

## ***Section 1***

# Effectiveness of Chemical Disinfection at the Laboratory Scale

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# Chapter 1



## Laboratory scale study of wastewater disinfection by means of PFA and the factors affecting its effectiveness

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### 1.1 INTRODUCTION

The Paris Metropolitan Area intends to authorize recreational bathing in the Seine River during the summer by 2024. The precondition to achieving this objective consists of limiting as much as possible the input of fecal bacteria into the river, as per current bathing regulation targets for *Escherichia coli* (*E. coli*) and intestinal enterococci (*Directive 2006/7/EC, dated 15 February 2006 concerning the management of bathing water quality, repealing Directive 76/160/EEC*,

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## 4 Disinfection of WWTP Discharges using Performic Acid

2006). One necessary (although insufficient) action is to disinfect the wastewater treatment plant (WWTP) discharge upstream of Paris.

In the case of the Paris Metropolitan Area, performic acid (PFA), peracetic acid (PAA), UV irradiation and ozonation seem to be among the disinfection techniques existing for wastewater application, effective options when considering how they respond to fecal bacteria. In addition, the application of chlorination processes has not been considered since the disinfection unit would be implemented to treat wastewater treatment plant (WWTP) effluents discharged into the Seine River.

PFA has recently been tested at both the laboratory scale (Chhetri *et al.*, 2014; Gehr *et al.*, 2009; Karpova *et al.*, 2013; Luukkonen *et al.*, 2015) and industrial scale (Chhetri *et al.*, 2015; Ragazzo *et al.*, 2013, 2017) in order to disinfect treated or partially treated wastewater. This technique would offer several operational advantages, for example, effectiveness at a relatively low dosage, lack of harmful byproducts, an onsite production just before injection and post-injection instability (Karpova *et al.*, 2013; Luukkonen *et al.*, 2015; Ragazzo *et al.*, 2013). In addition, such a technique could be easily activated during summer only (bathing period) and then switched off the rest of the year. Therefore, a multidisciplinary project was conducted covering the Paris Metropolitan Area in order to study the possibility of implementing a PFA disinfection unit at a plant within the SIAAP jurisdiction.

The first objective of this project was to study, at the laboratory scale, the wastewater disinfection by PFA and the factors affecting its effectiveness, and then to validate this choice before carrying out industrial-scale tests. Various experiments were thus performed to: (1) validate the choice of PFA in comparison with PAA; (2) quantify precisely the relationships between  $C \times t$  (concentration  $\times$  time of exposure) and fecal bacteria reduction in the targeted WWTP discharge; (3) assess the effect of water quality, especially particles, on PFA effectiveness; (4) evaluate the feasibility and implications of disinfecting partially treated wastewater by PFA; and (5) obtain information regarding the effect of PFA on other types of pathogens. This first chapter will present all the experiments and results associated with these five points.

## 1.2 TRIAL METHODS USED AT THE LABORATORY SCALE

### 1.2.1 PFA preparation method

PFA is produced at the laboratory scale in accordance with the two-step Kemira preparation protocol described in Luukkonen (2015). The first step consists of catalyzing formic acid by adding 10% by mass of sulfuric acid. This step is performed in an iced batch since the reaction is exothermic. The second step entails producing PFA from the catalyzed formic acid by addition into an iced bath of hydrogen peroxide with a mass ratio of 1/1. A maturation time during mixing is needed given that the reaction is slow and the mass concentrations

of hydrogen peroxide and PFA change until reaching equilibrium. Specific experiments have been conducted to determine an optimal maturation time of around 1 hour. In theory, at the end of preparation, the solution contains 20% hydrogen peroxide and 13.5% PFA. The solution is always controlled by dosing the exact PFA concentration. This method is summarized in [Figure 2](#). In theory, the final solution containing 13.5% of PFA also contains 30.9% of residual formic acid, hence the injection of 1 ppm of PFA leads to injecting 0.79 ppm of C (0.19 from PFA plus 0.60 from formic acid). The PFA solution is then directly stored at  $-18^{\circ}\text{C}$  in darkness for a maximum period of 3 weeks.

### 1.2.1.1 PFA titration method

The reference dosing technique consists of a redox colorimetric titration of hydrogen peroxide in the solution mixed with diluted sulfuric acid by adding potassium permanganate. The equivalency is determined by a persistent pink coloration of the solution. Next, potassium iodide is added, which leads to transforming PFA into a carboxylic acid along with the formation of 1 mole of iodine for each mole of carboxylic acid. Lastly, the iodine is dosed using thiosulfate in the presence of starch, leading to discoloration of the solution upon reaching equivalency. This method is summarized in [Figure 2](#).

### 1.2.1.2 Decay kinetics at different temperatures of PFA produced at the laboratory scale

PFA preparation and titration at the laboratory scale have been tested in order to evaluate: (1) repeatability of the titration technique; (2) repeatability of the preparation protocol; and (3) decay kinetics of PFA at various storage temperatures ( $-18$ , 4 and  $20^{\circ}\text{C}$ ) in darkness.

Regarding repeatability of the titration technique, five titrations of a given PFA solution were performed on the same day. This evaluation was also conducted on different days and with different PFA solutions. The average concentrations obtained for PFA and hydrogen peroxide were respectively:  $11.73 \pm 0.80$  and  $19.79 \pm 0.65\%$ . The variability of this method was therefore very low, with a coefficient of variation equal to 7 and 3%. As regards repeatability of the laboratory scale preparation protocol, five PFA solutions were prepared and dosed using the colorimetric method over five different days. For samples 3, 4 and 5, titration was performed three times. The PFA concentrations obtained were: 12.12% (sample 1), 11.91% (sample 2),  $12.40 \pm 0.98\%$  (sample 3),  $13.03 \pm 0.91\%$  (sample 4), and  $11.24 \pm 0.28\%$  (sample 5). The overall average obtained was thus  $12.18 \pm 0.94\%$ , for a limited variability of just 8% (coefficient of variation), which is comparable to the titration method variability. The laboratory scale PFA preparation protocol is hence reliable and repeatable.

As for decay kinetics, PFA concentration was monitored in one of the preparations stored in darkness at three different temperatures ( $-18$ , 4 and  $22^{\circ}\text{C}$ ).

Figure 3 displays the evolution in PFA concentration vs. time over a period of 150 days.

In the three cases studied, the PFA decay follows a pseudo-first-order kinetics ( $y = A e^{-k x}$ ). The influence of temperature is clear, with an increase in constant  $k$  as temperature increases: 0.004 at  $-18^{\circ}\text{C}$ , 0.041 at  $4^{\circ}\text{C}$ , and 0.16 at  $22^{\circ}\text{C}$ . PFA exhibits special behavior when stored at  $-18^{\circ}\text{C}$ , with a concentration rise during the first 3 days (28%), followed by a pseudo-first-order decay kinetics. The initial PFA concentration is then once again reached after 20–30 days. It can be assumed that PFA formation continues when the solution is kept at a temperature below  $0^{\circ}\text{C}$ . The half-life of PFA is thus 210, 17 and 4.5 days, respectively, at  $-18$ , 4 and  $22^{\circ}\text{C}$ . In more practical terms, if PFA use is considered to remain the same until its concentration reaches 90% of the initial concentration, then a PFA preparation can be stored for a maximum time of 63, 2.5 and 0.5 days, respectively, at  $-18$ , 4 and  $22^{\circ}\text{C}$ . Out of safety concerns, a PFA preparation should be titrated for each use, as was the case for this work.

### 1.2.1.3 Description of an experimental PFA disinfection method at the laboratory scale

Laboratory scale disinfection trials were performed in 2-L batches under strong mixing conditions (200 rpm) in order to guarantee batch uniformity. A Jar-test apparatus, which is normally used for coagulation-flocculation batch tests, was employed herein: 1.8 L of the wastewater sample is first introduced into the batch; then, mixing is started and a given volume of the solution containing the disinfectant, corresponding to the targeted dose, is injected. After the contact time, 20 mg/L of thiosulfate is added to stop the disinfection reaction, mixing is stopped and the samples removed for analysis. For all laboratory scale disinfection trials, a 10-min contact time was applied. This method is summarized in Figure 2.

Most trials were conducted at the Seine Valenton (SEV, Valenton, France) WWTP, with distinct discharge samples being drawn several hours before the trials. SEV is run by SIAAP and treats  $600,000 \text{ m}^3/\text{day}$  of wastewater from the eastern part of the Paris Metropolitan Area. In a normal configuration (dry weather), the treatment processes are pre-treatment (screening, grit and oil removal), followed by a primary settling unit and biological treatment by an extended aeration activated sludge process to achieve a complete treatment of carbon, nitrogen (nitrification and denitrification) and phosphorus. A physicochemical dephosphatation unit treats a portion of the treated water in order to raise the level of phosphorus removal. In a degraded mode of WWTP operations (wet weather or internal bypass due to insufficient treatment capacity), the excess wastewater is conveyed directly to the physicochemical dephosphatation unit for particle and phosphorus removal. WWTP discharge to

the Seine River depends on whether the water has been totally treated or is a mix of totally and partially treated. A complete description of SEV WWTP operations is given in Section 2, Chapter 1.

Various parameters were measured during most of these laboratory scale experiments, i.e. total suspended solids (TSS), dissolved organic carbon (DOC), chemical (COD) and biochemical (BOD) oxygen demands, total Kjeldahl nitrogen (TKN), total phosphorus (TP), and *E. coli* and intestinal enterococci (in MPN/100 mL). These analyses were performed according to the following methods: NF EN 872 for TSS, NF EN 1484 for DOC, ISO 15,705 for COD, NF EN 1899 for BOD, NF EN 25,663 for TKN, NF EN ISO 6878 for TP, NF EN ISO 9308-3 for *E. coli*, and NF EN ISO 7899-1 for intestinal enterococci.

Moreover, preliminary tests were conducted to consider the best analytical method for the quantification of the ions  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$  and  $\text{PO}_4^{3-}$  since the conventional method using cadmium column was not adapted. Indeed, the potential presence of residual PFA concentrations may cause damages to the column. These analyses were performed according to the following methods: NF EN ISO 11732 for  $\text{NH}_4^+$ , NF EN ISO 10304-1 for  $\text{NO}_3^-$  and  $\text{NO}_2^-$  and NF EN ISO 15681-2 for  $\text{PO}_4^{3-}$ . A significant impact from excess thiosulfate on the quantification of COD, BOD and DOC had been observed; these parameters were then analyzed in sub-samples free of thiosulfate.

## 1.3 COMPARISON OF PFA DISINFECTION EFFECTIVENESS WITH OTHER CHEMICALS

### 1.3.1 Description of the experiments performed

For starters, PFA was compared to peracetic acid (CAS 79-21-0) and hypochlorite (CAS 7681-52-9), both of which are commonly used disinfectants. An initial literature survey did lead to identifying PFA and peracetic acid (PAA) as promising disinfection alternatives for wastewater (Chhetri *et al.*, 2014, 2015, 2018; Luukkonen and Pehkonen, 2017; Luukkonen *et al.*, 2015; Ragazzo *et al.*, 2013). These initial experiments were aimed at both comparing their disinfection effectiveness on SEV WWTP discharge and estimating the overall dose required of these compounds to achieve a given fecal bacteria elimination rate. Hypochlorite was adopted as the disinfection reference even though its application in the environment had not been considered.

Peracetic acid (VWR 1.07222.1000, mass concentration of 38–40%) and hypochlorite (Nectra 156031, mass concentration of 10%) were commercial solutions available from VWR, whereas PFA was directly produced at the laboratory scale following the preparation previously described (Figure 1). The applied PFA solution was produced and dosed on the same day as the disinfection experiments in order to precisely determine the volume of PFA to inject.

The three products were tested simultaneously on six distinct SEV WWTP discharge samples, except for PFA at doses of 5, 8 and 10 ppm, which were only tested on the first three samples. The treated wastewater was sampled a few hours before each disinfection trial (Nov 14, Nov 28, Dec 5, Dec 19 and Dec 20, 2017 and Jan 15, 2018). The previously described laboratory scale experimental disinfection method was applied. For each trial, four disinfectant doses were tested simultaneously (2, 5, 8 and 10 ppm) with a contact time of 10 min. The quality of the wastewater samples was evaluated before a disinfection step aimed at respecting the quality standards described in Part 2.1.3. The overall quality of the six SEV WWTP discharge samples was normal, with average concentrations of:  $6.5 \pm 2.8$  mg/L for TSS,  $5.7 \pm 1.0$  mgC/L for DOC,  $21 \pm 4$  mgO<sub>2</sub>/L for COD,  $2.1 \pm 1.4$  mgO<sub>2</sub>/L for BOD<sub>5</sub>,  $1.4 \pm 0.5$  mgN/L for TKN, and  $1.1 \pm 0.8$  mgP/L for TP. Similarly, the *E. coli* and intestinal enterococci concentrations in the samples were close to what is generally encountered in this type of water with median  $\pm$  min-max concentrations of:  $13,288 \pm 1690$ – $123,603$  and  $5887 \pm 1929$ – $23,655$  MPN/100 mL, respectively (Rocher & Azimi, 2016).

### 1.3.1.1 Effectiveness of PFA, PAA and hypochlorite on SEV WWTP discharge

Figure 4 Presents the results of the six disinfection trials performed to compare PFA, PAA and hypochlorite on SEV WWTP discharge with a contact time of 10 mins. Depicted here are the median concentrations of *E. coli* or intestinal enterococci, with the observed minimum and maximum concentrations shown as error bars. These values were calculated from six trials, except for PFA at 5, 8 and 10 ppm (three trials).

These trial results indicate a lower fecal bacteria disinfection effectiveness of PAA compared to PFA at a comparable limited applied dose. At an applied dose of 2 ppm, the residual concentrations of *E. coli* and intestinal enterococci in the disinfected wastewater are in fact equal to  $38 \pm <38$ – $78$  MPN/100 mL (median  $\pm$  min-max) for PFA, and  $2625 \pm 1855$ – $23,695$  and  $3596 \pm 1511$ – $19,701$  MPN/100 mL, respectively, for PAA. This difference in effectiveness at 2 ppm is significant (Mann–Whitney test) for both *E. coli* and intestinal enterococci with *p*-values of 0.004. A higher dose is thus required to achieve a given fecal bacteria elimination rate with PAA compared to PFA. It can also be concluded that PFA disinfection effectiveness is comparable to hypochlorite at the same applied dose even though fecal bacteria concentrations after 10 min of disinfection at 2 ppm are slightly higher for hypochlorite than PFA. As an example, the residual *E. coli* concentrations in the disinfected wastewater are:  $38 \pm <38$ – $78$  MPN/100 mL (median  $\pm$  min-max) for PFA, and  $108 \pm <38$ – $2253$  MPN/100 mL for hypochlorite. The difference in effectiveness at 2 ppm for



these products is insignificant (Mann–Whitney test) for both *E. coli* and intestinal enterococci, with *p*-values of 0.177.

Karpova (2013) observed similar trends in concluding that 0.5 ppm of PFA had the same effectiveness in reducing fecal coliform concentration in biologically-treated wastewater as 1 ppm PAA and 8 ppm Cl<sub>2</sub>. The lower PFA dose requirement compared to other chemicals is commonly acknowledged in the scientific literature (Luukkonen & Pehkonen, 2017). More recently, Ragazzo (2020) reported that for a typical disinfection contact time (20–30 min) at doses set to guarantee the current effluent limit for *E. coli* of 5000 CFU/100 mL, PAA and hypochlorite required Ct values three and four times higher on average, respectively, than PFA.

These preliminary results highlight the consistency of using PFA to disinfect the SEV WWTP discharge since this chemical features high fecal bacteria disinfection effectiveness at relatively low doses, which would in fact limit the quantity of chemical injected into the Seine River, in addition to the advantage of being produced *in situ* due to its instability.

## 1.4 INFLUENCE OF PFA DOSE ON THE EFFECTIVENESS OF FECAL BACTERIA REMOVAL

### 1.4.1 Description of the experiments performed on SEV WWTP discharge

Given the high disinfection effectiveness of PFA with a limited applied dose and time, multiple disinfection trials were performed on SEV WWTP discharge at various doses and a contact time of 10 min in order to study the dose-effectiveness relationships for both *E. coli* and intestinal enterococci. The aim herein was to both determine the required PFA C × t to achieve a given fecal bacteria elimination rate and characterize the variability due to water quality variations.

In all, 24 distinct SEV WWTP discharge samples were collected for PFA disinfection trials, including the six previously presented, between Nov 14, 2017 and Feb 13, 2019. The previously described laboratory scale experimental disinfection method was applied. The SEV WWTP discharge was sampled several hours before each disinfection trial and various PFA doses were applied depending on the sample, resulting in nine values for the 0.2–0.3 ppm interval, 13 values for 0.35–0.50 ppm, nine values for 0.7–0.8 ppm, 16 values for 0.9–1.0 ppm, eight values at 1.2 ppm, 15 values for 1.8–2.0 ppm, and lastly three higher values at 4.5, 7.2 and 8.9 ppm of PFA. The wastewater sample quality was evaluated before a disinfection step aimed at respecting the quality standards described above. The overall quality and variability of the 24 SEV WWTP discharge samples were relatively normal, with average concentrations of:  $8.7 \pm 5.5$  mg/L for TSS,  $5.8 \pm 0.8$  mgC/L for DOC,  $23 \pm 8$  mgO<sub>2</sub>/L

for COD,  $2.0 \pm 1.2$  mgO<sub>2</sub>/L for BOD<sub>5</sub>,  $1.1 \pm 0.7$  mgN/L for TKN, and  $1.2 \pm 0.7$  mgP/L for TP. Similarly, the *E. coli* and intestinal enterococci concentrations in the samples were close to what is normally encountered in this type of water, with median  $\pm$  min-max concentrations of:  $14,290 \pm 1690$ – $678750$  and  $4630 \pm 707$ – $62,969$  MPN/100 mL, respectively (Rocher & Azimi 2016). The variability of water quality originates from differing SEV WWTP operating conditions during the sampling period (internal bypass, dry and wet weather, etc.).

#### 1.4.1.1 Chart of PFA effectiveness for the SEV WWTP discharge

Figure 5 displays the results of the 24 disinfection trials performed with PFA on SEV WWTP discharge with a contact time of 10 min; it depicts the median concentration of *E. coli* or intestinal enterococci, with the minimum and maximum concentrations observed as error bars (upper part of the figure), and the average logarithmic removal of both fecal bacteria, with the standard deviation shown as error bars (lower part of the figure). The quality limits (900 MPN/100 mL for *E. coli* and 330 MPN/100 mL for intestinal enterococci) for respecting European recreational bathing regulations (*Directive 2006/7/EC dated 15 February 2006 concerning the management of bathing water quality, repealing Directive 76/160/EEC 2006*) are listed as indications along with the bacteria limit of quantification (LOQ).

The strong influence of the PFA dose at a contact time of 10 min is clearly observable. The increase in the applied PFA dose leads to an increase in fecal bacteria reduction until doses of between 1.8 and 4.5 ppm ( $C \times t$  of 18–45 ppm·min), at which point the median concentrations of both bacteria reach the limits of quantification for this type of treated wastewater. Moreover, the PFA effectiveness is higher for *E. coli* than for intestinal enterococci, leading to a lower PFA dose requirement for these bacteria. This greater sensitivity of *E. coli* to PFA is particularly observable at low PFA doses, with more pronounced decreases of concentration from one dose to another for *E. coli* and higher logarithmic removal values. For example, the median *E. coli* concentration is lowered from 14,290 MPN/100 mL in the raw water to 179 MPN/100 mL in the disinfected water at 0.35–0.5 ppm PFA, while it is only reduced from 4630 to 1305 MPN/100 mL for intestinal enterococci at this same dose. The logarithmic removals are always higher for *E. coli* than for intestinal enterococci when considering doses below 1.8–2.0 ppm PFA, at which point the limits of quantification start to be reached. Such is particularly the case for a PFA dose of 0.35–0.5 ppm, with logarithmic removals of 0.66–2.85 and 0–1.71 respectively for *E. coli* and intestinal enterococci. Above this dose, the difference in logarithmic removals is due to higher initial concentrations for *E. coli* and similar limits of quantification. In the scientific literature, a comparable effectiveness of

PFA in disinfecting treated wastewater has been mentioned. Karpova (2013) obtained a removal rate of about 1 log for *E. coli* at 4–5 ppm.min of PFA applied to biologically-treated wastewater effluents at the laboratory scale, and 0.5–2.0 log for intestinal enterococci. Similarly, Luukkonen (2015) obtained, at the laboratory scale, a removal of 3.3 log for *E. coli* with an initial concentration of 29,200 CFU/100 mL and 15 ppm.min of PFA, compared to a removal of 2.5 log for intestinal enterococci with an initial concentration of 1840 CFU/100 mL. Next, industrial-scale trials for the disinfection of WWTP discharges with PFA were performed in Venice (Ragazzo *et al.*, 2013), concluding that 23 ppm.min or less of PFA led to *E. coli* and intestinal enterococci removals of respectively 2–4.2 and 0.7–3.2 log, while 60 ppm.min guaranteed removals always remained higher than 3 log. In these trials, the higher sensitivity of *E. coli* to PFA was also observed.

In addition, a strong variability in residual concentration and logarithmic removals was observed for a given applied PFA dose. For example, the residual *E. coli* and intestinal enterococci concentrations varied respectively between <15 and 1541 MPN/100 mL and between 38 and 20,488 MPN/100 mL for a PFA dose of 0.35–0.5 ppm, and between <15 and 419 MPN/100 mL and between <15 and 2720 MPN/100 mL for a dose of 0.9–1.0 ppm. Consequently, the logarithmic removal rate at a given PFA dose is also strongly variable, that is, approximately 1 log removal of variation from one sample to another. This variability is most likely indicative of an impact of the SEV WWTP discharge quality variations on PFA disinfection effectiveness. Among the 24 samples, 12 were in fact collected during nominal SEV WWTP operations (i.e., nominal flow capacity not being exceeded and no internal bypass), as opposed to the other 12, for which the SEV WWTP was experiencing partially degraded operations (i.e., flow capacity exceeded and/or internal bypass). This discrepancy led to variations of: TSS between 2 and 25 mg/L, COD between 6 and 42 mgO<sub>2</sub>/L, DOC between 3.9 and 7.0 mgC/L, TKN between <0.3 and 2.8 mgN/L, NH<sub>4</sub><sup>+</sup> between <0.3 and 1.3 mgN/L, NO<sub>3</sub><sup>-</sup> between 13.1 and 18.9 mgN/L, NO<sub>2</sub><sup>-</sup> between <0.02 and 0.32 mgN/L, and PO<sub>4</sub><sup>3-</sup> between <0.1 and 7.4 mgP/L.

Hence, in the case of SEV WWTP discharge disinfection, a  $C \times t$  of 9–12 ppm.min seems to be a good target since within this range, the concentrations of *E. coli* and intestinal enterococci most of the time lie below the European recreational bathing regulation targets of 900 and 330 MPN/100 mL, respectively. As regards regulating the applied PFA dose in recognition of both the contact time (flow rate) and water quality, a target of 10 ppm.min could be considered for ‘good quality’ water and 20 ppm.min in the event of quality degradation. However, the quality parameters leading to a variability in results should be better understood in order to correctly modulate the PFA dose injection as a function of water quality.

## 1.5 INFLUENCE OF WWTP DISCHARGE QUALITY ON FECAL BACTERIA REMOVAL

### 1.5.1 Normalization of the PFA effectiveness to the SEV WWTP discharge quality

As observed in the previous section, a strong variability in PFA disinfection effectiveness has been observed, along with a variability in the SEV WWTP discharge quality. To identify suspected causes of degraded quality parameters, statistical correlation tests (Spearman,  $\alpha = 0.05$ ) were performed between water quality parameters and the residual bacterial concentration or logarithmic removal at a PFA  $C \times t$  of either 7–9 ppm.min ( $n = 15$ ) or 9–12 ppm.min ( $n = 18$ ). For both cases, no significant correlations ( $p$ -value  $> 0.05$ ) were found between the logarithmic removals of both types of bacteria and TSS, COD, DOC and initial bacterial concentrations. For a PFA  $C \times t$  of 7–9 ppm.min, the residual *E. coli* concentration was statistically correlated with TSS ( $r = 0.773 - p$ -value = 0.001), COD ( $r = 0.542 - p$ -value = 0.039) and the initial *E. coli* concentration ( $r = 0.703 - p$ -value = 0.005), while the sole statistically correlated parameter with the residual intestinal enterococci concentration was COD ( $r = 0.572 - p$ -value = 0.028). For the higher PFA  $C \times t$  of 9–12 ppm.min, the sole statistically significant correlation was found between the residual concentration of *E. coli* and TSS ( $r = 0.637 - p$ -value = 0.006). This finding would indicate that the PFA disinfection effectiveness in reducing *E. coli* and intestinal enterococci contents depends on the initial concentrations of bacteria, TSS and COD of the water.

In considering this conclusion, the results of the 24 disinfection trials were plotted in different ways in [Figure 6](#), which represents the residual concentration of both types of bacteria after 10 min of disinfection vs. the normalized PFA  $C \times t$ . The normalization step was performed by dividing the applied  $C \times t$  by both initial bacterial concentrations, TSS or COD since they are correlated with the residual bacterial concentration after disinfection.

For one thing, [Figure 6](#) highlights that the normalization steps are consistent since no notable differences can be detected between samples from degraded operations and those from a normally operating SEV WWTP. These normalizations incorporate the normal variability of WWTP quality and can thus be used independently of upstream conditions.

From a logical standpoint, the residual bacterial concentration after disinfection is significantly correlated (Spearman,  $\alpha = 0.05$ ) with the  $C \times t$  of PFA normalized to the initial bacterial concentration for both *E. coli* ( $r = -0.604 - p$ -value  $< 0.0001$ ) and intestinal enterococci ( $r = -0.735 - p$ -value  $< 0.0001$ ), in following a decreasing power law. The higher the initial bacterial concentration, the higher the residual concentration after disinfection for a given applied  $C \times t$ . In addition, the variability in the residual concentration of intestinal enterococci is notably higher than that of *E. coli*. Using this normalized chart that takes into account influent variability, the PFA requirement in the SEV WWTP discharge to reach

the quality targets of 900 and 330 MPN/100 mL can be estimated at around 1.5 ppm.min of PFA per logarithmic concentration unit of *E. coli* and around 4 ppm.min of PFA per logarithmic concentration unit of intestinal enterococci.

Since an instantaneous in-line measurement of fecal bacteria is infeasible, it would be worthwhile to use a surrogate to regulate PFA injection. Given that TSS and COD were found to be correlated with the residual bacterial concentrations, both parameters were tested during the normalization step and for both, the residual concentrations were significantly correlated with the normalized  $C \times t$  of PFA applied for *E. coli* ( $r = -0.690 - p\text{-value} < 0.0001$  for TSS and  $r = -0.643 - p\text{-value} < 0.0001$  for COD) as well as intestinal enterococci ( $r = -0.706 - p\text{-value} < 0.0001$  for TSS and  $r = -0.643 - p\text{-value} < 0.0001$  for COD), in following a decreasing power law. According to these normalized charts, a normalized  $C \times t$  of 1 ppm.min of PFA/mg TSS or 0.5 ppm.min of PFA/mgO<sub>2</sub>-COD proves to be sufficient to ensure a reduction in *E. coli* concentration below the quality target of 900 MPN/100 mL. A normalized  $C \times t$  of 2 ppm.min of PFA/mg TSS or 1 ppm.min of PFA/mgO<sub>2</sub>-COD is sufficient to ensure a reduction in *E. coli* concentration below this same quality target of 900 MPN/100 mL. Since TSS can be easily estimated in-line and instantaneously by means of a turbidity probe, and COD by a 3D fluorescence probe (Goffin *et al.*, 2018), both parameters serve as good surrogates to regulate PFA injection, provided that the mathematical correlations for the SEV WWTP discharge between TSS and turbidity or between COD and 3D fluorescence are well established. A more in-depth analysis of PFA performance predictability with respect to wastewater quality parameters is performed at the industrial scale in Part 2 – Chapter 3.

## 1.5.2 Investigation of the role of TSS in the variability of PFA effectiveness

### 1.5.2.1 Description of the specific experiments performed to investigate the role of TSS

The effect of TSS alone is not directly observable by comparing PFA trials performed on different samples since the initial bacterial concentrations increase with TSS concentration in SEV WWTP discharge, as well as with other quality parameters. The TSS content in the 24 disinfection trials conducted previously is indeed significantly correlated with both *E. coli* ( $r = 0.773 - p\text{-value} = 0.001$ ) and intestinal enterococci ( $r = 0.637 - p\text{-value} = 0.006$ ) concentrations. It is thus impossible to directly determine if the correlation between disinfection effectiveness and TSS is due exclusively to the increase in bacterial content or if the TSS themselves have a protection effect against fecal bacteria.

To isolate the effect of TSS, specific laboratory tests have been performed in water samples spiked with different amounts of TSS collected from SEV WWTP discharge samples by means of settling in the laboratory. For each test, the TSS were collected from the same sample of water used for the disinfection tests;

these tests were carried out by spiking raw TSS (Oct 24–31, 2018, Nov 7, 2018 and Jan 30, 2019) or autoclaved TSS (Nov 7, 2019 and Feb 6–13, 2019). It was assumed that spiking autoclaved TSS would increase the TSS content yet without increasing the bacterial content, thus making it possible to isolate the effect of a TSS content modification and determine whether the TSS could protect bacteria from PFA. The tests were performed at a contact time of 10 min and a dose of 1.0 ppm of PFA ( $C \times t$  of 10 ppm.min), except for the trial conducted on Jan 30, 2019, in which a lower dose of 0.5 ppm ( $C \times t$  of 5 ppm.min) was applied in order to exacerbate the trends. The overall quality of the six SEV WWTP discharge samples (before TSS spiking) was normal, with average concentrations of:  $13 \pm 8$  mg/L for TSS,  $6.2 \pm 0.4$  mgC/L for DOC, and  $26 \pm 7$  mgO<sub>2</sub>/L for COD.

### 1.5.2.2 Effectiveness of PFA disinfection at increasing TSS concentration in SEV WWTP discharge

Figure 7 displays the results of these specific tests performed: (a) with raw TSS, and (b) with autoclaved TSS.

The spiking did not yield a major variation in fecal bacteria concentrations for the samples spiked with raw TSS. For these samples, the initial concentrations were quite comparable across the various samples, with a variability of less than a factor of 2 or 3, which is rather low considering the analytical method adopted for bacterial quantification. For example, *E. coli* concentrations for the Oct 24, 2018 samples were 13,800, 17,100, 10,100 and 15,700 MPN/100 mL respectively for TSS concentrations of 2, 7, 9 and 24 mg/L. Similarly, the intestinal enterococci concentrations for these same samples were 3150, 4630, 4520 and 2560 MPN/100 mL. The initial bacterial concentrations can thus be considered comparable in the samples on any given day.

Figure 7a shows two types of behavior for *E. coli*. For the Oct 24, 2018 and Oct 31, 2018 samples, no clear negative influence of TSS concentration can be observed as the residual bacterial concentration does not increase with TSS content in the sample after 10 ppm.min of PFA. For the Nov 7, 2018 and Jan 30, 2019 samples, an increase in residual bacterial concentration is observed above 20–30 mg/L of TSS. This phenomenon seems more pronounced on Jan 30, 2019, most likely because of the lower  $C \times t$  of applied PFA (5 ppm.min). For intestinal enterococci, a negative effect of TSS content in the sample to be disinfected is observed, except for the Oct 24, 2018 sample. An increase in residual bacterial concentration with TSS content in the sample after 10 ppm.min of PFA is observed above 20–30 mg/L for both the Oct 31, 2018 and Jan 30, 2019 samples, and above 12–20 mg/L on Nov 7, 2018.

Regarding the trials performed by spiking autoclaved TSS, the exact same observation can be made for the effect of TSS spiking on the variation in initial bacterial concentrations, which can be considered comparable in the samples for any given day.

The results obtained with autoclaved TSS (Figure 7b) are very consistent with those from raw TSS. Both the autoclaved and raw TSS spiking tests were in fact held on Nov 7, 2018. For this particular day, no negative influence of autoclaved TSS on the residual *E. coli* concentration was observable until a concentration of 23–26 mg/L of TSS, whereas such an influence could be observed as of a concentration of 30 mg/L of TSS with raw TSS. Similarly, the negative effect of autoclaved TSS was observable on the residual concentration of intestinal enterococci from a concentration of 14–15 mg/L of TSS, while observation could only be made from a concentration of 12–20 mg/L of TSS for raw TSS. For the other tests with autoclaved TSS (i.e., Feb 6, 2019 and Feb 13, 2019), no influence of autoclaved TSS was recorded during the Feb 6, 2019 tests for either *E. coli* or intestinal enterococci, yet an increase in the residual *E. coli* concentration was detected on the Feb 13, 2019 tests as of a concentration of 14–15 mg/L of TSS.

Such results tend to confirm that TSS concentration in the wastewater to be disinfected constitutes a key parameter with a potential negative effect on PFA disinfection performance as TSS content increases even if the initial bacterial concentrations are stable. In addition, the sensitivity of intestinal enterococci to TSS increases seems to be higher than that of *E. coli*; however, the exact mechanism explaining this effect has not been clearly identified. Further experiments should thus be conducted in order to confirm this effect and identify if the TSS truly protect bacteria from PFA or if TSS consume a fraction of the PFA, thereby reducing the actual applied dose.

## 1.6 IMPACT OF PFA APPLICATION IN PARTIALLY TREATED WASTEWATER ON PFA DOSE REQUIREMENTS

### 1.6.1 Description of disinfection experiments performed in raw and settled wastewater

Several PFA disinfection trials have been performed in partially treated wastewater; the aim here was to investigate the evolution of the PFA  $C \times t$  required to achieve a given removal effectiveness when PFA is applied to a highly degraded quality of wastewater. Few studies have actually reported on the disinfection effectiveness of PFA applied to settled wastewater (Gehr *et al.*, 2009) or to combined sewer overflow (Chhetri *et al.*, 2014, 2015; McFadden *et al.*, 2017; Tondera *et al.*, 2016), yet this solution is sometimes considered as an option to reduce the river's fecal bacteria inputs.

These experiments were conducted using the same laboratory scale disinfection method as previously described (Figure 1) with distinct raw wastewater and settled wastewater (physicochemical lamellar settling effluent) samples from the Seine Centre (SEC) WWTP. This WWTP treats 240,000 m<sup>3</sup>/day of Parisian wastewater by means of pre-treatment, physicochemical lamellar settling and three-stage

biofiltration that serves to eliminate carbon and nitrogen pollution. This WWTP layout is presented in detail in Rocher *et al.* (2012). The raw wastewater was also diluted with distilled water to create artificial sewer overflow samples. Four dilutions containing respectively 15, 40, 60 and 85% wastewater were applied. It is considered that samples containing 40% raw wastewater simulate the initial flow of a sewer overflow event, while 15% of the samples simulate the typical overflow (Chhetri *et al.*, 2014; Passerat *et al.*, 2011).

PFA disinfection trials were conducted on five different samples for settled wastewater (March 25, 2019, May 2, 6, 9 and 13, 2019), seven for raw wastewater and diluted raw wastewater (Dec 11, 13 and 18, 2018, May 2, 6, 9 and 13, 2019). For each trial, a contact time of 10 min was applied as well as PFA doses of 2, 6 and 10 ppm, resulting in a  $C \times t$  of 20–100 ppm.min. As regards the diluted raw wastewater, three samples (Dec 11, 13 and 18, 2018) corresponded to 60 or 85% wastewater and four samples (May 2, 6, 9 and 13, 2019) corresponded to 15 or 40% wastewater. The overall quality of the seven raw wastewater samples (before dilution) was usual, with average concentrations of:  $190 \pm 68$  mg/L for TSS,  $24.9 \pm 14.1$  mgC/L for DOC,  $356 \pm 101$  mgO<sub>2</sub>/L for COD,  $121 \pm 63$  mgO<sub>2</sub>/L for BOD<sub>5</sub>,  $38.7 \pm 6.1$  mgN/L for TKN, and  $3.8 \pm 0.8$  mgP/L for TP. The overall quality of the five settled SEC wastewater samples was normal, with average concentrations of:  $35 \pm 10$  mg/L for TSS,  $31.3 \pm 17.3$  mgC/L for DOC,  $161 \pm 49$  mgO<sub>2</sub>/L for COD,  $48.7 \pm 12.2$  mgO<sub>2</sub>/L for BOD<sub>5</sub>,  $37.5 \pm 7.5$  mgN/L for TKN, and  $1.5 \pm 0.8$  mgP/L for TP.

### 1.6.2 PFA effectiveness in removing fecal bacteria in raw and settled wastewater

Figure 8 displays the results of the PFA disinfection trials performed on raw, settled and diluted raw wastewater from the SEC WWTP, with the left side results comparing raw and settled wastewater and the right-side results from diluted raw wastewater. In both cases, the median concentrations of bacteria have been plotted on top of the figure with min and max values as error bars, while the average logarithmic removals with standard deviations as error bars are plotted at the bottom.

Regarding the case of partially treated wastewater, the initial concentrations of *E. coli* and intestinal enterococci are, logically, higher than in the SEV WWTP discharge (2–3 log for *E. coli* and 1–2 log for intestinal enterococci).

For raw wastewater, a  $C \times t$  of 100 ppm.min is insufficient to reduce the concentrations of both bacteria below the bathing quality limits of 330 and 900 MPN/100 mL. The increase of  $C \times t$  in this type of water allows increasing the logarithmic removal from  $0.96 \pm 0.78$  at 20 ppm.min to  $3.23 \pm 0.67$  at 60 ppm.min and to  $3.33 \pm 0.81$  at 100 ppm.min for *E. coli*, and from  $0.68 \pm 0.48$  at 20 ppm.min to  $3.10 \pm 0.89$  at 60 ppm.min and to  $3.35 \pm 0.85$  at 100 ppm.min for intestinal enterococci.



For settled wastewater, a  $C \times t$  of 100 ppm.min is insufficient to reduce the concentrations of both bacteria below the bathing quality limits of 330 and 900 MPN/100 mL. The increase of  $C \times t$  in this type of water serves to increase the logarithmic removal from  $2.41 \pm 0.56$  at 20 ppm.min to  $3.10 \pm 0.32$  at 60 ppm.min and to  $3.09 \pm 0.31$  at 100 ppm.min for *E. coli*, and from  $0.86 \pm 0.73$  at 20 ppm.min to  $3.46 \pm 0.28$  at 60 ppm.min and to  $3.46 \pm 0.28$  at 100 ppm.min for intestinal enterococci. The logarithmic removals are thus comparable (60 and 100 ppm.min) or slightly higher (20 ppm.min) in settled wastewater compared to raw wastewater, however the residual bacterial concentrations are lower thanks to lower initial concentrations. A  $C \times t$  above 100 ppm.min is thus required to efficiently disinfect raw or settled wastewater, in comparison with a  $C \times t$  of 10–20 ppm.min for the SEV WWTP discharge.

To the best of the author's knowledge, no results are available in the literature on PFA effectiveness on raw wastewater. In contrast, similar experiments were performed by Gehr *et al.* (2009) on physicochemical treatment effluent (10–100 mg/L of TSS and 37–238 mgO<sub>2</sub>/L of COD) at both the batch and pilot scales. At the batch scale for a contact time of 10 min, they obtained fecal coliform removals of approximately 3 log at 5 ppm.min of PFA, slightly above 3 log at 20 ppm.min and up to 6 log at 40 ppm.min. At the pilot scale for a contact time of 45 min, average fecal coliform removals of 0.5 log at 45–90 ppm.min, 2.5 log at 90–135 ppm.min, 3 log at 135–180 ppm.min and up to 5.5 log at 225–270 ppm.min were recorded with PFA. For intestinal enterococci, removals of 4–6 log were observed for a contact time of 45 min at 225–270 ppm.min of PFA.

As regards the case of artificial combined sewer overflows (CSOs), the initial concentrations of both *E. coli* and intestinal enterococci decreased with the dilution of raw wastewater, with a maximum difference of around 1 log between the concentrations in 100 and 15% raw wastewater.

For *E. coli*, the dilution rate increase led to a decrease in residual concentration after 20 ppm.min of PFA, with median concentrations of: 3,332,461, 1,792,500, 18,863, 2695 and 2598 MPN/100 mL respectively for 100, 85, 60, 40 and 15% raw wastewater. However, at 60 and 100 ppm.min, the residual bacterial concentrations were similar among the various dilution rates, that is, around 1000–3000 MPN/100 mL. These values were correlated with an increase in the logarithmic removal rate between 100 and 85% raw wastewater and more heavily diluted wastewater for a  $C \times t$  of 20 ppm.min, which rose from around 1 log to just below 3 log, in contrast with 60 and 100 ppm.min, at which logarithmic removal remained stable between 3 and 4.5 log.

For intestinal enterococci, the decrease in residual concentration with an increasing dilution rate was observable for all three  $C \times t$ . For example, the median concentrations after 100 ppm.min of PFA were 1495, 391, 107, 54 and 37 MPN/100 mL respectively for 100, 85, 60, 40 and 15% raw wastewater. As was the case for *E. coli*, the logarithmic removal of intestinal enterococci

increased with a dilution rate at 20 ppm.min of PFA, from below 1–3 log, but remained stable at 60 and 100 ppm.min between 3 and 4 log.

Consequently, for both bacteria and except for a low  $C \times t$  of 20 ppm.min, the logarithmic removal rate was relatively stable for the various dilution rates, and improved residual bacterial concentrations resulted from the initial decrease in concentration due to dilution.

Several papers have studied the disinfection of CSO by PFA (Chhetri *et al.*, 2014, 2015; McFadden *et al.*, 2017; Tondera *et al.*, 2016). In particular, Chhetri *et al.* (2014) performed laboratory scale disinfection tests on diluted raw wastewater with 5, 15 and 40% raw wastewater; they obtained logarithmic removals comparable to those in diluted raw SEC wastewater. The removals of intestinal enterococci were 1 and 3.5 log, respectively, for 40 and 80 ppm.min in 40% raw wastewater, which corresponds to the first flush. For 5% raw wastewater, corresponding to the maximum of an overflow event, removals were higher, i.e. respectively 4 and 3.5 log for *E. coli* and intestinal enterococci at 20 ppm.min of PFA or up to 5 log at 80 ppm.min. Tondera *et al.* (2016) studied the application of PFA at an industrial scale on CSO at a significantly higher  $C \times t$  compared to this study, with doses between 12 and 24 ppm and a maximum contact time of 30 min. They obtained bacteria reductions of 100–1000 CFU/100 mL for both *E. coli* (initial concentration:  $10^6$  CFU/100 mL) and intestinal enterococci (initial concentration:  $10^6$  CFU/100 mL). The associated logarithmic removals were:  $3.1 \pm 1.7$  log for *E. coli*, and  $2.6 \pm 1.5$  log for intestinal enterococci. Comparable removals were reported by Chhetri *et al.* (2015) at the industrial scale with comparable initial concentrations, lower PFA doses between 4 and 8 ppm and a contact time of 20 min ( $C \times t$  between 80 and 160 ppm.min). These authors also recommended regulating the PFA dose injection based on water quality and then treating the first 60 min of an event with a higher PFA dose than the rest of the overflow.

In terms of the PFA  $C \times t$  required to achieve a given disinfection effectiveness, a  $C \times t$  of 100 ppm.min was insufficient to reduce the median concentration of *E. coli* below the bathing quality limit of 900 MPN/100 mL for any type of diluted raw wastewater. However, residual concentrations after 100 ppm.min of PFA varied between 38 and 3050 MPN/100 mL for 15% raw wastewater in two of the four tests where concentrations were below 900 MPN/100 mL after disinfection. In contrast, a  $C \times t$  between 60 and 100 ppm.min was sufficient to reduce the median concentration of intestinal enterococci below the bathing quality limit of 330 MPN/100 mL for diluted wastewater containing 60% or less raw wastewater. For a 15% raw wastewater level, a  $C \times t$  of 20 ppm.min seems to allow reducing the median intestinal enterococci concentration below 330 MPN/100 mL. It can thus be assumed that a PFA  $C \times t$  of approximately 100 ppm.min would be required to disinfect Parisian CSO, hence 5–10 times higher than for SEV WWTP discharge. This finding means that in the case of in-line injection of PFA with very limited contact times, that is, between 1 and 5 min,

and in considering the hypothesis that concentration and time have the same effect on disinfection effectiveness, the required PFA dose would be 20–100 ppm, which represents a significant input of carbon into the river, theoretically 15.8–79 mgC/L respectively (1 ppm of PFA injected injects 0.79 ppm of C). To limit this carbon input to less than 1–2 mgC/L, as in the case of the SEV WWTP discharge, dedicated high-volume contact tanks ensuring a contact time of 50–100 min would need to be built.

Along with a notably higher required PFA  $C \times t$ , thus requiring long contact times or the discharge of large quantities of carbon into the river, the disinfection of non-biologically treated wastewater with PFA could result in a greater risk of byproduct formation since raw or settled wastewater and CSO possess a higher quantity of organic matter and particles. Chapters 3 and 4 of Part 1 provide more information on this topic.

## 1.7 PFA EFFECTIVENESS IN REMOVING OTHER MICROORGANISMS

In addition to *E. coli* and intestinal enterococci, F-specific bacteriophages and SSR (sulfite reducing bacteria) spore analyses were performed for five PFA disinfection tests (Sept 11–18, 2018, Jan 30, 2019 and Feb 6–12, 2019) to generate information on PFA effectiveness regarding other pathogens. As a reminder, these tests were conducted with PFA doses of between 0.8 and 2 ppm and a 10-min contact time, in using SEV WWTP discharge samples. Both parameters were analyzed according to Standards ISO 10705-3 and NF EN ISO 10705-1 for F-specific bacteriophages, and NF EN 26461-2 for SSR spores. The concentrations before and after disinfection, as well as logarithmic removals, are listed in [Table 1](#).

SSR spores were detected in the seven SEV WWTP discharge samples, with a median concentration of 5000 CFU/100 mL, while F-specific bacteriophages were only detected in two of the five samples considered, with a concentration close to the LOQ of 30 CFU/100 mL. The SEV WWTP operations (whether normal or degraded) had no impact on the initial concentrations of these pathogens. These concentrations were in the range of the data measured on SEV WWTP discharge by the SIAAP Authority over the period 2014–2017, with median  $\pm$  min-max values of  $860 \pm 4$ –2700 UFC/100 mL for SSR spores ( $n = 27$  values) and  $150 \pm 14$ –7800 UFC/100 mL for F-specific bacteriophages ( $n = 27$  values), even though they lie in the top of the range for SSR spores and the bottom of the range for F-specific bacteriophages.

PFA at a limited  $C \times t$  of 8–20 ppm.min seems to exert no or only a very limited effect on SSR spores for five of the seven tests, with logarithmic removals lying below 0.5, but better removals were achieved under these same conditions for the other two tests, that is, between 1 and 4 log. The effect of PFA on F-specific bacteriophages could not be determined in light of the very small initial concentrations close to the LOQ. The effect of PFA on pathogens other than

*E. coli* and intestinal enterococci in the SEV WWTP discharge is thus uncertain, and complementary experiments should be performed.

In the literature, information on PFA is limited although several papers deal with the effectiveness of peracids on pathogens in wastewater (Gehr *et al.*, 2009; Karpova *et al.*, 2013; Luukkonen & Pehkonen, 2017; Mora *et al.*, 2018; Tondera *et al.*, 2016). In particular, Luukkonen and Pehkonen (2017) conducted a critical review of PFA disinfection.

As regards bacteria, most authors have indicated the good effectiveness of PFA. For example, Tondera *et al.* (2016) reported removals of fecal coliforms *Aeromonas* spp. and *C. perfringens* of 1.8 to 3.1 log in CSO with a dose of 12–24 ppm of PFA and a contact time of 30 min ( $C \times t$  of 360–720 ppm.min). The good effectiveness of PFA on fecal coliforms has also been reported in most publications (Gehr *et al.*, 2009; Karpova *et al.*, 2013; Luukkonen & Pehkonen, 2017; Ragazzo *et al.*, 2013). In addition, Karpova *et al.* (2013) noted a logarithmic removal of *Salmonella* spp. equal to 3 log for a  $C \times t$  of 20 ppm.min.

Regarding spores and cysts, e.g. *Clostridia* spp. or *Giardia* spp., they have been identified as more recalcitrant to PFA (Karpova *et al.*, 2013) or PAA (Luukkonen & Pehkonen, 2017). A PFA  $C \times t$  of 10 ppm.min applied in a WWTP discharge does indeed lead to a limited removal of below 1 log for *Clostridia* spp. and *Giardia* spp. (Karpova *et al.*, 2013). In CSO, Tondera *et al.* (2016) reported no significant removal of *Giardia lamblia* despite a high  $C \times t$  of 360–720 ppm.min. Gehr *et al.* (2009) found *Clostridia* removals of 1–2 log at PFA  $C \times t$  of 450–540 ppm.min in physico-chemically treated wastewater effluent. Overall, the disinfection effectiveness of PFA is higher than PAA with respect to *Clostridia* (Mora *et al.*, 2018).

As for bacteriophages, MS2 and DNA bacteriophages have been reported as more sensitive to PFA than intestinal enterococci and *E. coli* (Karpova *et al.*, 2013). In fact, these authors reported MS2 and DNA bacteriophage removals of 1 log for a limited PFA  $C \times t$  of 17–22 ppm.min. Gehr *et al.* (2009) reported F-specific bacteriophage removals of 1–2 log at a PFA  $C \times t$  of 450–540 ppm.min in a physico-chemically treated wastewater effluent. Logarithmic removals of somatic coliphages equal to  $2.7 \pm 1.6$  in CSO were observed by Tondera *et al.* (2016) with a very high PFA  $C \times t$  of 360–720 ppm.min. In a WWTP discharge, Karpova *et al.* (2013) observed higher removals of somatic coliphages of 4 log for a significantly lower  $C \times t$  of 10 ppm.min.

Regarding human viruses like adenovirus, polyomavirus, norovirus, rotavirus and enterovirus, no results are available for PFA, but PAA has been reported as inefficient. Tondera *et al.* (2016) concluded that viruses are not inactivated by PAA, even at a high  $C \times t$  of 120–240 ppm.min. However, Luukkonen and Pehkonen (2017) indicated that the virus inactivation mechanism by PAA may occur by damaging the virus surface, for example, the protein coat of the sites needed to infect the host cells. Such information has not been reported for PFA.

These elements therefore suggest that in the case of viruses, spores, cysts or bacteriophages being present in WWTP discharge, a higher PFA  $C \times t$  would be required to remove them in comparison with bacteria such as *E. coli* or intestinal enterococci.

### Key Points

- In the SEV WWTP discharge, the required PFA  $C \times t$  to achieve a given disinfection rate is 2–4 times less than PAA, thus leading to a significantly lower potential carbon input into the river.
- Laboratory scale PFA disinfection trials performed with the SEV WWTP discharge indicate that a PFA  $C \times t$  of 10–20 ppm.min is sufficient to ensure a reduction in *E. coli* and intestinal enterococci concentrations to below 900 and 330 MPN/100 mL, respectively. Intestinal enterococci are more resistant to PFA in wastewater than *E. coli*.
- The residual concentrations of *E. coli* and intestinal enterococci after a given  $C \times t$  of PFA disinfection are correlated with not only the initial bacterial concentrations, but also TSS and COD, which serve as good surrogates to regulate the PFA dose injection.
- TSS content has an impact on the PFA disinfection effectiveness by means of both an increase in the initial bacterial concentration and an intrinsic effect above 20 mg/L of TSS.
- PFA is efficient in removing fecal bacteria from Parisian combined sewer overflows or partially treated wastewater, yet the required  $C \times t$  is at or above 100 ppm.min. This finding would lead to applying a high PFA dosage, which then implies high carbon inputs into the river or the necessity of long contact times, in addition to higher risks in terms of organic matter evolution and byproduct formation.
- Limited information is available regarding the effect of PFA on other pathogens, but the scarce literature available and the results obtained in the SEV WWTP discharge indicate a limited effect at a  $C \times t$  of 10–20 ppm.min on spores, cysts, bacteriophages and human viruses. This issue should however be investigated more thoroughly.