Removal of Organic micropollutants (OMPs) with Subsurface Iron Removal (SIR)

MSc Thesis

by

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Aknowledgements

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Abstract

This research explores the potential effect of Subsurface Iron removal (SIR) on the removal of organic micropollutants (OMPs). The presence of OMPs and their transformation products in the water environments globally, have raised concerns due to the potential environmental and human health risks they are posing. Recent technologies often fail to remove OMPs completely or require high energy levels and costs. Previous findings by Vitens water company have indicated that SIR application resulted in the attenuation of certain OMPs. Therefore, the effect of SIR as an alternative, cost-effective removal method of OMPs was investigated.

A continuous flow column experiment was conducted in order to simulate the processes which take place under oxic conditions at SIR for the removal of 5 targeted OMPs (bentazone, metformin, caffeine, carbamazepine and atrazine). Two columns were filled with iron oxides (FeOx) coated sand and manganese oxides (MnOx) coated sand respectively, in order to simulate the two precipitation zones created in the subsurface. The aim of the study was to investigate the removal efficiencies of the selected OMPs in both columns in order to understand if the SIR environment is favourable for the removal of OMPs.

Results indicated that for most compounds there was removal observed after 65 pore volumes of continuous flow. Metformin was hardly removed (<10% removal rate) in both materials. A higher removal efficiency was observed at the FeOx column for bentazone (65%), caffeine (54%) and carbamazepine(29%) , while atrazine was the only compound which had a greater affinity for MnOx, with a removal rate of 87%.

These findings suggest that SIR has a potential on the removal of certain OMPs. It is suggested that during SIR the OMPs existing in the subsurface, pass through the two precipitation zones and undergo removal processes within both zones. However, based on their respective affinities to each of these zones, their removal extents vary accordingly. Ultimately, the water extracted from the undergoing SIR exhibits a reduced concentration of OMPs, which is a result of the combined removal mechanisms operating within both precipitation zones.

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List of Abbreviations

Abbreviation	Definition
AOB	Ammonia Oxidizing Bacteria
AOPs	Advanced Oxidation Processes
DO	Dissolved Oxygen
EC	Electrical Conductivity
Fe(II)	Iron in +2 oxidation state
Fe(III)	Iron in +3 oxidation state
FeOx	Iron oxides
GC-MS	Gas Chromatography - Mass Spectrometry
LC-MS	Liquid Chromatography - Mass Spectrometry
Mn(II)	Manganese in +2 oxidation state
Mn(IV)	Manganese in +4 oxidation state
MnOx	Manganese oxides
NF	Nanofiltration
OMPs	Organic Micropollutants
PVC	Poly-Vinyl Chloride
PTFE	Polytetrafluoroethylene
RO	Reverse Osmosis
ROS	Reactive oxygen species
SIR	Subsurface Iron Removal

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Introduction

1.1. OMPs

1.1.1. The Occurrence of OMPs

Organic micropollutants (OMPs) are compounds which are found at very low concentrations in the ecosystem, usually from ng/L to μg/L (Arslan et al. 2017). The category of OMPs consists of different classes, such as pesticides, pharmaceutically active compounds, personal care products, endocrine-disrupting chemicals and plasticizers (Omar et al. 2019).

OMPs are frequently referred to as “emerging contaminants”. The term ”emerging contaminants” is commonly used to describe substances that were not previously recognized or considered to be of significant concern. However, with advancements in analytical techniques, previously unnoticed OMPs are now being detected in water environments. While many of these emerging contaminants currently lack regulation, it is expected that the number of regulated contaminants will gradually increase in the coming decades (Survey et al. 2011).

It is highly important to understand the way that these OMPs enter the environment, as well as the pathway they follow after their entry. Two of the main sources of OMPs in the environment are wastewater and agriculture. Figure 1.1 gives an overview of the OMPs fate after their entry in the environment.

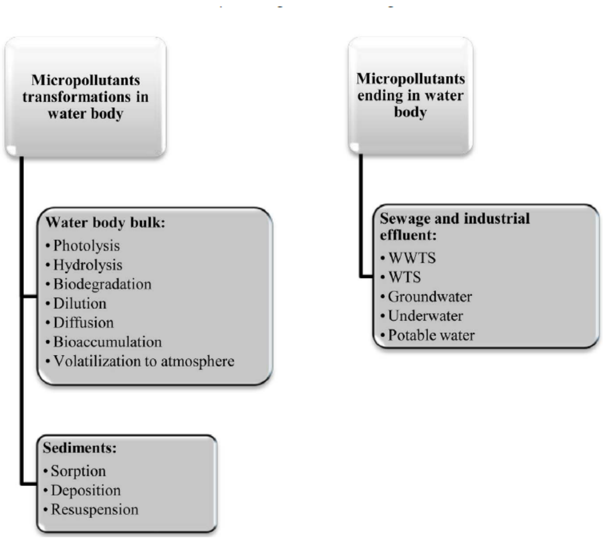


Figure 1.1: OMPs pathway of environmental contamination (Silva et al. 2017)

According to figure 1.1, after their entry, the pathway an OMP can follow varies. It can be (bio)chemically transformed, dissolved in water, or attached to solids (Farré et al. 2008, Metcalfe et al. 2013). The OMPs which are not quickly degraded, end up at different places and forms in the environment, based on their physicochemical properties (Corcoran et al. 2010, Daughton et al. 2001). Specifically, the less soluble OMPs in water tend to be more persistent and toxic compared to the ones with higher transformation rates and solubility, as the latter are highly dispersed (Farré et al. 2008).

1.1.2. Concern regarding OMPs

Recent studies have revealed that a significant quantity of OMPs, along with their transformation products, have been discovered in aquatic systems worldwide (Escher et al. 2014). While these compounds are generally found in very low concentrations and do not typically pose a significant risk of severe toxicity at such levels, their long-term persistence in the environment may give rise to chronic health issues (Schriks et al. 2010). The increased prevalence of diabetes, obesity, hormonal imbalances, cancer, cardiovascular, and reproductive ailments among humans in recent years could be due to long-term exposure to one or more of these micro-pollutants (Gautam et al. 2020). Furthermore, the presence of OMPs in the ecosystem over extended periods has been found to have detrimental effects on its biological characteristics, leading to the disruption of its functioning and purpose (Westergaard et al. 2001). Another reason for the growing concern surrounding these compounds is that OMPs with low Kow values are easily absorbed by aquatic plants, thereby entering the food chain (Yebra-Pimentel et al. 2015). Furthermore, they not only present ecotoxicity but they also have the potential to cause genotoxicity, such as mutations, chromosomal alterations and DNA modifications (Hoffmann et al. 2008).

The fact that OMPs exist at very low concentrations and their structures highly differ from one to another, makes the detection and the investigation of their degradation pathways a difficult procedure (Bila et al. 2003, Bila et al. 2007). Two main processes for their attenuation are sorption and (bio)degradation (Gerritse et al. 2009). The technologies used in the drinking water industry to remove them in order to ensure the safety of water are reverse osmosis, advanced oxidation and adsorption onto different media (Hofman-Caris et al. 2020).

1.1.3. OMPs Removal Pathways in the Environment

A. Sorption of OMPs in groundwater

The sorption of OMPs is an important process of their environmental behaviour (Schmidt et al. 2005). The process of sorption affects transport and bioavailability, which consequently affects the biotransformation of OMPs in porous media. OMPs adsorb onto the available surfaces, but can also remain in bulk phase. The process of adsorption has been found to be more important at lower concentrations, while partition in the water phase is of higher importance when the concentrations are higher (Kleineidam et al. 2002). The physical property which plays an important role in sorption is hydrophobicity. There are hydrophobic and hydrophilic OMPs. An indication to distinguish if an OMP is hydrophobic or hydrophilic is the octanol-water partition coefficient (Kow), which can be measured in the laboratory. OMPs with low Kow are considered hydrophilic, while OMPs with higher Kow values (e.g. more than 3-3.5) are characterised as hydrophobic (Gerritse et al. 2009). The hydrophobic ones present low affinity for solution in water. Therefore, are easily adsorbed to the organic matter of sediment and are rarely found in groundwater, whereas the hydrophilic get dispersed in the groundwater and are not adsorbed to the sediment (Gerritse et al. 2009).

B. Biodegradation

Another pathway OMPs can follow is biodegradation. It is considered the most important process for their complete attenuation in groundwater systems. Biodegradation refers to the transformation of a compound through microbial activity. It can be measured, by the detecting of degradation end products or by discovering degradation pathways, metabolites and active bacteria or enzymes. The bacteria which are responsible for the decomposition of the OMPs, are present in the groundwater systems in the soil. The role of the bacteria is to transfer electrons from the substrates to the electron acceptors, with the help of the appropriate enzymes (Gerritse et al. 2009). In this way, bacteria gain the necessary energy and elements they need for their growth and production of new cells. The OMPs usually act as the main source of energy and electrons. Depending on the type of bacteria, the electron acceptors vary. For example, when the bacteria are aerobic, O2 is used as the final electron acceptor for the oxidation of the OMPs. Some other compounds in the groundwater which can also act as electron acceptors are nitrate, Mn(IV) oxides, Fe(III) oxides, sulphate, carbon dioxide and humic acids. With "halorespiring" or "dehalorespiring" bacteria, OMPs act as the electron acceptors and get reduced. Another possible process is fermentation, where OMPs serve both as electron donors and acceptors, leading to mixture of oxidised and reduced products. Finally, there is also the process of "cometabolism", which can occur in oxic and anoxic conditions, and refers the process where OMPs are degraded but the microbes do not use any energy or carbon from them. The microbes, use enzymes to degrade their natural growth substrates, but because they have a wide substrate range, they also degrade the OMPs (Gerritse et al. 2009).

1.2. Removal Technologies of OMPs

1.2.1. Current Technologies

In industry, a number of technologies have been established for the removal of OMPs for drinking water production. Some examples of these are activated carbon, chemical oxidation and membrane separation.

A. Activated Carbon

In industry, activated carbon is widely used as the primary adsorbent for the removal of OMPs. It is derived from carbonaceous sources, such as coal or coconut husks. It is activated through chemical or thermal processes, and it has great properties, due to its significant inner surface (in the range of 800 – 1800 m2/g) and its hydrophobic surface (Lawtae et al. 2021). The compounds that are best removed with activated carbon are found to be non-polar, neutral compounds. Examples of compounds that are efficiently removed through adsorption with activated carbon include ibuprofen, ketoprofen, atrazine, and metoprolol (Sponar 2020). Nonetheless, activated carbon fails to remove most of the hydrophilic OMPs, while after some cycles of operation it needs either regeneration or disposal. However, for its regeneration still great amounts of energy are needed (Alsbaiee et al. 2016).

B. Chemical Oxidation

Research has shown that OMPs' removal has been achieved through chemical oxidation and specifically, with ozonation and advanced oxidation processes (AOPs). They have managed to transform a wide range of OMPs to less harmful products (Ikehata et al. 2006). While the hydroxyl radical (•OH) serves as the primary oxidizing agent in these processes, its application often leads to the generation and involvement of other reactive oxygen species (ROS). These additional ROS include superoxide radical anions, hydroperoxyl radicals, singlet and triplet oxygen, and more (Ikehata et al. 2006). For ozonation, there are two distinct mechanisms of action. In the alkaline pH range, ozonation predominantly operates through a radical mechanism, where radicals generated from ozone play a crucial role. Conversely, under acidic and neutral conditions, ozone directly reacts with the organic substances (Szabová et al. 2020). However, still these processes have drawbacks as they are highly energy and oxidant consuming, while the non-selectivity of hydroxyl radicals lead to the formation of a number of unwanted products (Chiron et al. 2000).

C. Membrane Separation

Another common technology used for the removal of OMPs is membrane separation, and especially nanofiltration (NF) and reverse osmosis (RO). RO and NF membranes have been found efficient for a wide range of organic micropollutants, specifically for the ones with a molecular weight of 200 - 400 g/mol (Habert et al. 2020, Sui et al. 2010). The removal efficiency of the membranes depends on a number of factors such as size exclusion, electrostatic repulsion, adsorption, diffusion, fouling (Silva et al. 2017). However, fouling poses a significant challenge to the effective operation of membranes.

It can result to reduced permeate flux, increases operational expenses, and a shortened lifespan of the membrane (Xu et al. 2006).

1.2.2. Iron Redox Cycling and Removal of OMPs

Previous research has shown that the couple of Fe(II)(aq) – Fe(III)(s) can potentially reduce organic and inorganic pollutants, nitroaromatics (Elsner et al. 2003, Hartenbach et al. 2006, Klausen et al. 1995, Strehlau 2016), pesticides (Sivey et al. 2012, Strathmann et al. 2003), as well as antibiotics (Mohatt et al. 2011). The mechanism that drives this chemical reduction of oxidised pollutants by Fe(II), takes place in three stages (Strehlau 2016):

The first step begins with the adsorption of Fe(II) to the iron oxide surface, causing an electron delocalization, which is the second stage of the interfacial electron transfer (Williams et al. 2004). This means that the electrons do not belong to a single atom or participate at a covalent bond but are expanded over different neighbouring atoms. This causes a decrease in the redox potential of the Fe(II) – Fe(III) couple, the Fe(III) oxidising state is stabilised, resulting in a more favourable transfer of an electron from Fe(II) (Farley et al. 1985, Schaefer et al. 2010, Stumm 1987). The third and final stage occurs when a contaminant approaches the surface of the iron oxide, and electrons are transferred to it, leading to its reduction (Strehlau 2016).

The three stages of the reduction of a nitroaromatic compound are shown in figure 1.2.

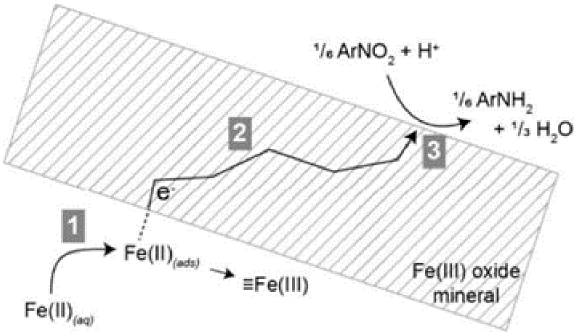


Figure 1.2: Schematic overview of the reduction of a nitroaromatic compound at the surface of iron hydroxide (Strehlau 2016)

1.2.3. Subsurface Iron Removal

Another potential technology for the removal of OMPs is the subsurface iron removal (SIR). SIR refers to the method where oxidation and filtration processes take place in the aquifer (in-situ) for the removal of iron, manganese, arsenic and other water compounds which need to be removed to meet drinking water quality standards.

For the subsurface treatment, two or more wells are needed, as well as a station for oxidising agent water enrichment, a degassing tank and a pipe-network for the uptake and infiltration of water from and to the aquifer. The process of the subsurface treatment begins with the delivery of water from the well (Figure 1.3). The delivered water is treated and a part of it passes through the oxidation station, where the oxidising agent is injected to the water. Subsequently, the oxygen enriched water flows through the degassing tank to remove the excess of gas and then it is reinfiltrated in the second well. As oxygen is introduced in the aquifer where there is little or no oxygen present, the redox potential is increased and an oxidation zone is created, where different physical, chemical and biological processes occur (U. Rott et al. 2002).

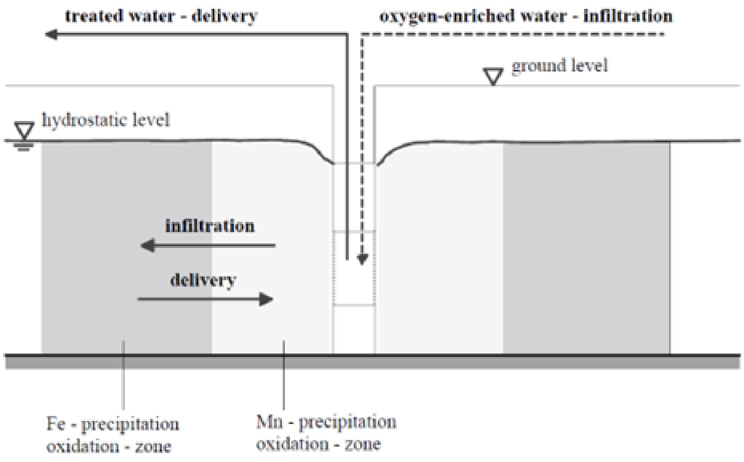


Figure 1.3: Creation of spatial, isolated oxidation zones of Fe and Mn in the aquifer (U. Rott et al. 2002)

The groundwater system is rich in soluble Fe(II) and Mn(II). The soil grains in the aquifer are partly coated with previously deposited oxidation products and bacteria. These grains adsorb Mn(II) and Fe(II) on their surface. Thus, during the next infiltration period, the oxygen, which is transferred along with the infiltrated water, oxidises the metals which are deposited on the soil surface into insoluble ferric and manganese oxides (U. Rott et al. 2002).

The reactions related with the iron and manganese oxidation are shown below with equations 1.1, 1.2:

$$2Fe^{2+} + \frac{1}{2}O_2 + (x+2)H_2O \rightarrow Fe_2O_3xH_2O + 4H^+ \tag{1.1}$$

$$Mn^{2+} + O_2 \rightarrow MnO_2 \tag{1.2}$$

As the subterranean treatment has begun, more and more iron and manganese oxides are precipitated in the aquifer, and these consequently adsorb more Mn(II) and Fe(II), leading to the increase of the adsorption rate of the bivalent ions (U. Rott et al. 2002).

A schematic overview of the above-mentioned process during the delivery and infiltration phases is shown in figure 1.4.

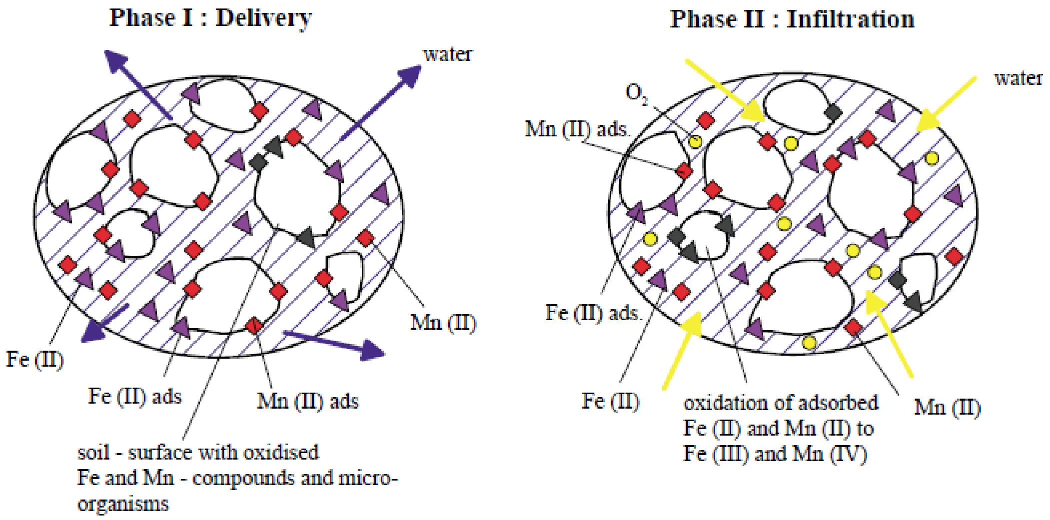


Figure 1.4: Schematic overview of the delivery and infiltration phases on the soil grains of the aquifer (U. Rott et al. 2002)

Since iron and manganese are oxidised at a different redox potential (Fe precipitation zone: -100 mV – 100 mV, Mn precipitation zone: +200 mV – 500 mV), the removal of iron and manganese occurs at isolated regions. This is illustrated at figure 1.3, where the Fe precipitation zone is the one further away from the well.

Apart from the oxidation of the Fe(II) and Mn(II) in the aquifer, biological activity also takes place. A variety of bacteria exist at the aerobic and anaerobic zones of the aquifer, which are adapted at the low nutrient supply, the existing water compounds, the pH, as well as the redox conditions (U. Rott et al. 2002). The oxygen, which is introduced with the infiltrated water, improves the environment for the bacteria, leading to an increase of the biological activity (U. Rott et al. 2002). Therefore, in the surface of the soil grains, a thin biofilm is formed by the present bacteria, and due to active and passive mechanisms the metals are restricted by it (Rott et al. 2000). Examples of these bacteria are the Gallionella ferruginea and Thiobacillus ferrooxidans, which are able to enhance iron oxidation and adsorb the bivalent ions on the soil surface, as well as the bacteria Sphaerotilus and Leptothrix which oxidise Mn(II) to Mn(IV) (Bouwer et al. 1988).

The literature review showed that there is potential in the removal of OMPs during the SIR technique. However, to the best of the author’s knowledge, little research has been conducted to examine the potential removal of OMPs during the SIR, which is already established for years in the drinking water production. During SIR, the environment of the iron and manganese oxides and the soluble Fe(II) and Mn(II), which are adsorbed on the available surface of the oxides, creates favourable conditions for the chemical reduction of the present OMPs. Additionally, the processes of sorption and biodegradation are also possible for the enhancement of the OMPs’ removal from the groundwater, since there is available surface for OMPs to attach, as well as microbial communities present.

1.3. The Vitens Case

In 1994, Vitens started the application of SIR at the Dinxperlo production site. The continuous supply of oxygen in the naturally oxygen-depleted sand layer, resulted in the oxidation and removal of various substances, including the target pollutants: ferrous iron and soluble manganese. Analysis of the iron content trend led to the conclusion that both the infiltration-extraction cycle and oxygen supply were well-adjusted.

Before the implementation of SIR at the Dinxperlo production facility, there were elevated concentrations of bentazone. However, following the application of SIR, a surprising shift occurred, with concentrations dropping below the Dutch drinking water quality standards of 0.1 µg/L for individual pesticides. This led to speculation that the reduction in bentazone concentration might be directly related to the implementation of SIR.

Figure 1.5 shows the results obtained from one of the wells of the Dinxperlo production site.

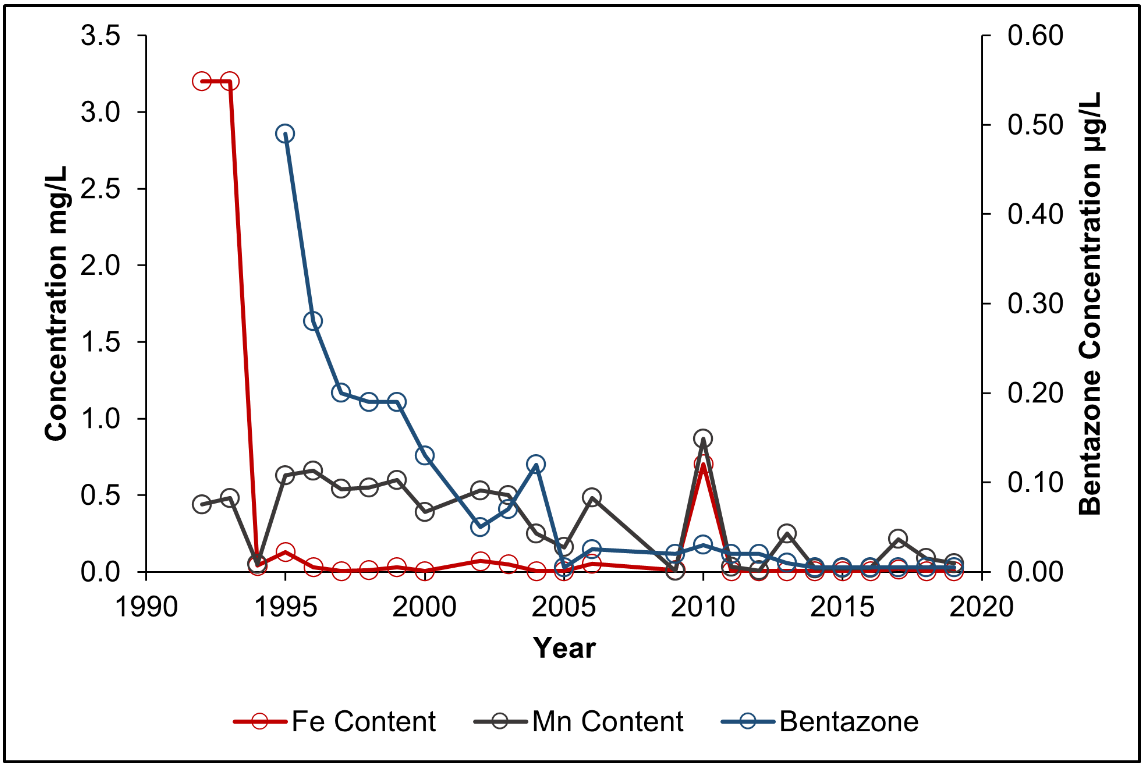


Figure 1.5: Fe, Mn and bentazone concentration at the Vitens well

It is worth noticing that the pattern of bentazone is more comparable with that of manganese than with the pattern of iron, since iron concentrations immediately decreased in contrast to manganese and bentazone which presented fluctuations.

However, the reduction of bentazone during SIR is still not well explored. The goal of this study is to confirm if OMPs including bentazone can be removed during the FeOx and/or MnOx zones of SIR.

1.4. Research Questions

The following research questions arise:

- Are the conditions created during subsurface iron removal favouring OMP removal?

Sub-questions:

1. Which zone (Mn vs Fe oxidation zone) has greater influence on the organic micropollutants' removal?
2. Which selected organic micropollutants are removed better with subsurface iron removal?
3. Is it possible to distinguish the mechanisms which take place during the removal of OMPs in the two zones?

2

Materials and Methods

2.1. OMPs

2.1.1. OMPs selection

The targeted OMPs were bentazone, metformin, caffeine, carbamazepine and atrazine. Bentazone was selected due to its promising results during SIR at the Vitens production site. Furthermore, all compounds have been detected in the groundwater systems (Ebrahimzadeh et al. 2021, Ambrosio-Albuquerque et al. 2021, Sjerps et al. 2019).

The physicochemical properties of the five OMPs present differences and are shown at table 2.1.

Table 2.1: Properties of the selected OMPs

Name	Category	CAS no.	Formula	MW	Charge [a, b]	Strongest acidic pKa [b]	Strongest basic pKa [b]	logD [a,b]	Solubility in Water (mg/ml) [a, b]
Bentazone	Pesticide	25057-89-0	C10H12N2O3S	240.28	Negative	2.03	n.a	-0.19	240
Metformin	Pharmaceutical	657-24-9	C4H11N5	129.17	Positive	n.a.	12.3	-5.62	8340
Caffeine	Pharmaceutical	58-08-2	C8H10N4O2	194.19	Neutral	n.a.	-1.16	-0.55	70.5
Carbamazepine	Pharmaceutical	298-46-4	C15H12N2O	236.27	Neutral	15.96	n.a.	2.77	0.04
Atrazine	Pesticide	1912-24-9	C8H14ClN5	215.68	Neutral	15.84	4.2	2.20	0.03

[a] : at pH 7.4 [b] : Obtained from http://www.chemicalize.org

2.1.2. OMPs Feed Solution Preparation

Firstly, the OMPs Stock solution (Sigma-Aldrich) was prepared by the laboratory of Sanitary engineering of the Civil Engineering Faculty of TU Delft. The aimed concentration of the stock solution was 100 µg/L. The stock solution was preserved in the fridge under 4°C .

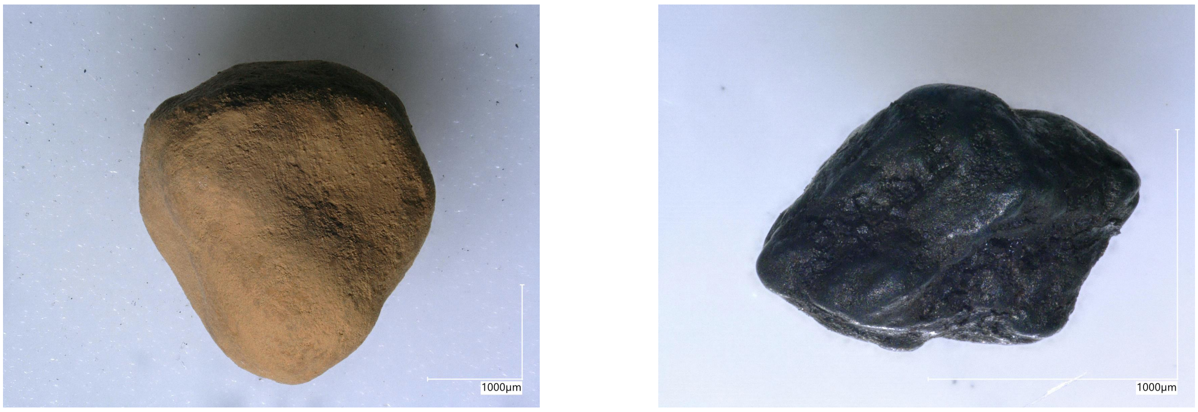
The feed solution for each phase was prepared by diluting the stock solution with the effluent water from the PIDPA Drinking water treatment plant. The bottles used for the storage of the feed solution were Duran bottles in different sizes (2 L, 3.5 L, 5 L, 10 L). Prior to use, the bottles were firstly rinsed with technical methanol (VWR Chemicals), afterwards with ultrapure water (ELGA, water purity at 18.2 MΩ.cm) thrice and were left inside the fume hood for 24 hours. The rinsing procedure took place to reassure that there were no previously deposited OMPs attached on the glass, while the use of fume hood aimed to the evaporation of any methanol leftovers. Multiple feed solutions were prepared at different stages of the experiment. Feed solutions aimed to achieve a target concentration of approximately 1 µg/L for each OMP. For the measurement of the stock solution's volume a 10 mL pipette (Thermo Scientific) was used, while for the tap water's volume measurement, Duran measurement balloons of different sizes (100 mL, 250 mL, 500 mL, 2000 mL) were used depending on the target size of the feed solution.

During the main experiment, for the FeOx column there were 3 changes in total (4 feed solutions at the moments where PV=0, PV = 9.3, PV= 18 and PV= 32.2) while for the MnOx column, there were 2 changes (3 feed solutions at the moments where PV=0, PV= 27.1 and PV = 36.3). It is noted that, for the time span of the pore volumes 18 – 73.6 of the FeOx column , and the time span of 27.2 – 82.7 pore volumes for the MnOx column, the feed solutions were the same for both columns and direct comparison between the concentrations is possible.

2.2. Sand Material

The FeOx and MnOx coated sand which was used for the column setup was collected from the two sand filters of the PIDPA Drinking water treatment plant, located in Mol, Belgium on the 09/12/2022. The sand grains coated with FeOx, were collected from the pre-filter of the plant, where iron removal takes place. The sand grains which are coated with MnOx were collected from the post-filter of the plant. In the post filter, nitrification takes place, thus it is highly probable that AOB communities are present on the coated grains as well.

The sand grains were collected from the top layer of the filters when operation was paused for backwashing. Both types of the collected sand were stored at the refrigerator at 4°C for 4 months until use. Prior to the experiment, the material was soaked in tap water for at least 24 hours in order for the entrapped air bubbles in the pores of the material to escape and be saturated with water.



(a) FeOx coated sand grain

(b) MnOx coated sand grain

Figure 2.1: Microscopic pictures of the FeOx and MnOx coated sand grains used at the experiment

2.3. Water

The water used is tap water which was collected from the PIDPA drinking water treatment plant, located in Mol, Belgium on the 09/12/2022. It was stored at the refrigerator at 4°C for 4 months until use. Tap water was selected for the feed solutions due to the absence of OMPs. This, enabled the determination of the exact initial OMPs concentrations which were spiked to both columns.

2.4. Column System

The experimental setup consisted of two identical columns. Both columns consisted of three individual sections connected via Teflon tubing to allow for sampling at different bed heights. The first column was packed with FeOx coated sand, while the other column set, was packed with MnOx coated sand. Two columns were used in order to simulate the two zones of the SIR. Thus, the FeOx precipitation zone in the subsurface was simulated with the column filled with Feox coated sand, while the MnOx zone was simulated by the column filled with MnOx coated sand. The material of the columns was glass, while the caps were made out of PVC. Teflon tape was used for the attachment of the caps to the columns. All columns were covered in aluminium foil for photodegradation to be prevented.

At table 2.2, the characteristics of the columns are shown.

Table 2.2: Column characteristics

Column Data		
Column Height	50	cm
Radius	1.2	cm

Each column set was connected to a 120U Watson & Marlow peristaltic pump. The connections in the system were made with PTFE tubes (6 mm). The system consisted of 6 sampling points, one after each section. The system was operated in uplfow mode. The system is presented at figure 2.2.

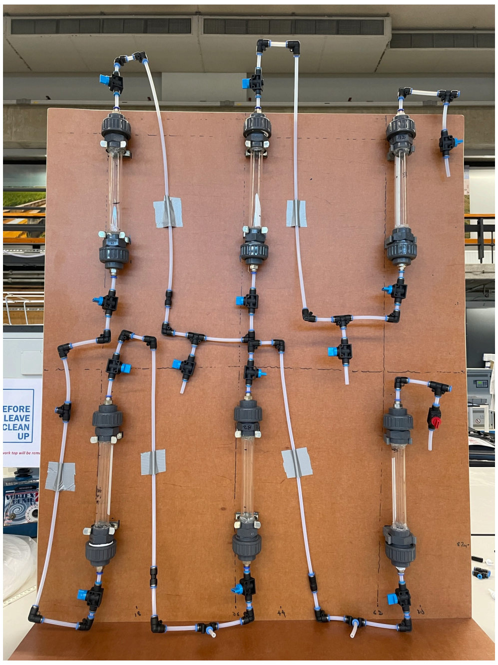


Figure 2.2: Column set-up and tubing, before filling with FeOx and MnOx coated sand

For clarity and simplification reasons, throughout the report the FeOx column is referred to as column A, while the MnOx filled column is referred to as column B.

2.5. Experiments

2.5.1. Tracer Test with NaCl

In order to determine the porosity of the system, a tracer test was performed in both columns. For the tracer test, NaCl (Carl Roth) was used as the inert tracer and measurement were carried out using an EC-meter. The feed solution was prepared in a 1L Duran bottle, with an initial EC of 2.77 mS/cm (2.1 g/L of NaCl). After the initiation of the experiment with the introduction of the NaCl solution, there was constant measurement of the effluent's EC.

The volume of water which passed through the columns at the of 50% breakthrough (EC/ECo = 50%) was used for the calculations. This volume consisted of the pore volume and the dead volume, which in this case was the volume of the tubes. Hence:

$$Pore\ Volume = Volume\ at\ 50\%\ breakthrough - tubes'\ volume \tag{2.1}$$

Since there was the assumption that each column is identical, equation 2.1 refers to the pore volume of the system.

Finally, according to equation 2.2 the porosity of the system was found:

$$Porosity = \frac{Pore\ Volume}{Empty\ Column\ Volume} \tag{2.2}$$

After the determination of the pore volume of the two systems, the flow rate for the column sets was chosen. For column A, the flow rate was set equal to 45 mL/hr, while for column B, the flow rate was equal to 46 mL/hr, which remained unchanged throughout all stages. The filtration rate for columns A was 0.17 m/h, while for columns B filtration rate = 0.16 m/h. The contact time of the systems was calculated as follows:

$$Contact\ Time = \frac{Pore\ Volume}{Flow\ Rate} \tag{2.3}$$

2.5.2. Column Start-up and operation

The system was operated for 6 days under continuous flow in oxic conditions. The feed of the experiment was the tap water from the drinking water treatment plant, without OMPs. Samples were taken from both sets on the first and sixth day of the experiment. The samples were analysed for their pH and DO levels with a WTW 3630 IDS Multimeter. Results can be found in the Appendix.

2.5.3. Column Experiment

Both columns were operated for 10 consecutive days in oxic conditions. The feed solutions prepared by the stock solutions were used as the influent of the columns. For both sets the feed solution changed multiple times during the whole duration of the experiment. For column A, there were 3 changes of feed solution, on days 2, 3 and 8. For column B, there were 2 feed solution changes on days 4 and 8. During the first day of the experiment, samples were taken from all the sampling points, but after the second day samples were only taken from the sampling point at the exit of the third column of each set.

The same experiment was repeated with a shorter duration and a higher feed solution. The duration of the duplicate experiment was 8 pore volumes, while the target concentration of the feed solution was 10 µg/L. The scope of the experiment was the investigation of atrazine's behaviour and the detection of atrazine's transformation products, desethylatrazin and desisopropylatrazin. The results of the experiment can be found in the appendix.

2.6. Analysis

2.6.1. Sampling

Three different types of samples were collected during the experimental phases. For the main experiment samples were collected only for LC-MS analysis, while for the duplicate experiment samples were collected only for GC-MS analysis by an external lab in order to detect the levels of atrazine and its transformation products.

All the samples that were collected for the LC-MS and GC-MS, were collected in 40 mL TOC free glass vials with screws cap with hole with Teflon/silicone septum (Supelco), in order to prevent OMPs from getting adsorbed to possible carbon sources present at the sampling vials. After the sample collection, the sampling vials were covered with aluminium foil.

During the main experiment, which lasted in total 73.6 and 82.7 pore volumes for column A and B respectively, 12 samples were collected from the effluent of each column for LC-MS analysis and 2 from each feed solution.

During the duplicate experiment, 8 samples were collected in total for the GC-MS analysis. 1 sample of each column was collected prior to spiking OMP water and were considered as the blank samples, 2 samples from the feed solution and 2 samples from each column's effluent after 3.5 pore volumes had passed.

2.6.2. Sample Preparation

Prior to the LC-MS and GC-MS analysis, all samples had to be filtered through a 0.20 µm filter (CHROMAFIL Xtra). 2.5 mL Terumo syringes were used for the extraction of the sample from the vials and filtered with the 0.20 µm filters. Subsequently, the filtered samples were transferred to 15 mL Sarstedt PP tubes, where a 100 – 1000 µL Eppendorf pipette was used to collect 490 µL of the sample. A 2 - 20 µL Eppendorf pipette was used to collect 5 µL of the Internal Standard solution. The collected sample and internal standard solution were placed in a 1.5 mL glass vial (Macherey - Nagel).

2.6.3. LC-MS Analysis

High performance liquid chromatography combined with tandem mass spectrometry (LC-MS) were used to analyze the OMPs concentrations. An ACQUITY HSS T3 Column (1.8 µm particle size, 2.1 x 150 mm) was used. A qualitative analysis was performed with two daughter ions of OMPs and deuterated internal standards were used for OMP quantification.

2.7. Feed Solution Problems

The feed target concentration of 1 ug/L was not achieved for pollutants such as atrazine, carbamazepine and bentazone (concentrations as low as 0.09 ug/L) and varied substantially throughout the duration of the operation. The low concentrations in the feed were a consequence of too low pollutant concentration in the stock solution and it is hypothesized that these were a consequence of expired standards and weighing errors. The variations in the feed coincide with the change of the feed bottles were most likely a consequence of errors in the preparation of the feed solution. Additionally, for some compounds, the LC-MS analysis was not successful, since the concentrations were below the detection limit, resulting into inability to retrieve measurements. The results of the concentration of each compound at the 7 feed solutions that were used are presented in the Appendix.

3

Results & Discussion

3.1. OMP removal by FeOx column

In order to investigate the removal of OMPs in the FeOx precipitation zone, results obtained from the FeOx packed column are presented.

At figure 3.1, the breakthrough curves of the five compounds are presented. The graph refers to the first 7.3 pore volumes, when the first feed solution was introduced to the column. On the y-axis the OMPs concentration over the highest concentration in the effluent (cmax) during this range of pore volumes is presented.

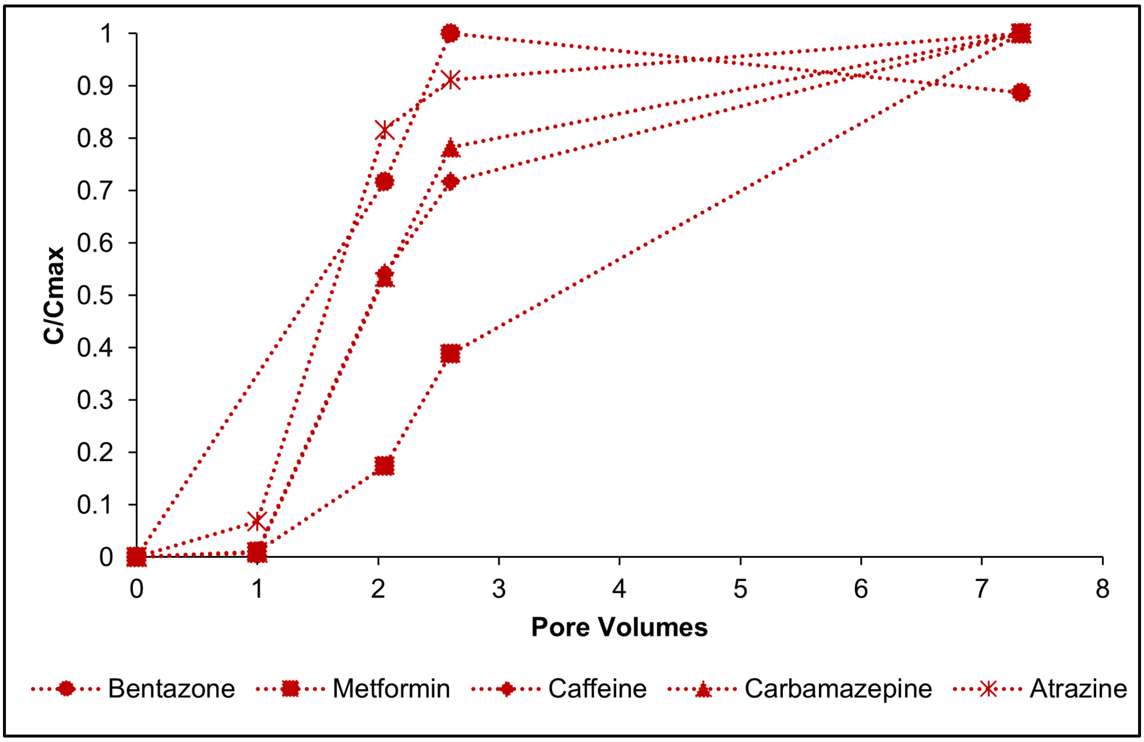


Figure 3.1: Breakthrough curves of the OMPs at the FeOx column during 0 - 7.3 pore volumes

First of all, bentazone's breakthrough curve is not complete since concentration results during pore volumes 0 – 2 were not available. However, from the rest of the concentration points it is obvious that bentazone reached full breakthrough after 2.5 pore volumes, which is the fastest compared to the other compounds. For the other four compounds, the breakthrough curves were complete. It is apparent from the graph that atrazine was the second compound to break through the system. Carbamazepine and caffeine were the next ones, with carbamazepine passing through the column more rapidly since its curve is higher than the curve of caffeine. The last compound which presented a very different trend compared to the others was metformin. However, metformin's first three concentration points are in great distance with the final concentration point, so the linear trend presented on the graph from 2.5 – 7.6 pore volumes cannot be considered accurate, since another point in between would have indicated its trend more precisely.

In order to quantify the retardation that each compound faced during their passage through the FeOx column, the indicator of the retardation factors at the 50% breakthrough are used in terms of pore volumes. This indicates the pore volumes passed, when 50% of the compound has passed through the system.

At table 3.1 the retardation factors of each compound at the FeOx column are presented.

Table 3.1: Retardation Factors at 50% breakthrough at the FeOx column

Retardation Factor	FeOx
Atrazine	1.6
Bentazone	-
Metformin	>2.6
Caffeine	2
Carbamazepine	2

For bentazone, the retardation factor was not taken, since the first concentration point available was after 2 pore volumes. However, since bentazone was the first compound to reach complete breakthrough already from 2.5 pore volumes, it is assumed to be the compound with the lowest retardation factor. For metformin, the exact retardation factor cannot be determined. However, since there was a concentration point at 2.6 pore volumes, where the $C/C_{max} < 0.5$, the retardation factor can be assumed that is higher than 2.6.

However, the results obtained are contradictory to previous research. According to Clausen et al. 2001, when the adsorption ability of certain OMPs onto iron oxides was studied, it was found that for bentazone, adsorption onto FeOx was significant, especially when compared to other pesticides such as atrazine. From figure 3.1 though, it is shown that atrazine presented a later breakthrough than bentazone, indicating that atrazine has a greater affinity compared to bentazone.

Furthermore, previous research has underlined the importance of the carboxyl group for the adsorption onto FeOx, suggesting that carboxyl group has greater affinity for FeOx compared to other functional groups. However, as outlined in prior investigations (Wang et al. 2023), caffeine was found to be completely removed by synthetic FeOx sand, despite the fact that it lacks carboxyl groups. From figure 3.1, caffeine presented indeed a later breakthrough compared to bentazone, atrazine and carbamazepine, but not from metformin.

Figure 1.4 illustrates the OMP loading in the FeOx column over the volume of the FeOx coated sand grains during the initial 7.3 pore volumes. The highest concentration of each compound during the range of the pore volumes was taken to represent the inlet concentration.

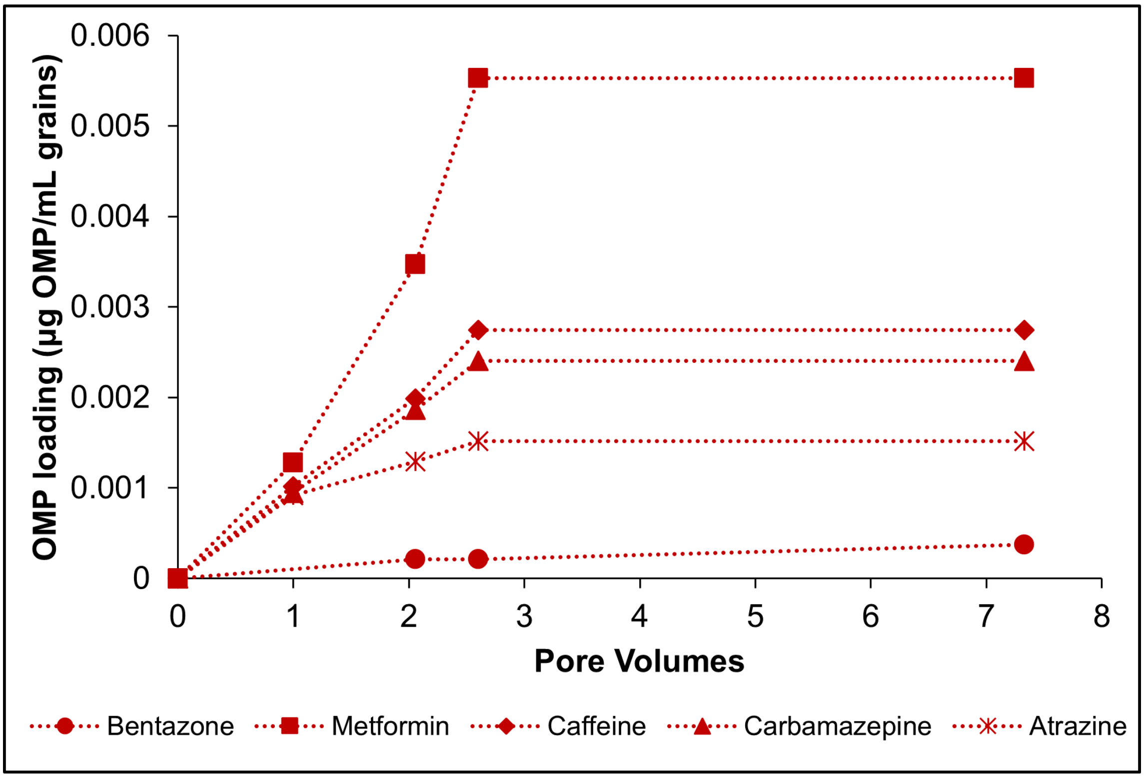


Figure 3.2: Loading graphs of the adsorbed mass of OMPs over the volume of the FeOx grains

it is apparent that all OMPs, except bentazone, present a similar trend. If bentazone is excluded, the other four compounds show an increasing trend in the first 2.5 pore volumes, and afterwards they all reach a plateau. However, for bentazone the trend is linear. This can be justified due to the fact that for bentazone, the initial concentration points in the FeOx column were not available (0-2 pore volumes), so it is assumed that the part of the graph presented in figure 3.2, is the part where the plateau has already been reached and probably in the pore volumes 0 – 2 an increase would have been observed.

First of all, it is observed that the loading for all compounds is quite low (less than 0.006 µg/L). This indicates that the adsorption capacity of the oxides is low. Furthermore, the order of the OMPs based on their loading capacity, from highest to lowest is: metformin, caffeine, carbamazepine, atrazine and bentazone. It is notable that metformin reaches a significantly higher value of loading compared to the other four compounds, almost double than the second highest which is caffeine. The results align with the outcome of the breakthrough results. However, it is worth noticing that the initial concentration taken might play a role in the outcome, since bentazone maximum concentration was equal to 0.261 µg/L, substantially lower than the maximum concentrations of the other compounds.

After focusing on the initial 7.3 pore volumes of the FeOx column, a closer look on the final 65.3 - 73.5 pore volumes was taken. During this phase, it is assumed that a steady state has been reached at the system and OMPs concentrations were expected to be stable.

For the calculation of the average concentration, two concentration points were used for each compound, except for carbamazepine in which three concentration points were available. However, it is noted that for carbamazepine in the FeOx column, the 3 concentrations used for the calculation of the average concentration presented great differences (range: 0.1474 µg/L - 0.6998 µg/L), so it was not considered stabilised. However, the average calculation was calculated.

Figure 3.3 shows the average concentration during steady state in comparison with the measured influent concentration, as well as the error bars which indicate the minimum and the maximum concentrations. Error bars of the influent concentrations are not shown, since the concentrations presented are the maximum concentrations obtained from the measurements.

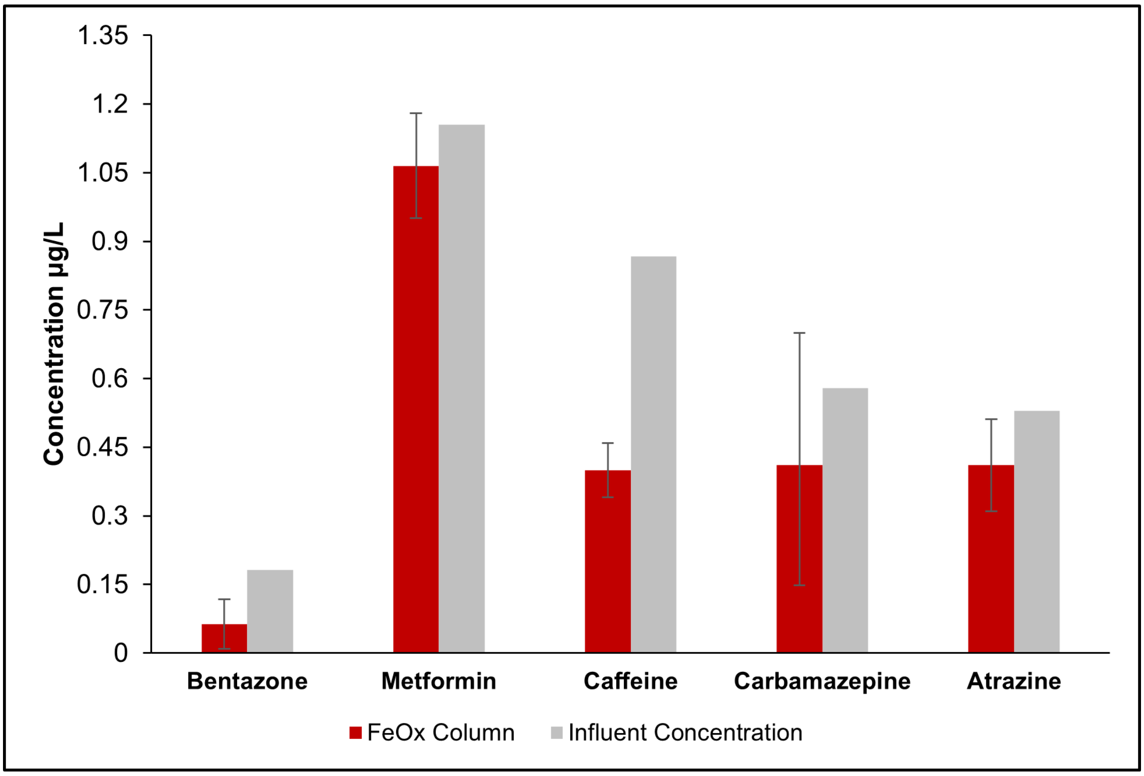


Figure 3.3: Average concentrations of OMPs during steady state at the FeOx column with error bars indicating the minimum and maximum concentrations

Compared to the influent concentrations spiked to the FeOx column, the average effluent concentration of all compounds was lower, so it is apparent that removal occurred for all compounds. The removal rates of each compound are presented in table 3.2.

Table 3.2: OMPs removal rates at the FeOx column during steady state

Compound	Removal Rate (%)
Bentazone	65.02
Metformin	7.76
Caffeine	53.88
Carbamazepine	28.94
Atrazine	22.45

The OMPs removal rates vary from 7.76% to 65.02 %, with the lowest to be achieved by metformin and the highest by bentazone. The second highest removal rate was observed by caffeine (53.88%), while carbamazepine (28.94%) and atrazine (22.45 %) presented a moderate removal.

The results obtained during steady state are in contrast to the results obtained during the initial pore volumes (Figure 3.1 & Figure 3.2), in which bentazone presented the lowest affinity to the FeOx and metformin the highest. This can be an indication that after a specific amount of pore volumes have passed, other mechanisms of OMP removal take place besides adsorption for their removal.

3.2. OMP removal by MnOx column

In order to explore the elimination of OMPs within the MnOx precipitation zone, findings derived from the packed column filled with MnOx are presented.

Figure 3.4 depicts the breakthrough curves of the OMPs at the MnOx column, during the initial pore volumes 0 - 8.7. For the calculations, the highest effluent concentration during this period was taken as the maximum concentration (Cmax). It is noted that since atrazine presented constantly a concentration below 0.1 µg/L, Cmax was assumed to be the same as the Cmax at the FeOx column.

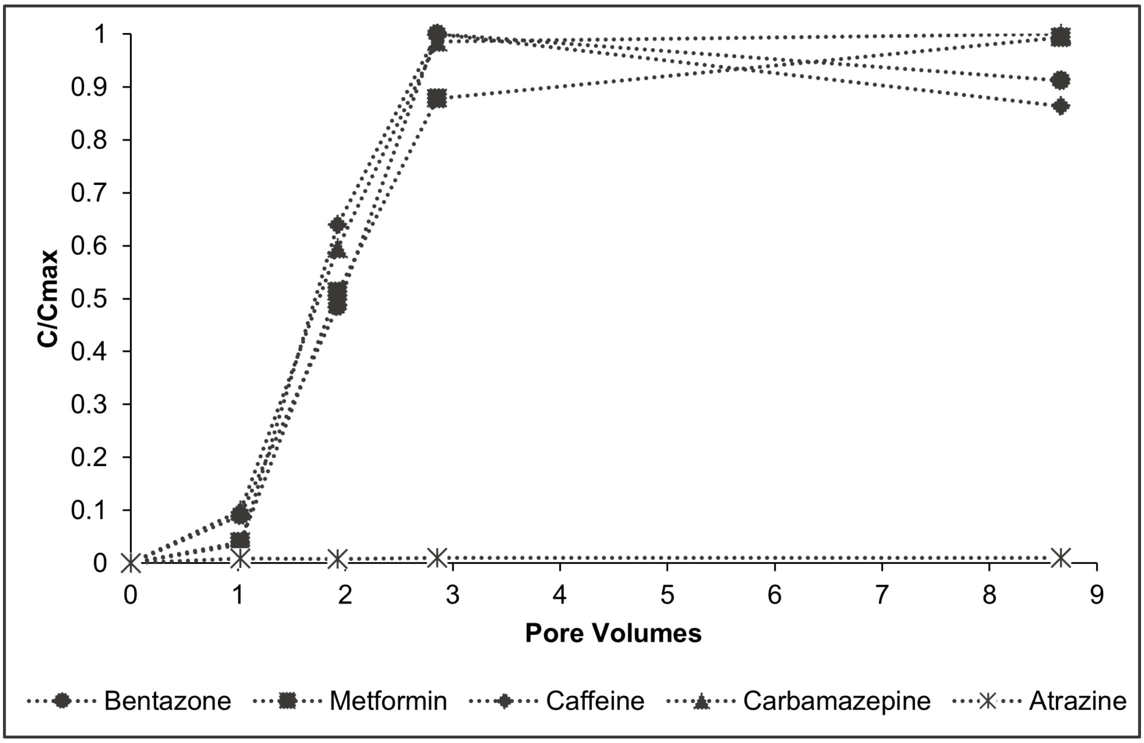


Figure 3.4: Breakthrough curves of the OMPs at the MnOx column

For the MnOx column all OMPs, except atrazine, presented a similar trend at their breakthrough curves. In the case of atrazine, there was no breakthrough observed at the MnOx column and the trend was linear. From the other four compounds, bentazone, carbamazepine and caffeine reached a full breakthrough at 2.9 pore volumes. Metformin was the only compound that had a later breaktrhough until the 8.7 pore volumes.

The OMPs retardation factors at 50% breakthrough at the MnOx column are shown at table 3.3.

Table 3.3: Retardation Factors at 50% breakthrough at the MnOx column

Retardatation Factor	MnOx
Bentazone	1.9
Metformin	1.9
Caffeine	1.7
Carbamazepine	1.8
Atrazine	-

Previous research has shown that electrostatic interactions play an important role at the mechanism of adsorption onto MnOx. The positively charged OMPs are adsorbed more efficiently onto MnOx compared to the negatively charged or neutral OMPs (Wang et al. 2023). This aligns with the results of metformin at figure 3.4. Metformin presented a later breakthrough indicating that adsorption was taking place, causing a retardation in the breakthrough of the compound. However, atrazine indicated a high affinity for the MnOx, despite the fact that is it a neutral OMP. Preceding studies have found that oxidation is also possible for the removal of certain OMPs when interacting with MnOx. Hence, it is possible that atrazine's behaviour in the MnOx column might be a result of oxidation.

Regarding the loading of the adsorbed mass of OMPs over the volume of the MnOx coated sand grains, results are shown at figure 3.5.

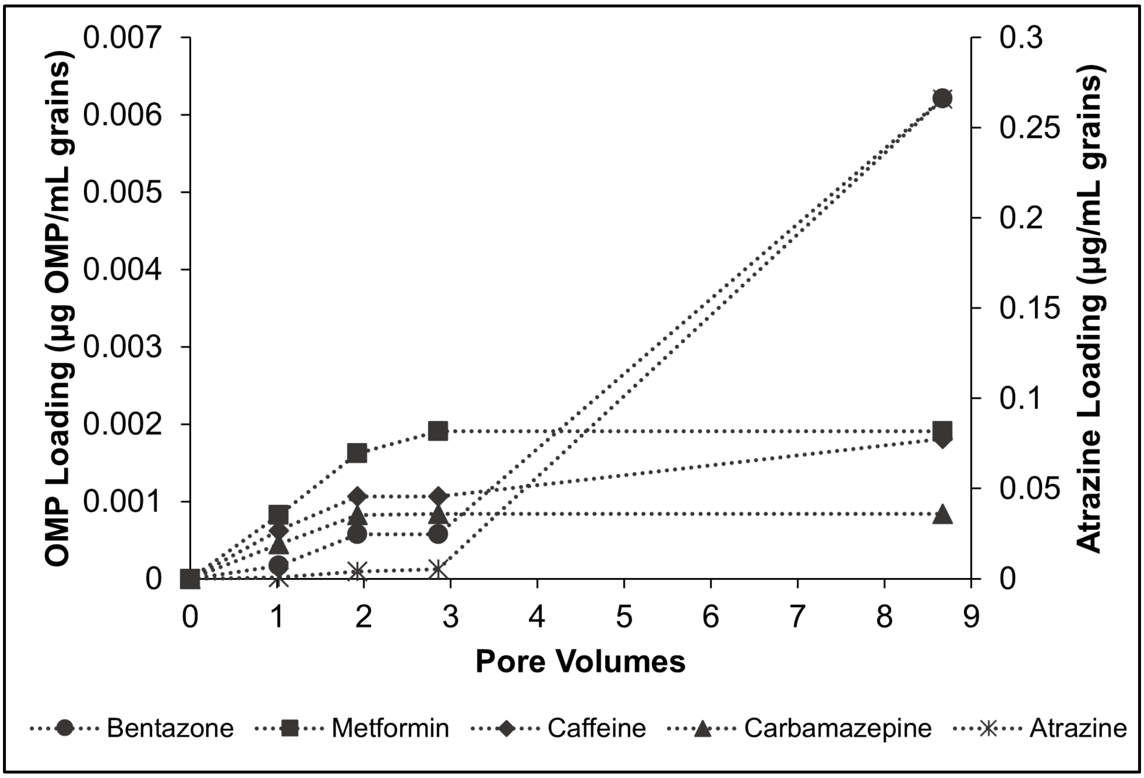


Figure 3.5: Loading graphs of the adsorbed mass of OMPs over the volume of the MnOx grains

It is is notable that metformin, caffeine and carbamazepine presented a similar trend; an initial increase at the first 3 pore volumes followed by a plateau. For bentazone, an initial gradual increase was observed until 3 pore volumes, however, a plateau was never reached and the loading increased reaching the value of 0.006 µg/mL, which is still considered a low value. Atrazine on the other hand, presented low values in the beginning (less than 0.05 µg/mL) and experienced an increase up to 0.26 µg/mL, which is a difference of several decades higher than the other four compounds.

This difference in the scale of atrazine's loading compared to the loading of the other four compounds can be explained due to the maximum concentration taken for the calculation of the loading. As in the breakthrough curves, the maximum concentration of atrazine was assumed to be the same as in the FeOx column, which was significantly higher than the concentrations obtained at the MnOx column's effluent.

Finally, results obtained during the period of 64.1 - 82.7 pore volumes, which was considered the steady state at the MnOx column, are presented at figure 3.6. The concentrations presented are the average concentrations calculated by the three concentration points measured during this period. They are compared to the influent concentrations spiked to the columns during this period, along with the error bars which indicate the minimum and maximum concentrations of the concentration points used for the calculation of the average concentration.

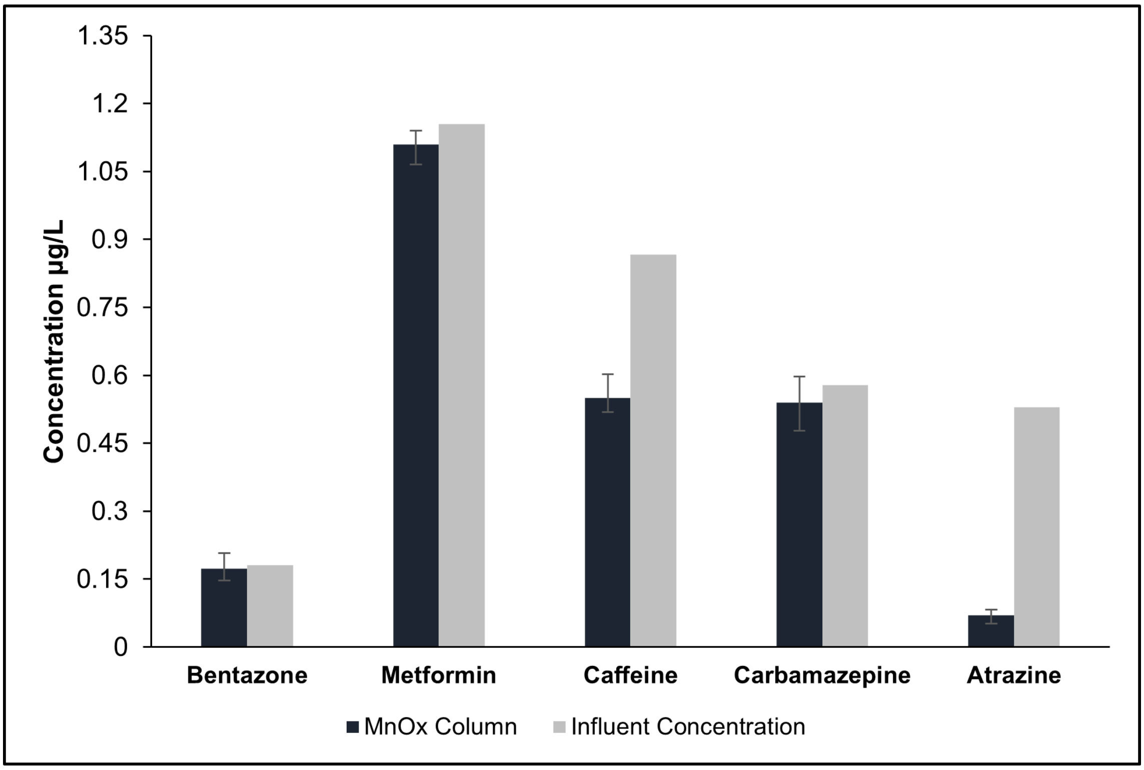


Figure 3.6: Average concentrations of OMPs during steady state at the MnOx column with error bars indicating the minimum and maximum concentrations

Compared to the influent concentrations introduced to the MnOx column, all average effluent concentrations were lower, indicating that removal took place for all compounds at the MnOx column.

At table 3.4, the removal rates during steady state are presented.

Table 3.4: OMPs removal rates at the MnOx column during steady state

Compound	Removal Rate (%)
Bentazone	4.56
Metformin	3.94
Caffeine	36.58
Carbamazepine	6.77
Atrazine	86.71

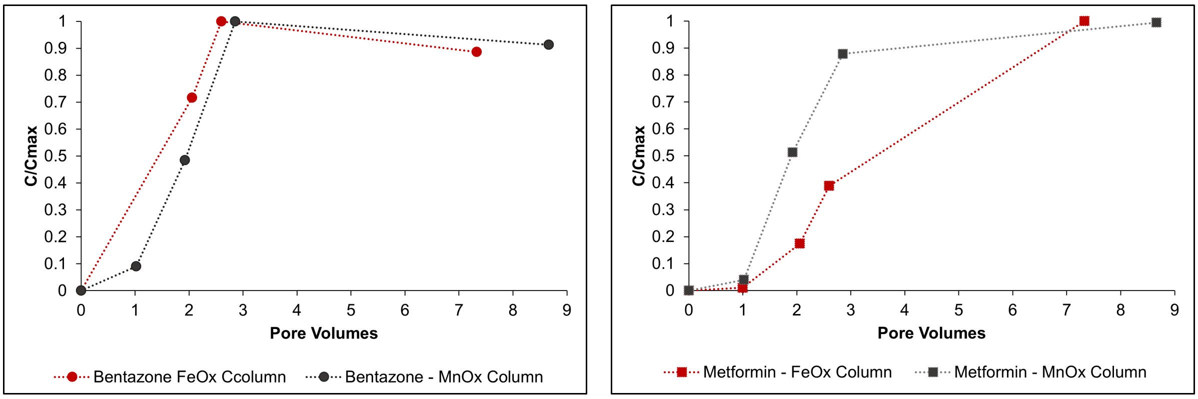
It is clear that all compounds except atrazine, presented a low or moderate removal during interaction with MnOx. The lowest removal rate was observed for metformin, (3.94 %), followed by bentazone (4.56%), carbamazepine (6.77%) and caffeine (36.58%). Atrazine, had the highest removal which reached amost 87%, showing that atrazine remained low throughout the experiment.

Metformin's behaviour during the initial range of 8.3 pore volumes indicated that adsorption was probably taking place. The fact that during the steady state, metformin concentration was almost equal to the influent concentration and almost none removal was observed, indicated that metformin's initial decline was due to adsorption.

3.3. FeOx vs MnOx column

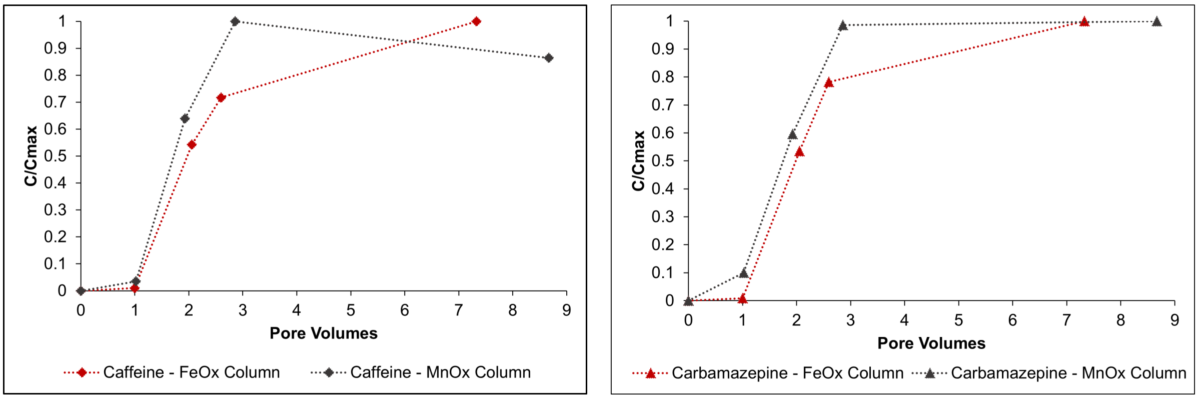
An aspect of the research project is the comparison between the two precipitation zones of the SIR. After the investigation of the behaviour of the targeted OMPs at each zone separately, direct comparison of the zones is of great importance.

At figure 3.7, graphs 3.7a - 3.7e show the breakthrough curves of each compound in both columns. The range of the pore volumes for column A was 0 - 7.3, while for column B the range was 0 - 8.7.



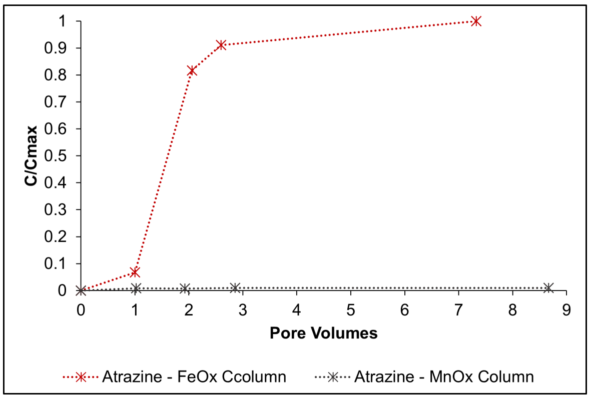
(a) Bentazone

(b) Metformin



(c) Caffeine

(d) Carbamazepine



(e) Atrazine

Figure 3.7: Comparison of the OMP breakthrough between the FeOx and the MnOx column

Upon review of the graphs, it is shown that each compound presented a different behaviour based on the material used. Bentazone's behaviour with MnOx and FeOx was very close, experiencing a full breakthrough faster at the FeOx column (0.3 pore volumes difference). For metformin, it is obvious that when interacting with MnOx, it reached almost a full breakthrough at 2.8 pore volumes, while at the same time step c/cmax at the FeOx column was almost 0.4. Same as metformin, caffeine and carbamazepine experienced a faster breakthrough at the MnOx column. Atrazine was the compound with the greatest difference between the two materials, presenting no breakthrough when interacting with the MnOx.

After the comparison between the breakthrough of each compound in the two columns, comparison between the materials is shown at the steady state of the two columns at figure 3.8. For both columns the feed solution was the same, so direct comparison can be made. The OMP concentrations presented were calculated with the same procedure as in graphs 3.3 and 3.6.

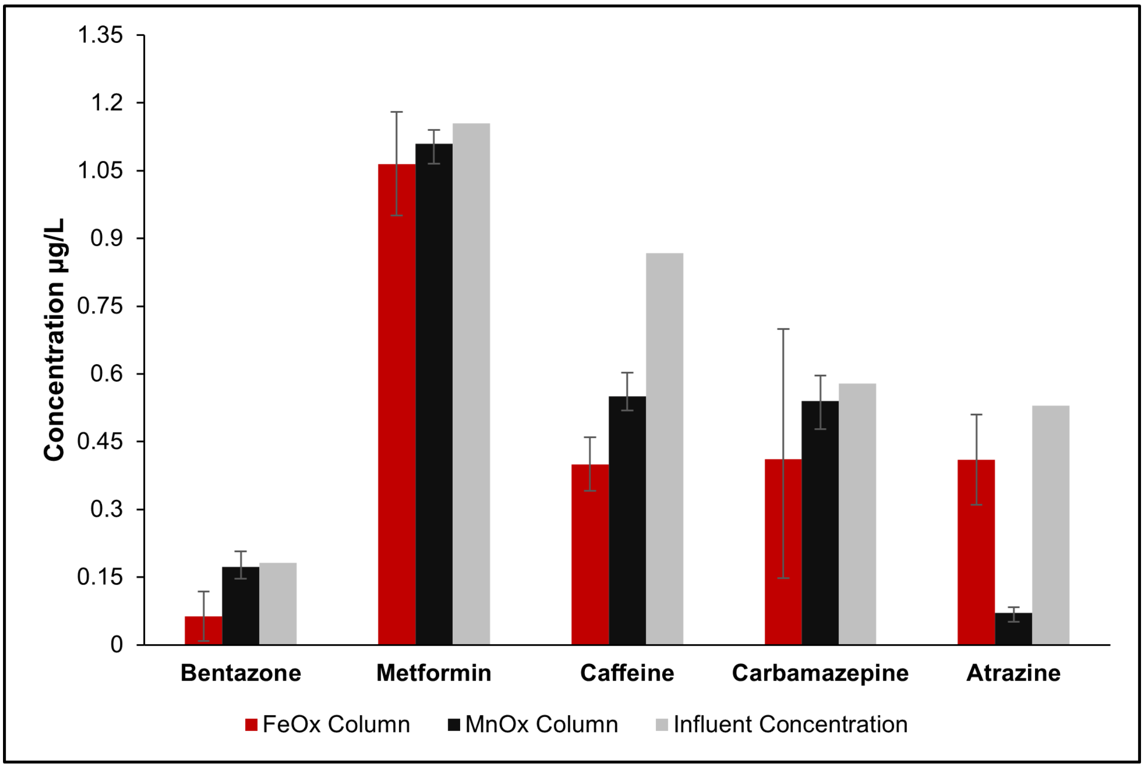


Figure 3.8: Average concentrations of OMPs during steady state in the FeOx and MnOx columns with error bars indicating the minimum and maximum concentrations

When comparison between the two materials is made for the better removal of compounds, it is evident from the graph that only atrazine presented better performance in the MnOx column, while for the other four compounds, the average concentration was lower at the steady state of the FeOx column.

Table 3.5 illustrates the difference in the removal rates between the two columns.

Table 3.5: OMPs removal rates at the FeOx and MnOx column during steady state

Compound	Removal Rate with FeOx (%)	Removal Rate with MnOx (%)
Bentazone	65.02	4.56
Metformin	7.76	3.94
Caffeine	53.88	36.58
Carbamazepine	28.94	6.77
Atrazine	22.45	86.71

It is worth noticing that after comparing the removal rates by the two materials, the compounds can be classified in different categories. Bentazone and carbamazepine were the compounds removed substantially only by the FeOx column. Caffeine was removed by both columns, but interaction with MnOx led to a moderate removal. Atrazine was the only compound that was removed better in the MnOx column, but also presented a moderate removal after interaction with FeOx. Finally metformin was the only compound which indicated very low removal in both columns.

The difference between metformin and the other targeted OMPs might be attributed to the fact that metformin is not an aromatic compound (PubChem 2023) and can be a potential reason for its lower performance in both materials.

3.4. Potential of FeOx and MnOx zones for OMP removal during SIR

Results have shown that interaction with both the materials, FeOx and MnOx, resulted into removal for all the compounds during steady state. Metformin was the compound that presented the lowest removal (less than 10%) in both columns, while for the other four compounds it was obvious that in at least one of the two columns they indicated a considerable reduction.

Linking the findings of the column experiments to the system of SIR, it is indicated that, the environment created in the subsurface can be a potential favourable environment for the removal of OMPs, since compounds pass through both of the zones. Hence, the fact that a compound might not perform well in one of the two zones is not a limiting factor of the potential SIR has on the OMPs removal.

During SIR, oxygen enriched water passes through the oxidation zones, resulting into the oxidation of Fe(II) and Mn(II) to FeOx and MnOx respectively. During the subsequent stage (water delivery phase), it is suggested that OMPs that presented a better performance with the FeOx, get removed in the first precipitation zone (FeOx) and then continue to the MnOx oxidation zone in lower concentrations.The OMPs that indicated a better performance when reacted with MnOx will firstly pass through the FeOx zone where they will not or slightly get decreased and continue to the subsequent precipitation zone of MnOx, where removal will take place.

Figure 3.9 gives a schematic overview of the removal of the five targeted OMPs of the research in the two zones during the subterranean treatment.

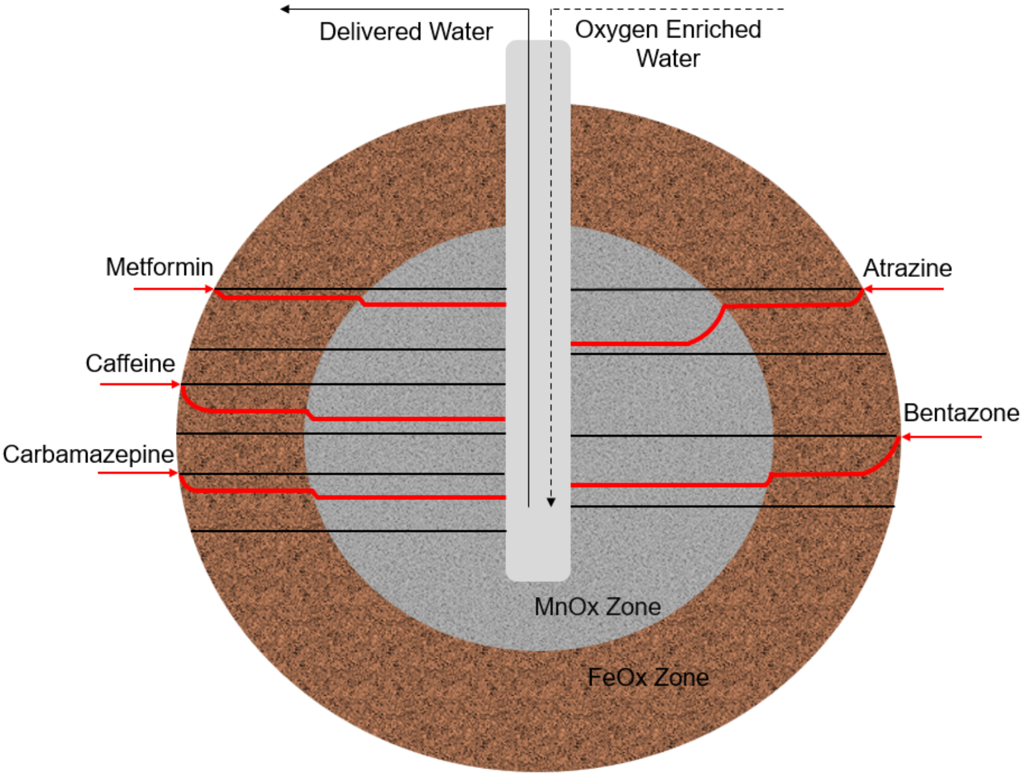


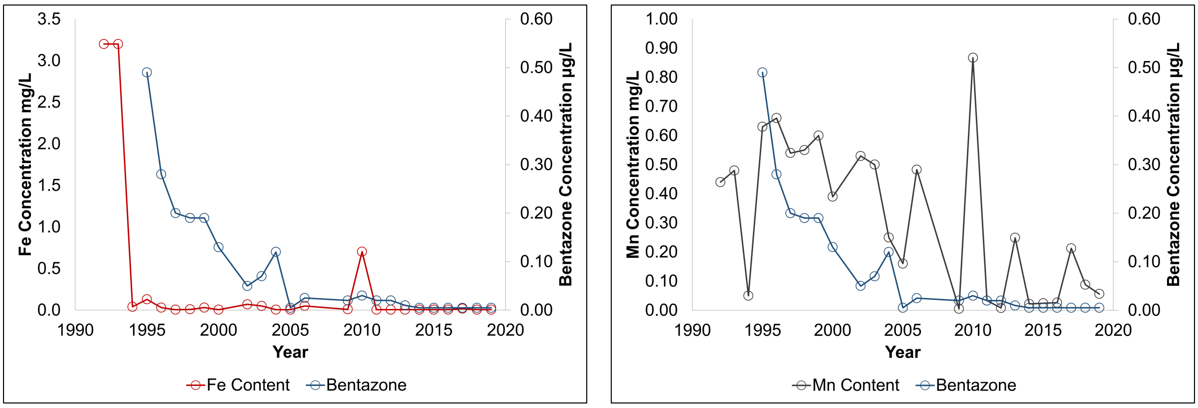
Figure 3.9: Conceptual Model of SIR and OMPs Removal

As illustrated in figure 3.9, the removal of the OMPs during SIR is a combination of their removal in each zone. Thus, in order for SIR to be effective on the removal of a compound, it is suggested that the compound has to be substantially removed in at least one of the two zones.

The outcome of the research gives a better understanding of the Vitens findings in the Dinxperlo production site. For Vitens, the compound of interest was bentazone, for which they observed a significant removal some years after the implementation of SIR. However, Vitens investigation of the relationship of bentazone removal and SIR, was focusing mainly on the effect of FeOx, without taking into account the effect of MnOx.

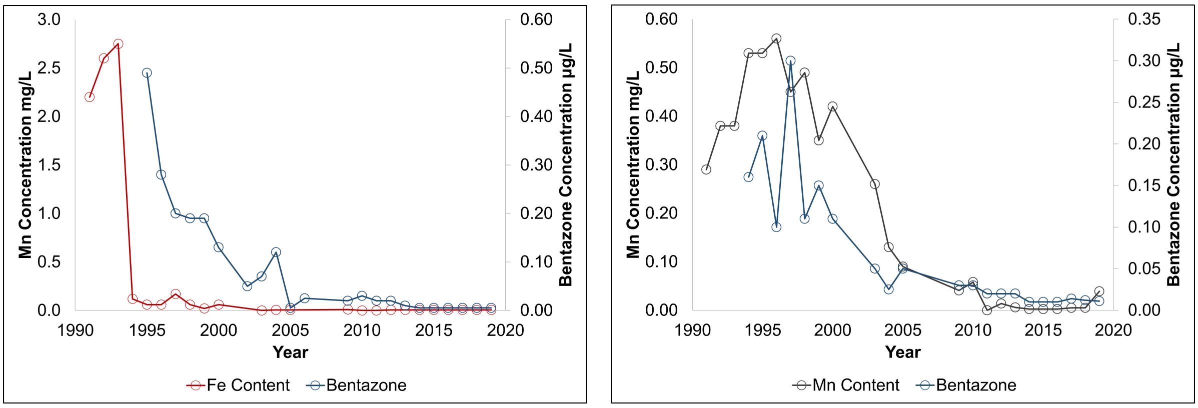
SIR was applied in multiple wells at the production site. Figure 3.10 gives an overview of the Fe, Mn and bentazone concentrations in the main wells of the Dinxperlo site, throughout the years of the application of SIR.

Figures 3.10a - 3.10f support the hypothesis that MnOx can be a potential reason for the removal of bentazone observed. More specifically this is supported by the fact that the behaviour of bentazone in the first two wells was more comparable with the pattern of manganese than the pattern of iron, since iron concentrations immediately decreased in contrast to manganese and bentazone concentrations, which experienced fluctuations after SIR application and decreased later. However at well no 3, there were no bentazone data available for the years prior to 1999, and bentazone concentration trend seems more similar to the iron trend compared to manganese concentration pattern, especially after year 2005.



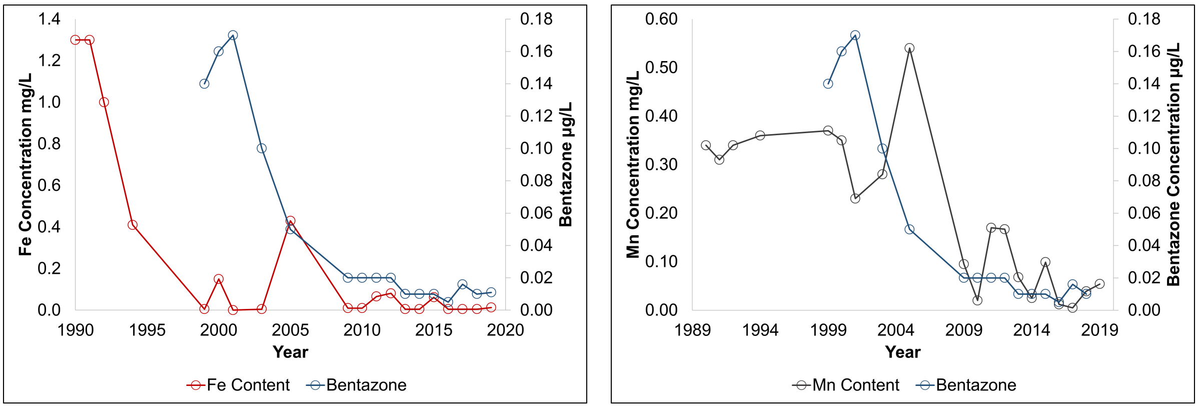
(a) Fe and Bentazone concentration at Vitens well No 01

(b) Mn and Bentazone concentration at Vitens well No 01



(c) Fe and Bentazone concentration at Vitens well No 02

(d) Mn and Bentazone concentration at Vitens well No 02



(e) Fe and Bentazone concentration at Vitens well No 03

(f) Mn and Bentazone concentration at Vitens well No 03

Figure 3.10: Fe, Mn and bentazone concentrations in the main wells at the Vitens Dinxperlo production site

The importance of MnOx in the removal of OMPs has been highlighted previously. Preceding research showed that paracetamol following adsorption, was oxidatively degraded by MnOx (Wang et al. 2023). Furthermore, it has been proposed that the main degradation pathway for phenolic compounds during interaction with MnOx is the hydrolysis - oxidation mechanism (Stone et al. 1984, Zhong et al. 2019). These findings, provide additional support for further research on the removal of OMPs by MnOx.

4

Conclusions

In this research, the method of subsurface iron removal was simulated, in order to investigate its effects on the removal of 5 targeted OMPs in tap water. A continuous flow column experiment was conducted, and two types of material were used, FeOx and MnOx. The main conclusions of this research can be drawn:

- Based on the results obtained on the average concentrations during steady state, for all the targeted OMPs there was some removal observed compared to the concentration spiked to the columns, at least in one of the two columns, except metformin. This indicates that SIR might be a potential method for the removal of OMPs. Despite the fact that, none of the targeted compounds had a good performance when interacting with both materials, this is not a limiting factor for the potential of SIR as a method of OMP removal, since both oxidation zones exist in the subsurface where SIR is applied. The OMPs that present a better performance with FeOx, will decrease in the first precipitation zone (FeOx) during the delivery phase and then continue to the MnOx oxidation zone in lower concentrations. The OMPs that indicate a better performance when reacting with MnOx will firstly pass through the FeOx zone where they will not or slightly get decreased and continue to the subsequent precipitation zone of MnOx, where removal will take place.

- Metformin was the only compound of the research which presented low removal rates during steady state of the experiment in both columns. One potential reason this can be attributed is the fact that it is the only non-aromatic compound of the targeted OMPs and does not contain any aromatic rings.

- In the case of atrazine, despite the fact that the influent concentrations were not determined, it is evident that in the column of MnOx coated sand, atrazine was removed, proving that there is possibility of atrazine removal during the subsurface iron removal when water containing atrazine passes through the manganese precipitation zone during SIR.

- Regarding atrazine's observed removal, no clear conclusion can be drawn for the distinction of the mechanisms which are accountable for its removal.

- Despite the fact that atrazine showed promising results for its removal with the method of SIR, and some removal was observed at the last pore volumes of the experiment, conclusion cannot be drawn on the efficiency of SIR and the mechanisms that are responsible for the removal of OMPs, since the outcome of the research is very limited.

5

Limitations & Recommendations

Based on the conclusions drawn, as well as the problems encountered during the performance of the column experiments, some recommendations and further research suggestions are listed, for the better investigation of the research topic:

- During this research, the column experiment for the investigation of the OMPs concentrations was conducted only once. For further research it would be advisable to have duplicates of the experiments, in order to investigate the margin of problematic measurements of the concentrations of OMPs. OMPs are very sensitive substances in terms of laboratory use. They are very sensitive to the containers they are stored, since they can strongly adsorb onto plastic materials (Yu et al. 2021). Low temperature is also a key factor for storage, since with higher temperature the removal efficiency increases for a variety of OMPs (Abdelrady et al. 2019), as well as the time span of their storage. Since, there are many factors which affect the concentration of OMPs and problems in their measurements and their precision is easy to happen, duplicates or even triplicates of the experimental phases are necessary.

- In regards to the feed solutions used, the multiple changes along with the aforementioned sensitivity of OMPs concentrations' measurement, created many problems with the understanding of the initial OMPs concentrations spiked to the system, making it impossible to calculate the overall removal of OMPs, which was the main goal of the research. For further research, the least possible changes of the feed solution should be done, in order to minimise the error in the determination of the influent concentrations. Furthermore, for better comparison between the two precipitation zones, the same feed should be used, as occurred during the steady state.

- In order to understand better the different mechanisms which take place at the removal of organic micropollutants during SIR, more research has to be conducted. Since, the main problem is the distinction between adsorption, biodegradation or oxidation, additional experiments should be conducted in parallel. An experiment with sterilised and decontaminated material should be performed, in order to explore biodegradation as a potential pathway of OMP removal. Additionally, analysis of the oxidative by-products of the selected OMPs can be done, for the exploration of the oxidation mechanism.

- Another important alternation that would lead to better understanding of the potential effect SIR has on the removal of OMPs is temperature. In this research project, the temperature chosen was higher than the common groundwater temperature. However, since the project had as an objective to provide evidence to support whether SIR is or not beneficial for OMP removal, a higher temperature was set. Despite the fact that it was not representative, it would lead to more intense results since higher temperature promotes OMP removal. However, it is important to perform an experiment set to the usual groundwater temperature of 14°C and compare the results with the experiment of the higher temperature.

- In order for the simulation of SIR to be complete, it is necessary to simulate all the processes which take place in the subsurface. During the column experiment, only the phase of oxygen enriched water spiked with OMPs was simulated. However, it is suggested that an anoxic conditions experiment with injection of soluble Fe(II) and Mn(II) to the system, followed by an oxic conditions experiment are added. In this way, results will be obtained on how OMPs removal is affected when FeOx and MnOx are generated in the system.

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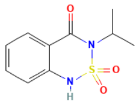
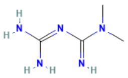
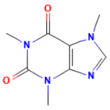
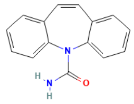
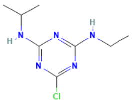
A

Appendix

A.1. OMPs Structures

Table A.1: OMPs structure

Compound	Structure[a]
Bentazone	
Metformin	
Caffeine	
Carbamazepine	
Atrazine	

[a]: Obtained from https://pubchem.ncbi.nlm.nih.gov/

A.2. Vitens Case

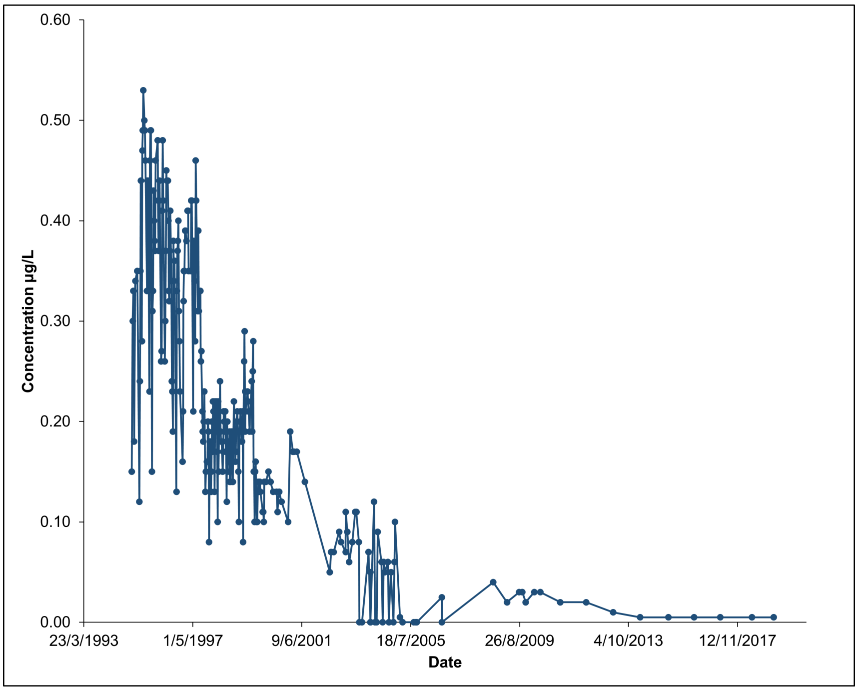


Figure A.1: Bentazone Concentration at Vitens well No 01

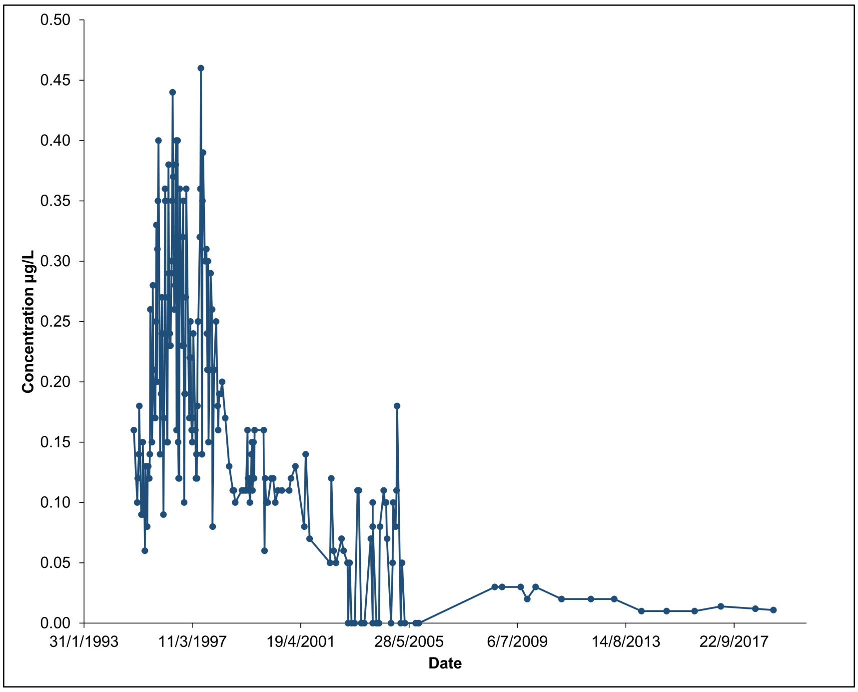


Figure A.2: Bentazone Concentration at Vitens well No 02

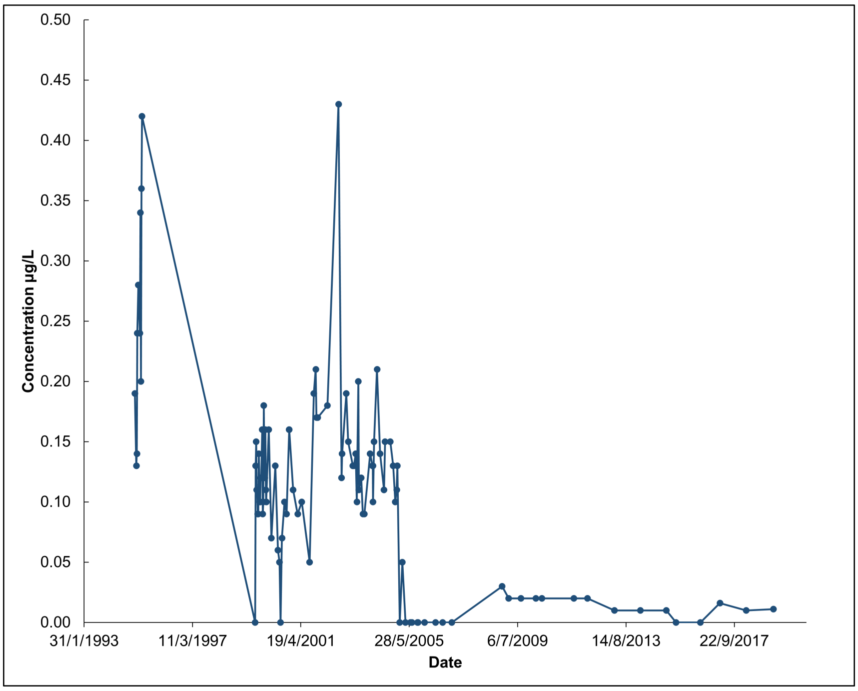


Figure A.3: Bentazone Concentration at Vitens well No 03

A.3. Tracer Test and Porosity Calculation

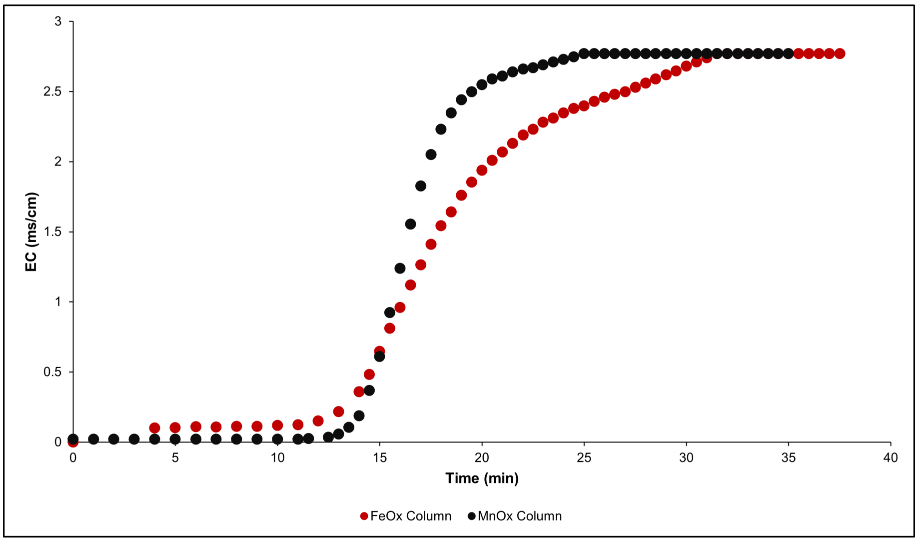


Figure A.4: EC Curves vs Time at the FeOx and MnOx column

In order to calculate the porosity of the system, the average concentration was used, thus the concentration at 50% breakthrough of NaCl.

First of all to calculate the pore volume, the volume of water passed through the columns up to the moment when c/c0 = 50% was calculated (Flow rate * Time). This volume consisted of the pore volume in addition with the dead volume, which in this case was the volume of the tubes. Afterwards, the volume of the empty columns was calculated by dividind the pore volume with the empty column volume, porosity was found. The assumption that each column is identical was made.
The flow rate of each column was decided in order for the contact be higher than 1 hour. The flow rates of column A and B were chosen equal to 45 mL/hr and 46 mL/hr and the corresponding contact time

Table A.2: Data for the calculation of the system's porosity

Column	FeOx	MnOx
Flow rate (mL/hr)	601.25	577.57
Time c/c0 [min]	16.5	15.5
Volume up to c/c0 = 50% [mL]	165.34	149.06
Dead Volume = Tubes volume [mL]	34.02	29.11
Pore Volume [mL]	131.32	119.94
Empty Column Volume	75.4	75.4
Porosity	0.58	0.53

of column A and B are 2.91 hr and 2.56 hr respectively.

A.4. Column Start-Up

Table A.3: DO, pH and Temperature results in both columns after 6 days of continuous flow with tap water

	pH	DO (mg/L)	T (oC)
Feed	7.29	9.27	19.1

Day 1	pH	DO (mg/L)	T (oC)
FeOx Column	6.67	7.76	19.2
MnOx Column	8.24	7.57	19.2

Day 6	pH	DO (mg/L)	T (oC)
FeOx Column	6.68	8.27	19.4
MnOx Column	7.99	8.45	19.2

Table A.4: Influent concentrations of the FeOx column

FeOx Column					
Range in pore volumes	Bentazone	Atrazine	Metformin	Caffeine	Carbamazepine
0-9.3	-	-	0.773	-	0.238
9.3 - 18	0.038	0.394	0.998	0.762	0.366
18 - 32.2	0.067	0.09	0.253	0.195	0.106
32.2 - 73.6	0.181	0.529	1.05	0.867	0.579

Table A.5: Influent Concentrations of the MnOx column

MnOx Column					
Range in pore volumes	Bentazone	Atrazine	Metformin	Caffeine	Carbamazepine
0 - 27.1	0.21	0.052	0.587	0.654	0.423
27.1 - 36.3	0.067	0.09	0.253	0.195	0.106
36.3 - 82.7	0.181	0.529	1.05	0.867	0.579

A.5. Concentrations during the first feed solution

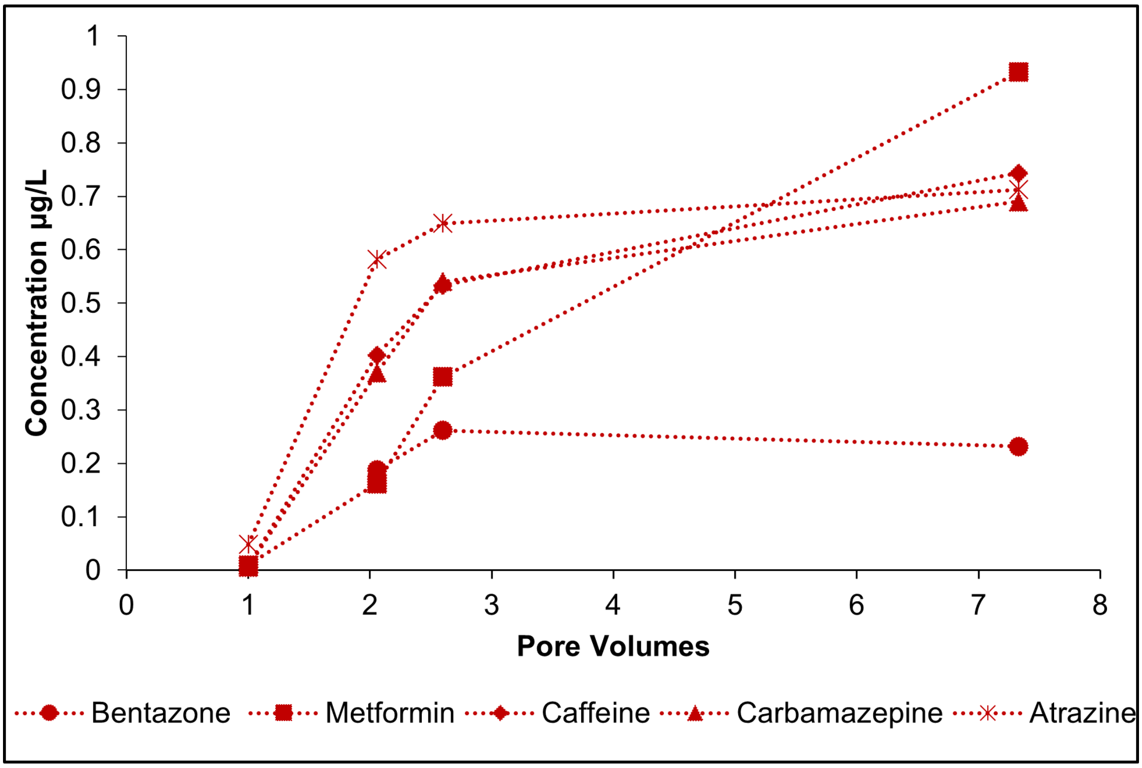


Figure A.5: OMPs concentration during the first feed solution at the FeOx column. Range of pore volumes 0 - 7.3

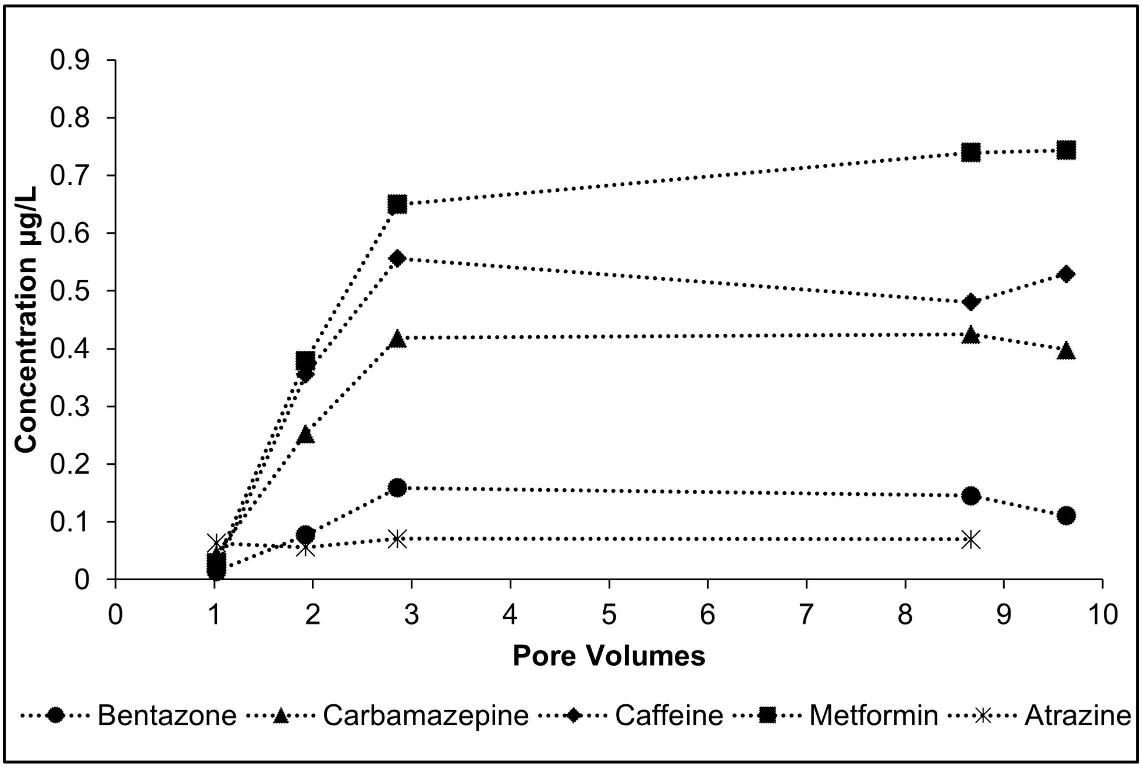
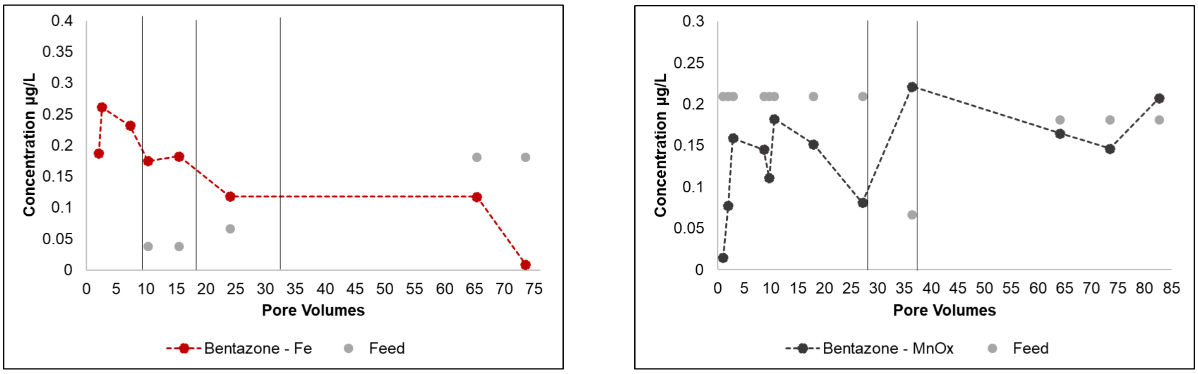


Figure A.6: OMPs concentration during the first feed solution at the MnOx column. Range of pore volumes 0 - 8.7

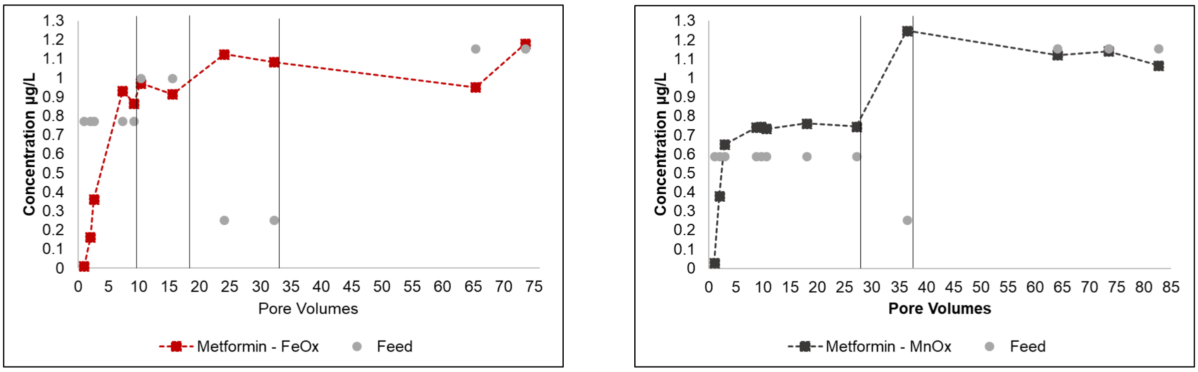
A.6. Complete OMPs concentrations



(a) FeOx

(b) MnOx

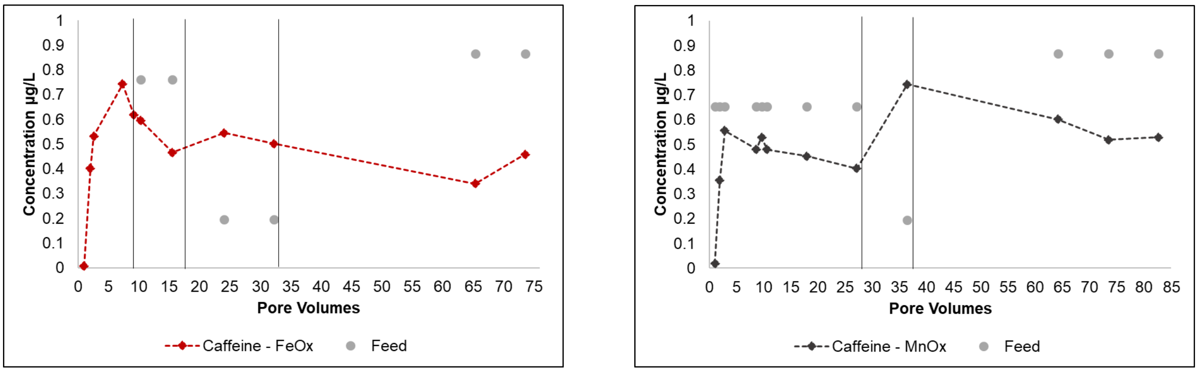
Figure A.7: Bentazone concentration vs Pore volumes at the FeOx and MnOx column



(a) FeOx

(b) MnOx

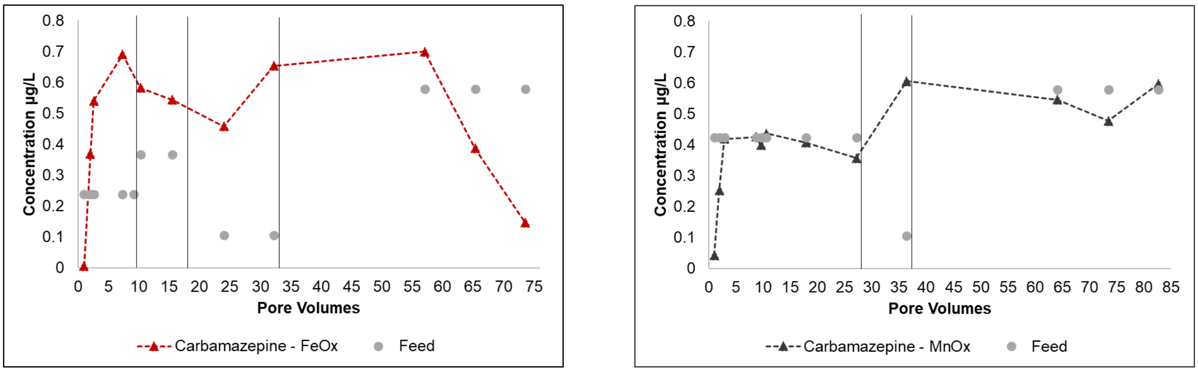
Figure A.8: Metformin concentration vs Pore volumes at the FeOx and MnOx column



(a) FeOx

(b) MnOx

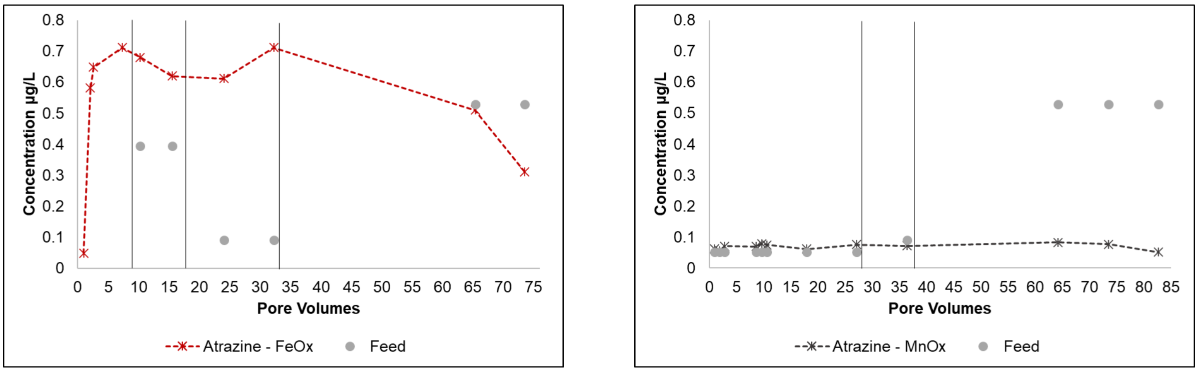
Figure A.9: Caffeine concentration vs Pore volumes at the FeOx and MnOx column



(a) FeOx

(b) MnOx

Figure A.10: Carbamazepine concentration vs Pore volumes at the FeOx and MnOx column



(a) FeOx

(b) MnOx

Figure A.11: Atrazine concentration vs Pore volumes at the FeOx and MnOx column

A.7. Duplicate experiment for the detection of atrazine's transformation products

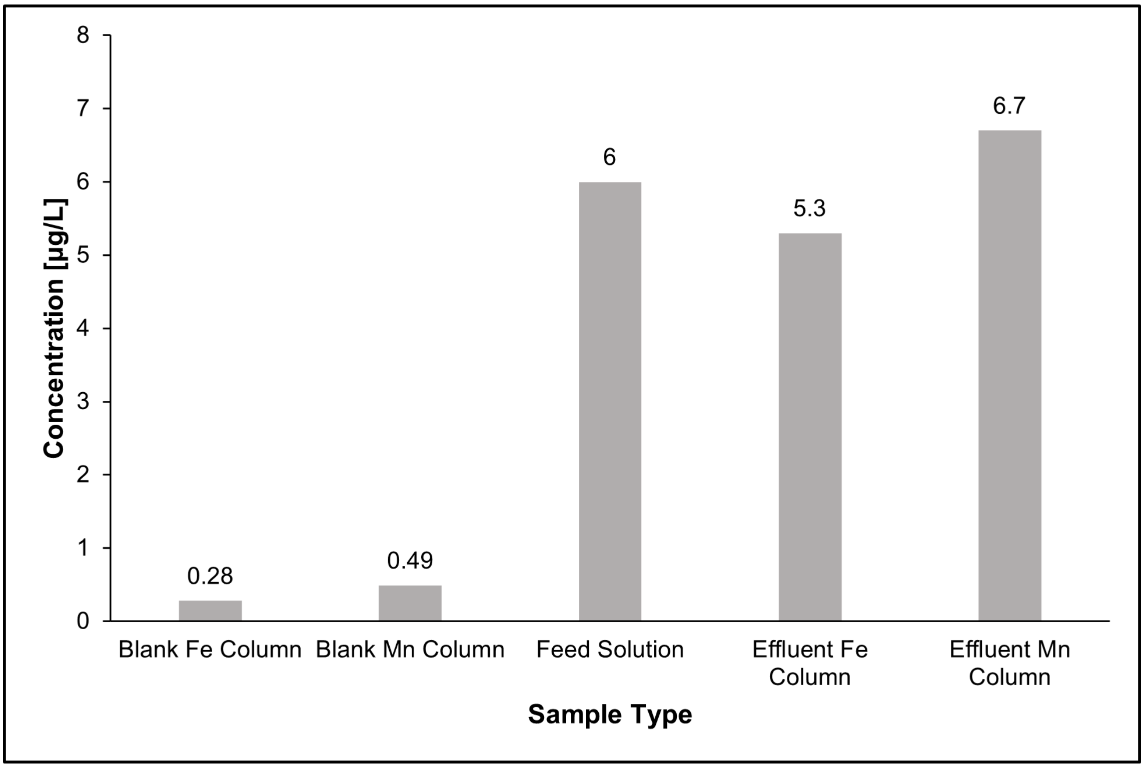


Figure A.12: Atrazine concentration at the different sample types during the duplicate experiment

The compounds targeted during the GC-MS analysis were atrazine, as well as desethylatrazin and desisopropylatrazin, which are two metabolites of atrazine. First of all, there was no detection of desethylatrazin and desisopropylatrazin in any of the samples. Furthermore, atrazine's results indicated that the concentration of atrazine in the feed solution was equal to 6 µg/L, instead of the 10 µg/L which was the intended atrazine concentration. The concentrations of the effluent in column A and B were 5.3 µg/L and 6.7 µg/L respectively. Additionally, the blank measurements, gave insight to the amount of atrazine present in the columns, even without spiking OMPs in the influent. This can be explained since the materials used, were previously used for the main experiment and despite the fact that in between the two experiments, there were 3 pore volumes of tap water introduced for the "cleaning" of the system, there were still deposits which leaked into the water. For column A, results showed that there was 0.28 µg/L of atrazine present, while for column B, there was 0.49 µg/L present.

For column A, there was a 0.7 µg/L difference between the feed solution and the effluent. However, taking into account the amount of atrazine present in the system because of previous deposits, the amount of atrazine removed would have been higher. Furthermore, since there were no metabolites of atrazine detected, the difference in the amount of atrazine spiked to the columns and the one measured in the effluent can be assumed that was not due to biodegradation. For column B, results were different compared to column A. First of all, the amount of atrazine present in the clean system was higher (blanc Mn > blanc Fe), but also the final concentration reached in the effluent was 0.7 µg/L higher than the one in the feed solution.

Results obtained from the duplicate experiment do not contribute in drawing any further conclusions and deeper exploration needs to be done.