latter cases an insulation cover or wrap is applied around the column or, alternatively, an elastic pipe through which a cooling or heating fluid circulates is coiled around the column to maintain column temperature constant during the experiment.

5.6. Start-up acclimatisation

A critical issue that is not always adequately addressed in soil-column experiments based on biotic processes deals with the establishment of favourable conditions for the biodegradation to evolve. It must be kept in mind that the presence of microorganisms (in terms of quantity, composition...) at a specific site

is dependent on a multitude of environmental variables. How to reach the same environmental conditions inside the experimental columns in a reasonable amount of time emerges as a crucial issue.

Even if site soil is used with caution to avoid disturbances when filling the column, it is evident that initial environmental conditions within the column will differ from those prevailing in the site, due to the inherent variations in the initial phases regarding temporal air consumption, evolution of redox conditions, adaptation of the microbial community... and that a certain period of time will be required to eventually reproduce the underground environmental conditions prevailing in the MAR site of study (referred to as the "time-lag").

With this in mind, which moment should be considered as the initial time of the experiment (i.e. for the routinely monitoring to begin)?

In most cases, and because the aim of the study is to reproduce steady-state operating MAR sites, the initial time of experiments is considered by many studies to be the time when steady-state conditions have first been achieved (evidenced by near constant parameters in effluent samples). Unfortunately, this criterion is not always practical, because the time-lag may be too long (weeks, months or even years) and therefore a reliable performance of the soil columns may be not obtained if laboratory studies are not operated for sufficient time.

The lag-time can be partially mitigated by reducing the column dimensions (i.e. lowering scale), but this should be done by taking into account the considerations discussed above in sections 4.4 and 5.2). In general, the more different the initial conditions within the column compared to field (due to the fact that e.g. pristine soil is used instead of site soil) the longer the time-lag.

A second issue relates to whether biomass adapted in the column differs (in terms of amount of biomass, microbial activity and community structure) from that in the aquifer of the MAR site. It must be taken into account that microorganisms do not live in isolation but in communities in which they interact and may cooperate in the biodegradation of EOCs. Therefore, reproducing a complex consortium of microorganisms, and in short times, is not an easy or trivial task.

Preconditioning the column prior to the start of the experiment with the purpose of accelerating the acclimatization of a consortium of microorganisms has been carried out in the revised literature in the following manners:

- By employing soil and feed water from the MAR site itself as an attempt to rapidly inoculate the column with native microorganisms of the MAR system. This action, together with the adjustments of operational conditions to better mimic the field site, may help minimise time-lag.
- By spiking feed water with a media containing additional elements (KH₂PO₄, K₂HPO₄, Na₂HPO₄, CaCl₂, FeCl₃, NH₄Cl, MgSO₄), nutrients and vitamins not necessarily present in the original site water but helpful to promote and stabilize the population of microorganisms. Once the stable conditions are reached, these additional elements can be gradually removed.
- By inoculating the column with an enriched solid source of microorganisms (e.g. sludge from sewage treatment plant or sediment rich in microorganisms) not necessarily present in the native site soil.
- By temporally modifying the operation conditions of the column. For instance, the column could be left in stagnant conditions for a certain period of time or be operated in recirculation conditions to help grow and stabilize the population of microorganisms until steady state conditions are observed.



- By inoculating the column with an acclimated culture towards the EOCs of interest (i.e. spiking the culture with EOCs of interest and, optionally, with a nutrient solution, organic matter and/or specific electron acceptors).
- By incubating the columns for a certain period of time at increased temperature to favour biological activity. Once the stable conditions are reached, temperature can gradually returned to the initial value.

5.7. Control experiments

Although rarely performed due to associated costs, separate control soil-column experiments should be performed as part of the quality assurance/quality control (QA/QC) when investigating biodegradation. These additional experiments can help correct EOC removal via other processes (e.g. sorption). These may include abiotic control, in which biological activity is inhibited by autoclavation or the addition of a biocide (e.g. sodium azide, mercuric chloride) and allows identifying which fraction of EOC is removed by other processes than biodegradation. Blank control, in which soil is absent too so that it allows account for losses of EOC due to the column material, is almost never considered due to the associated costs.

6. Sampling and monitoring

Proper sample collection and storage are crucial factors in any column experiment. Failure to properly collect and preserve a sample can invalidate any results subsequently obtained on a well-designed and well-operated column.

Issues that need to be carefully addressed in the sampling and monitoring include the following: sample representative and size, number of samples, sample collection frequency, sampling location and methods, sample preservation and sample manipulation during analysis.

6.1. Sample representativeness and size

The sample (either aqueous or solid from within the column) should be representative of its location and be free of any contamination arising during its collection. The amount of sample to be extracted is dictated, on the one hand, by the quantification limits of the analytical method. It must be bear in mind that some processing procedures prior to the analysis may be needed to isolate targeted EOC from each other and potential interferences, resulting in larger sample size requirements. On the other hand, the maximum amount of sample is dictated by the dimensions of the system, in the sense that large samples can alter the hydrodynamics and chemical conditions within a comparatively small column.

6.2. Number of samples

The number of samples collected over the study is a reasonable compromise between the number of samples which can be taken, defined by sample availability and funding, and the degree of precision required of that can be tolerated by the study objectives. When collecting samples, the amount of uncertainty associated with the sampling decreases with increasing number of samples.

6.3. Sample collection frequency

The appropriate sample collection frequency should adequately define the performance history to enable interpretation of the results. This implies collection at varying time intervals, with sampling frequency being highest when conditions (e.g. DO contents, redox conditions, EOC concentrations, trace concentrations if a tracer test is being conducted...) are expected to change rapidly. Of course, frequency may need to be modified as the experiment proceeds depending on the performance of the column.

6.4. Sampling locations and methods

6.4.1. Water samples collection

Evaluating the removal of EOCs by a soil column requires at least analysing the EOCs concentration in the feed water (inflow) and the treated water (outflow). The collection of samples from these streams is easy by means of an adequate collection device (e.g. T valve) for the collection.

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Some studies also extract pore water at different heights of the soil column to maximise the interpretability of its performance (i.e. by monitoring the EOC concentration profile and identifying where EOC removal is occurring most to gain information on how fast is the removal). This sampling is achieved by strategically placing along the length of the column a number of lateral sampling ports equipped with gastight and watertight fittings. The ports are designed to extract water from the inner edge of the column or, alternatively, from the centre of the column cross section by protruding a tube from the wall into the centre of the column. In this latter case, caution should be taken to minimise disturbances of flow by the inserted tube. An advantage of extracting core pore water samples from the center of the column is that the sample is a flux-weighted average of the solution and therefore more representative than the fluid adjacent to the wall of the column.

For the withdrawal of pore water, the ports are usually fitted with a valve with a luer lock adapter or a rubber septum to allow sampling with the aid of a syringe. The sample is then drawn very slowly to minimise any disturbance in the flow. Alternatively, and for saturated columns only, extraction of pore water can be done by clamping the column outlet tubing closed while keeping the influent peristaltic pump operating and opening the chosen lateral side port. Fluid is thus driven to the height of the side port and discharged passively into a collection vial, while the saturated section of column (above this height in upflow mode or below this height in downflow mode) is held static by the back pressure of the closed effluent tubing. This method eliminates the need to apply suction to the side ports in order to obtain samples and thus provides a more representative measure of flux-weighted fluid chemistry at each location.

Regardless the method used for its extraction, water samples sensitive to atmospheric exchange should be collected not by passively discharging it into a vial but using a degassed glass syringe with a low-friction plunger. Sampling the effluent or soil solution in such a way that the column remains unsaturated is challenging. The pressure potential in unsaturated soil is always negative due to capillary and other forces, becomes zero at the water table and increases below the water table and increases below the water table due to the pressure from to overlying water. This means that suction must be applied to unsaturated soil in order to extract the pore water. When choosing a rigid porous material for an experimental apparatus, the bubbling pressure of the material must be considered. This is the maximum suction that can be applied to soil water by a rigid porous material before air will begin to enter the plate instead of pore water. Table 3 shows the bubbling pressures and operational suction ranges of the most common materials used for suction plates. The interested reader is addressed to Lewis and Sjöstrom (2010) for further details.

The key to obtain the most representative soil water samples is to apply a suction equivalent of the ambient matric potential which exists at the same depth in the soil. However, higher-than-ambient suctions will allow a faster collection of leachate. While this will create an artificial flow field within the column, this may be an acceptable trade-off depending on the experimental objectives, particularly in soils which have very low permeabilities.

Porous material	Maximum pore diameter (μm)	Bubbling pressure (bar)	Operational suction range (bar)
Ceramic	1.1 - 2.1	>1	<0.6 - 0.8
Stainless steel	0.6 - 14	0.2 - 0.5	<0.2 - 0.5
PTFE	25 - 35	0.07 - 0.2	<0.07 - 0.2
Quartz	6 - 7	0.4 - 0.5	<0.4 - 0.5
Fritted glass	6	0.5	<0.5

Table 3:Porous plate material characteristicsSource: Lewis & Sjöstrom (2010)

Analysis of the other parameters (pH, Eh, electrical conductivity, T...) can be done either in-situ with invasive instrumentation inserted in the soil column itself or, as mentioned above for samples sensitive to the exposure to the atmosphere, ex-situ in a sealed flow-through cell where the probes are inserted. Pressure gages or transducers can also be inserted into the column if hydrodynamics is also studied beyond the EOC removal. Whatever the inserted measure device is made of, it must be water-tight to avoid any leakage and gas-tight to avoid any introduction of oxygen, which might perturb local equilibrium and/or insitu Eh measurements.

Core pore water samples should be small enough to avoid disturbances of the flow pattern within the column (see section 4.5) but large enough for a reliable analysis of the EOC of interest. Furthermore, sampling should be started at the top of the column and be continued to the lower part to again minimise flow pattern within the column.

Unfortunately, little guidance is available in the literature with respect to structural considerations for sampling ports or instruments beyond ensuring that they are water-tight and gas-tight.

6.4.2. Soil samples collection

For some of the examined published studies soil is also analysed together with aqueous samples. In these cases, soil is collected only after the experiment is completed and the column dismantled. The soil is then sectioned into slices so that a profile of the analysed parameters (EOC concentration in the soil, biomass on soil measurements...) can be determined over the entire length of the column. None of the reviewed studies reports extraction of soil cores during the operation of the column. Approaches of soil cores extraction from within a column in operation applied with other filling materials (e.g. granular activated carbon) under quasi fluidized conditions (e.g. during a backwash of a column) seem difficult to perform with hard and compacted materials like soils.

6.5. Sample preservation

Because immediate sample analysis after collection is not always possible and various processes such as chemical transformation, biodegradation, adsorption or volatilization may take place even during relatively short sample shipment and storage times resulting in losses of EOC, caution must be paid on the proper sample storage conditions. Failing to preserve the sample properly can render the sample collection useless.

Sampling of EOC from a soil column is mostly carried out according to existing tradition or standard laboratory protocols, i.e. by collecting a sample by hand directly into the sample container. Aspects to consider for a proper stabilization of the sample are:

- Temperature and UV radiation: samples are usually stored chilled (<4-6°C) until analysis to prevent alteration. If EOCs are potentially sensitive to UV radiation, amber-coloured bottles are used to prevent photo degradation.
- Material of the storage container: samples must be stored within containers made of an inert material to avoid any adsorption or desorption from/into the collected samples. The most appropriate materials are acryl glass, PTFE, HDPE, PP, stainless steel and aluminium. In the contrary, the use of Pharmed©, silicone, NBR70, Tygon©, and LDPE is not recommended. Since plasticisers and flame retardants are commonly targeted EOCs, plastics containing high levels of these chemicals should not be used. More accounts on materials compatibility with EOC can be found in Hebig *et al.* (2014).

Addition of chemicals: additives may be helpful as stabilizing agents (e.g. biocides to inhibit biological activity such as sodium azide). Thus, sample stabilization methods are applied to minimise concentration changes between sampling and analysis. These methods are most common in inorganic analysis and include addition of chemicals, cooling, pH-modifications and choice of storage container. To inhibit biological degradation in water samples containing EOCs, the following methods are the most applied (see Table 4).

Stabilization method	Description
Sodium azide (biocidal additive)	Sodium azide (NaN ₃) is frequently used in laboratory studies, especially to produce abiotic reference samples in degradation experiments. Sodium azide concentration: 1 mL of dissolution of sodium azide in a final concentration of 5 g/L NaN ₃ for each 100 mL sample of water.
Copper sulphate (biocidal additive)	Copper sulphate pentahydrate ($CuSO_4 \cdot 5H_2O$) is particularly applied for the stabilization of phenols and phenolics. Copper sulphate concentration: 1 mL of dissolution of Cu in a final concentration of 1 g/L CuSO ₄ for each 100 mL sample of water.
Solid phase extraction (SPE)	Reduces the water activity, so the microbial growth can be controlled

Table 4:	Stabilization methods for sampling conservation	
	Source: Hillebrand et al (2013)	

In cases when the immediate sample analysis is difficult or impossible (e.g. remote areas) or the sampling is intended to be realized over longer periods (e.g. weekly-integrated sampling) the storage conditions become highly relevant. Especially for easily degradable compounds, their reliable determination largely depends on proper sample storage conditions. Various processes such as microbial degradation, chemical reactions, volatilisation or adsorption may occur even during relatively short sample storage times resulting in low analyte recoveries.

According to the studies of Hillebrand *et al.* (2013), which evaluate the efficiency of the 3 methods described, the following recommendations for sample preparation and storage can be derived (from best, to worst alterative):

- Immediate analysis of samples (before 48 hours after sampling)
- SPE directly after sampling with SPE cartridge, store as cool as possible.
- Stabilisation of the samples with sodium azide and store as cool as possible.
- Storage of non-stabilised samples as cool as possible.
- The storage time should be minimised
- Due to the high number of adapted micro-organisms, the stabilisation of samples coming from waste water effluents is most urgent.
- For groundwater and drinking water samples, which are known to be less loaded with microorganisms, much less alteration of the analytes is expected. Hence, the analysis or stabilisation of respective samples need to be performed the least urgent.

Advanced sampling methods have been developed for cases where EOCs concentrations are very variable and/or very low, isolation of targeted EOC is required to avoid interferences or conventional collections does not guarantee a proper preservation of the sample. In these cases, extraction, pre-concentration and purification steps may be necessary prior to analysis. Among the most widely reported methods are the liquid-liquid extraction (LLE) and solid phase extraction (SPE), which are based on tailor made materials able to selectively retain the EOC of interest. Fuller accounts on these sampling methods can be found in Alvarez and Jones-Lepp (2010) and Gros *et al.* (2008) and references therein.

6.6. Sample manipulation during analysis

The requirements that need to be fulfilled by the sample container material also apply to any material in contact with the sample during its analysis, including filters used for sample filtration prior to analysis. It has been observed that even if the contact time during a sample filtration is often too short for sorption onto the filter material to take place, significant losses of certain EOCs (loratadine, fluoxetine, sertraline, and diuron) can occur. This problem can be overcome by filtering and discarding a significant volume (>25 mL) of aqueous sample before collecting the sample. Regarding filter materials, some recommended materials have been recommended in Hebig *et al.* (2014) and summarised in Table 5:

Table 5: Recommended filter materials Source: Hebig et al. (2014). Modified

		Cellulose – Acetate (CA)	
	Filter papers	Polycarbonate (PC)	(July)
Recommended		Fiber Glass	
filters materials		Regenerated Cellulose- Acetate (RCA)	
	Syringe filters	Hydrophilic Nylon	Rente Street
		Regenerated Cellulose	

6.7. Monitored parameters

6.7.1. Biodegradation-related parameters

The observed removal of EOCs, if any, by its passage through the column can be caused by various processes such as chemical transformation, biodegradation and adsorption. It is thus essential to determine the contribution of each process to the EOCs removal, in particular that of biodegradation, as it is the only irreversible means of contaminant reduction. However, there is no reliable method of directly quantifying in situ biodegradation of specific compounds in a given system.

A number of approaches based either on chemical or microbiological parameters are used to "prove" biodegradation. Some are well established and included in several recommendations (e.g. USEPA recommendations for the monitoring of natural attenuation in field sites), while others are recent and still at their early ages for routine application. They consist in:

- 1) **Demonstrating a decrease of EOC concentrations** along the water flow path through the column. While such decrease provides evidence that removal is occurring within the column, restricting the investigation only to the monitoring of EOCs concentrations may not be conclusive enough, because other processes such as sorption may also occur.
- 2) Confirming the presence of EOC-degrading microorganisms within the column (more specifically on the filling material). These microorganisms with biodegradation potential can originate from the soil itself (if it is collected from the field site) or from further inoculation with enriched material and/or feed water (see section 4.3). The microbiological monitoring parameters include number of total organisms (e.g. plate counts, most probable number (MPN) counts, direct DAPI counts...), number of specific organisms (e.g. counts on selective plates, MPN determinations with specific substrates...), live/dead cell counts...
- 3) Analysing biochemical parameters related to cell metabolism and activity (such as adenosine triphosphate (ATP), dehydrogenase activity, volatile fatty acids.... but also DNA, mRNA, rRNA analyzed by means of molecular techniques such as PCR or fluorescence in situ hybridization).
- 4) Monitoring changes in bulk parameters such as redox potential (Eh), total organic carbon (TOC), nutrients (N- and P- compounds) and terminal electron acceptors (TEA), as these parameters can be useful in identifying microbial processes occurring within the column. The value in Eh, the availability of TOC and nutrients and the consumption/production of oxidants/reductors can give insight into the type(s) of biodegradation processes related with the decrease of EOCs concentrations.
- 5) Detecting metabolites specific for certain degradation pathways (metabolic biomarkers or signature metabolites), giving evidence that biodegradation is active in the column. These biomarkers should be intermediate products of the degradation pathway and highly specific to the process being monitored, readily biodegradable so that their presence indicates recent activity, not earlier degradation that has already ceased, and not compounds that are common products of many metabolic processes (e.g. short-chain fatty acids). Identification of metabolites is however often difficult because of their trace concentrations and difficulties in isolating and reliably analysing them.
- 6) Analysing stable isotope composition of individual contaminants in water samples, taking advantage of the fact that microbially mediated redox reactions are capable of generating large stable isotope fractionation based on the higher reactivity of lighter isotopes.

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6.7.2. Additional parameters to monitor

Natural organic matter (NOM) fractionation

NOM is ubiquitous in aquatic ecosystems and present to a certain degree in the feed water of any MAR system. It comprises a heterogeneous mixture of organic compounds with very different physicochemical properties, including, humic and fulvic substances, proteins, aminoacids, lipids, polysaccharides, biopolymers, among others.

NOM content is expressed through a wide array of parameters such as total organic carbon (TOC), dissolved organic carbon (DOC), UV-absorbance at 254 nm (UV254), colour or KMnO₄ number. Comparison among these parameters shows, however, that they yield different results with no univocal relationship between them and, in practice, none of them alone is sufficient to predict the behaviour of NOM in a given system. The reason of such variability is that these surrogates do not take into account the different constituents of NOM, which do not necessarily react in the same way or degree within a MAR system. For instance, some organic fractions may affect differently than others the degradation of EOCs by serving as a co-substrate in microbiologically facilitated transformations. Characterizing such NOM contents as long as water flows through a MAR system (or through a column mimicking it) may help understand which organic fractions are preferentially removed.

A variety of methods have been developed to characterize NOM. Current approaches focus on grouping organic compounds into fractions according to their physicochemical properties such as hydrophobicity, molecular weight (MW), etc. The isolation of such fractions rely on adsorption/desorption on resins, membrane filtration, fluorescence excitation emission matrices and high-performance size exclusion chromatography (HPSEC), among other methods.

NOM fractionation is widely used in a variety of fields in the water sector (drinking water treatment, wastewater treatment), and it is being increasingly applied also in natural systems.

Biofilm

Monitoring biofilm (and in particular the consortium of microorganisms living in it) formed on the soil may give an insight on the ability of a column system to biodegrade targeted EOC (and also NOM dissolved in water). Biofilm-related parameters are among those described above in section 3.3 (viable cell counts, total cell counts, ATP measurements...), with the difference that an extraction step is necessary to detach biofilm from the soil particles. Details on biofilm characterization techniques can be found in Lazarova and Manem (1995) and Bricheux *et al.* (2013).



7. Interpretation of results using numerical models

7.1. Literature review of numerical modelling applied to EOCs in MAR

It has been observed that a multitude of field parameters influence EOCs removal. Therefore, the development of soil-column experiments is a general approach to investigate EOCs removal during soil passage considering different field parameters and the main reactions in soils and aquifers. These laboratory column studies can be focused on different aspects as redox conditions, temperature effects, saturated conditions, soil capacity of cationic exchange, pH influence, type of organic carbon source, etc.

Modelling exercises try to reproduce soil-column experiments in order to describe contaminant behaviour, main removal mechanisms and to obtain the parameters that control these mechanisms. Very few studies have attempted modelling of the EOCs breakthrough curves to differentiate between sorption (retardation factor) and biodegradation (biodegradation rate). In most cases, modelling does not take into account the main removal mechanisms and considers the results as a whole, trying to relate some changes with some initial varying conditions.

Numerical modelling is not widely applied to study the fate of EOCs in soil-column experiments due to the complexity and the large number of influencing factors. The different mechanisms that control EOCs removal (mainly sorption and biodegradation) are rarely differentiated. This differentiation is very important in the development of numerical models as predictive models need the parameters and constants of these two main removal processes.

Several assumptions are made in most of the modelled experiments in order to simplify the processes and the unknown parameters of the equations. For most of the compounds, it has been observed that most of the removal is expected by biodegradation, since more compounds show higher? biodegradation values than high log D values. Table 10 in the appendix includes the main references where the selected trace organic compounds are modelled in a column experiment. The biodegradation of EOCs can be studied by comparing the processes in a biotic (active biomass) sand column to those in an abiotic (inactive biomass) sand column at a certain time point.

The literature review has been focused in those studies that develop numerical models to reproduce EOCs behaviour during experimental columns. Those studies have not been taken into account that use numerical models to reproduce field EOCs removal. Therefore, this review has been analysed more than 50 literature studies of columns with EOCs but only 17 of these implemented numerical models. The following conclusions are based on these 17 studies.

7.2. Examples of numerical models applied at column tests

The numerical approaches to simulate EOCs behaviour in columns experiments depend on assumptions made and the main objective of the study. All of analysed column numerical models are 1D type (column radius influence is not considered). Field models instead take into account at least a second dimension.

Transport is simulated trying to reproduce, at a first instance, the conservative transport of a tracer. This simulation allows the identification of the hydraulic parameters (physical transport parameters, i.e.

hydraulic conductivity, dispersion, effective porosity) fitting the breakthrough curves of the tracer by means of different codes. CXTFIT is one of the most common software to predict concentrations for both of conservative (e.g. tracer tests) and EOCs contaminants (some of them not conservative) in the posterior reactive transport model, as it is further indicated.

The reactive transport of contaminants is usually modelled solving the one-dimensional advectiondispersion equation or convection-dispersion equation with variable water flow characteristics: dual/single/ homogeneous media porosity; constant/variable water flux conditions: saturated/unsaturated/variably saturated flow. The transport parameters are considered differently depending on the column and study objectives: non-equilibrium sorption or physical non-equilibrium transport (mobile and immobile pore domain¹); linear and reversible equilibrium sorption; instantaneous sorption/desorption; equilibrium transport following the advection-dispersion equation; only biodegradation (ultimate and primary biodegradation²); exchange of solute between the mobile pore domain and an immobile pore domain, etc.

The different evaluated studies suggest that there is a need to study the processes e.g. sorption, (bio) degradation, irreversible sorption and any transformation or loss of mass in general of pharmaceuticals under field conditions. Sorption on various materials (organic matter, mineral surfaces) at different pH values and ionic strengths could help to predict the occurrence of pharmaceuticals in the unsaturated zone.

In summary, the general type of models and considerations used in experimental columns are:

- Conservative (non-reactive) transport (e.g. tracer)
- Reactive transport
 - Linear degradation (see examples in Bertelkamp *et al.*, 2013; Strauss *et al.*, 2011)
 - First order kinetics (linear adsorption and degradation) (see examples of application in Arye et al., 2011; Bertelkamp et al., 2013; Burke et al., 2013; Scheytt et al., 2006; Siemens et al., 2010; Strauss et al., 2011)
 - Sorption models (one-site chemical non-equilibrium sorption model). The sorption process is the sink term included in the simulation and this is approximated expressed by the sorption equation (Herny, Ferundlich or Langmuir are the most used). This sorption processes can be modelled as a surface complexation reaction (see examples of application in Arye *et al.*, 2011; Gillis *et al.*, 2012; Strauss *et al.*, 2011)

As a result, two main approaches to numerical models have been applied to reproduce trace organic compound behaviour in aquifers, showing a good agreement between measured and modelled compounds:

• Standard first order kinetics in combination with linear and (reversible) equilibrium sorption (Strauss *et al.*, 2011; Bertelkamp *et al.*, 2014; Burke *et al.*, 2013). The fact is that this

¹ Two dual-porosity models assume existence of mobile and immobile flow domains (pores with mobile and immobile water). These models thus lead to non-equilibrium flow conditions (between mobile and immobile domains).

² Biodegradation is understood as the transformation of a substance into new compounds through biochemical reactions or the actions of microorganisms such as bacteria. The primary biodegradation refers to the alteration of the chemical structure of a substance resulting in loss of a specific property of that substance. In this case, the modification caused by activity of micro-organisms affects only some physical and chemical properties of the substance. Instead, the Ultimate biodegradation is the complete breakdown of a compound to either fully oxidized or reduced simple molecules (such as carbon dioxide/methane, nitrate/ammonium, and water) (http://toxics.usgs.gov/definitions/biodegradation.html).

assumption (one-site linear and equilibrium sorption) can consider the other different processes together (microbial transformation, irreversible sorption, mineralization...) as a type of dissipation or general removal. Hence, kinetic sorption is a good approach to reproduce data recorded at the laboratory scale but for some compounds it plays a minor role at the field scale.

• Two-site kinetic sorption model with degradation and/or retardation that allows estimation of parameters for non-equilibrium, irreversible sorption (Unold *et al.*, 2009; Unold *et al.*, 2010; Wehrhan *et al.*, 2007; Brusseau *et al.*, 2012, Teijón *et al.*, 2014, Gillis *et al.*, 2012; Scheytt *et al.*, 2006).

The applicability of these two approaches depends on site characteristics but also on the chemical properties of compounds. Some of the behaviours of the target organic pollutants of DEMEAU are listed below:

- **Carbamazepine** can be retarded in the presence of soil organic matter based on laboratory results but field data seems to relate the removal with dilution processes. Retardation is governed by carbamazepine desorption kinetics from adsorbing sites. Advection-dispersion equation fail to reproduce the breakthrough curves of carbamazepine in the upper soil layers where adsorption takes place. Instead, a two-site model gives better results particularly of the desorption phase. This implies that chemical non-equilibrium conditions prevail during the transport of carbamazepine in the upper soil layers. In contrast, in deep layers, the retardation factor decreases and the advection-dispersion equation fits better (Arye *et al.*, 2011).
- Naproxen, bezafibrate and ibuprofen could not be well predicted assuming linear sorption due to rather nonlinear sorption of these compounds (Siemens *et al.*, 2010).
- **Ibuprofen** is significantly retarded and biodegraded and hence, a non-equilibrium sorption model is not adequate to predict its concentrations (Scheytt *et al.*, 2007).
- **Diclofenac** has a higher transformation under unsaturated conditions rather than under saturated conditions. Hence, a non-equilibrium sorption model fails in predicting Diclofenac groundwater concentrations (Scheytt *et al.*, 2007).
- **Iopromide** transport was poorly described with the non-equilibrium model as for ionisable compounds as iopromide the sorption to organic matter is not the main process (Gillis *et al.*, 2012).
- **Diazepam** transport was well predicted applying a one-site chemical non-equilibrium sorption model in a single porosity media (Gillis *et al.*, 2012).
- Acetaminophen, ibuprofen, ketoprofen, gemfibrozil, trimethoprim, caffeine, propranolol and metoprolol are characterised by different degrees of degradation making difficult the implementation of a reversible equilibrium sorption (Bertelkamp *et al.*, 2014).
- **Phenazone**-type pharmaceuticals are transported similar to a non-reactive tracer. A model based on a one-dimensional advection-dispersion and one-site kinetic linear sorption model is able to reproduce phenazone data (Burke *et al.*, 2013).

• The behaviour of **sulfonamines** (**sulfamethoxazole**) during soil passage can be described by standard first-order kinetics in combination with linear and equilibrium sorption (Burke *et al.*, 2013).

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7.3. Available software tools

The evaluated studies have used different software tools to interpret the breakthrough curves and to predict the compounds removal in columns experiments:

- PHREEQC and PHREEQC-2 (Parkhust and Appelo, 1999). This code is designed to perform a wide variety of low-temperature aqueous geochemical calculations. PHREEQC is based on an ion-association aqueous model and has capabilities for (1) speciation and saturation-index calculations; (2) batch-reaction and one-dimensional (1D) transport calculations involving reversible reactions, and (3) inverse modelling.
- BIOWIN model 4. This numerical model created by US EPA predicts biodegradation potential using the group contribution approach.
- HYDRUS-1D (Simunek *et al.*, 2009), a software package for simulating water, heat and solute movement in one-dimensional variably-saturated porous media. The HYDRUS program numerically solves the Richards equation for variably-saturated water flow and advection-dispersion type equations for heat and solute transport.
- CXTFIT (Parker and van Genuchten, 1984; Toride *et al.*, 1995). This program uses an inverse modelling technique to fit the model data to the observed data in order to estimate reaction and transport parameters. This model is based on the advective dispersion equation.
- MARTHE (Thiery, 1990) is for hydrodynamic and hydrodispersive modelling of groundwater flow in porous media. MARTHE can be used to simulate numerous types of groundwater flow, for saturated and unsaturated conditions, in monophasic and diphasic media.
- MODFLOW-96 (Harbaugh and McDonald, 1996) coupled with the solute transport model MT3D (Zheng, 1990). MODFLOW is the USGS's three-dimensional (3D) finite-difference groundwater model. It has a modular structure that allows it to be easily modified to adapt the code for a particular application. MT3D is a Modular 3-D Multi-Species transport model for simulation of advection, dispersion, and chemical reactions of contaminants in groundwater systems. This software has been applied in simulating an experimental column where different aquifer layers are built, transferring the column systems into a 1D model in a confined layer, with a constant-flow and a fixed-head boundary condition on the up and downstream boundary, respectively (Shaffer *et al.*, 2015). More specifically, this code has been implemented in the Software Processing Modflow (PMWIN, version 5.3.1 and 8.040; Chiang and Kinzelbach, 1998).

7.4. Linear distribution coefficient

The literature review has included a compilation of different constants both calculated and compiled in different studies (see Table 6). This summary includes both the constants calculated experimentally and those used in the publications consulted in these articles. The appendix (Table 10) includes more constants that have been calibrated in numerical models of experimental columns.

Table 6: Linear distribution coefficient estimated by soil-column experiments

NOTE: reported time: duration of experimental columns; experiment: data obtained in the experiment described in the reference paper; literature: experimental data has been compared with available literature data; ref literature: author of the paper used in the example).See more information of the literature review in Appendix D

			K _D	units: [- adimensiona	I - L/kg - g/cm]
	Reported time	Compound	Experiment	Literature	Comments
12		Carbamazepine	0.2 [-]	0.3 - 8.4 [-]	High sorption
л!., 20		Sulfamethoxazole	0.15 [-]	0.1 - 1.5 [-]	Low sorption
ner <i>et</i> (Benzotriazole	0.15 - 0.2 [-]		Low sorption
Kazı		lopromide	No sorption	-	Sorption Neglected
14		Gemfibrozil			
ıl., 20		Trimethoprim			
ip et c	Adaptation period of 4	Metoprolol			
telkam	months	Carbamazepine	_	0.49 - 37 [L/kg]	
Beri		Sulfamethoxazole		0.23 - 37.6 [L/kg]	
nens <i>et</i> , 2010		Benzafibrate	0.35 +/- 0.06 [g/cm]		
Sieı al.		Diclofenac			
eytt <i>al.</i> , 06		Carbamazepine	0.131 [L/kg]		
Sch et 20		Diclofenac	0.572 [L/kg]		
Jia <i>et al.,</i> 2007		Benzotriazole	0.011 - 0.042 [L/kg] subsoil column 1.29 - 2.58 [L/kg] Fe0 column test	0.195 - 0.399 [-]	
Gillis et al, 2012	48 hours	lopromide	1,49	157	
Strauss <i>et al.</i> , 2011		Sulfamethoxazole	0.297 +- 0.005 pH 5.0 0.128 +- 0.003 pH 6.5 0.111 +- 0.012 pH 8.5 0.09 +- 0.001 pH 8.5		
al.,		Primidone	0.02 [L/kg]	0.02 - 0.75 [L/kg]	
rke <i>et</i> 2013		Phenazone	0.02 [L/kg]		
Bu		Metoprolol	0 [L/kg]	-	



7.5. Constraints and difficulties in the use of numerical modelling

One of the limitations in numerical modelling is the different data structure between the numerical code and the collected data and the data resolution. Sometimes the available data has lower resolution than data required in numerical codes. This fact implies some assumptions over available data, which can lead to a lack of precision in parameters. For instance, it would be difficult to obtain representative samples at even 1 cm resolution from a column study as some codes requires, since mixing would likely occur during sampling (Gillis *et al.*, 2012).

Models based on distribution coefficients assume that sorption to organic matter is the main process affecting the solutes, but this assumption may not be true in the case of ionisable compounds (Cunningham, 2008), as this is the case with iopromide. This compound has multiple groups that can become protonated, so sorption processes would be highly pH dependent. In these cases it is very difficult to describe the transport and to adjust the mass balance.

Nevertheless, the main limitation in reproducing the contaminants' behaviour is the lack of information about the main processes that determine contaminant attenuation and how some site characteristics can have influence over these intrinsic characteristics of trace organics regarding its fate and transport. Sorption is essential in organic pollutant removal but the sorption coefficient cannot be directly derived from the K_{ow} values. Then, other mechanisms have to be considered.

7.6. Recommendations for the use of numerical modelling

The following list includes the main considerations to take into account in the numerical modelling of the experimental columns with EOCs:

- To evaluate if the collecting data phase (after setting up the column) take into account the type and format of input data required in the numerical model together with code requirements.
- It should be ensured that all physical parameter information that is necessary is collected before conducting the soil-column experiments (i.e., bulk density, moisture content, pore volume, ...)
- To determine if the type of solutes to be modelled can be reproduced with the reactions considered in the modelling tool (e.g., iopromide transport is poorly described by HYDRUS-1D).
- To take into account if the EOCs concentrations in the columns are higher than those present in the environment. Some compounds at higher concentration show significantly better removal (Bertelkamp *et al.*, 2014), thus, models in columns dosing higher EOCs concentrations than present in the environment, and could significantly overestimate the biodegradation rates.
- Numerical models should be applied to data from columns after adaptation time. This is the needed time in a column to reach stable conditions. Usually, biomass needs some months to reach this state.
- Neutral compounds (those with low Log D values except sulfamethoxazole -) and negatively charged compounds are more biodegradable due to the presence of ethers and carbonyl groups. In these cases, the main process to be modelled can be the biodegradation.



- Laboratory experiments that address the combination of sorption and degradation are important when studying micropollutants such as pharmaceuticals. The different influence of both processes in contaminant mobility can be compared considering a relative "apparent retardation factor" (Banzhaf *et al.*, 2012).

Some aspects which are also important to consider:

- Comparability: in contrast to removal % at a specific site, degradation rates and distribution coefficients allow for comparison between sites.
- Calibration: possibility of parameter estimation by calibration (see e.g. Henzler *et al.* 2014, Modeling the fate of organic micropollutants during river bank filtration (Berlin, Germany).

8. Conclusions

From this review it can be concluded, on the one hand, that is seems clear that is virtually impossible to simulate environmental conditions prevailing in a MAR system by a soil column experiment. Acknowledging the large range of variables that play a key role in a MAR performance and that are never precisely reproduced in laboratory systems (flow rate fluctuations, redox conditions, temperature, DO content, consortium of microorganisms...), a column experiment must be regarded at best only as an exsitu representation of a small section of a MAR site. This circumstance emphasizes the importance of appropriately designing and operating a column experiment to reproduce conditions of the simulated MAR system as much as possible, otherwise the column experiment might result in erroneous or irrelevant results not directly applicable to the MAR system of study. Thus, a reasonable compromise must be found between the achievement of such field-like conditions and practicability (in terms of time, cost, existing knowledge...) in lab-scale conditions.

One the other hand, the review in the scientific literature shows that, as pointed out by Lewis and Sjöstrom (2010), "despite at least 300 years of experience in the use of soil columns, no standardization of experimental methods has occurred". In fact, the review has shown that design and operation approaches of soil columns mimicking MAR systems are unique to a single researcher or to a research team, making direct comparison of results from different experiments are difficult. Within the context of this absence of an accepted protocol or guidelines, the present document aims at summarising and providing insight into the present-day practices for the construction of soil columns simulating a MAR system.

Following the Lewis and Sjöstrom (2010) observation, the numerical modelling of soil columns when dealing with trace organic compounds is poorly developed. Previously to the selection of the model type to be implemented, it is necessary to define the conceptual model of the contaminants degradation. The main processes that takes place in each contaminant and site are poorly known and the value of these parameters that reproduces the conceptual model are highly variable depending on local site characteristics. Nevertheless, the main limitation in reproducing the contaminants behaviour is the lack of information about the main processes that determine contaminant attenuation and how some site characteristics can have influence over this intrinsic trace organics fate and transport.

References

- Alvarez D.A., Jones-Lepp T.L. Sampling and analysis of emerging pollutants (Chapter 11). In Y. Li & K. Migliaccio (Eds), Water quality concepts, sampling and analyses (pp. 199-226), CRC Press - Taylor & Francis Group, LLC, Boca Raton, FL (2010).
- ASTM D4874-95(R2001) Standard Test Method for Leaching Solid Material in a Column Apparatus.
- Azaroual, M., Pettenati, M., Casanova, J., Besnard, K., & Rampnoux, N. (2011). Challenges of artificial recharge of aquifers: Reactive transport through soils, fate of pollutants and possibility of the water quality improvement. In Water Security in the Mediterranean Region (pp. 111-128). Springer Netherlands.
- Banzhaf S., Nödler K., Licha T., Krein A., Scheytt T. Redox-sensitivity and mobility of selected pharmaceutical compounds in a low flow column experiment. Science of the Total Environment 438 (2012) 113-121.
- Baumgarten B., Jährig J., Reemtsma T., Jekel M. Long term laboratory column experiments to simulate bank filtration: factors controlling removal of sulfamethoxazole. Water Research 45 (2011) 211-220.
- Bergström, L. Leaching of agrochemicals in field lysimeters a method to test mobility of chemical in soil. In: Cornejo J., Jamet P., Lobnik F. (Eds), Pesticide/Soil Interactions: Some Current Research Methods, INRA, Paris, p. 479.
- Bertelkamp C., Reungoat J., Cornelissen E.R., Singhal N., Reynisson J., Cabo A.J., van der Hoek J.P., Verliefde A.R.D. Sorption and biodegradation of organic micropollutants during river bank filtration. A laboratory column study. Water Research 52 (2014) 231-241.
- Borgman O., Chefetz B. Combined effects of biosolids application and irrigation with reclaimed wastewater on transport of pharmaceutical compounds in arable soils. Water Research 47 (2013) 3431-3443.
- Bouwer, E. J., & McCarty, P. L. (1984). Modeling of trace organics biotransformation in the subsurface. Groundwater, 22(4), 433-440.
- Bricheux G., Le Moal G., Hennequin C., Coffe G., Donnadieu F., Portelli C., Bohatier J., Forestier C. Characterization and evolution of natural aquatic biofilm communities exposed in vitro to herbicides. Ecotoxicology and Environmental Safety 88 (2013) 126-134.
- Burke V., Treumann S., Duennbier U., Greskowiak J., Massmann G. Sorption behaviour of 20 wastewater originated micropollutants in groundwater Column experiments with pharmaceutical residues and industrial agents. Journal of Contaminant Hydrology 154 (2013) 29-41.
- Burke V., Greskowiak J., Asmuβ, Bremermann R., Taute T., Massmann G. Temperature dependent redox zonation and attenuation of wastewater-derived organic micropollutants in the hyporheic zone. Science of the Total Environment 482-483 (2014) 53-61.
- Carballa, M., Fink, G., Omil, F., Lema, J. M., & Ternes, T. (2008). Determination of the solid–water distribution coefficient for pharmaceuticals, estrogens and musk fragrances in digested sludge. Water research, 42(1), 287-295.
- Chen H., Gao B., Li H., Ma L.Q. Effects of pH and ionic strength on sulfamethoxazole and ciprofloxacin transport in saturated porous media. Journal of Contaminany Hydrology 126 (2011) 29-36.
- Chen Q., Shi J., Liu X., Wu W., Liu B., Zhang H. Simulation of estrogen transport and behaviour in laboratory soil columns using a cellular automata model. Journal of Contaminant Hydrology 146 (2013) 51-62.
- Cordy G.E., Duran N.L., Bouwer H., Rice R.C., Furlong E.T., Zaugg S.D., Meyer M.T., Barber L.B., Kolpin D.W. Do pharmaceuticals, pathogens, and other organic waste water compounds persist when waste water is used for recharge? Ground Water & Remediation 24 (2004) 58-69.
- Cunningham, V.L. Special characteristics of pharmaceuticals related to environmental fate. In: Kümmerer K. (ed), 2008. *Pharmaceuticals in the environment*. 23-24. Berlin Heidelberg New York: Springer-Verlag.
- Das B.S., Lee L.S., Rao P.S.C., Hultgren R.P. Sorption and degradation of steroid hormones in soils during transport: column studies and model evaluation. Environmental Science & Technology 38 (2008) 1460-1470.

Durán-Álvarez J.C., Prado B., Ferroud A., Juayerk N., Jiménez-Cisneros B. Sorption, desorption and displacement of ibuprofen, estrone, and 17β estradiol in wastewter irrigated and rainfed agricultural soils. Science of the Total Environment 473-474 (2014) 189-198.

DEMEAU

- Drillia, P., Stamatelatou, K., & Lyberatos, G. (2005). Fate and mobility of pharmaceuticals in solid matrices. Chemosphere, 60(8), 1034-1044.
- Gillis, J. D., Prasher, S. O., & Price, G. W. (2012). Modelling pharmaceutical concentration in the soil profile using HYDRUS 1D.
- Engelhardt, I., Prommer, H., Schulz, M., Vanderborght, J., Schüth, C., & Ternes, T. A. (2013). Reactive Transport of Iomeprol during Stream-Groundwater Interactions. Environmental science & technology, 48(1), 199-207.
- Essandoh H.M.K., Tizaoui C., Mohamed M.H.A., Amy G., Brdjanovic D. Soil aquifer treatment of artificial wastewater under saturated conditions. Water Research 45 (2011) 4211-4226.
- Fan Z., Casey F.X.M., Hakk H., Larsen G.L., Khan E. Sorption, fate, and mobility of sulfonamides in soils. Water Air & Soil Pollution 218 (2011) 49-61.
- Fand R.M., Thinakaran R. The influence of the wall on flow through pipes packed with spheres. Journal of Fluids Engineering Transactions of the ASME 112 (1990) 84-88.
- Fang, Y., Karnjanapiboonwong, A., Chase, D. A., Wang, J., Morse, A. N., & Anderson, T. A. (2012). Occurrence, fate, and persistence of gemfibrozil in water and soil. Environmental Toxicology and Chemistry, 31(3), 550-555.
- Fenoll J., Ruiz E., Flores P., Vela N., Hellin P., Navarro S. Use of farming and agro-industrial wastes as versatile barriers in reducing pesticide leaching through soil columns. Journal of Hazardous Materials 187 (2011) 206-212.
- Greenhagen A.M., Lenczewski M.E., Carroll M. Natural attenuation of pharmaceuticals and in illicit drug in a laboratory column experiment. Chemosphere 115 (2014) 13-19.
- Greskowiak, J., Prommer, H., Massmann, G., & Nützmann, G. (2006). Modeling seasonal redox dynamics and the corresponding fate of the pharmaceutical residue phenazone during artificial recharge of groundwater. Environmental science & technology, 40(21), 6615-6621.
- Gros M., Petrovic M., Barceló D. Analysis of emerging contaminants of municipal and industrail origin (Volume 5, Part S/1). In O. Hutzinger, D. Barceló, A. Kostianoy (Eds), Handbook of Environmental Chemistry (pp. 37-104), Springer-Verlag, Berlin Heidelberg (2008).
- Hebig K.H., Nödler K., Licha T., Scheytt T.J. Impact of materials used in lab and field experiments on the recovery of organic micropollutants. Science of the Total Environment 473-474 (2014) 125-131.
- Hillebrand, O.; Musallam, S.; Scherer, L.; Nödler, K.; Licha, T. (2013). The challenge of sample-stabilisation in the era of multi-residue analytical methods: A practical guideline of the stabilization of 46 organic micropollutants in aqueous samples. Science of the Total Environment 454-455 (3013) 289 298.
- Hu D., Coats J.R. Laboratory evaluation of mobility and sorption for the veterinary antibiotic, tylosin, in agricultural soils. Jornal of Environmental Monitoring 11 (2009) 1634-1638.
- Jia, Y., Aagaard, P., & Breedveld, G. D. (2007). Sorption of triazoles to soil and iron minerals. Chemosphere, 67(2), 250-258.
- Kay P., Blackwell P.A., Boxall A.B.A. Column studies to investigate the fate of veterinary antibiotics in clay soils following slurry application to agricultural land. Chemosphere 60 (2005) 497-507.
- Ke J., Gin K.Y.H., Tan L.H., Reinhard M. Fate of endocrine-disrupting and pharmaceutically active substances in sand columns fed with secondary effluent. Journal of Environmental Engineering 138 (2012) 1067-1076.
- Kibbey, T. C., Paruchuri, R., Sabatini, D. A., & Chen, L. (2007). Adsorption of beta blockers to environmental surfaces. Environmental science & technology,41(15), 5349-5356.
- Kwon J.W. Mobility of veterinary drugs in soil with application of manure compost. Bulletin of Environmental Contamination and Toxicology 87 (2011) 40-44.
- Lazarova V., Manem J. Biofilm characterization and activity analysis in water and wastewater treatment. Water Research 29 (1995) 2227-2245.

Lekkerker-Teunissen, K., Chekol, E. T., Maeng, S. K., Ghebremichael, K., Houtman, C. J., Verliefde, A. R. D., ... & Van Dijk, J. C. Pharmaceutical removal during managed aquifer recharge with pretreatment by advanced oxidation. Water Science & Technology, 2012: Water Supply, 12(6), 755-767.

DEMEAU

- Lewis J., Sjöstrom J. Optimizing the experimental design of soil columns in saturated and unsaturated transport experiments. Journal of Contaminant Hydrology 115 (2010) 1-13.
- Maeng S.K., Ameda E., Sharma S.K., Grützmacher G., Amy G.L. Organic micropollutant removal from wastewater effluent-impacted drinking water sources during bank filtration and artificial recharge. Water Research 44 (2010) 4003-4014.
- Mansell J., Drewes J.E. Fate of steroidal hormones during soil-aquifer treatment. Ground Water Monitoring & Remediation 24 (2004) 94-101.
- Massmann G., Dünnbier U., Heberer T., Taute T. Behaviour and redox sensitivity of pharmaceutical residues during bank-filtration Investigation of residues of phenazone-type analgesics. Chemosphere 71 (2008) 1476-1485.
- Maszkowska J., Kołodziesjska M., Białk-Bielińska, Mrozik W., Kumirska J., Stepnowski P., Palavinskas R., Krüger O., Kalbe U. Column and batch tests of sulfonamide leaching from different types of soil. Journal of Hazardous Materials 260 (2013) 468-474.
- Mersmann, P., Scheytt, T., & Heberer, T. (2002). Column experiments on the transport behaviour of pharmaceutically active compounds in the saturated zone. Acta hydrochimica et hydrobiologica, 30(5), 275-284.
- Mioska, M.J. (2006). PhD thesis. A column experiment for Groundwater remediation post-mine closure at the Wolverine mine, Yukon. B.A.Sc., University of British Columbia, 2006
- Müller B., Scheytt T., Grützmacher G. Transport of primidone, carbamazepine, and sulfamethoxazole in thermally treated sediments laboratory column experiments. Journal of Soils and Sediments 13 (2013) 953-965.
- NEN 7343. 1995. Leaching Characteristics of Building and Solid Waste Material, Leaching Tests, Determination of the Leaching of Inorganic Components from Granular Materials with the Column Test. Netherlands Nonnalization Institute, Delft.
- OECD / OCDE (2004). OECD Guidelines for the testing of chemicals. Leaching in Soil Columns. 312. Adopted: 13 April 2004.
- Onesios K.M., Bouwer E.J. Biological removal of pharmaceuticals and personal care products during laboratory soil aquifer treatment simulation with different primary substrate concentrations. Water Research 46 (2012) 2365-2375.
- Patterson B.M., Shackleton M., Furness A.J., Bekele E., Pearce J., Linge K.L., Busetti F., Spadek T., Toze S. Behaviour and fate of nine recycled water trace organics during managed aquifer recharge in an aerobic aquifer. Journal of Contaminant Hydrology 122 (2011) 53-62.
- Parker J.C., van Genuchten MTh. Determining transport parameters from laboratory and field tracer experiments. Va Agric Exp St Bull (1984): 194, 84-3.
- Parkhurst, D.L. and Appelo, C.A.J., User's guide to PHREEQC (version 2)--A computer program for speciation, batchreaction, one-dimensional transport, and inverse geochemical calculations: U.S. Geological Survey Water-Resources Investigations Report 1999. 99-4259, 312 p.
- Ramil, M., El Aref, T., Fink, G., Scheurer, M., & Ternes, T. A. (2009). Fate of beta blockers in aquatic-sediment systems: sorption and biotransformation.Environmental science & technology, 44(3), 962-970.
- Relyea, J.F. Theoretical and experimental considerations for the use of the column method. Radioactive Waste Management and Nuclear Fuel Cycle 3 (1982) 151-166.
- Schaffer, M.; Kröger, F.; Nödler, K.; Ayora, C.; Carrera, J.; Hernández, M.; Licha, T. (2015 in press). Influence of a reactive layer on the attenuation of 28 selected organic micropollutants under realistic soil aquifer treatment conditions: insights from a large scale column experiment. Water Research. In press.
- Scheytt T., Mersmann P., Leidig M., Pekdeger A., Heberer T. Transport of pharmaceutically active compounds in saturated laboratory columns. Ground Water 42 (2004) 767-773.
- Scheytt T.J., Mersmann P., Heberer T. Mobility of pharmaceuticals carbamazepine, diclofenac, ibuprofen, and propyphenazone in miscible-displacement experiments. Journal of Contaminant Hydrology 83 (2006) 53-69.

- Sentenac P., Lynch R., Bolton M., Measurement of the side-wall boundary effect in soil columns using fibre-optics sensing. International Journal of Physical Modelling in Geotechnics 4 (2001) 35-41.
- Shackelford C.D. Laboratory diffusion testing for waste disposal a review. Journal of Contaminant Hydrology 7 (1991) 177-217.
- Siemens, J., Huschek, G., Walshe, G., Siebe, C., Kasteel, R., Wulf, S., ... & Kaupenjohann, M. (2010). Transport of pharmaceuticals in columns of a wastewater-irrigated Mexican clay soil. Journal of environmental quality, 39(4), 1201-1210.
- Simunek, J., M. Sejna, H. Saito, M. Sakai, and M. Th van Genuchten. The HYDRUS-1D software package for simulating one-dimensional movement of water, heat and multiple solutes in variably-saturated media. 2009. Riverside, CA, USA. Department of Environmental Sciences, University of California Riverside.
- Stevens-Garmon, J., Drewes, J. E., Khan, S. J., McDonald, J. A., & Dickenson, E. R. (2011). Sorption of emerging trace organic compounds onto wastewater sludge solids. Water research, 45(11), 3417-3426.
- Strauss, C, Thomas H., and . Radke. "Effects of pH and manure on transport of sulfonamide antibiotics in soil." Journal of environmental quality 40.5 (2011): 1652-1660
- Teijón, G., Candela, L., Simunek, J., Tamoh, K., and J. Valdés-Abellán. Fate and Transport of Nanoproxen in a Sandy Aquifer Material: Saturated Column Studies and Model Evaluation. Soil and sediment Contamination (2014), 23: 736-750.
- Thiery D. Logiciel MARTHE. Modélisation d'Aquifêres par un Maillage Rectangulaire en régime Transitoire pour le calcul Hydrodynamique des Ecoulements. 1990. Version 4.3. Rapport BRGM n° R32210
- Tiehm A., Schmidt N. Stieber M., Sacher F., Wolf L., Hoetzl H. Biodegradation of pharmaceutical compounds and their occurrence in the Jordan Valley. Water Resources Management 25 (2011) 1195-1203.
- Toride, N., leij, F.J, van Genuchten, M.T. The CXTFIT Code for Estimating Transport Parameters from laboratory or Field Tracer Experiments, Version 2.0. research Report No. 137. 1995. US Salinity Laboratory, USDA, ARS, Riverside, CA.
- Scheytt, T. J., Mersmann, P., Rejman-Rasinski, E., & These, A. (2007). Tracing Pharmaceuticals in the Unsaturated Zone (10 pp). Journal of Soils and Sediments, 7(2), 75-84.
- Unold M., Kasteel R., Groeneweg J., Vereecken H. Transport and transformation of sulfadiazine in soil columns packed with a silty loam and a loamy sand. Journal of Contaminant Hydrology 103 (2009) 38-47.
- Unold, M.J. Simunek R., Kaastel, J. groeneweg, and H. Vereecken. Transport of manure-based applied sulfadiazine and its main transformation products in soil columns. Vadose Zone. J. 2009. 8: 677-689. Doi: 10.2136/vzj2008.0122
- Wehrhan A., Kasteel R., Simunek J., Groeneweg J. Vereecken H. Transport of sulfadiazine in soil columns Experiments and modelling approaches. Journal of Contaminant Hydrology 89 (2007) 107-13.
- Yu, L., Fink, G., Wintgens, T., Melin, T., & Ternes, T. A. (2009). Sorption behaviour of potential organic wastewater indicators with soils. Water research, 43(4), 951-960.
- Zearley, T. L., & Summers, R. S. (2012). Removal of trace organic micropollutants by drinking water biological filters. Environmental science & technology, 46(17), 9412-9419.



Appendix

Table 7:Summary of set-up and design aspects of column studies simulating fate and transport of EOCs
Note: n.r. means not reported

teed water origin	Water Target micropollutants (MP)	Spiking	Casing material	Filling material	Grain size (average)	Porosity	Hydraul. Cond.	Type packing	Column dimensions	Ref
econdary effluent from WWTP	Tβ-estradiol, testosterone, estrone,	[MP]=200 ng/L	nır.	nr.	nr.	nır.	nr.	ur.	L=4x1m, Ø=14 cm	
OM fractionated WWTP effluent	and rost enedione	[M P]=200 ng/L [M P]=480 ng/L	acrylic glass	silica sand	1 mm	0.41 0.41	nr. nr.	n.r.	L=0.3 m, Ø=8 cm	Mansell et al., 2004
Surface water of lake Tegel SMX]=0,25 µg/L	Sulf amethoxazole (SM X)	[SM X]=0-3.93 µg/L [SM X]=0-4.15 µg/L	nı.	quartz sand p=2507 kg/m3	0.7-1.2 mm	0.4	nr.	nr.	L=2 m, Ø=15.5 cm	Baumgarten et al., 2011
econdary effluent from WWTP	131 compounds (including MP)	no	Stainless steel	sandy loam soil p=1.63 g/cm3	≪ mn	0.38	280 mm/d	hand-packed	L=2.4 m, Ø=32.5cm	Cordy et al., 2004
ynthetic wastewater (rich in DOC 16-50 mg/L), N and P)	nore	QU	acrylic tube	silica sand p=1.55 g/cm3	0.51 mm	0.41	nr.	ur.	L=2.0 m, Ø=14 cm	Essandoh et al., 2011
buf ace lake water	phenazone (0.5 µg/L), 4- azerylaminoantipyrine (AAA) (0.53 µg/L), 4- formylaminoantipyrine (FAA) (0.34 µg/L), 15- dimethyl-12-dehydro-3-syvrazolone (DP)(0.03 µg/L), AMDOPH (0.10 µg/L)	Ŋ	יני.	lake sediment core	ur.	ы.	b/mn/06	Ur.	L=10 m, Ø≡n.r.	M assman et al., 2008
WMTP difluent amended with NO3- to 30 mg//L IO3N	Bisphenol A (BPA), 778-estradiol (E2), 77a- ethynylestradiol (EE2), N- ritrosodimethylamire (NDM A), N- introsomorphine (NM CR), cabamazepire, oxazepam, iohexol, lodip amde	E2: 90 µg/L; EE2: 400 µg/L; BPA: 500 µg/L; 0XAZ: 400 µg/L; CARB; 680 µg/L; NDMA: 590 µg/L; NMOR; 680 µg/L; IOX: 630 µg/L; IDP: 700 µg/L	stainless steel	aquifer sediment quarz (75%), calcite (12%), others (13%) p=1.66 g/cm3	UL.	0.46	ß m'd	The baller, corntaining the sediment and groundwater, was sediment and groundwater, was repeatedly tisterbaged inside the columns, displacing wcss groundwater and gradually filling the columns on-site.	L=2.0 m,Ø=14.5 cm	Patterson et al., 2011
WMTP effluent media containing 8.5 mg/L 4:PEO4, 12 mg/L 1:X2:PEO4, 3.3 mg/L 4:2:PEO4, 28 mg/L CaCl2, 0.25 1:2,7 mg/L NH4C1, and 23 mg/L FeCl3, 2.7 mg/L NH4C1, and 23 mg/L MgO4, Optionally acetate ras supplied).	Acetaminopher, Biosol, Biphenylol, p- Chloro-m-cresol, p-Chloro-m-xylerol, Chlorophen Eloiloienes, F-Liuoruradi, Gabapentin, Gemithorotal, Iupprofen, Ketoprofen, Naproxen, Phenytoln, Triclosan, Valproic	[PPCP]=0- ນັ ມຊ/L ຂອດ [acetate]=0-1000 ມຊ/L [HgCl2]=0-ນັ ກຊ/L	Glass	dry sand (30-40 mesh)	30-40 rresh	ž	ч.	Two centimeter-layers and were tamped 25 times before the next sand layer was added.	L=0.3 m, Ø=2.5 cm	Oresios et al., 2012
3ynthetic solutions	ጥያ-estratiol, testosterone, estrone, androstenedione	Estradioi: 2.5.3.5 mg/L Testosterone: 5.5.6.5 mg/L	Glass	M ixtures of: Sand (silica), surface soil: sand (15%, silt (66%, clay (2 %, OC: 2.9% Freshwater sediment (sand 94% dap 6%, OC: 0.2%	20-60 mesh	0.34-0.42	ъг.	лг.	L=0.07 m, Ø=2.5 cm	Das et al., 2004
yrthesized water, representing an tfluert fromsewage rearment.	carbamazepine, dickofenas, ibuprofen, and propyphenazone	1 µg /L in the spiked water	st äinless steel	sediment from the unsuranced zone. Clay (2.cum): 0% Sitt (2-33.un) 0.7% Fine sand (63.200) un): 42.7% Medium sand Con-630 um) 56.5% Coarse sand (200-2000 un): 02% Coarol 35% p=173-187 g/cm6.	si <i>e</i> ved through a 2-mm sieve,	.'J'	8.64 m′d	The sediment was added in the sediment was added in increments and tap-om increments and taped lightly with a plunger. Care was taken to with a plunger. Care was taken to more addition of material or segregation of sediment by particle size.	L=0.29 m,Ø=13.6 cm	Scheytt et al., 2006



Feed water origin	Target micropollutants (M P)	Spiking	Casing material	Filling material	Grain size (average)	Porosity	Hydraul. Cond.	Type packing	Column dimensions	Ref
natural surface water. Concentrations of SMX, CBZ, DCL and IBU between 775 and 852 ng/L.	suftamethoxazole SM X), carbamazepine (CBZ), diclofenac (DCL), and ibuprofen (IBU)	[SM X], [CBZ], [DCL], and [IBU] between 165 and 295 µg/L.	stainless steel	natural organic rich sediment (fOC=0.01) from a field site. p=1.4 g/cm3.	<2mm	0.42	200 mm/d	The dry sediment was then filled in small portions into the column and compacted after each addition.	L=0.35 m, Ø=13.6 cm	Banzhaf et al., 2013
Synthetic leaching solutions (CaCl2: 0.01 mol L-1)	suf adiazine (SDZ)	0.57 mg SDZ L-1 (in 0.01M CaCl2)	Stainless steel	2 Solis from the upper 30 cm. Sity loam: Sand (5.9%), Siti (78.7%), clay (15.4%), OC (1.24%). Loamy sand: Sand (68.2%), Siti (26.7%), Clay (4.9%), OC (10.7%).	~2 mm	nr.	ייני.	During the packing procedure, layers of about 1 cm thickness were filled into the columns and compacted by a weak pressing with a pestle.	L=0.10 m, Ø=8.5 cm	Unold et al., 2009
surface water from the local Sche Canal	Ibup nofen, Ketoprofen, Gerrlib nozil, Acetamino phen, Trimethop rim, Caffeine, Proprarouol, Atrezin, Metoprolo, Atrazin, Carbamzzejne, Prevytoin, Sulf amethoxazole, Hydrochtorothizzide, Linoomycin	4 OM Ps (200 rg/L per solute)	transparent PVC	sand	(d=14-2 mm, d50=1.83 mm)	0.31-0.42	חיר.	Columns were filled with sand in incontensits of 4-5 cm while tapping on the column, to prevent layering in the columns.	L=1m, Ø=3.6 cm	Bertelkamp et al., 2014
Synthetic feed water	meptobaned clazes and oxazepan, pyrithydione, primdore as well as its met &olite phenytetryhmalonamide (PEMA), phenazone and propypherazone, 1-acetyl-1- methyl-2-dimethyl-oxaroyl-2- phenythydrazide (AM PD), 1-zeryl-1- methyl-2-dimethylorazide (AM PH), acetylarinoantipyrine (FAA), metporiol, ormyfarmoantipyrine (FAA), metporiol, totytri zzole and pare-toluensul formande (p- riSA). Phenazeline, N-ethytherazetire	Spiking: 5 µg/m of each mcropollutart.	st ainless steel	Aquifer sediment. Particle sardy sediment of the sardy sediment determined by seving analysis was N630 µm (19%, 830-2006 µm (17%, 830-2006) µm (19%, 8020 µm (19%, OC: 0.20%(w/w).		0.45		ż	L=0.3 m, Ø=0.1 m	Вике ега., 2013
Groundwater from a local well	Methamphetamine, caffeine and acetaminophen	M ethamphetamine: 0-100 mg/L caffeine: 0-1000 mg/L acetaminophen: 0-250 mg/L M ethamphetamine: 100 mg/L caffeinion: 1000 mg/L	PVC	Undisturbed soil (0.9 – 1.3 m deep). Sity clay. P= 1.7 g cm3, foc=0.01 sand		0,28	95 mm/d 86.4 m/d	Undisturbed	square section (0.3 mx0.3 m) L=0.3 m	Greenhagen et al., 2014
Irrigation with treated wastewater	diclofenac, bezafibrate, naproxen, carbamazepine, diatrizoic acid, ibuprofen	5 µm/L for each micropollutant	Stainless steel	natural vado se zone sediment. Low organic content of 0.04 mgC/g.	0.2-2 mm	nr.	n.r.	n.r.	n.r.	Tiehm et al., 2013
Simulated rairs (ultrapure water) wereapplied weekly with a rainfall rate of 3 cm, over a 6-h period to the soli colum.	Tylosin	1500 µg/ column (incorporated into the top 2 cm soil surface)	PVC	OC: 0.5-4.0% Clay (~2 μm): 3.6% Salt (2-63 μm): 6- 3.6% Sand (63-2000 μm): 36-90% solt: 1.56 cm3/g spiked with manure + tylosin	12 mm sieved	лг.	ייני	Disturbed	L=0.30 m, Ø=0.10 m	Hu et al., 2009
Secondary effluent ultrafiltered water	estrone (E1), 7(B-estratiol (E2), estriol (E3), 7(a-ethynylestradiol (EE2), 4-tetr- octyphenol (4-t-OP), bisphenol A (BPA), ibyprofen (IBU) and reproxen (NAP)	Feed water spiked to obtain a concentration of app ro.x. 100 ug/L	טג.	Aquifer sand. Fraction of organic carbon=0,29%	2 mm sieved	0.44	ייני	ы.	8 columns in series L≡1.00 m, Ø=0.10 m	Ke et al ,2012
Surface (lake) water and intermitently Ozonated surface (lake) water (DO=21mg/L)	primidone (PMD); carbamazepine (CBZ); and sulfamethoxazole (SMX)	Spiked to CBZ=0.8 µgl-1, PM D=0.7 µgl-1, SM X=0.9 µg/L	חני	Sediment from an infiltration pond. Fraction of organic carbon=0, 9%	medium grain size of 0.38 mm (medium sand)	0.35	48.4 m/d	n.r.	L=0,35 m Ø=0,135 m	M uller et al., 2013
Ground water	clofibric æcid, propypherezore, and dicloferac	Spiked to 10 μg/L in the spiked water. 5 d ground water (acclimatization) + P 10 d ground water (to wash M P 5 d ground water (to wash out M P)	stainless steel	Sediment: Fraction of organic cashor – 0.24% Clay organic cashor – 0.24% Clay (~2.0m); nd.% Silt (2–63 um); 0.2% Fine sand (63–200 um); 145% Medium sand (200-630 Mm); 15.3% Coartes Sand (630-2000 um); 2.8%		0.32	44.1m/d		L=0,35 m, Ø=0,14 m	Scheytt et al., 2004





Table 8:Summary of operational parameter of column studies simulating fate and transport of EOCs
Note: n.r. means not reported; H.R.T means hydraulic residence time

Flow mode	Infilt ration rate	Pore water velocity	HRT (d)	Tracer experiment	Preferent ial flowpaths minimisation	Redox conditions	Flow regime cond.	bio conditions	How conditions were achieved	Ref
	1mL/min	4.4 cm/d	23 d	n.r.	n.r.	Anoxic	Saturated flow regime	Biotic	Stripping DO using medical grade N2.	
n.r.	nr.	11.5 cm/d	0.75 d	n.r.	n.r.	Aerobic	Saturated flow regime	Biotic	2 2 2	Mansell et al., 2004
n.r. (recirculation)	n.r.	851 cm/d	n.r.	n.r.	n.r.	n.r.	Unsaturated flow regime	Abiotic (NaN3 2mM)		
						Aerobic			feed water in an open tank	
up flow	υĽ	0.13 m/d	14 d	n.r.	n.r.	A no xic (DO=1.2 mg/L, consumed rap idly $\rightarrow 0$ mg/L)	Saturated flow regime	Biotic	degæsed with N2	Baumgartenet al., 2011
						Anaerobic			deg assed and additionally spiked with 1 mg/L starch as carbon so urce	
downflow (gravity -10 cm water co lumn)	n.r.	16.5 cm/d \rightarrow 7.5 cm/d \rightarrow 4.5 cm/d (clogging) (average: 5.3 cm/d)	n.r.	n.r.	n.r.	n.r.	Saturated flow regime	Biotic	nr.	Cordy et al., 2004
up-flow (A 10 mm thick PVC distributor cut out in the form of a tabytim was mound on the inner surface of bottom cap to facilitate even distribution of water over the entire cross section of the column.	5 mL/min	44-169 cm/d	0.5-2.2 d	Y es (fluorescein sodium salt)	ur.	Anoxic (dentrification) and anaerobic (sulphate reduction) processes occurred in the soil column in addition to aerobic degradation.	Saturated conditions	Biotic	Water saturated condition in the column was achieved by ensuring that the water level in the column was always above the surface of the sand during packing.	Essandoh et al., 2011
downwards with a pulsating pump at the bottom. This was done in order to maintain the field conditions since turning the core around might have disturbed the clogging layer.	600 mL/d	0.52 m/d	Jr.	Yes (NaCl)	עי.	Ожс		Biotic	Bubbling air to maintain constant saturation with O2.	M assman et al., 2008
						Araerobic (in columi)		Biotic	A rearobic in column by the delivery of ethanol to promete readureng conditions. Delivery system designed to minimise alterations of the water flow rate through the outurn. To promete the arabicition conditions, ethanol delivery on menced 101 d after delivery of the trace organics	
40104	360 mU d	4. cmd	24 2	Y es (Br-)	Ye	Aerobic (influent)	saturation	Abiotic (0.65 g/L) NaN3	commerced. Colum water entanol concentration of 700 mg/L (360 mg/L C). Aerobic inrifiluent. A saturated DO concentration (7.8 mg/L) of the influent water for each colum was maintained by continuous aeration using a small air pump dishcarging into the base of each influent water container.	Pattersonet al., 2011
		0 072-0 0 75 cm/min (5th	6,7-6,9 d → 8,1-9,7			n.r. The effluents from the active columns		Abiotic control Biotic		
Upflow direction	approx. 0,1mL/min	day of operation) $\rightarrow 0.05$ -0.05-0.05-0.05-0.05-0.05-0.05-0.05	d. Increase likely caused by clogging	tritiated water (³ H2O)	u.r.	all exhibited lower dissolved o xygen	n.r. (saturated??)	Biotic	חוי	Oneosis et al., 2012
		of operation) (clogging)	of tubing and column.			concentrations, which is indicative of aerobic resoliration within the		Biotic		
						colums.		Background control		
nr.	1 ml/min	29-36 cm/h	n.r.	Br	n.r.	A erobic (A naerobic degradation processes were likely to be minimal in	Saturated	Biotic and abiotic (sorption mechanisms)	Columns were saturated by pumping N2- purged electrolyte solution to minimise any trapped air in the soil column. O2	Das et al, 2004
Downflow (irrigationhead system) Drained by gravity (free drainage)	0.216 m/d	0,71-0,88 m/d	nr.	LiCI	nr.	nr.	Unsaturated flow regime	Abiotic/Biotic	υr.	Scheytt et al., 2006



Flow mode	Infiltration rate	Pore water velocity	HRT (d)	Tracer experiment	Preferential flowpaths minimisation	Redox conditions	Flow regime cond.	bio conditions	How conditions were achieved	Ref
Upflow (from bottom to top)	14.1mUh	6.3-6.5 cm/d	nr.	L L	л.: Л	Different denitrifying conditions	Saturated	ur.	Applying different NO3- concentrations in the feed (range 20-131 mg/L), different nitrate concentrations were established in the influent water	Banzhaf -2013
Dowrflow. The soil columns were irrigated with a 0.01M CaCl2- solution using an irrigation device	n.r.	0.25 cm h1	nr.	CI-	nr.	n.r.	near water saturation	n.r.	The soil columnswere slowly saturated from the bottom with tap water for 3 to 4 days.	Unold et al., 2009
Bottomto top	١Ld	1m'd	ż	NaCI (5 g/L)	1	Ойс		Biotic (sorption + biodegradation) Inactivated biomass (with 400 mg/LNaN3) (sorptiononto biomass) sorptiononto sorptiononto sand)		Bertelkamp et al., 2014
Bottom to top	5.6 × 10-9 m3/s	1.7 × 10–6 m/s		NaCI (50 mg/L)		Oxigen saturation 100%		Sorption experiments (Prior to the sediment was sterilized by autoclavation (121°C, 1 bar and 15 min).		Burke et al., 2013
Upward	600 mL/d			KCI (0.75 mg/L)			Saturation (upward to achieve saturation)	Yes		Greenhagen et al., 2014
Downward	n.r.	n.r.	6-7 days			1	Unsaturated flow regime	Yes		Tiehm et al., 2013
Downgradient	rairfal I rate: 3 cm rairfal I rate: 3 cm Rain events carried out 4 times for the whole experiment quantity applied: 4400 mL).			2			Saurated	Leaching experiment	Columns were kept at 25% for a one- week pre-incubation period and then for a 4-week strein period an an environmental carrier as Soll in the columns was saturated with 0.01 M CaCl2 and allowed to draing overright prio to the experient. After the treatment was applied, simulated raing (utreature wats) were applied weekly with a rainfall rate of 3 om over a 6-h period to the soil.	Huetal., 2009
Downward	0.55 mL/min	n.r.	35 d	CI-		n.r.	Saturated	Biodegradation	veure colurma acclimatization	Ke et al.,2012
Upward	0.060-0.078 L/h 1.0-1.3 mL/min	1.20-1.56 cm/h	n.r.	LiBr		Anoxic (even when ozone was ap plied)	Saturated	No		M uller et al., 2013
Upward	5.9 10 ⁻⁶ m3/h	0.3 m/d		LiCi		the prevailing conditions were anaerobic with an oxygen content between 0 and 1mg/L and a redox potential between 0 to 200 mV.	Saturated			Scheytt et al., 2004



 Table 9:
 Summary of monitoring strategies of column studies simulating fate and transport EOCs

	Sampling			
Pore water at different heights	Soil collection	Syringe/filter material	Monitoring	Ref
ou	ou	cellulose acetate membrane filters Teflon		
no	по	tubing glass containars	DOC, AbsUV, pH, cond, [MP]	Mansell et al., 2004
no	по	LUDING, BIRDO CONTRINETO		
yes -"the samples were taken very slowly to avoid disturbances of the column flow and aeration of the columns"	по	cellulose nitrate acetate (for SMX and DOC analyses) and cellulose acetate for all other	DO, pH, [SMX], SEC-OCD	Baumgarten et al., 2011
ou	ПО	Glass bottles, Teflon tubing	TOC, UV254, cond, T, MP, micro (PCR)	Cordy et al., 2004
Water sampling points consisting of 3.2 mm inner diameter stainless steel tubes were provided at ten points from the bottom of the column. These sampling tubes extended to the centre of the column's cross section. The sampling ports were closed by means of flexible tubing and a clip.	Q	u.r.	DOC, COD, BOD, TKN, TN, Org-N, NH3-N, NO3-N, NO2-N, PO4-P, SO4,DO, pH	Essandoh et al., 2011
		see Zuehlke et al., 2004	DO	Massman et al., 2008
Yes (19 sampling ports)	о	u.r.	MP	Patterson et al., 2011
QL	All columns were sectioned for biomass analysis on day 300 when column operation ceased.	polyethersulfone membranes	PPCP, pH, DO, ¹⁴ C	Oneosis et al., 2012
ou	ou	Amber-colored glassware was used to avoid photochemical reactions	MP	Das et al, 2004
The column was dismantled immediately after the end of each experiment and the water content was determined at different lengths within the column.	After the experiment the sand column was segmented.	n.r.	(EH, pH, temperature, oxygen saturation, specific conductance), MP	Scheytt et al., 2006
ę	At the end of the experiment, sand samples (2-5 g) were taken from the bottom and top of the columns, to determine adenosine triphosphate (ATP) concentrations as a measure of biological activity.	The pump tubes were connected to the columns by black polyethylene tubing (di ¼ 4 mm, Festo, The Netherlands).	DOC, UV254, DO, T, pH	Bertelkamp et al., 2014
Qu	Qu	The entire tubing and tube connections used during the experiment were made of polytetrafluoroethylene (PTFE).	pH, temperature and the electrical conductivity (EC)DO,	Burke et al., 2013
ou		Tygon tubing, PVC manifold pump tubing, vinyl tubing, brass compression fittings, and	Mn, Fe, Eh, pH, ConductivityNO3-, SO42-	Greenhagen et al., 2014
ou	Yes			Hu et al., 2009
Yes	No	Glass syringe		Ke et al., 2012
No	No		Cations, Anions, DOC, TOC, Carbonate hardness (CH) and Total hardness (TH), MP.	Muller et al., 2013
			anions. cations, MP.	Schevtt et al 2004





Table 10: Summary of numerical modelling approaches of column studies simulating fate and transport EOCs

Values of constants compiled from different studies (time: duration of experimental columns; experiment: data obtained in the experiment described in the reference paper; literature: experimental data has been compared with available literature data; ref literature: author of the paper used in the example)

			2	and an and an and a second	1/1	[]	-1		[70]	
			۸D	units: [- adimension	ai - L/Kg - g,	/cm]	Average C/Co		Recovery [%]	
	Reported time	Compound	Experiment	Literature	Ref literature	Comments	Experiment	Experiment	Literature	ket terature
'le		Carbamazepine	0.2 [-]	0.3 - 8.4 [-]		High sorption				
12 1 6f		Sulfamethoxazole	0.15 [-]	0.1 - 1.5 [-]		Low sorption				
0Z Əuze		Benzotriazole	0.15 - 0.2 [-]			Low sorption				
R		lopromide	No sorption			Sorption Neglected				
ʻ'le		Gemfibrozil								
¢ d وژ	Adaptation	Trimethoprim								
107 We>	period of 4	Metoprolol								
llətr	months	Carbamazepine		0.49 - 37 [L/kg]	[11]					
əg		Sulfamethoxazole		0.23 - 37.6 [L/kg]	[11]					
0T0 1ə suə		Benzafibrate	0.35 +/- 0.06 [g/cm]							
omei2 le		Diclofenac								
al, 2007 Scheytt et	48 h(*)	Diclofenac					0.18 [-]			
0006 مراد ور		Carbamazepine	0.131 [L/kg]				0.93 [-]	102	93-105% saturated conditions 102% unsaturated conditions	16] [17]
z 'le əys		Diclofenac	0.572 [L/kg]				0.55 [-]	63	97-106% saturated conditions 63% unsaturated conditions	
Jia et al., 2007		Benzotriazole	0.011-0.042 [L/kg] subsoil column 1.29-2.58 [L/kg] Fe0 column test	0.195 - 0.399 [-]	[9]					
Gillis et al, 2012	48 hours	lopromide	1,49	157						
12 1 et		Sulfamethoxazole					0,85	45		
OZ ' eyzı		Carbamazepine					0,62	74		
i68 I6		Diclofenac					0,84	66		
, le i			0.297 +- 0.005 pH 5.0					0.56 pH 5.0		
TTOZ Strauss ei		Sulfamethoxazole	0.128 +- 0.003 pH 6.5 0.111 +- 0.012 pH 8.5 0.09 +- 0.001 pH 8.5					0.62 pH 6.5 0.77 pH 8.5 0.92 pH 8.5		
13 6£		Primidone	0.02 [L/kg]	0.02 - 0.75 [L/kg]	[12]					
" 50 مېلاھ		Phenazone	0.02 [L/kg]							
B		Metoprolol	0 [L/kg]							



							;; ;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;					
		Half-life time	e [d days/h hours/m n	[nir	μ (first order decay) [d -1]		Degradation rate [h-:	1]			Log Koc	
	Compound	Experiment	Literature	Ret literature	Comments	Experiment	Experiment	Literature	Ref literature	Experiment	Literature	Ret literature
'le	Carbamazepine	7 days	328 days		High persistence							
15 L G£ :	Sulfamethoxazole	No degradation	Few months		Moderate persistence							
07 Əuze	Benzotriazole	No degradation	29 +/- 4 days		No degradation							
к	Iopromide	1 - 3 d			Moderate persistence							
"I¢	Gemfibrozil	1 h	4 m; 17.8 m; 20.6	[13] [14]		12,7						
e tə o	Trimethoprim	1 h	3 m	[13]		11,5	_					
7074 dwe	Metoprolol	12 h	4.1; 8.7	[15]		1,4						
: Ylətr	Carbamazepine					0						
Be	Sulfamethoxazole					0	-					
0T0 1ə sua	Benzafibrate					0.033 +/- 0.03						
əməi2 X ,.le	Diclofenac						_				2.2 - 3.42	[19]
3cheytt et 3cheytt et	Diclofenac					not aplicable	not aplicable					
0006 ۸۴۴ פל	Carbamazepine					0,006	1.84 usaturated cond	2.8 - 3.3 saturated cond.	[16] [17]			
gʻle Əys	Diclofenac					0,37	4.8 unsaturated cond	2.0 - 2.6 saturated cond.	[16] [17]			
,la et al., 2007	Benzotriazole						1.05 - 1.19 subsoil column 14 - 27 Fe0 column test					
Gillis et al, 2012	lopromide											
12 f et	Sulfamethoxazole											
07 " eyzu	Carbamazepine										1.9 - 2.11	[20]
e8 e	Diclofenac											
Strauss et al.,	Sulfamethoxazole	3.2 pH 5.0 3.92 pH 6.5 8.9 pH 8.5 26.8 pH 8.5				0.219 +- 0.005 pH 5.0 0.178 +- 0.002 pH 6.5 0.078 +- 0.008 pH 8.5 0.026 +- 0.002 pH 8.5						
13 6£	Primidone						1,1			0,91	- 0.04 - 1.07	[12]
י' 50 חוגאפ	Phenazone						1,1			1,01	-	
e 8	Metoprolol						1	16	[18]	0,17	1.75 - 2.22	[15]

REFERENCE LIST OF APPENDIX TABLE 10

- EC, IWA, Kazner (2012). Water Reclamation Technologies for Safe Managed Aquifer Recharge Editor(s): Christian Kazner, Thomas Wintgens, Peter Dillon. Publication Date: 15 Apr 2012 ISBN: 9781843393443
- [2] Bertelkamp C., Reungoat J., Cornelissen E.R., Singhal N., Reynisson J., Cabo A.J., van der Hoek J.P., Verliefde A.R.D. Sorption and biodegradation of organic micropollutants during river bank filtration. A laboratory column study. Water Research 52 (2014) 231-241.
- [3] Siemens, J., Huschek, G., Walshe, G., Siebe, C., Kasteel, R., Wulf, S., & Kaupenjohann, M. (2010). Transport of pharmaceuticals in columns of a wastewater-irrigated Mexican clay soil. Journal of environmental quality, 39(4), 1201-1210.
- [4] Scheytt T., Mersmann P., Leidig M., Pekdeger A., Heberer T. Transport of pharmaceutically active compounds in saturated laboratory columns. Ground Water 42 (2004) 767-773.
- [5] Scheytt T.J., Mersmann P., Heberer T. Mobility of pharmaceuticals carbamazepine, diclofenac, ibuprofen, and propyphenazone in miscible-displacement experiments. Journal of Contaminant Hydrology 83 (2006) 53-69.
- [6] Jia, Y., Aagaard, P., & Breedveld, G. D. (2007). Sorption of triazoles to soil and iron minerals. Chemosphere, 67(2), 250-258.
- [7] Gillis, J. D., Prasher, S. O., & Price, G. W. (2012). Modelling pharmaceutical concentration in the soil profile using HYDRUS 1D.
- [8] Banzhaf S., Nödler K., Licha T., Krein A., Scheytt T. Redox-sensitivity and mobility of selected pharmaceutical compounds in a low flow column experiment. Science of the Total Environment 438 (2012) 113-121.
- [9] Strauss, C, Thomas H., and . Radke. "Effects of pH and manure on transport of sulfonamide antibiotics in soil." Journal of environmental quality 40.5 (2011): 1652-1660
- [10] Burke V., Treumann S., Duennbier U., Greskowiak J., Massmann G. Sorption behaviour of 20 wastewater originated micropollutants in groundwater – Column experiments with pharmaceutical residues and industrial agents. Journal of Contaminant Hydrology 154 (2013) 29-41.
- [11] Drillia, P., Stamatelatou, K., & Lyberatos, G. (2005). Fate and mobility of pharmaceuticals in solid matrices. Chemosphere, 60(8), 1034-1044.
- [12] Yu, L., Fink, G., Wintgens, T., Melin, T., & Ternes, T. A. (2009). Sorption behaviour of potential organic wastewater indicators with soils. Water research,43(4), 951-960.
- [13] Zearley, T. L., & Summers, R. S. (2012). Removal of trace organic micropollutants by drinking water biological filters. Environmental science & technology, 46(17), 9412-9419.
- [14] Fang, Y., Karnjanapiboonwong, A., Chase, D. A., Wang, J., Morse, A. N., & Anderson, T. A. (2012). Occurrence, fate, and persistence of gemfibrozil in water and soil. Environmental Toxicology and Chemistry, 31(3), 550-555.
- [15] Ramil, M., El Aref, T., Fink, G., Scheurer, M., & Ternes, T. A. (2009). Fate of beta blockers in aquaticsediment systems: sorption and biotransformation. Environmental science & technology, 44(3), 962-970.
- [16] Scheytt T.J., Mersmann P., Heberer T. Mobility of pharmaceuticals carbamazepine, diclofenac, ibuprofen, and propyphenazone in miscible-displacement experiments. Journal of Contaminant Hydrology 83 (2006) 53-69.
- [17] Mersmann, P., Scheytt, T., & Heberer, T. (2002). Column experiments on the transport behaviour of pharmaceutically active compounds in the saturated zone. Acta hydrochimica et hydrobiologica, 30(5), 275-284.
- [18] Kibbey, T. C., Paruchuri, R., Sabatini, D. A., & Chen, L. (2007). Adsorption of beta blockers to environmental surfaces. Environmental science & technology,41(15), 5349-5356.
- [19] Carballa, M., Fink, G., Omil, F., Lema, J. M., & Ternes, T. (2008). Determination of the solid-water distribution coefficient for pharmaceuticals, estrogens and musk fragrances in digested sludge. Water research, 42(1), 287-295.
- [20] Stevens-Garmon, J., Drewes, J. E., Khan, S. J., McDonald, J. A., & Dickenson, E. R. (2011). Sorption of emerging trace organic compounds onto wastewater sludge solids. Water research, 45(11), 3417-3426.