Characterisation of the impact of dissolved organic matter on iron, manganese, and arsenic mobilisation during bank filtration

Abdelrady, Ahmed; Sharma, Saroj; Sefelnasr, Ahmed; Kennedy, Maria

DOI
10.1016/j.jenvman.2019.110003

Publication date
2020

Document Version
Accepted author manuscript

Published in
Journal of Environmental Management

Citation (APA)
Abdelrady, A., Sharma, S., Sefelnasr, A., & Kennedy, M. (2020). Characterisation of the impact of dissolved organic matter on iron, manganese, and arsenic mobilisation during bank filtration. *Journal of Environmental Management*, *258*, Article 110003. https://doi.org/10.1016/j.jenvman.2019.110003

Characterisation of the Impact of Dissolved Organic Matter on Iron, Manganese, and Arsenic Mobilisation during Bank Filtration

Ahmed Abdelrady[1, 2*], Saroj Sharma[2], Ahmed Sefelnasr[3], and Maria Kennedy[1, 2]

[1]Delft University of Technology, P.O. Box 5048, 2600 GA Delft, The Netherlands, A.R.A.Mahmoud@tudelft.nl.

[2]IHE Delft Institute for Water Education, P.O.Box 3015, 2601 DA, Delft, The Netherlands, s.sharma@un-ihe.org, m.kennedy@un-ihe.org.

[3] Geology Department, Faculty of Science, Assiut University, 71516 Assiut, Egypt, ahmed.sefelnasr@aun.edu.eg

[*] Corresponding author: A.R.A.Mahmoud@tudelft.nl. Tel: 0020111546898.

Abstract

Bank filtration (BF) has been used for many years as an economical technique for providing high-quality drinking water. However, under anaerobic conditions, the aquifer release of undesirable metal(loid)s, such as iron manganese, and arsenic, reduces the bank filtrate quality and thus restricts the application of this technique. This study investigates the impact of the organic-matter composition of source water on the mobilisation of Fe, Mn, and As during the anaerobic BF process. A laboratory-scale column study was conducted at a controlled-temperature (30±2°C) using different feed water sources. The organic matter characteristics of the feed water were elucidated using excitation-emission spectroscopy techniques integrated with parallel factor framework clustering analysis (PFFCA) model. The experiment was performed at redox conditions between 66 mv and -185 mv. Moreover, batch studies were implemented to study the effect of natural organic matter type (humic, fulvic and tyrosine) and concentration on the mobilisation of the selected metal(loids). The laboratory experiments demonstrated that the mobilisation of Fe, Mn and As during the BF are varied with the organic water concentration and composition of the source water. The fluorescence results revealed that terrestrial and condensed structure humic compounds are more capable to release Fe into the filtrate water. In contrast, Mn exhibited an equal tendency of mobilisation towards all the humic compounds regardless of its origin and structure. However, at a humic concentration higher than 5 mg-C/L, Mn showed more affinity towards lower molecular weight humic compounds. Arsenic was found to be the least impacted by the alteration in the source water organic matter composition; its mobilisation was highly correlated with iron releasing process. On the other hand, the biodegradable organic matter at high concentration (>10 mg-C/L) was found to be highly effective to turn the infiltration area into Fe-reducing environment and thereby elevating Fe and As concentrations in the pumped water. In conclusion, this study revealed that the DOM composition and concentration of the raw water could play an important role in the mobilisation of metal(loids) during the BF processes.

Keywords: Bank filtration, Iron, Manganese, Arsenic, Organic Matter

1. Introduction

Bank filtration (BF) has been known to be a sustainable and natural treatment technique for water supplies worldwide (Eckert et al., 2006). This technique is based on inducing surface water to flow towards a vertical or horizontal well located near a surface water system. The river bank acts as a robust barrier filter to reduce the pollutant concentration. Irmscher et al. (2002) reported that there are more than 100 BF fields in Europe; many of them have been operated for more than 100 years. Recently, BF has been getting increasing attention as a desirable technique for treating water supplies in several developing countries with different and extreme environmental conditions (Wahaab et al., 2019).

BF is an effective technique to remove presistent pollutants and produce high drinking water quality. Sandhu et al. (2019) reported a 50% removal of dissolved organic matter (DOM) and 13-99% of micro-organic pollutants for BF fields along the Yamuna River (India). Moreover, BF can also be used as a pre-treatment step to improve the quality of the water and reduce the treatment cost. Haas et al. (2018) revealed that BF could reduce the fouling development in membrane treatment plant and this subsequently will reduce the energy consumption, increase the efficiency and life-time of the membrane, and therefore, reduce the operation cost of the plant.

BF is an effective technique to remove persistent pollutants and produce high drinking water quality. Sandhu et al. (2019) reported a 50% removal of dissolved organic matter (DOM) and 13-99% of micro-organic pollutants for BF fields along the Yamuna River (India). Moreover, BF can also be used as a pre-treatment step to improve the quality of the water and reduce the treatment cost. Haas et al. (2018) revealed that BF could reduce the fouling development in membrane treatment plants and this subsequently will reduce the energy consumption, increase the efficiency and life-time of the membrane, and therefore, reduce the operation cost of the plant. However, other BF processes (e.g., mixing the infiltrate water with the contaminated ambient groundwater and reduction of toxic metals from soil into the filtrate water) might also have an adverse effect on the quality of the pumped water. In the last decades, the quality of the River Rhine at Dusseldorf (Germany) was deteriorated and an anaerobic environment was developed in the infiltration area that led to increase the concentrations of Fe and Mn in the pumped water. In the last years, the water quality of the raw water improved; however, the periodic changes of river water quality and hydraulics as a result of climate conditions should be considered. Recently, granular activated carbon combined with ozonation and filtration are used as a further treatment of bank filtrate to remove the chemical pollutants (Eckert et al., 2006). Thus, it can be concluded that the BF processes and environmental condition of the infiltration area highly determine the quality of the pumped water.

Biodegradation and adsorption are the main mechanisms to remove chemical pollutants during the filtration process (Bertelkamp et al., 2014). Biodegradation is a process in which the microorganisms degrade organic matter using acceptor electrons. Organisms use oxygen as the primary electron acceptor for the organic-matter biodegradation process, followed by nitrate, Mn, and Fe. This process is highly useful to reduce the concentration of organic matter and nitrogen and consequently increase the quality of the pumped water. However, turning the environment into anaerobic, where the insoluble Fe and Mn are the primary electron acceptor, will increase the metals concentrations in the infiltrate water (Massmann et al., 2008). The microbial reduction and mobilisation of Fe and Mn are considered as significant sources of elevated toxic substances (e.g., arsenic (As)) in pumped water, which adversely affects human health and degrades bank filtrate quality (Yang et al., 2015). These processes are mainly controlled by environmental conditions along the subsurface flow path, such as the temperature, hydraulic conductivity of the soil, redox potential, metal speciation in the ores, and the organic and inorganic compositions of source water (Vega et al., 2017).

DOM is considered as the primary energy source for the metal and metalloids (has intermediate properties of metals and non-metals) mobilisation taking place during the subsurface water flow process (Vega et al., 2017). DOM can be subdivided into two major categories namely, biodegradable and non-biodegradable. Biodegradable compounds enrich the biological activity along the flow path and subsequently accelerate the microbial reduction of metal(loid)s into the filtrate water (Schittich et al., 2018). Non-biodegradable compounds (i.e., humics) have high electron shuttle capacities and thus could play a dual role in these mobilisation processes. First, they could enhance the mobilisation of metal(loid)s biotically by mediating the microbial reduction processes (Brune et al., 2004). Second, they might chemically form aqueous complexes with metal(loid)s and thereby increase their concentrations in filtrate water (Liu et al., 2011). On the other hand, the microbial reduction of Fe and Mn might also affect the dynamics and alter the chemical structures of DOM during infiltration. Vega et al. (2017) highlighted that the microbial reduction process is concurrent with the oxidation of labile compounds (e.g., phenol) into refractory humic compounds, as well as the destruction of high-molecular-weight organic compounds into smaller compounds that can serve as electron donors for microorganisms during the microbial reduction processes. The dynamics of DOM and its impact on the mobilisation of metal(loid)s during the subsurface flow of water is highly dependent on the chemical structure of DOM and environmental conditions such as the redox potential and the temperature.

The main objective of this research was to assess the effectiveness of this technique in providing high-quality water in hot-climate environments and to address the problems that restrict the extended application of this technique. The bank filtrate temperature of wells located along the Nile River (Egypt) was 26.4 °C (Ghodeif et al., 2016), whereas, it was reported as 28.6 and 30 °C along the Ganga River and Yamuna River (India) (Sprenger et al., 2012). Moreover, recent climate models expect a 12.6 °C global average temperature rise by 2050 (R.K. Pachauri et al., 2014). The depletion of oxygen in surface water systems is more likely in arid environments. Hence, there is a higher potential of developing an anaerobic environment during the BF processes, which subsequently leads to the enrichment of pumped water in metal(loid)s and degrades the bank filtrate quality. This is one of the major drawbacks that restrict the widespread application of the BF technique in hot-climate regions. Therefore, this research investigated the role of DOM composition in the mobilisation of Fe, Mn, and As during the BF processes under hot-climate conditions. This is an important step to predict and control their concentrations in pumped bank filtrate water. During this research, laboratory-scale column and batch studies were conducted using different feed water sources. The organic composition of the feed water was investigated using different fluorescence techniques.

2. Research Methodology

2.1. Soil and feed water characteristics

Manganese iron coated sand (MICS) used in this research was obtained from the groundwater water treatment plant Brucht (Netherlands). The media was sieved through a 3 mm mesh screen, washed gently with water to discard the deposits, and then dried at 70 °C. The size of the used media was 1-3 mm. The physical and chemical properties of the media were determined and presented in table S1.

During this study, four different types of waters were fed to the columns to assess the impact of organic matter composition on the mobilisation of Fe, Mn and As during soil passage. The quality parameters of the feed water (pH, conductivity, ammonia, nitrate, total phosphorus, and chlorides) are summarized in table S2. The redox potential of the effluent water was ranged between -66 mv and -185 mv and pH varied between 7.56 and 8.14 during the experimental period.

2.2. Column experiment

A laboratory-scale column study was performed to evaluate the role of the organic composition of water in the release of Mn, Fe and As from the soil into the bank filtrate at a high temperature. Four PVC columns with 2.1 cm internal diameter and 50 cm height were developed. The columns were packed at the bottom with a support layer of graded gravel with a diameter 3-5 mm to a height of 5 cm and then filled with MICS in deionised water to ensure the homogeneous packing. The feed water was introduced to the columns in an up-flow mode (saturated flow), and a variable-speed peristaltic pump was used at the top of the column providing at a constant hydraulic rate (0.5 m/d) to avoid the entrapment of air bubbles in the soil bed. This hydraulic rate has been experienced in many BF fields (Ghodeif et al., 2016; Paufler et al., 2018). The tracer test using NaCl was conducted to estimate the retention time; the empty bed contact time was 16 hours. Sub-oxic conditions were maintained in all columns by continuously degassing the feed water tank with a nitrogen stream to dissipate the air until the dissolved oxygen concentration was lower than 0.2 mg/L. Moreover, the column was fed continuously with water during the whole experiment to prevent the penetration of air into the soil bed. Then, the columns were acclimated using Delft canal water (DCW) for more than 70 days. After that, the columns were fed with waters of different organic composition. The first column continued to be fed with DCW. The second column was fed with DCW mixed with secondary treated wastewater effluent from Hoek van Holland, the Netherlands (DCWW). The third column was fed with DCW mixed with water-extractable organic matter (WEOM) that had high humic content. The procedures used for WEOM preparation are described in detail in (Abdelrady et al., 2018). The last column was fed with non-chlorinated tap water (NCTW), representing low-organic-matter-content water. The experiment was conducted in a controlled-temperature room (at 30 °C). The pore volume (PV) of each column was changed 10–15 times during the whole experiment. Influent and effluent samples were taken regularly (at every PV change) to characterise their quality parameters. Physical and chemical parameters (i.e., pH, redox potential, temperature, and dissolved oxygen concentration) were measured continuously to ensure that the experiment was conducted under the desired environmental conditions.

2.3. Batch experiment

Laboratory-scale batch reactors were employed to determine the impact of the type and concentration of natural organic matter (NOM) on the mobilisation of Fe, Mn, and As from the soil into the filtrate water. Each reactor (0.5 L brown glass bottle containing 100 g MICS) was ripened with 400 mL of DCW and the ripening process was continued for 70 days. The feed water was degassed with a nitrogen stream to dissipate the air. Then, the reactors were sealed tightly and placed on a reciprocal shaker at 100 rpm in a controlled-temperature room (30 °C). The renewal process was conducted inside an anaerobic chamber to ensure that the experiment was conducted under anaerobic conditions. After ripening, three NOM types (humic, fulvic, and tyrosine) were spiked at four different concentrations (5, 10, 15, and 20 mg-C/L) in the reactors (one type and one concentration in each), and the experiment was conducted for 30 days at the same experimental conditions. This residence time was recommended by several previous studies to remove chemical and biological contaminants from the raw water during the BF processes (Ray et al., 2011). The humic acid and tyrosine were purchased as powders from Sigma-Aldrich (Netherlands) and the powdered fulvic acid was bought from the International Humic Substances Society. Control (DCW without sand) reactors were operated under the same environmental conditions.

2.4. Analytical methods

Influent and effluent samples were collected and analysed directly to avoid the degradation of the organic matter. The samples were first filtered using 0.45 µm filtration (Whatman, Dassel, Germany). The Fe and Mn concentrations were determined using inductively coupled plasma–mass spectrometry instrument (Xseries II Thermo Scientific, Bermen, Germany). The arsenic concentration was analysed using a graphite furnace atomic absorption spectrophotometer (Solaar MQZe, Thermo Electron Co). The limit of quantitation (LOQ) of Fe, Mn and As was 10, 10 and 2 µg/L, respectively.

The organic matter content of the feed waters was measured as dissolved organic carbon (DOC, in mg-C/L) using the combustion technique with a total organic carbon analyser (TOC-VCPN (TN), Shimadzu, Japan). The organic composition of the influent and effluent water was determined using the fluorescence excitation–emission technique (F-EEM). A Fluoromax-3 spectrofluorometer (HORIBA Jobin Yvon, Edison, NJ, USA) was used to determine the fluorescence intensity (FI) of the water samples at excitation wavelengths (λex) of 240–452 nm (interval = 4 nm) and emission wavelengths (λem) of 290–500 nm (interval = 2 nm).

2.5. Fluorescence indices

Fluorescence indices, including the humification index (HIX), the fluorescence index (FIX), and the biological index (BIX), were estimated based on the F-EEM measurements. HIX is used as a marker of the humification (polycondensation) degree of the water, and higher HIX values refer to higher humic content (lower H:C) (Gabor et al., 2014). This parameter was estimated following the equation proposed by (Ohno, 2002):

$$HIX = \frac{\sum FI_{\lambda em\ (434\text{–}480\ \mathrm{nm})}}{\sum FI_{\lambda em\ (434\text{–}480\ \mathrm{nm})} + \sum FI_{\lambda em\ (300\text{–}344\ \mathrm{nm})}} \quad at\ \lambda ex\ (254\ nm) \qquad (1)$$

FIX is used widely to identify the origin of DOM in water. It is estimated following the method developed by Hansen et al. (2016) (see Equation 2). Its values range between 1.2 and 1.8, with higher values for terrestrial DOM and lower values for microbial DOM origin (Gabor et al., 2014).

$$FIX = \frac{FI_{\lambda \mathrm{em}\ (450)}}{FI_{\lambda \mathrm{em}\ (500)}} \quad at\ \lambda ex\ (370\ nm) \qquad (2)$$

BIX is used as an indicator of the contribution of recently produced and microbial-derived organic compounds to the fluorescence DOM pool. It was determined following the method of following the method of Huguet et al. (2009) (Equation 3).

$$BIX = \frac{FI_{\lambda \mathrm{em}\ (380)}}{FI_{\lambda \mathrm{em}\ (430)}} \quad at\ \lambda ex\ (310\ nm) \qquad (3)$$

2.6. Fluorescence modelling

Although F-EEM is a qualitative technique, it is still effective in quantifying the characteristics of DOM. A parallel factor framework-clustering analysis (PFFCA) model was recently stipulated by Qian et al. (2017) for decomposing the F-EEM dataset into major fluorescence components representing different NOM compounds. Briefly, PFFCA decomposes the F-EEM datasets into several factors (7–13). Afterwards, the highly correlated factors are clustered into one component representing organic matter with the same fluorescence characteristics.

To ensure the quality of the data and the robustness of the fluorescence dataset interpretation, parallel factor (PARAFAC) analysis was used as well to decompose the fluorescence dataset into major components and to assess the contribution of each component to the full fluorescence spectrum. The development and validation of the model developing were described in details in Murphy et al. (2013). Split-half validation technique was used to validate the fluorescence model. This technique is based on the comparison of multiple models generated by splitting the dataset. In this research, the dataset was divided into four groups, and the samples were assigned alternately into the groups. Then, the groups were assembled into six combined groups; each combined group contains half of the dataset. After that, the PARAFAC test was applied for each combined group and the produced models were compared (Harshman et al., 1994). The validation process was implemented using drEEM MATLAB toolboxes developed by Murphy et al. (2013).

The redox index (RI) is used as an indicator of the reducibility of quinone-like moieties in the DOM of raw water. This parameter was calculated following the definition of Miller et al. (2006), by dividing the sum of the FI of the reduced quinone-like moieties to the total of the (reduced and oxidised) quinone-like moieties of the fluorescence components, with values close to 1 indicating a higher reducing capacity of the feed water (Gabor et al., 2014).

2.7. Statistical analysis

The relationship between Fe, Mn, and As concentrations in the effluent waters and the fluorescence organic characteristics of the feed water were explored using Pearson correlation (r) and nonparametric Spearman rank correlation (ρ) analysis. The strength of the correlation was considered high when the correlation value (ρ) was higher than 0.7 and moderate when it ranged between 0.7 and 0.5 (Hinkle et al., 1988). The relationship was considered significant if the criterion level of significance (*p*) was lower than 0.05.

3. Results

3.1. Impact of DOM composition on metal(loids) mobilisation (column experiment)

3.1.1.Fluorescence components

A F-EEM dataset of 80 water samples collected from the influents and effluents of the columns was used to develop and validate a PFFCA-EEM model. The dataset was decomposed into 11 factors and afterwards clustered into four main components (FC1–FC4). To ensure the reliability and interpretability of the F-EEM dataset, it was also analysed using the PARAFAC technique. A model with four fluorescence components (PC1–PC4) was successfully split-half-validated and explained 99.7% of the data variability. The footprints of the PFFCA components and their corresponding PARAFAC components is presented in Figure 1 and Figure S1. A comparison between the spectral characteristics of the recognised components and those reported in earlier studies was conducted using OpenFluor online database (Table S1). Component FC1 exhibited maximum wavelengths of λex = 332 nm and λem = 460 nm and therefore it could be allocated to a terrestrial humic component (Coble, 1996). Singh et al. (2013) reported that this component is ubiquitous in a reduced environment and holds reduced quinone-like moieties in its structure. Component FC2 showed a maximum peak at λex = 310

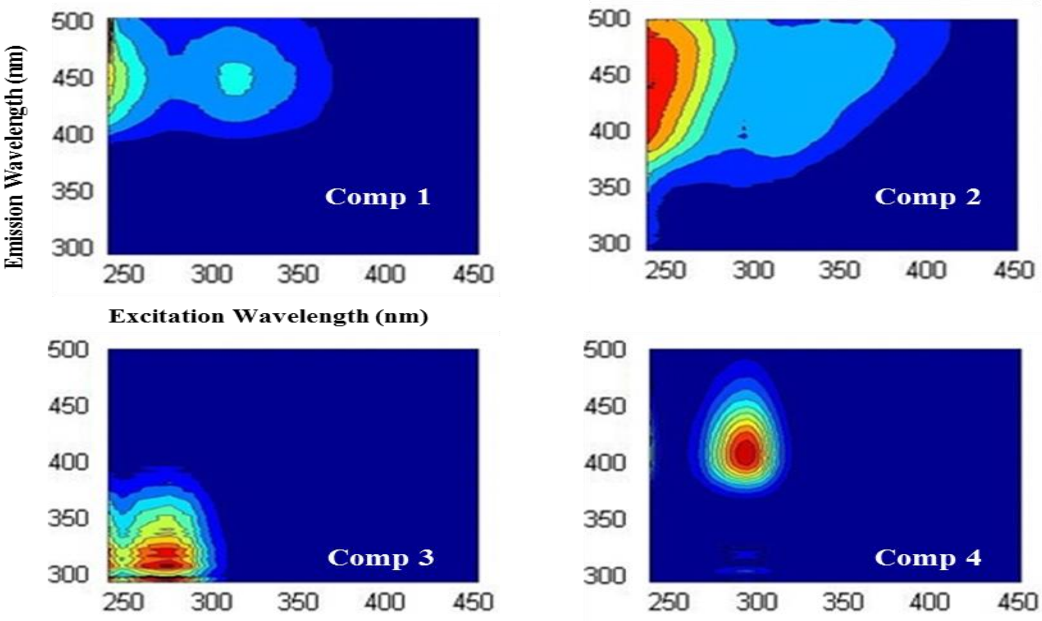

Figure 1. Contour plots of the four PFFCA components (PF1-PF4) identified from the complete measured F-EEMs dataset for the influents and effluents water of column experiment.

nm and λem = 410 nm, and therefore it was as attributed to a combination of terrestrial fulvic acid and microbial humic compounds (Gonçalves-Araujo et al., 2016; Li et al., 2016). Component FC4 displayed a maximum peak at λex = 300 nm and λem = 410 nm. This component is frequently associated with marine and/or microbial humic fluorophores and was recently connected to humic/fulvic compounds of agricultural origin (Baghoth et al., 2011). According to Singh et al. (2013) component FC2 and component FC4 contain oxidised moieties in their structures. Based on these definitions, the RI was calculated as the ratio of the first component (FC1) to the sum of the three humic components (FC1, FC2, and FC4). Component FC3 exhibited maximum fluorescence at the shortest wavelengths (λex = 240 nm, 268 nm) and (λem = 308 nm), which corresponds to a protein-like fluorophore (tyrosine and tryptophan-like fluorophores) (Wünsch et al., 2017).

3.1.2.Feed water DOM characteristics

Four feed waters (DCW, DCWW, WEOM, and NCTW) with different organic compositions were used in the experiments. Table 1 shows that WEOM had the highest concentration of organic matter (DOC ranged between 15.8 and 19.3 mg-C/L) and the NCTW influent had the lowest one (DOC varied from 1.98 to 4.1 mg/L). However, the DOC levels of DCW and DCWW were 10.8–13.6 mg-C/L and 10.2–13.7 mg/L, respectively.

The fluorescence indices were used to elucidate the DOM characteristics of the feed waters (Table 1). The results showed that DCW and DCWW had relatively similar fluorescence DOM characteristics. The HIX, FIX, and BIX of the DCW feed water were 0.85, 1.25, and 0.54, respectively, whereas they were 0.83, 1.26, and 0.61 for DCWW. WEOM had the highest humic content (HIX = 0.9) and the lowest microbial-derived (autochthonous) DOM content (BIX = 0.47), and its ratio of terrestrial humic DOM to microbial DOM (FIX) was 1.08. By contrast, NCTW retained a lower humic content (HIX = 0.62) and higher fresh DOM (BIX = 0.73). There were no notable changes in the fluorescence indexes values for DCW, DCWW, and WEOM feed water during the filtration process. However, an increase in the terrestrial humic content (HIX = 0.79, FIX = 1.2) for the NCTW effluent was recorded.

The PFFCA-EEM technique was used to gain insight into the DOM characteristics of the influent waters. Table 1 shows the average FI of PFFCA-EEM components for all of the feed-water types. The results demonstrated that the WEOM influent had a considerably higher concentration of humic compounds than the other influents. Terrestrial humic (FC1) was present in a proportion (45–49%) of the fluorescence spectrum of WEOM feed water; however, it only represents 43–46%, 41–42%, and 33–34% of the DCW, DCWW, and NCTW fluorescence spectrum, respectively. The average FIs of microbial humic FC2 and humic-like from agricultural sources, FC4, were 2.36±0.42 and 0.24±0.04 RU, while their values for NCTW were 0.2±0.09 and 0.1±0.03 RU, respectively. The humic-like components (FC1, FC2, and FC4) exhibited a decreasing behaviour during the filtration; the FI of the humic components decreased by 8–26% for DCW, 11–24% for DCWW, and 20–32% for WEOM influent water. An exception was the terrestrial and processed humic compounds of the NCTW influent, which followed an increasing behaviour during the filtration process. On average, the FI of FC1 and FC2 increased by a factor of two and three, respectively, during the filtration process. The enrichment of humic compounds in the effluent water might be attributed to: (i) the dissolution of soil organic compounds into the filtrate water, (ii) the presence of micro-organisms that are able to bio-transform the labile organic matter into more condensed and refractory compounds (Abdelrady et al., 2018). DCWW and WEOM had the highest concentration of protein-like fluorescent compounds. The average FI of FC3 was 0.47±0.19, 0.52±0.14, 0.15±0.08, and 0.65±0.23 RU for DCW, DCWW, NCTW, and WEOM influents, respectively. For all feed-water types, the protein-like component FC3 exhibited a decreasing trend during the filtration process; its removal ranged between 67% and 80%, which is in agreement with Abdelrady et al. (2019), who observed an average removal of 80% of labile organic compounds during the filtration process.

Table 1. The organic characteristics of the feed waters

Parameter	**Units**	**DCW**	**NCTW**	**DCWW**	**WEOM**
DOC	mg-C/L	11.64±3.51	3.98±0.73	11.73±1.06	18.23±1.6
HIX	----	0.85±0.02	0.62±0.04	0.83±0.06	0.9±0.02
FIX	----	1.25±0.07	1.35±0.02	1.26±0.14	1.08±0.13
BIX	----	0.54±0.11	0.73±0.04	0.61±0.17	0.47±0.11
FC1	RU	1.48±0.22	1.44±0.24	0.23±0.09	2.63±0.64
FC2	RU	1.10±0.19	1.53±0.21	0.20±0.09	2.36±0.42
FC3	RU	0.47±0.19	0.52±0.14	0.15±0.08	0.65±0.23
FC4	RU	0.20±0.03	0.15±0.06	0.10±0.03	0.24±0.04

3.1.3.Iron, manganese and arsenic mobilisation

Figure 2 shows the concentrations of Fe, Mn, and As in the effluents of the columns fed with different water sources. The figure shows that the mobilisation of Mn was much higher than that of Fe and As during the filtration processes. The concentration of Fe, Mn, and As for the four different water types were 10–20 µg/L, 1500–3900 µg/L, and >2–7.1 µg/L, respectively. The concentrations of the tested metal(loid)s in the effluents were found to be dependent on the feed-water source. The WEOM feed water exhibited the highest capacity to release Fe, Mn, and As from their solid forms into the filtrate water. The mean concentration of Fe, Mn, and As in the WEOM effluent were 18.28±1.5 µg/L, 3590±185.3 µg/L, and 5.48±1.2 µg/L, respectively. The DCW and DCWW effluents showed a lower capacity of releasing these metal(loid)s during the filtration process. The Fe, Mn, and As concentrations of the DCW

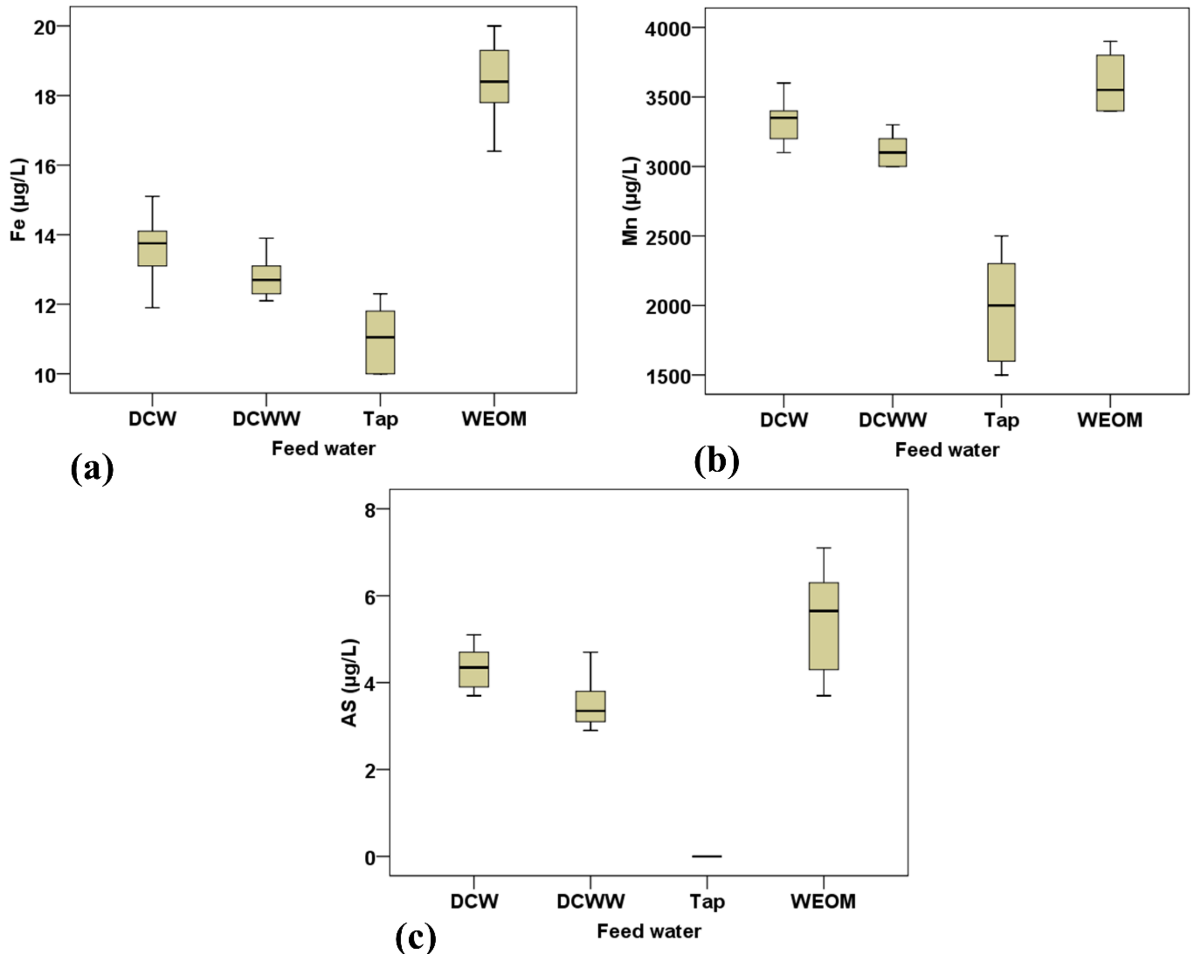

Figure 2. Fe (a), Mn (b), and As (c) concentrations in the effluents of columns operated using different water sources (DCW, DCWW, WEOM, NCTW) (anaerobic, 30°C, HRL=0.5 m/d)

effluent were 11.9–15.1 µg/L, 3100–3600 µg/L, and 3.7–5.1 µg/L, respectively, and those of the DCWW effluent were 12.1–13.9 µg/L, 3000–3600 µg/L, and 2.9–4.7 µg/L, correspondingly. By contrast, NCTW exhibited the lowest capability of releasing the assessed metal(loid)s, with Fe and Mn concentrations of 10.98±0.9 µg/L and 1990±384.3 µg/L, respectively. Moreover, the As concentration was always below the detection limit (<2 µg/L). A strong correlation (ρ = 0.77) was observed between Fe and As concentrations in the effluent waters. By contrast, a weak correlation (ρ = 0.35) was detected between the As and Mn concentrations.

3.1.4.Relationship between DOM composition and metal(loid) mobilisation

Figure 3 illustrates that the release of metal(loid)s (Fe, Mn, and As) during the filtration process is highly dependent on the DOM concentration of the feed water. The feed DOM concentration was highly correlated with Fe (ρ=0.89) and Mn (ρ=0.87) concentrations in the effluent waters,

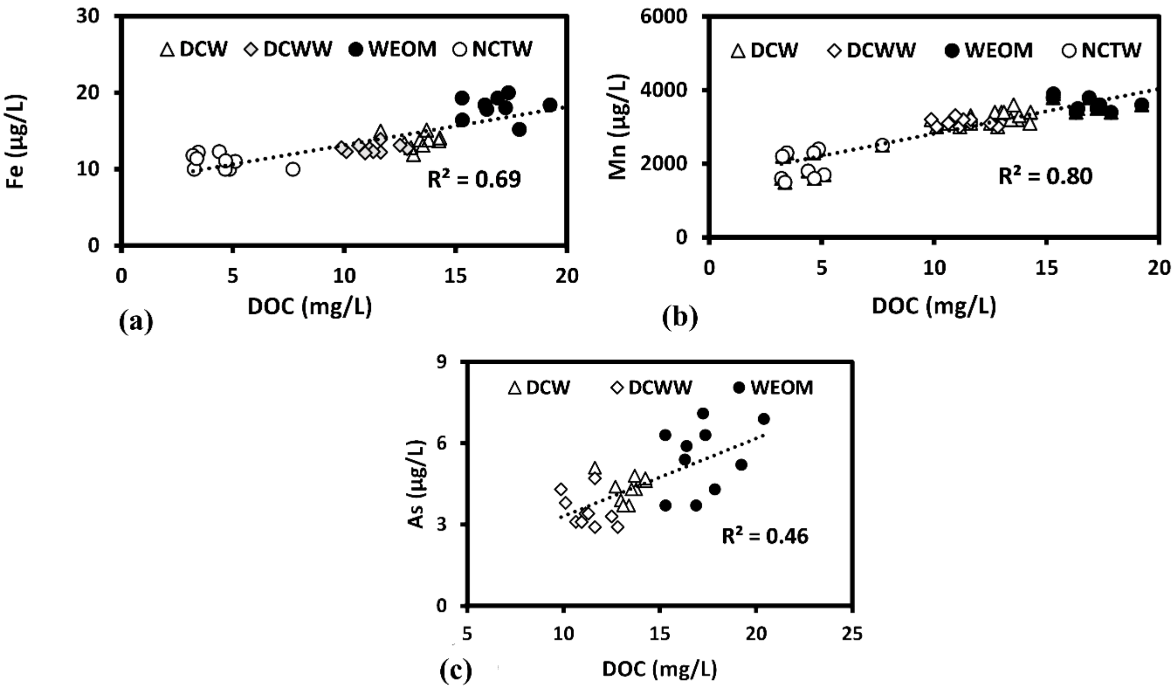

Figure 3. Impact of DOC concentration (mg-C/L) of different water sources (DCW, DCWW, WEOM, NCTW) on Fe (a), Mn (b), and As (c) mobilisation during column experiment (anaerobic, 30°C)

whereas a moderate positive relationship was observed between DOM concentration and effluent As concentrations (ρ = 0.63).

The fluorescence indexes results illustrate that Fe, Mn, and As release during the anaerobic filtration process is much more dependent on the humic content of the feed water than its autochthonous microbial DOM concentration (Table 2). The correlation between HIX and the effluent Fe concentration was observed to be ρ = 0.87, whereas it was recorded as ρ = 0.82 for the Mn concentration. However, a moderate correlation was observed between HIX and the effluent As concentration (ρ = 0.51). On the other hand, the mobilisation of Fe, Mn, and As was observed to be in a negative relationship with the microbial and terrestrial DOM ratio, and the correlation between the FIX of the feed waters and the released metal(loid)s was ρ = -0.71 for Fe, ρ = -0.64 for Mn, and ρ = -0.39 for As.

The correlation between the released metal(loid) concentrations and the FI of the fluorescence components of the feed waters was estimated and is presented in Table 2 and figures S2-S4. A strong positive correlation was observed between the Fe concentration and the FI of the humic components (FC1, FC2, and FC4) in the feed waters. The Mn mobilisation, in contrast, exhibited a strong correlation with the FI of humic components from different sources; the correlations between the Mn concentration and the FI of the PFFCA humic components (FC1, FC2, and FC4) were 0.7, 0.82, and 0.73, respectively. Conversely, the As concentration in the column effluent water was found to be in a moderate correlation with microbial humic component (FC2) and in weak correlations with the other humic components (FC1 and FC4). Furthermore, the RI demonstrated a moderate correlation with Fe mobilisation and a weak correlation with Mn and As mobilisation. This infers a role for condensed-structure humic compounds in the mobilisation of Fe into filtrate water. On the other hand, labile fluorescence compounds (FC3) were found to have a greater influence on the mobilisation of Mn than on those of Fe and As.

Table 2. Correlations between the tested metal(loid)s and the fluorescence characteristics of the feed waters

		DOC	**FC1**	**FC2**	**FC3**	**FC4**	**RI**	**HIX**	**FIX**	**BIX**
Fe	*spearman Correlation (ρ)*	0.89^{**}	$.82^{**}$	$.88^{**}$	$.6^{**}$	$.68^{**}$	$.64^{**}$	$.87^{**}$	$-.71^{**}$	$-.76^{**}$
	Pearson correlation (r)	0.83^{**}	$.83^{**}$	$.89^{**}$	$.58^{**}$	$.68^{**}$	$.60^{**}$	$.77^{**}$	$-.71^{**}$	$-.71^{**}$
	n	40	40	40	40	40	40	40	40	40
Mn	*spearman Correlation (ρ)*	0.87^{**}	$.70^{**}$	$.82^{**}$	$.77^{**}$	$.73^{**}$	$.33^{**}$	$.82^{**}$	$-.64^{**}$	$-.85^{**}$
	Pearson correlation (r)	0.89^{**}	$.77^{**}$	$.84^{**}$	$.75^{**}$	$.67^{**}$	$.21^{**}$	$.85^{**}$	$-.59^{**}$	$-.72^{**}$
	n	40	40	40	40	40	40	40	40	40
As	*spearman Correlation (ρ)*	0.63^{**}	.32	$.57^{**}$	.05	$.42^{*}$	$.37^{*}$	$.51^{**}$	$-.39^{*}$	$-.57^{**}$
	Pearson correlation (r)	0.68^{**}	$.48^{**}$	$.64^{**}$	.08	$.47^{**}$	$.41^{*}$	$.52^{**}$	$-.51^{**}$	$-.58^{**}$
	n	30	30	30	30	30	30	30	30	30

***P*-value is less than 0.001

**P*-value is less than 0.05

3.2. Impact of NOM concentrations on metal(loid) mobilisation (batch study)

The effect of NOM (humic, fulvic, and tyrosine) concentrations on the release of metal(loid)s (Fe, Mn, and As) from the soil into the filtrate water under anaerobic conditions was studied in established batch reactors. The fluorescence characteristics of the injected NOM is presented in Figure S5. The experimental results illustrated that the Fe mobilisation increased steadily with humic and fulvic concentrations (Figure 4.a). Fe exhibited relatively higher affinity with humic (high molecular weight) compounds compared to that with fulvic ones (low molecular weight). The concentration of soluble Fe reached 162±19 µg/L when the humic concentration was 20 mg-C/L, whereas it was 114±28 µg/L at the same concentration of fulvic acid. On the other hand, tyrosine exhibited lower ability to release Fe at low concentrations; the concentrations of Fe in the effluent water in the batch reactors injected with 5 and 10 mg-C/L of tyrosine were 30±17 and 32±11 µg/L, respectively. However, an immense increase in Fe concentration was observed for the batch reactors injected with 15 mg-C/L and 20 mg-C/L of tyrosine, where the soluble Fe concentrations were 290±47 µg/L and 340±24 µg/L, respectively.

Figure 4.b illustrates the impact of NOM type and concentration on the mobilisation of Mn during the filtration process. It can be observed that fulvic compounds have the highest capacity of releasing Mn into the filtrate water. The concentration of Mn increased from 250±47 µg/L to 1041±69 µg/L as the concentration of fulvic acid increased from 5 mg-C/L to 20 mg-C/L. The same trend was noted for humic compounds, where a humic acid concentration of 20 mg-C/L resulted in increasing the released Mn concentration five times compared with its effluent concentration in the reactors injected with 5 mg-C/L humic acid. Likewise, a positive relationship was observed between Mn concentration in the batch reactor effluents and tyrosine concentration. The concentration of Mn was increased by 35%, 65%, and 77% in the batch

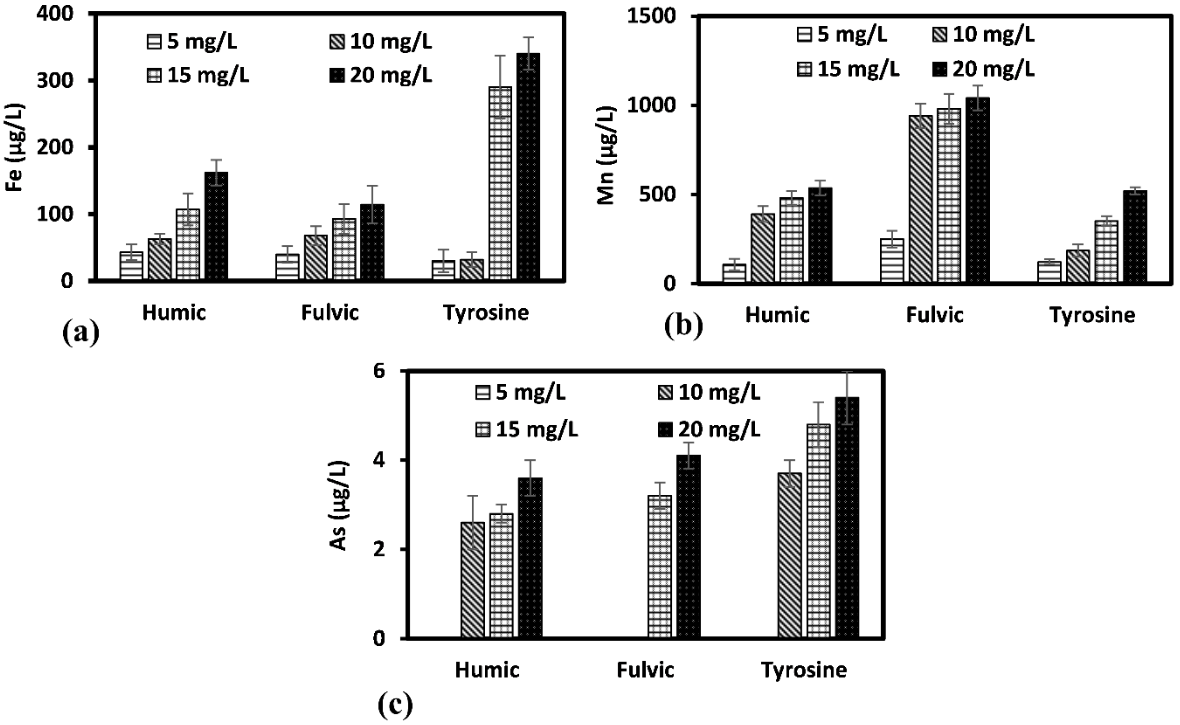

Figure 4. Effect of NOM type (humic, fulvic, and tyrosine) and concentration (5, 10, 15, 20 mg-C/L) on (a) Fe, (b) Mn, and (c) As mobilisation during the batch experiment (anaerobic, 30 °C, HRL = 0.5 m/d)

reactors injected with 10, 15, and 20 mg-C/L, respectively, compared with its concentration in the batch reactors injected with 5 mg-C/L.

The batch study results showed that the mobilisation of As is obviously affected by the type and concentration of NOM (Figure 4.C). NOM at low concentration exhibited a poor capacity of releasing As from its precipitated form into the filtrate water. No As concentration was quantitatively (LOQ = 2 µg/L) detected in any of the batch reactor effluents at DOC = 5 mg-C/L for the three NOM types. At higher concentrations (20 mg-C/L), tyrosine exhibited the highest capacity of releasing As into the filtrate water; the As concentrations in the batch reactors injected with humic, fulvic, and tyrosine were 3.6±0.4, 4.1±0.3, and 5.4±0.6 µg/L, respectively.

4. Discussion

4.1. Mobilisation of Fe, Mn and As during BF

The mobilisation of Mn was two orders of magnitude higher than that of Fe during the infiltration process under the experimental conditions. From stoichiometry, 1 mole of simple organic matter (e.g., acetate) could act as an electron donor to mobilise 4 moles of Mn and 8 moles of Fe from the soil into the filtrate water (Lovley et al., 1988). However, the higher mobilisation of Mn compared with those of Fe and As observed during this study was probably due the combination of three factors:

(i) The reducing environment was still not high enough to be dominated by the Fe microbial reduction process.

(ii) Mn oxide was used as an agent for the Fe oxidation process and thereby could be precipitated as Fe oxides. This process would increase the re-adsorption of As on the surface of iron oxides and thus reduce the concentrations of Fe and As in the filtrate water (Vega et al., 2017). Neidhardt et al. (2014) illustrated that Fe (oxyhydr)oxide redox processes control the concentration of As in filtrate water.

(iii) The column experiment was conducted at a high temperature (30 °C) and a low infiltration rate (0.5 m/d), which greatly enhanced the microbial reduction of manganese.

Low infiltration rate increases the contact time and interaction between the metals of the soil and the DOM of the raw water. Moreover, it promotes the reducing conditions along the flow path, which leads to increase the mobilisation of metals into the infiltrating water. Paufler et al. (2018) conducted column studies to assess the impact of the temperature (15–35 °C) and flow rate on the Mn mobilisation during the BF process. It was found that raising the temperature from 20 to 30 °C at a low hydraulic rate (1 ml/min) resulted in increasing the Mn release rate (K_{Mn}) 10–15 times, whereas K_{Mn} was negligible when the feed-water temperature was below 10 °C. Bourg et al. (1994) reported that increasing the temperature (>10 °C) triggers the microbial reduction of manganese in an alluvial aquifer. Based on these findings, it is presumed that the higher Mn mobilisation rate in the column experiment relative to Fe and As mobilisation is primarily ascribable to the microbial reduction of Mn at high temperature (30 °C) that stimulates simultaneously the associated Fe (II) and As (III) oxidation and precipitation processes. This plausible mechanism was observed and reported in many BF and alluvial aquifer fields (Bourg et al., 1993, 1994; Eckert et al., 2006; Jacobs et al., 1988; Kedziorek et al., 2008; Thomas et al., 1994; Vega et al., 2017). However, it is worth noting that other mechanisms (e.g., the simultaneous mobilisation of Fe and Mn) have also been observed in many BF fields (Grischek et al., 2017; Hamdan et al., 2013; Matsunaga et al., 1993).

4.2. Influence of composition and concentration of DOM on metal(loid) mobilisation

The strong correlation between DOC and metal(loid) (Fe, Mn, and As) concentrations in the effluent water of the column indicates that DOM plays a key role in the mobilisation of these metal(loid)s during infiltration. In this research, NCTW with low organic content demonstrated lower efficiency in releasing Fe, Mn, and As into the filtrate water compared with those of other source-water types. This is consistent with the findings of recent studies (Hossain Md Anawar et al., 2013; Vega et al., 2017), which reported an increase in the mobilisation rate of Fe and As associated with higher DOM in Daudkandi (Meghna delta) and Marua of the Ganges delta plain aquifer in Bangladesh (Hossain M. Anawar et al., 2003; Hossain Md Anawar et al., 2013). Wang et al. (2012) illustrated that DOM influences the mobilisation and release of metal(loid)s during the passage of the soil through a redox process, complexation, and competitive adsorption. Therefore, it can be concluded that the organic composition of feed water controls the concentration of Fe, Mn, and As in bank filtrate water.

Refractory compounds (i.e., humic) play a vital role in the mobilisation of Fe, Mn, and As during the subsurface flow of water. The experimental results revealed that the mobilisation of Fe and Mn has a strong positive relationship with the humic content of the feed water (HIX), whereas As mobilisation was the least affected by changes in the humic content of the feed water. Several previous studies highlighted the multiple roles of humic compounds in the mobilisation of metal(loid)s during the filtration process (Brune et al., 2004; Liu et al., 2011; Yuan et al., 2018). Owing to their high electron shuttle capacities, humic compounds might act as catalysts for the iron microbial reduction process by transferring electrons between the insoluble metal(loid)s and the reducing microorganisms; this was investigated in many field studies (Mladenov et al., 2010; Mladenov et al., 2015; Poggenburg et al., 2018). In addition, these electron-rich compounds have high capabilities of binding to the soil metal(loid)s and increasing their solubility (Sharma et al., 2010). Chen et al. (2003) pointed out that humic compounds are more soluble at higher pH (>4); thus, they are subjected to more trapping of metal(loid)s from the soil and are maintained in their soluble forms by forming soluble complex compounds.

The effect of humic compounds on the metal(loid) mobilisation is relatively dependent on the origin and characteristics of the organic compounds and type of metal(loid). In this research, a moderate correlation was detected between RI and Fe concentration in the filtrate water, indicating that terrestrial humic compounds (with condensed structures) have relatively higher capability to trap Fe into filtrate water than lower molecular weight humic compounds. According to Yuan et al. (2018), high-molecular-weight humic compounds have more binding sites, and therefore higher capability of forming chemically stable compounds with Fe, than less-condensed-structure and labile compounds. Therefore, it can be deduced that humic compounds of terrestrial origin are more triggered to release iron from its solid forms into filtrate water. This was confirmed by the batch experiment results, which showed a relatively higher increase in Fe mobilisation with humic than with fulvic acid (lower-molecular-weight humic compounds). By contrast, a weak correlation was observed between RI and Mn mobilisation, demonstrating comparable abilities of humic compounds with low and high condensation (i.e., terrestrial and microbial humic) to mobilise Mn; this indicates that Mn metal has a high affinity to both low- and high-molecular-weight humic compounds. This is in agreement with Vega et al. (2017), who observed higher concentrations of Mn to be associated with higher humic content in shallow aquifers at West Bengal (India). Nevertheless, the batch experiment showed that fulvic compounds at higher concentrations (>5 mg-C/L) have a higher capability of mobilising Mn than higher-molecular-weight humic compounds; this could be due to their high capacity to form soluble and stable Mn complexes at high pH (>6) compared with humic compounds, as proven previously by Du Laing (2010).

The mobilisation of Mn during the filtration process was observed to be highly influenced by the biodegradable organic matter content of the source water. The high correlation between Mn concentration in the filtrate water and protein-like fluorescent components indicates that the microbial reduction of Mn is the primary mechanism of Mn release. However, a moderate correlation was observed between Fe concentration and protein-like components. The batch experiment showed that a protein-like (i.e., tyrosine) compound is the most effective NOM for releasing Fe and As at high concentrations (>10 mg-C/L). This is probably due to the increased concentration of biodegradable compounds, which increases the biological activity associated to sand, increases the mobilisation of Mn and decreases the redox potential to a level that permits bacteria to use Fe from the soil as a source of energy, thus increasing the Fe concentration in the effluent water. This process is concurrent with the release of As adsorbed on Fe (oxyhydr)oxides into the filtrate water.

5. Conclusions

The mobilisation of geogenic metal(loid)s, such as Fe, Mn, and As, during the BF process restricts their application, particularly in arid-climate countries. Based on the results of laboratory-scale column and batch studies, which were conducted to assess the impact of the organic composition of raw water on the mobilisation of these metal(loids) during anaerobic BF, the following conclusions are drawn:

- The mobilisation of Mn under the applied experimental conditions was two and three orders of magnitude higher than those of Fe and As, respectively.
- The dissolved organic matter concentration and composition of the raw water could change the capacity of mobilisation of metal(loids) during the filtration process
- The humic content of the source water was found to significantly affect the release of Fe and Mn during the BF process; a positive relationship was found between the mobilisation of the metal(loids) and the HIX of the source water. This might be attributed to the high electron shuttle capacity of the humic compounds, which enables them to act as mediators for the microbial reduction processes and to form soluble complex compounds with the released metals.

- Terrestrial humic compounds with complex structures showed a higher capability of releasing Fe from the soil into the filtrate water. On the other hand, source water with lower-molecular-weight humic compounds at a concentration of >5 mg-C/L was able to mobilise Mn at a higher rate than higher-molecular-weight humic compounds. However, the metal(loid) species in the soil may alter the behaviours of NOM compounds, which should be investigated.
- Arsenic mobilisation was observed to have a high correlation with Fe mobilisation and a weak correlation with the variations in the organic composition of source water.
- Biodegradable organic matter was found to be effective in mobilising Mn into the filtrate water; a strong correlation was observed between the FI of protein-like components in the source water and Mn mobilisation. However, a moderate correlation was found between Fe mobilisation and the FI of protein-like components. Nevertheless, the experimental results showed that a high concentration (>10 mg-C/L) of a protein-like compound is enough to produce a Fe-reducing environment in the infiltration area and thereby increase the Fe concentration in the filtrate water.
- In summary, this study revealed that the organic matter composition of source water determines the redox environment during the BF process and affects the mobilisation process of the metal(loid)s that should be considered during the BF design process. Moreover, this research highlights the efficiency of the fluorescence spectroscopy technique as a monitoring tool for characterisation the organic composition of the raw water as well as for prediction and control the redox process and the mobilisation of metal(loid)s during BF.

Acknowledgements: We would like to acknowledge the support of Mr. Abdullahi Mohamed (IHE Delft Institute for Water Education, Delft, The Netherlands) for his assistance in laboratory measurements. This work was financially supported by the Netherlands Fellowship Programme NFP

6. References

Abdelrady, A., Sharma, S., Sefelnasr, A., Abogbal, A., & Kennedy, M. (2019). Investigating the impact of temperature and organic matter on the removal of selected organic micropollutants during bank filtration: A batch study. *Journal of Environmental Chemical Engineering, 7*(1), 102904. doi:https://doi.org/10.1016/j.jece.2019.102904

Abdelrady, A., Sharma, S., Sefelnasr, A., & Kennedy, M. (2018). The Fate of Dissolved Organic Matter (DOM) During Bank Filtration under Different Environmental Conditions: Batch and Column Studies. *Water, 10*(12), 1730.

Anawar, H. M., Akai, J., Komaki, K., Terao, H., Yoshioka, T., Ishizuka, T., . . . Kato, K. (2003). Geochemical occurrence of arsenic in groundwater of Bangladesh: sources and mobilization processes. *Journal of Geochemical Exploration, 77*(2), 109-131. doi:https://doi.org/10.1016/S0375-6742(02)00273-X

Anawar, H. M., Tareq, S. M., & Ahmed, G. (2013). Is organic matter a source or redox driver or both for arsenic release in groundwater? *Physics and Chemistry of the Earth, Parts A/B/C, 58-60*, 49-56. doi:https://doi.org/10.1016/j.pce.2013.04.009

Baghoth, S. A., Sharma, S. K., & Amy, G. L. (2011). Tracking natural organic matter (NOM) in a drinking water treatment plant using fluorescence excitation-emission matrices and PARAFAC. *Water Res, 45*(2), 797-809. doi:10.1016/j.watres.2010.09.005

Bertelkamp, C., Reungoat, J., Cornelissen, E., Singhal, N., Reynisson, J., Cabo, A., . . . Verliefde, A. R. (2014). Sorption and biodegradation of organic micropollutants during river bank filtration: A laboratory column study. *Water Research, 52*, 231-241. doi:http://dx.doi.org/10.1016/j.watres.2013.10.068

Bourg, A. C. M., & Bertin, C. (1993). Biogeochemical processes during the infiltration of river water into an alluvial aquifer. *Environmental science & technology, 27*(4), 661-666. doi:10.1021/es00041a009

Bourg, A. C. M., & Bertin, C. (1994). Seasonal and Spatial Trends in Manganese Solubility in an Alluvial Aquifer. *Environmental science & technology, 28*(5), 868-876. doi:10.1021/es00054a018

Brune, A., Schink, B., Benz, M., & Kappler, A. (2004). Electron shuttling via humic acids in microbial iron(III) reduction in a freshwater sediment. *FEMS Microbiology Ecology, 47*(1), 85-92. doi:10.1016/S0168-6496(03)00245-9 %J FEMS Microbiology Ecology

Chen, J., Gu, B., Royer, R. A., & Burgos, W. D. (2003). The roles of natural organic matter in chemical and microbial reduction of ferric iron. *Science of The Total Environment, 307*(1), 167-178. doi:https://doi.org/10.1016/S0048-9697(02)00538-7

Coble, P. G. (1996). Characterization of marine and terrestrial DOM in seawater using excitation-emission matrix spectroscopy. *Marine Chemistry, 51*(4), 325-346. doi:https://doi.org/10.1016/0304-4203(95)00062-3

Du Laing, G. (2010). Analysis and Fractionation of Trace Elements in Soils. In P. S. Hooda (Ed.), *Trace Elements in Soils*.

Eckert, P., & Irmscher, R. (2006). Over 130 years of experience with Riverbank Filtration in Düsseldorf, Germany. *Journal of Water Supply: Research and Technology - AQUA, 55*(4), 283-291. doi:10.2166/aqua.2006.040

Gabor, R. S., Baker, A., McKnight, D. M., & Miller, M. P. (2014). Fluorescence Indices and Their Interpretation. In A. Baker, D. M. Reynolds, J. Lead, P. G. Coble, & R. G. M. Spencer (Eds.), *Aquatic Organic Matter Fluorescence* (pp. 303-338). Cambridge: Cambridge University Press.

Ghodeif, K., Grischek, T., Bartak, R., Wahaab, R., & Herlitzius, J. (2016). Potential of river bank filtration (RBF) in Egypt. *Environmental Earth Sciences, 75*(8), 1-13. doi:10.1007/s12665-016-5454-3

Gonçalves-Araujo, R., Granskog, M. A., Bracher, A., Azetsu-Scott, K., Dodd, P. A., & Stedmon, C. A. (2016). Using fluorescent dissolved organic matter to trace and distinguish the origin of Arctic surface waters. *Scientific Reports, 6*, 33978. doi:10.1038/srep33978

Grischek, T., & Paufler, S. (2017). Prediction of Iron Release during Riverbank Filtration. *9*(5), 317.

Haas, R., Opitz, R., Grischek, T., & Otter, P. (2018). The AquaNES Project: Coupling Riverbank Filtration and Ultrafiltration in Drinking Water Treatment. *Water, 11*(1), 18.

Hamdan, A. M., Sensoy, M. M., & Mansour, M. S. (2013). Evaluating the effectiveness of bank infiltration process in new Aswan City, Egypt. *Arabian Journal of Geosciences, 6*(11), 4155-4165. doi:10.1007/s12517-012-0682-7

Hansen, A. M., Kraus, T. E. C., Pellerin, B. A., Fleck, J. A., Downing, B. D., & Bergamaschi, B. A. (2016). Optical properties of dissolved organic matter (DOM): Effects of biological and photolytic degradation. *61*(3), 1015-1032. doi:doi:10.1002/lno.10270

Harshman, R. A., & Lundy, M. E. (1994). PARAFAC: Parallel factor analysis. *Computational Statistics & Data Analysis, 18*(1), 39-72. doi:https://doi.org/10.1016/0167-9473(94)90132-5

Hinkle, D. E., Wiersma, W., & Jurs, S. G. (1988). Applied statistics for the behavioral sciences.

Huguet, A., Vacher, L., Relexans, S., Saubusse, S., Froidefond, J. M., & Parlanti, E. (2009). Properties of fluorescent dissolved organic matter in the Gironde Estuary. *Organic Geochemistry, 40*(6), 706-719. doi:https://doi.org/10.1016/j.orggeochem.2009.03.002

Irmscher, R., & Teermann, I. (2002). Riverbank filtration for drinking water supply - a proven method, perfect to face today's challenges. *Water Science and Technology: Water Supply, 2*(5-6), 1-8. doi:10.2166/ws.2002.0143 %J Water Science and Technology: Water Supply

Jacobs, L. A., von Gunten, H. R., Keil, R., & Kuslys, M. (1988). Geochemical changes along a river-groundwater infiltration flow path: Glattfelden, Switzerland. *Geochimica et Cosmochimica Acta, 52*(11), 2693-2706. doi:https://doi.org/10.1016/0016-7037(88)90038-5

Kedziorek, M. A., Geoffriau, S., Bourg, A. C. J. E. s., & technology. (2008). Organic matter and modeling redox reactions during river bank filtration in an alluvial aquifer of the Lot River, France. *42*(8), 2793-2798.

Li, P., Lee, S. H., Lee, S. H., Lee, J.-B., Lee, Y. K., Shin, H.-S., & Hur, J. (2016). Seasonal and storm-driven changes in chemical composition of dissolved organic matter: a case study of a reservoir and its forested tributaries. *Environmental Science and Pollution Research, 23*(24), 24834-24845. doi:10.1007/s11356-016-7720-z

Liu, G., Fernandez, A., & Cai, Y. (2011). Complexation of Arsenite with Humic Acid in the Presence of Ferric Iron. *Environmental science & technology, 45*(8), 3210-3216. doi:10.1021/es102931p

Lovley, D. R., & Phillips, E. J. (1988). Novel mode of microbial energy metabolism: organic carbon oxidation coupled to dissimilatory reduction of iron or manganese. *Applied and Environmental Microbiology, 54*(6), 1472-1480.

Massmann, G., Nogeitzig, A., Taute, T., & Pekdeger, A. (2008). Seasonal and spatial distribution of redox zones during lake bank filtration in Berlin, Germany. *Environmental Geology, 54*(1), 53-65. doi:10.1007/s00254-007-0792-9

Matsunaga, T., Karametaxas, G., Von Gunten, H., & Lichtner, P. J. G. e. C. A. (1993). Redox chemistry of iron and manganese minerals in river-recharged aquifers: A model interpretation of a column experiment. *57*(8), 1691-1704.

Miller, M. P., McKnight, D. M., Cory, R. M., Williams, M. W., & Runkel, R. L. (2006). Hyporheic Exchange and Fulvic Acid Redox Reactions in an Alpine Stream/Wetland Ecosystem, Colorado Front Range. *Environmental science & technology, 40*(19), 5943-5949. doi:10.1021/es060635j

Mladenov, N., Zheng, Y., Miller, M. P., Nemergut, D. R., Legg, T., Simone, B., . . . McKnight, D. M. (2010). Dissolved Organic Matter Sources and Consequences for Iron and Arsenic Mobilization in Bangladesh Aquifers. *Environmental science & technology, 44*(1), 123-128. doi:10.1021/es901472g

Mladenov, N., Zheng, Y., Simone, B., Bilinski, T. M., McKnight, D. M., Nemergut, D., . . . Ahmed, K. M. (2015). Dissolved Organic Matter Quality in a Shallow Aquifer of Bangladesh: Implications for

Arsenic Mobility. *Environmental science & technology, 49*(18), 10815-10824. doi:10.1021/acs.est.5b01962

Murphy, K. R., Stedmon, C. A., Graeber, D., & Bro, R. (2013). Fluorescence spectroscopy and multi-way techniques. PARAFAC. *Analytical Methods, 5*(23), 6557-6566. doi:10.1039/C3AY41160E

Neidhardt, H., Berner, Z. A., Freikowski, D., Biswas, A., Majumder, S., Winter, J., . . . Norra, S. (2014). Organic carbon induced mobilization of iron and manganese in a West Bengal aquifer and the muted response of groundwater arsenic concentrations. *Chemical Geology, 367*, 51-62. doi:https://doi.org/10.1016/j.chemgeo.2013.12.021

Ohno, T. (2002). Fluorescence Inner-Filtering Correction for Determining the Humification Index of Dissolved Organic Matter. *Environmental science & technology, 36*(4), 742-746. doi:10.1021/es0155276

Paufler, S., Grischek, T., Benso, M. R., Seidel, N., & Fischer, T. (2018). The Impact of River Discharge and Water Temperature on Manganese Release from the Riverbed during Riverbank Filtration: A Case Study from Dresden, Germany. *10*(10), 1476.

Poggenburg, C., Mikutta, R., Schippers, A., Dohrmann, R., & Guggenberger, G. (2018). Impact of natural organic matter coatings on the microbial reduction of iron oxides. *Geochimica et Cosmochimica Acta, 224*, 223-248. doi:https://doi.org/10.1016/j.gca.2018.01.004

Qian, C., Wang, L.-F., Chen, W., Wang, Y.-S., Liu, X.-Y., Jiang, H., & Yu, H.-Q. (2017). Fluorescence Approach for the Determination of Fluorescent Dissolved Organic Matter. *Analytical Chemistry, 89*(7), 4264-4271. doi:10.1021/acs.analchem.7b00324

R.K. Pachauri, & Meyer, L. A. (2014). *Climate Change 2014 Synthesis Report*. Retrieved from Geneva, Switzerland:

Ray, C., & Shamrukh, M. (2011). Riverbank Filtration for Water Security in Desert Countries. *NATO Science for Peace and Security Series C: Environmental Security, 2011*.

Sandhu, C., Grischek, T., Börnick, H., Feller, J., & Sharma, S. K. (2019). A Water Quality Appraisal of Some Existing and Potential Riverbank Filtration Sites in India. *11*(2), 215.

Schittich, A.-R., Wünsch, U. J., Kulkarni, H. V., Battistel, M., Bregnhøj, H., Stedmon, C. A., & McKnight, U. S. (2018). Investigating Fluorescent Organic-Matter Composition as a Key Predictor for Arsenic Mobility in Groundwater Aquifers. *Environmental science & technology, 52*(22), 13027-13036. doi:10.1021/acs.est.8b04070

Sharma, P., Ofner, J., & Kappler, A. (2010). Formation of Binary and Ternary Colloids and Dissolved Complexes of Organic Matter, Fe and As. *Environmental science & technology, 44*(12), 4479-4485. doi:10.1021/es100066s

Singh, S., Inamdar, S., & Scott, D. (2013). Comparison of Two PARAFAC Models of Dissolved Organic Matter Fluorescence for a Mid-Atlantic Forested Watershed in the USA. *Journal of Ecosystems, 2013*, 16. doi:10.1155/2013/532424

Sprenger, C., Lorenzen, G., & Asaf, P. (2012). Environmental Tracer Application and Purification Capacity at a Riverbank Filtration Well in Delhi (India). *Journal of Indian Water Works Association, Special Issue on River Bank Filtration, 1*, 25-32.

Thomas, N. E., Kan, K. T., Bray, D. I., & MacQuarrie, K. T. B. (1994). Temporal Changes in Manganèse Concentrations in Water from the Fredericton Aquifer, New Brunswick. *32*(4), 650-656. doi:doi:10.1111/j.1745-6584.1994.tb00901.x

Vega, M. A., Kulkarni, H. V., Mladenov, N., Johannesson, K., Hettiarachchi, G. M., Bhattacharya, P., . . . Datta, S. (2017). Biogeochemical Controls on the Release and Accumulation of Mn and As in Shallow Aquifers, West Bengal, India. *Frontiers in Environmental Science, 5*, 29.

Wahaab, R. A., Salah, A., & Grischek, T. (2019). Water Quality Changes during the Initial Operating Phase of Riverbank Filtration Sites in Upper Egypt. *Water, 11*(6), 1258.

Wang, Y., Jiao, J. J., & Cherry, J. A. (2012). Occurrence and geochemical behavior of arsenic in a coastal aquifer–aquitard system of the Pearl River Delta, China. *Science of The Total Environment, 427-428*, 286-297. doi:https://doi.org/10.1016/j.scitotenv.2012.04.006

Wünsch, U., Murphy, K., & Stedmon, C. (2017). The One-Sample PARAFAC Approach Reveals Molecular Size Distributions of Fluorescent Components in Dissolved Organic Matter. *Environmental Science and Technology, 51*(20), 11900–11908. doi:10.1021/acs.est.7b03260

Yang, C., Li, S., Liu, R., Sun, P., & Liu, K. (2015). Effect of reductive dissolution of iron (hydr)oxides on arsenic behavior in a water–sediment system: First release, then adsorption. *Ecological Engineering, 83*, 176-183. doi:10.1016/j.ecoleng.2015.06.018

Yuan, Y., He, X., Xi, B., Li, D., Gao, R., Tan, W., . . . Zhao, X. (2018). Polarity and molecular weight of compost-derived humic acid affect Fe(III) oxides reduction. *Chemosphere, 208*, 77-83. doi:https://doi.org/10.1016/j.chemosphere.2018.05.160