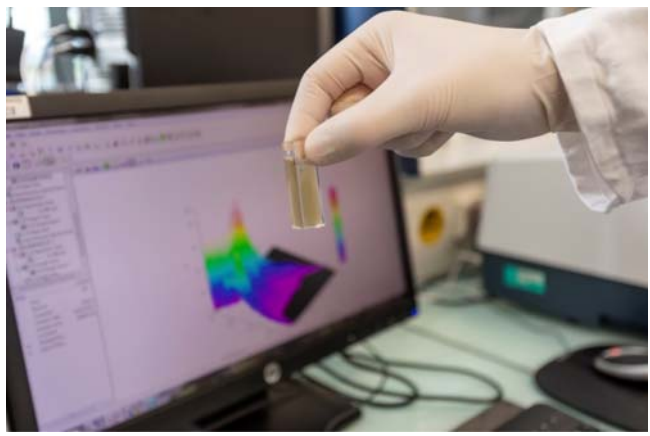
Chapter 3

Impact of PFA on organic matter and post-injection consequences



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3.1 INTRODUCTION

Performic acid (PFA) is an organic oxidant, which consequently is capable of affecting organic matter in wastewater. The injection of an organic compound will indeed increase the dissolved organic carbon of wastewater. This DOC addition constitutes a mix of PFA and formic acid, and the PFA instability will result in a PFA degradation to the formic acid once injected into the wastewater. The kinetics of this degradation process in wastewater and Seine River water needs to be investigated, along with the PFA degradation products, in order to

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determine whether the environmental fate of PFA after injection is an issue. In addition, the oxidative power of PFA could cause changes in the organic matter nature, and this remains an outstanding question.

This chapter aims to present the results obtained relative to the PFA impact on SEV WWTP discharged organic matter and its fate in both wastewater and Seine River water after treatment. First, the DOC increase caused by PFA injection will be quantified and compared with the theoretical input of the PFA mixture. Next, the effect of PFA on wastewater organic matter nature will be evaluated based on 3D fluorescence. Lastly, the fate of PFA after injection will be investigated both quantitatively and qualitatively. PFA degradation kinetics are determined in both SEV WWTP discharge and Seine River water, as are the PFA half-lives. PFA degradation products can then be measured by means of liquid chromatography with conductive detection and UV detection so as to verify that only formic acid and H_2O_2 are formed.

3.2 IMPACT OF PFA ON THE SOLUBLE ORGANIC MATRIX

3.2.1 Increase in dissolved organic carbon concentration

The injection of PFA into a WWTP discharge leads to injecting dissolved organic carbon (DOC). In theory, the DOC content of the prepared PFA solution equals 0.79 ppm C/ppm PFA injected (0.19 from PFA and 0.60 from the residual formic acid), as described in Part 1, Chapter 1. To verify this assertion, DOC values from the 24 laboratory scale PFA disinfection trials performed in Part 1, Chapter 1 on SEV WWTP discharge samples, are plotted in Figure 14, which displays the average DOC concentrations measured and the standard deviations as error bars for each C × t, as well as the average values and standard deviations for the theoretical DOC concentrations. These theoretical concentrations are obtained by adding the 0.79 ppm C/ppm PFA injected to the initial DOC values.

The DOC concentrations measured after disinfection are very consistent with those obtained theoretically by adding 0.79 ppm C/ppm PFA injected to the initial DOC concentrations. Both series are indeed significantly comparable (Mann-Whitney, p-value = 0.8397). In addition, the average increase in calculated DOC based on actual measurements equals 0.78 ppm C/ppm PFA injected. The slight observable difference between actual measurements and theoretical values in Figure 14 can be explained by the variability of the DOC analytical method. It can thus be confirmed that injecting PFA preparation to achieve a PFA dose between 1 and 2 ppm would result in a limited increase of 0.79 and 1.58 mgC/L of the DOC.

By comparison, applying a dose of 8 ppm of peracetic acid (PAA) in SEV WWTP discharge, which is the dose required to obtain the same bacteria reduction as 2 ppm of PFA (Part 1, Chapter 1), would theoretically result in a minimum DOC increase of 2.53 mgC/L since 1 ppm of PAA contains 0.32 mgC/L and provided the PAA preparation does not contain any other organic

compounds. Similarly, since high doses of 10 ppm of PFA or more are required to disinfect partially-treated Parisian wastewater or combined sewer overflows with a contact time of 10 min (Part 1, Chapter 1), the DOC increase in such a case would be very high, that is, 7.9 mgC/L or more.

3.2.2 Modifications to dissolved organic matter quality, as monitored by 3D fluorescence spectroscopy

3.2.2.1 Experimental description

The analytical protocol described below has been applied to the PFA addition tests performed on the following dates: Sept 4, 2018, Sept 11, 2018, Sept 18, 2018, Oct 30, 2018, and Nov 6, 2018. Before analysis by 3D fluorescence spectrometry, the selected samples from SEV WWTP discharge water (both with and without PFA) were filtered at 0.45 µm (GF/F, glass fiber, Whatman®). Fluorescence spectrometry measurements were performed using a 3D spectrofluorimeter (Jasco FP-8300, Japan) equipped with a 150-W xenon lamp as the excitation source. This device is controlled by the Spectra Manager II software. Measurements were conducted in a 1-cm quartz cell at a controlled temperature of 20°C in order to avoid thermal fluorescence extinction (Watras *et al.*, 2011). Fluorescence spectra (excitation-emission matrix: EEM) were measured for excitation wavelengths (Ex) ranging from 240 to 550 nm every 5 nm and for an emission wavelength (Em) ranging from 260 to 700 nm with a measurement step of 2 nm. The widths of the emission and excitation slots were set to 5 nm, with a scanning rate of 1000 nm/min.

To avoid internal filter effects due to highly absorbent species present in the samples, the species were diluted with ultrapure water to obtain an absorbance of 0.05 cm^{-1} at 254 nm before fluorescence analysis (Alberts & Takács, 2004; Lakowicz, 2010). The absorbance at 254 nm was measured in a standard 1.0-cm quartz cuvette using a UV-Vis spectrophotometer (UviLine 9400, Seconam – Xylem S.A.S., White Plains, USA). The EEM measurements (both blank and sample) were normalized by the area of the Raman peak of ultrapure water at 350 nm excitation (measured each day of analysis), thus allowing fluorescence data to be obtained in Raman units (RU) (Determann *et al.*, 1998; Lawaetz & Stedmon, 2009). Moreover, an EEM of ultrapure water (blank) was subtracted from the sample EEMs measured on the same day. The resulting EEMs were plotted using Matlab® R2013b software (Mathworks, Natick MA, USA). The 'peak-picking' fluorescence data processing protocol was applied in this study since the number of samples was not large enough to perform a mathematical decomposition of EEM into its fluorescent components (parallel factor analysis). The 'peak-picking' method consists of extracting a maximum value of fluorescence intensity observed within a delimited area of the fluorescence spectrum. Each zone delimitations and related chemical compounds from

dissolved organic matter (DOM) have been compiled in Table 2 and illustrated in Figure 15.

3.2.2.2 Results

3D EEM fluorescence spectra. 3D fluorescence spectrometric analyses were performed for SEV WWTP discharge samples with the following PFA concentrations: 0, 8, 10, 12, 20, 300, and 1000 ppm.min. An example of the 3D EEM spectra obtained for two disinfection test campaigns is shown in Figure 16.

An initial approach to qualitatively interpreting 3D fluorescence spectra consists of locating fluorescence maxima with the 'peak-picking' method, as described above. For all spectra shown of SEV WWTP discharge, whether or not exposed to a PFA concentration, a similar fluorescence signature is apparently observed. The highest fluorescence intensities recorded are related to the 'humic substances-like' fluorescent component of DOM, which is known to be more resistant to biodegradation (Parlanti *et al.*, 2000) and located in the excitation-emission wavelength region called the α band (Ex/Em 330–370/420–480 nm). Other areas of interest are also observed, with lower fluorescence intensities: peak α' (Ex/Em 230–260/380–480 nm) associated with 'humic substances-like' fluorescent components mixed with a recent DOM material and peak δ related to the 'protein-tryptophan-like' component of fluorescent DOM.

Analysis of SEV WWTP discharge EEM spectra according to the operationally applicable PFA processing rates (0–20 ppm.min). Since DOM fluorescence quality and quantity indicate very similar fluorescence intensities among the three disinfection testing campaigns carried out (results not shown, relative standard deviation less than 4%), only the average results will be discussed herein. By comparing the average fluorescence intensities (Figure 17a) obtained for both the non-disinfected and disinfected SEV WWTP discharges at various PFA concentrations (operating rates: 0–20 ppm.min), a similar amount of fluorescence intensity has been observed (relative standard deviation: 3% for all peaks). It should be noted though that between the non-disinfected and disinfected SEV WWTP discharges at a 20 ppm.min PFA rate, a slight increase (less than 9%) in the average fluorescence intensity is noticed for all fluorescence peaks (α: 1.73 to 1.85 RU; β: 1.56 to 1.66 RU; α': 1.45 to 1.51 RU; δ: 1.26 to 1.32 RU; γ: 0.75 to 0.82 RU). The quality of SEV WWTP discharge fluorescent DOM (Figure 17b) is mainly composed of a 'humic substances-like' signal (α: 0.29 RU $\text{mgC} \cdot \text{L}^{-1}$; β: 0.26 RU $\text{mgC} \cdot \text{L}^{-1}$; α': 0.24 RU $\text{mgC} \cdot \text{L}^{-1}$), followed by lower protein compound contributions (δ: 0.21 RU $\text{mgC} \cdot \text{L}^{-1}$; γ: 0.12 RU $\text{mgC} \cdot \text{L}^{-1}$). A small decrease (about 15%) in the average DOC-standardized fluorescence intensity is observed for all peaks between non-disinfected and disinfected samples treated at 20 ppm.min of PFA (Figure 17b). This variation is primarily due to an increase in the average measured DOC (DOC: 6.0 to 7.3 $\text{mgC} \cdot \text{L}^{-1}$,

+27%) caused by adding PFA. This phenomenon has also been demonstrated in Part 1.1 of this chapter.

In light of these results, any modification of the fluorescent DOM nature from SEV WWTP discharges was observed for PFA treatment rates between 0 and 20 ppm.min. It should also be noted that more PFA adds non-fluorescent DOC in solution, resulting in a decrease of total fluorescence intensities recorded per gram of carbon in solution. Moreover, it has been shown that this range of PFA treatment rates (0–20 ppm.min) exerts no influence on the total amount of fluorescent DOM observed in SEV WWTP discharge.

Analysis of SEV WWTP discharge EEM spectra according to extreme PFA processing rates (300 and 1000 ppm.min). Disinfection tests of SEV WWTP discharge with PFA concentrations of 300 and 1000 ppm.min were performed to determine the impact of high treatment rates on the DOM fluorescence signature. The fluorescence intensities obtained for two campaigns (Oct 30 and Nov 6, 2018) are shown in Figure 18.

The Oct 30 and Nov 6, 2018 campaigns display a similar fluorescent DOM nature (Figure 18a) mainly correlated with 'humic substances-like' fluorescent compounds (average fluorescence intensity of α: 2.02 RU), followed by the other DOM types (β: 1.69 RU; δ: 1.60 RU; α': 1.48 RU; γ: 1.19 RU). Let us note that unlike previous campaigns carried out (Figure 17), the measured non-disinfected SEV WWTP discharge contains a higher amount of 'protein-tryptophan-like' fluorescent compounds. Disinfection tests performed at 300 ppm.min PFA on SEV WWTP discharge do not significantly influence the average amount of fluorescent DOM observed, as opposed to the non-disinfected sample (relative standard deviation: less than 5% for all peaks). For a treatment rate of 1000 ppm.min PFA, decreases in the mean fluorescence intensity are mostly detected for 'protein-like' fluorescent components (γ: –33%, 1.19 to 0.80 RU; δ: –25%, 1.62 to 1.20 RU), in comparison with the other fluorescent components being monitored (α: –11%, 2.03 to 1.80 RU; β: –5%, 1.69 to 1.60 RU; α': +8%, 1.49 to 1.60 RU). One explanation for this phenomenon could be that the previous studies were carried out with PAA (Peracetic acid). A study by Domínguez Henao *et al.* (2018) demonstrated that proteins are the organic molecules with the greatest impact on the instantaneous demand for PAA due to their protein denaturation action. In addition, the study by Zhang *et al.* (2016) on the action of PAA on extracellular soluble compounds derived from sludge, from a membrane bioreactor fed by wastewater, also revealed a decrease in the fluorescence of 'protein-like' compounds. The oxidation action of PAA would thus result in the degradation of protein-like fluorescent compounds into smaller and potentially non-fluorescent molecules. The results found in our study for the 'protein-like' component in the case of significant PFA additions (i.e., above 1000 ppm.min) seem to be very consistent. It should be noted however that this range of treatment rates (PFA: 300–1000 ppm.min) has only been tested for exploratory purposes and will not be applied under actual operating conditions.

3.3 STUDY OF PFA INSTABILITY AFTER INJECTION

3.3.1 PFA degradation kinetics in WWTP discharge and surface water

3.3.1.1 Experimental description

For starters, long-term degradation kinetics were evaluated by monitoring over time the PFA concentration in a given PFA-doped matrix (SEV discharge water either unfiltered or filtered at 0.45 µm, or Seine River water filtered at 0.45 µm). The study matrix was temperature balanced for at least one night in a temperature-controlled chamber. Several temperatures were studied: 12, 20, and 25°C. One liter of water was then doped with PFA at a concentration between 1.5 and 2 ppm. Regular samples were then extracted every 10 min, and the PFA concentration was determined by means of ABTS, which is an alternative spectrophotometric method adapted from a peracetic acid determination (Pinkernell *et al.*, 1997). The ABTS method allows for high-frequency monitoring of PFA concentrations and thus yields a determination of low PFA concentrations. It is therefore well adapted to studying the decomposition of PFA and its monitoring after wastewater disinfection. Absorbance can be measured at two different wavelengths: 415 nm for colorless working samples, and 732 nm for colored working samples. The limit of quantification equals 0.05 ppm (at 415 nm, 1-cm light pass). The samples were stored in the temperature-controlled chamber until the absorbance measurement had been completed. Kinetic tracking continued for 90 mins.

Complementary experiments were then performed using raw SEV WWTP discharge samples in order to both identify the effect of fecal bacteria on PFA degradation kinetics and focus on the first 10 mins. A PFA dose of 1–1.2 ppm was applied to three distinct samples, and the PFA concentration was measured several times by the ABTS method with contact times ranging from 30 seconds to 10 mins. The experiments were performed on both raw and filtered (0.45 µm) samples.

3.3.1.2 Long-term degradation kinetics in WWTP discharge and surface water

Figure 19 shows the evolution in the concentration of PFA in SEV WWTP wastewater discharge (upstream) and in Seine River water (downstream). In both cases, decomposition kinetics were studied at three temperatures: 12, 20 and 25°C. To preserve sample homogeneity and prevent potential disturbance of absorbance readings due to the presence of TSS, the samples were filtered at 0.45 µm.

All kinetics have been correctly fitted by pseudo-first-order kinetics ($R^2 > 0.97$). The results allowed determining half-lives, in minutes, for both matrices at all three temperatures. These results are summarized in Table 3. For each matrix, the

kinetics established at 20°C were performed in triplicate. The uncertainty was estimated at 10% and applied to the various temperatures studied.

For the two matrices analyzed, decomposition occurs faster as temperature increases. In SEV WWTP wastewater discharge, the half-lives varied from 33 mins (12°C) to 13 mins (25°C), whereas in Seine water the half-lives varied from 87 mins (12°C) to 29 mins (25°C). By way of comparison, Luukkonen *et al.* (2015) had obtained half-lives of 58 mins at 15°C in Finnish wastewater treated by physicochemical settling, biological treatment and tertiary filtration, under pseudo-first order kinetics.

It should be noted that the half-life of PFA in Seine water is less than 1 hour in summer (with a water temperature close to 20°C) and moreover that PFA is mostly decomposed in the WWTP discharge channel since the hydraulic residence time in this channel lies between 10 and 20 mins.

These results confirm the unstable nature of PFA compared to other peracids and particularly PAA since the half-life of PAA varies from 18 mins in primary effluent to 710 mins in tap water (Luukkonen & Pehkonen, 2017).

Let us also point out that the decomposition of PFA in wastewater showed quite significant variability at 20°C (half-life between 17 and 33 mins). This finding could probably be explained by variations in the quality of the water discharged (conductivity, TSS, DOC). Nevertheless, low concentrations of TSS do not seem to exert a major influence on the decomposition of PFA, as corroborated by the same half-lives of filtered and unfiltered samples (29 mins).

This decomposition reaction behavior is rather common and can be modeled by Arrenhius' Law ($\ln k = A + B \times (1/T)$, k = pseudo-first-order constant). The B factor in this model is directly related to the activation energy Ea of the studied reaction ($B = -Ea/R$, R = perfect gas constant), that is, the energy required for this chemical reaction to take place. In this case, the activation energy can be estimated at 57.8 kJ/mol for decomposition in Seine River water and 51.3 kJ/mol for decomposition in WWTP water. These values remain relatively low and are in agreement with the unstable nature of performic acid; they lie within the range of values found in the literature by various authors who have studied performic acid decomposition during the PFA synthesis process: 72.6 kJ/mol (Filippis *et al.*, 2009), and 52 kJ/mol (Santacesaria *et al.*, 2017).

3.3.1.3 Short-term degradation kinetics in WWTP discharge in the presence of fecal bacteria

Figure 20 displays the evolution in PFA concentration measured by the ABTS method in the three raw (non-autoclaved, non-filtered) samples of SEV WWTP discharge. The *E. coli* and intestinal enterococci concentrations in those samples were: 18,400 and 6,870 NPP/100 mL for Experiment 1, 40,600 and

11,200 NPP/100 mL for Experiment 2, and 51,700 and 13,800 NPP/100 mL for Experiment 3. The TSS contents were respectively 2, 10 and 12 mg/L, while the initial PFA concentration was 1–1.2 ppm.

PFA degradation kinetics are comparable in all three samples, with an initial instantaneous PFA consumption of 30–35% and then a slow concentration decrease. The PFA concentration is reduced by 40–50% after 10 mins in the presence of fecal bacteria. By means of extrapolation, it is possible to evaluate a half-life of 19–24 mins, which is highly comparable to the half-lives previously determined on autoclaved samples. This finding indicates that the presence of fecal bacteria does not significantly modify the PFA degradation kinetics in treated wastewater. Based on these results, it can be calculated that the initial PFA concentration is reduced by 58–69% after 20 mins, 73–87% after 30 mins and >90% after 50 mins. This calculation is most interesting since the actual PFA contact time observed at SEV during the industrial-scale trials (Part 2) was between 20 and 50 mins, with an average of 30 mins.

3.3.2 Analysis and fate of PFA degradation byproducts

The decomposition of performic acid was followed by liquid chromatography with both conductive detection (detection of ionized species such as acids) and UV detection (for detection of H_2O_2) of a solution containing about 100 ppm PFA, that is, a concentration 100 times higher than that actually used to generate favorable conditions for detecting potential byproducts. The only compounds detected were formic acid and hydrogen peroxide. These results are consistent with all published studies on the decomposition of performic acid, whereby the only stable products observed are formic acid, hydrogen peroxide and CO_2 (Filippis *et al.*, 2009; Leveneur *et al.*, 2014; Santacesaria *et al.*, 2017; Sun *et al.*, 2011).

During the experimental decomposition of PFA, the formation of hydroxyl radicals was also investigated by adding terephthalic acid (TA) to a PFA solution. TA specifically reacts with hydroxyl radicals to form a fluorescent compound, that is, hydroxyterephthalic acid (HTA) (Barreto *et al.*, 1994). Since no fluorescence signal of HTA has been detected, it can be concluded that the decomposition of PFA does not occur by means of homolytic rupture of the peroxide O-O bond and, consequently, no hydroxyl radicals are formed during the PFA decomposition process.

This result is in agreement with the low reactivity of PFA on DOM and organic micropollutants (see Section 1.2 of this chapter and Chapter 4) since it is well known that hydroxyl radicals react with DOM and numerous organic compounds (Wenk *et al.*, 2011).

Key points

- The increase in dissolved organic carbon in wastewater by PFA injection equals 0.78 ppm C/ppm PFA injected, which confirms the theory.
- 3D fluorescence highlights a negligible impact of PFA on fluorescent organic matter quality and quantity at a conventional PFA dose. A decrease in the 'protein-like' fluorescent organic matter is observed at a very high dose of PFA (1000 ppm.min).
- PFA degradation kinetics in SEV WWTP discharge and Seine River water follow a pseudo-first order with half-lives of 26 $\pm$ 9 min in wastewater and 53 min in Seine water at 20°C, after an instantaneous reduction of 30–35%.
- Temperature has a significant acceleration effect on PFA degradation, while TSS and fecal bacteria do not affect the degradation kinetics.
- The PFA degradation products are both formic acid and H_2O_2, with no other products being detected.