

Section 4

Feedback from other Municipalities on the use of Chemical Disinfection with PFA

Chapter 1

Case of Biarritz (France)



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1.1 INTRODUCTION

The tightening of the bacteriological quality thresholds for bathing water, following the revision of the European Directive (DCE 2006/7/EC), raises an issue for cities

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or urban areas discharging their treated wastewater into or near bathing areas. The Urban Waste Water Treatment Directive (91/271/EEC) has imposed the implementation of a secondary treatment before discharge, but this is generally insufficient to achieve the required level of quality for bathing. The implementation of a disinfection process is then required.

There are several options available for disinfecting wastewater treatment plant (WWTP) effluents at the industrial scale: ultraviolet (UV) irradiation, chlorination, ozonation, and injection of organic peracids. UV has proven its effectiveness, despite its sensitivity to the amount of suspended solids in water. Bacterial regrowth, with the capability of damaged bacteria to adapt and repair DNA, has also been reported in the context of this technology. Chlorination is a known standard method to disinfect effluent, in particular for potable water production. However, due to the potential formation of toxic disinfection byproducts (DBP), like trihalomethanes or haloacetic acids, its use is not recommended for the disinfection of wastewater, which is rich in organic matter. Ozonation forms active species capable of disinfecting wastewater efficiently; however, bacterial regrowth and formation of DBP are also potential issues with this process.

In recent years, the use of organic peracids (peracetic acid or performic acid) has been developed for the disinfection of wastewater. Kemira (Helsinki, Finland) sells the KemConnect™, which proposes the on-site production and use of a performic acid solution (DEX solution). Compared to ozone and UV, organic peracids have lower operating and capital costs; they are also less sensitive to effluent quality changes, for example TSS and organic load.

In 2014, the city of Biarritz decided to upgrade its WWTP (Marbella) with the KemConnect™ process to disinfect the treated wastewater being discharged into the Atlantic Ocean (Bay of Biscay). Consequently, the effectiveness of this process was studied. The City of Biarritz's sanitation system, mainly unitary, collects wastewater and rainwater that are then treated at the Marbella WWTP. The treated wastewater is discharged into the ocean 800 m from the Bay of Biscay beaches via a sewer (called Milady and Marbella).

The city is coping with the potential deterioration of water quality for bathing on the bay's southern beaches, caused by a return of the outfall plume under certain oceanographic conditions and weather. This deterioration may lead to temporary closures of bathing on those beaches.

The implementation of a tertiary disinfection process in the Marbella WWTP was therefore decided in order to guarantee better bacteriological water quality at the discharge point and thus to minimize the impact on beaches during episodes of plume return.

In this chapter, the results from 18 months of full-scale operation of KemConnect™ at Marbella WWTP will be presented. The impact of KemConnect™ on the WWTP effluent quality as well as on the environment will be evaluated.

1.2 MATERIALS AND METHODS

1.2.1 Presentation of the Marbella WWTP

The Marbella WWTP has been in operation since January 1, 2004 and has a nominal capacity of 92,000 population equivalents (5500 kg BOD₅/day). Due to the specificity of the sanitation network, which is mainly unitary, the WWTP comprises a treatment line for dry weather (wastewater flow reaching the station at up to 1300 m³/h) coupled to a treatment line for rainy weather (flow arriving at the station above 1300 m³/h and up to 3000 m³/h).

Beyond the rain occurring at a monthly frequency, that is when storm basins are full, the fraction of flow higher than 3000 m³/h is discharged into the environment after a single fine screening.

Briefly, the raw effluent is first pretreated (screening, grease and sand removal) before treatment with a physicochemical lamellar decanter (Densadeg type). The dry weather system (flow rate up to 1300 m³/h) includes an additional biological treatment by biofiltration (Biofor type biofilters), which performs nitrification and denitrification.

The treated effluents pass through a treated water storage tank and then a counting channel to be finally discharged into the ocean via an 800-meter long outfall (DN 1600) located between the Milady and Marbella beaches. Since 2014, a disinfection unit (KemConnect™) provided by Kemira offers tertiary disinfection. Performic acid (PFA) is produced *in situ* by mixing formic acid and hydrogen peroxide in the presence of a catalyst. This mixture (commercially called DEX® and containing around 12% PFA (w/w%)) is then injected into the WWTP effluent at a dose ranging from 0.8 to 1.0 ppm.

1.2.2 Sampling points and bacteria removal determination

Fecal bacteria (*E. coli* and *Faecalis enterococci*) removals were evaluated using single samples collected at two distinct points in the network. The first point lies upstream of the PFA injection point; this point allows for an estimation of the fecal bacteria load at the station outlet. The second sampling point is located downstream of the PFA injection point and constitutes the last possible sampling point before effluent discharge into the drop well and the outfall.

The effluent/PFA contact time from the injection point to the downstream sampling point was measured by means of colorimetry and estimated at 3 min, while the total contact time was estimated at 18 min until the end of the pipe and discharge into the ocean.

The upstream samples were collected in a single-use sterile plastic bottle (500 mL), and the downstream samples ($t + 3$ min, $t + 18$ min) were collected either in sterile disposable plastic bottles containing excess thiosulfate (20 mg/L) (for $t + 3$ min) or in single-use sterile plastic bottles; the reaction stopped after 15 min, with an excess of thiosulfate.

Determination of *E. coli* and *Faecalis enterococci* was performed according to standard methods (NF EN ISO 9308-3 for *E. coli*, and NF EN ISO 7899-1 for *E. faecalis*).

1.2.3 Evaluation of the environmental impact of disinfected effluent

1.2.3.1 Ecological inventory at the outfall of the WWTP discharge pipe

The objective here was to perform a qualitative and quantitative assessment of the species present at the outfall. This assessment took seasonal variations into account and was conducted over an entire season (late winter, late spring and end of summer). The observations and census protocol were carried out by two divers simultaneously and optimized in order to limit bias (size and positioning of the quadrats).

1.2.3.2 Monitoring of a bio-indicator: common mold

The biomonitoring step focused on *Mytilus edulis* (common mussel), which is a bio-indicator widely used in biomonitoring; hence, extensive data are available in the literature (Bachelot, 2012; Gosling, 2003; Kerambrun *et al.*, 2012; Swiacka *et al.*, 2019).

For starters, the general condition of mussels has been evaluated using conventional morphological type descriptors based on metric and weight parameters as well as a physiological state index. To describe and compare the morphology of individuals with regard to sites and sampling dates, seven conventional biometric indices have been used (Figure 48): Length (L), Height (H), Width (W), Thickness (T), Elongation index (H/L), Compactness index (W/L), Convexity index (W/H), and Thickness index (T/L). In addition, a physiological state index was included: the Walne & Mann condition index, denoted 'IC' (Walne & Mann, 1975). This index provides information on the individual's condition (filling rate indicator) and moreover makes it possible to identify growth and reproduction anomalies; it is derived by dividing the dry mass of meat by the dry mass of shell. The higher this index value, the better the overall condition. The index varies greatly during the breeding season depending on the state of gonad development (Seed & Suchanek, 1992). Since samples are taken during the breeding period, the condition of the gonads is also observed for purposes of interpreting the results.

This approach was then completed by genetic analysis. The objective was to determine whether the individual *Mytilus edulis* present on the outfall, and continuously exposed to the PFA disinfected discharge, overexpress the genes involved in the resistance to various stresses (oxidative stress, xenobiotics, energy requirements, etc.). Twelve genes of interest were targeted for the genetic study from the sequences available in the database for *Mytilus edulis*. Individuals living

on the outfall were sampled during dives conducted during the outfall ecological study (February, June and September 2015). The individuals at a reference site were collected from the Marbella dike on the days of the dives. The studied genes can be sorted into five categories, four of which are stress-response genes. The studied genes are all involved in the response to: oxidative stress (sod Cu/Zn, sod Mn, cat), mitochondrial metabolism (cox1), DNA repair mechanisms (rad51), and apoptosis (cas8, bax, bd2). The reference genes, whose expressions are constant in all cells, were studied to normalize the amount of RNA between samples. The ribosomal protein gene L7 (rpl7) is involved in protein synthesis, while the second reference gene used was the elongation factor (ef1).

1.3 EFFECTIVENESS OF FECAL BACTERIA DISINFECTION

Figure 49 displays the boxplots of the logarithmic removals obtained during the trial period until early June 2017 for both types of fecal bacteria. This removal is expressed in logarithmic units (Removal = $\log N_t/N_0$, where N_t = count after treatment time t and N_0 = count before treatment).

Several important observations can be drawn based on Figure 50, namely:

- For *E. coli*, with a contact time of 18 min, the average removal equals 3.3 u. log.
- For Enterococci, under these same conditions, the removal is about 1 u.log less than for *E. coli*, with an average value of 2.2 u.log. This difference is probably due to the alteration in membrane structure between the two types of bacteria, as the cell wall of Enterococci (Gram negative bacteria) is much thicker than that of *E. coli* (Gram positive).
- Significant variability exists in the removal rates for both *E. coli* and Enterococci, as demonstrated in other studies (Ragazzo *et al.*, 2013). This variability is related not only to the load of microorganisms (which can vary by a factor of 1000 from one sample to another), but also to the TSS content of the outlet water, with lower removals often being observed at high TSS concentration values. However, no simple relationship exists between fecal bacteria removal and TSS content.

In order to rationalize these experimental results, a statistical study was conducted to better define the turbidity thresholds that impact PFA effectiveness. The most suitable statistical model to account for the influence of various parameters (turbidity, TSS, temperature, conductivity, chemical oxygen demand) on a target variable (in this case the value of the bacteriological quality of water) is the conditional tree. This tool allows to show:

- which parameter exerts the primary influence on the target variable;
- what parameter value triggers a noticeable threshold effect.

Turbidity data and bacteria removal results were therefore compiled and analyzed statistically according to this methodology (using the R software *rattle* package, Williams, 2011); Figure 50 shows the conditional tree obtained with the bacteriological analysis value for the *E. coli* organism after 18 min of treatment with PFA. For this analysis, three target values were chosen, each corresponding to a 'bathing water' threshold: 0–500, 500–1000, >1000 (MPN/100 mL).

This conditional tree can be interpreted as follows: the most impactful parameter is turbidity, and the threshold value is 15.7 NTU, corresponding to total suspended solids of around 20 mg/L. Above this value, the proportion of analysis higher than 1000 MPN/100 mL becomes significant (about 50% of the total 14 analyses above 1000). The second parameter with a significant impact appears to be conductivity: for conductivities above 3200 $\mu\text{S}/\text{cm}$, the proportion of analyses lower than 500 MPN/100 mL is only 60%. A separation of dry weather/rainfall data does not significantly modify the analysis of the results.

All results converge to indicate that PFA effectiveness is high for turbidity below 16 NTU at a dose of 1.2 ppm ($C \times t$ of 21.6 ppm.h). Above this turbidity value, it is proposed to increase the treatment dose to 2 ppm ($C \times t$ of 36 ppm.h) and possibly to 4 ppm ($C \times t$ of 72 ppm.h) in case of extreme turbidity values.

1.4 ENVIRONMENTAL IMPACT OF THE DISINFECTED EFFLUENT

1.4.1 Ecological inventory at the outfall of the WWTP discharge pipe

The impact of WWTP discharges on benthic communities in hard substrates has been poorly documented. Several works do exist (Andral *et al.*, 2011; Cabral-Oliveira *et al.*, 2014; Terlizzi *et al.*, 2002), but the conditions are not necessarily comparable to those at the Marbella outfall. Therefore, a census of species present at the outfall has been carried out. The spatial distribution of species at the outfall (Figure 51) and its temporal evolution were monitored in 2015 and 2016, after the start of the PFA disinfection campaign in 2014. The objective of this monitoring mission was to determine whether or not ecological diversity was changing over time as a result of PFA use.

For both years monitored, the average recovery percentages show that the majority of species are *Actinothoe sphyrodeta* (47%), *bryozoans* (16%) and *Chartella papyracea* (12%).

A statistical comparison was performed in order to highlight a possible spatial distribution of colonization between the north-facing part of the outfall and the south-facing part. The result of the Wilcoxon test conducted to compare colonization between the north and south faces indicates insignificant differences (p -value = 0.285), which means that colonization and communities do not differ

between the two areas. Consequently, the two colonization faces can be treated together without introducing bias into the analysis. The spatial distribution of benthic fauna reveals homogeneous colonization over the entire structure. In conclusion, the quadrats carried out in 2015 and 2016 do not display an effect of discards on the distribution of taxa of fixed fauna. Within these two years, a similarity is found between the dominant taxa, but with differences in average representation, particularly for *Actinothoe sphyrodeta*, *Hydrozoa* and *Sabellaria alveolata*. The presence of species considered opportunistic or, in contrast, highly sensitive to changes in environmental conditions, was not been observed during either year.

It can be concluded that the Marbella WWTP outfall is an artificial habitat where a particular biodiversity has been concentrated. This biodiversity is characteristic of hard substrates, tolerant of strong hydrodynamics, regular sedimentation and desalination (de Casamajor, 2004). In fact, the tertiary treatment does not seem to have a negative impact on the site's biodiversity.

1.4.2 Monitoring of a bio-indicator: common mold

The performance of the biological functions of bivalves is known to be strongly influenced by environmental conditions. As a result, their use as sentinel organisms and pollution controls is common (Gosling, 2003). Their mode of feeding by filtration leads to the concentration of various types of pollutants (chemical, bacteriological) and/or viruses. Thus, they are sensitive to the different stresses caused by pollution, and their growth, reproduction and longevity can be directly affected (Gosling, 2003). Among the organisms frequently used for coastal environmental biomonitoring, mussels are preferred because, as 'bioaccumulators' (i.e., capable of accumulating contaminants at levels higher than those of the environment), they allow us to study the levels and trends of chemical contamination in the aquatic environment. Accumulation performance varies with age and stage in the organism's reproductive cycle (Bachelot, 2012). Studying the biological response of organisms to pollutants combines multiple indicators, namely: physiological, biochemical, molecular and/or cellular parameters that are altered by the action of contaminants (Kerambrun *et al.*, 2012). In studies dealing with the biological effects of urban discharges in the sea, implementation strategies are generally of three types:

- (1) mussel 'caging', which consists of exposing the mussels close to the outfall for a given period of time by transplanting them into cages with a control site,
- (2) controlled environmental experiments in mesocosms,
- (3) *in situ* sampling (De los Ríos *et al.*, 2012; Turja *et al.*, 2015).

This latter strategy has been selected for the present study. Caging tests would have been unsuccessful due to extremely unfavorable hydrodynamic conditions at the discharge point (strong swell). Moreover, mesocosm tests would require the presence of certain equipment close to the PFA production unit, which was not possible in this study.

1.4.2.1 Morphological parameters

First of all, the general condition of the mussels, as studied using conventional morphological-type descriptors based on metric and weight parameters along with and a physiological condition index, will be presented. The relationships between the various indices, which did not change substantially between 2015 and 2017, are depicted in [Figure 52](#) via a principal components analysis (PCA). This depiction could reflect a relative stability of the environment containing the studied individuals and is consistent with their adaptation to the disinfected effluent.

Statistical tests were conducted on the condition index IC in order to compare the same sampling point in both studied years (2015 and 2017). These tests concluded an insignificant difference in this index between sampling years, meaning that the tertiary treatment implemented at the Biarritz WWTP does not degrade the condition index of mussels living on the outfall.

1.4.2.2 Genetic analysis

The morphological approach was complemented by a genetic analysis to determine if the genes involved in the resistance to various stresses (oxidative stress, xenobiotics, energy requirements, etc.) are being overexpressed. [Figure 53](#) summarizes the results obtained on two groups of genes in 2015 and 2017: oxidative stress genes and DNA repair. For a given site and date, inter-individual variability can be high (i.e., high 'error' bars), which has also been verified herein. It is therefore generally accepted that a minimum factor of 2 for induction or less than 0.5 for repression must be achieved in order to dismiss physiological variations in expression levels between individuals (red lines in [Figure 53](#)). For a given site, the temporal variation can be extremely large and the expression levels of a gene can differ considerably depending on the sampling period. As such, outfall/reference site comparisons should only be conducted on the same date.

In considering the above remarks, no significant differences exist in terms of oxidative stress genes and DNA repair genes between the individuals in the reference site and those in the outfall ([Figure 53](#)). All results obtained indicate that the induction factors observed more heavily favor an adaptive response of organisms to the disinfection of treated wastewater by PFA rather than an acute toxicity response.

Key points

As regards PFA disinfection performance:

- The disinfection performance of limited doses of PFA (1.2 ppm of PFA and 18 min of contact time) applied to treated wastewater has been confirmed and quantified.
- The average removal for *E. coli* is 3.4 u.log.
- The average removal for *E. faecalis* is 2.2 u.log.
- A systematically lower removal of one log unit for *E. faecalis* compared to *E. coli* has been observed.
- The disinfection effectiveness is highly dependent on the outlet water quality and, in particular, on the TSS load.

In studying the impact of PFA disinfection on the natural environment:

- The WWTP outlet pipe behaves like an artificial reef and contains an ecosystem different from the surrounding sandy seabed.
- Biodiversity appears to be normal given the environmental constraints (swell), and the identified species are those commonly found in the Bay of Biscay.
- A more detailed study on a bio-indicator (common mussel) was conducted from both a physiological (biometric indices) and genetic (comparative response of certain gene stresses) point of view. All results obtained to date suggest that the observed responses are adaptive in nature. Further anatomical-pathological studies would provide additional information on process safety.