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Full scale evaluation of combined sewer overflows disinfection using performic acid in a sea-outfall pipe

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Highlights

- Combined Sewer Overflow was disinfected with performic acid in a sea-outfall pipe
- Dosing 1-4 ppm performic acid removed indicator bacteria by 1-5 log units
- Laboratory and field disinfection agreed fraction wise and detected known errors
- Laboratory disinfection correlation with dose for $\leq 4$ ppm initial performic acid
- Performic acid water quality limits upheld through fast degradation, high dilution
Abstract
Pollution of surface waters with pathogens from combined sewer overflows limits recreational use of surface waters. Large retention basins are a satisfactory solution but they are rarely sufficient for economic or space reasons. Fast disinfection during the overflow is an alternative, but few methods are known and each has problems. This work evaluated for the first time the full-scale disinfection using performic acid by the removal of the two currently regulated indicator bacteria for bathing water quality, \textit{E. coli} and \textit{Enterococcus}. Experiments were performed at a sewage bypass through a sea-outfall pipe with a minimum hydraulic retention time of 24 min.

The disinfection efficiency in the field was measured by analyzing samples taken before and after the treatment. Samples were also treated with performic acid in the laboratory to measure the disinfection effectiveness and kinetic of degradation of performic acid. Doses of 1-8 ppm of performic acid achieved 1.0-3.5 log removal of \textit{E. coli} and 1.0-2.44 log removal of \textit{Enterococcus} in the field, but were somewhat higher in laboratory conditions at 1.69-4.38 and 1.0-4.27 log units, respectively. Studies of the degradation of performic acid in collected real samples showed more than 50 % was degraded in 20 min, and mostly degraded by 120 min. Comparison of field and laboratory dosed samples detected that performic acid synthesis didn’t start in one event and clogging of the sampler in another event.

Overall the tests showed that the treatment was successful but it is indicated that online control could benefit treatments efficiency.

Keywords: Disinfection, Combined sewer overflow, Performic acid, Disinfix, Sewer system, Bathing water.

1. Introduction
Combined sewer overflow (CSO) is a well-known phenomenon in combined sewer systems where wastewater and rain water are transported in the same sewer network. Discharge of untreated CSOs deteriorates the quality of receiving surface waters, since CSOs contain a variable mixture of rain water, raw sewage, watershed run-off pollutants, variable pathogenic organisms, viruses, cysts, suspended solids, chemicals and floatable materials [1]. In recent years, the effect of CSOs on water bodies used for recreational purpose has caught significant attention in Europe. Particularly the dedication in 2002 of Copenhagen harbor for recreational purposes including swimming and water sports has yielded an economically significant added service and tourism industry to the harbor area. Corresponding economic losses when CSO events close the harbor for bathing has inspired the construction of significant retention basins which was meant to limit the CSO event frequency. However, due to the climate change related increased number of extreme rain events in 2000-2011, 20 rain events caused temporary closing of bathing in the harbor [2].

According to European Union directive 2006/7/EC for the good quality of bathing water, the number of indicator organisms should not exceed 500 MPN \textit{E. coli} and 200 MPN \textit{Enterococcus} per 100 mL water (based upon 95 percentile evaluation) in surface water intended for recreational purposes [3]. Microbial safe bathing water quality can be maintained by disinfecting the CSO water, and can be achieved in the existing sewer systems where sufficient holding time is available in an outlet pipe or detention tank, by adding a disinfectant at the beginning of the structure. The amount of disinfectant to be added will depend on the quality of CSO and the available residence time in the system. According to Tchobanoglous et al. [4], an ideal disinfectant should guarantee the maximum efficiency in pathogenic microorganism removal, without generating toxic and undesirable by-products. In addition, it should be inexpensive and technologically compatible [4]. There are various well known disinfectants used in the water industries such as hypochlorite and chlorine dioxide [5], which could be used to reduce contamination by microorganisms from CSO events, but the by-products of these are of environmental concern [6]–[10]. The organic peroxide, performic acid (PFA) emerged as a well-known disinfectant in the medical field and food industry [11]. In recent years, PFA has been used to disinfect primary and secondary WWTP effluents and can efficiently remove fecal coliforms [11], [12].

PFA degrades into formic acid and water. Formic acid is not toxic to aquatic fauna and is easily biodegradable [11], [13]. Moreover, PFA is unstable and needs to be generated on-site, when needed, as a quaternary equilibrium mixture of performic acid (PFA), formic acid, hydrogen peroxide and water:

$$\text{CH}_2\text{O}_2+\text{H}_2\text{O}_2 \leftrightarrow \text{CH}_2\text{O}_2+\text{H}_2\text{O} \quad (\text{Eq. 1})$$

PFA has shown high disinfection efficiency on treated wastewater effluents, but to our knowledge PFA has not been used to disinfect CSOs.

If microbiological bathing water quality is the only concern from a CSO structure PFA can be a very economically attractive solution as e.g. a PFA generator with capacity to disinfect up to 4,500 m³/h with 4 ppm PFA costs about 100,000 € and can deliver chemical for 0.06 €/m³ (Kemira Water, Denmark) while construction of a retention basin of 4,000 m² is estimated to cost about 2,800,000 € depending on the land cost.

In our previous study Chhetri et al. [14], the degradation profile of PFA, disinfection efficiency on indicator organisms and residual toxicity on marine bacteria \textit{Vibrio fischeri} were studied in both laboratory simulated CSO water and real CSO water. Furthermore, a PFA dose required to disinfect CSO water in full-scale operations was recommended based
on the experimental results from batch scale tests.

The aim of this study was to test the full scale design and predicted performance of a disinfection system for combined sewer overflow (CSO) using performic acid based on our previous work on the characterization of the disinfection and degradation kinetics of performic acid in simulated and real CSO water. We constructed a dosing system where performic acid was synthesized using the commercial available Disinfix® system, and delivered to an overflow point in an existing CSO structure from a pumping station. To evaluate the performance, we collected water samples using two auto samplers connected to the water flow before and after the dosing point in order to collect untreated and treated water samples during the CSO events. We evaluated the disinfection performance by comparing the concentration of bathing water indicator organisms (E. coli and Enterococcus) in samples taken both before and after the treatment. Experimental dosing of field collected samples with performic acid in the laboratory was used to confirm the dose delivered in the field by comparing the achieved disinfection effect. Furthermore, the experiment was used to measure the kinetic of degradation of PFA in water.

2. Materials and methods

2.1 Chemicals
Formic acid 85% w/w, hydrogen peroxide (50% w/w.), ABTS (2, 2’’-azino-bis [3-ethylbenzothiazoline-6-sulfonic acid] diammonium salt) and catalase from bovine liver were all purchased from Sigma-Aldrich (Brøndby, Denmark). All chemicals were reagent grade.
Performic acid for laboratory use was prepared in two steps. Firstly, 11 mL formic acid (85% w/w.) was mixed with 1.0 mL sulphuric acid (95%) in a glass test tube. Secondly, 0.9 mL of the this mixture was added to 1.1 mL of hydrogen peroxide (50 % w/w) in a 5 mL test tube, and immersed in a water bath controlled at 20° C. The product was allowed to react for 10 min before use in the experiments and was quantified in parallel by dilution of a subsample in demineralised water (125 µL to 100 ml) to yield a solution of approximately 2 mg-L⁻¹. This solution was analyzed using the colorimetric method described by Chhetri et al. [14] based on selective oxidation of ABTS by PFA without interference from hydrogen peroxide.
The field production of PFA was done continuously in a similar way using commercial chemical mixtures and reaction inside a tube reactor under automated temperature control in the Desinfix unit (Dex-135) from Kemira Water (Denmark).

2.2 Full scale disinfection system
The field experiment was performed at a large wastewater pumping station north of Copenhagen, in Skovshoved, which relays wastewater from Gentofte municipality and a part of Lyngby municipality to the Lynetten wastewater treatment plant. When the pumping capacity is exceeded during rain events CSO water bypasses the facility via a 1.6 km long outfall pipe into the Øresund. The hydraulic retention time in the pipe is, at minimum 24 min prior to discharge.
For the experiment, CSO water bypassed into the sea was disinfected with PFA which was generated onsite from a Desinfix unit (provided by Kemira Water, Denmark). PFA was dosed to an overflow point in the existing CSO structure (See Figure 1).
In order to be able to determine the effect of treatment two automatic sample collectors were installed to collect fractions of water before and after the dosing. It was not possible to collect disinfected water from the end of the sea-outfall pipe which is required to evaluate the disinfection effect with the correct contact time. Therefore a tube reactor was made from a flexible polyethylene pipe (1.55 cm diameter and 100 m long) which was wound around a metal pillar. One end of the polyethylene pipe was inserted 6 m into the sea-outfall-pipe from the land side and the other end of the polyethylene pipe was connected to a pump (1 L·min⁻¹) which delivered water to the sample collector with a 20 min retention time. Each sample collector was set to collect 1 L sample time proportionally every 20 min with a capacity of 24 samples. As there is 20 min retention time between the samplers the first sample collected in autosampler 1 correspond to the second sample collected in the second sampler. In order to make the naming straightforward the samples in autosampler 2 was named starting with fraction 0 while autosampler 1 started with fraction 1.
Initiation of the performic acid synthesis, dosing and activation of the two auto samplers were automatized based on signals from the digital control system of the pumping station and CSO system.
2.3 Laboratory disinfection
In order to confirm the PFA dose delivered in the field, comparable PFA treatments were made on three representative field collected (untreated) samples in the laboratory. Three PFA doses were applied to each fraction, in order to match the onsite disinfection dose in low and maximal flows of CSO in the sea out-fall pipe. After 20 min of contact time, a fraction of each sample was processed for *E. coli* and *Enterococcus* enumeration and in parallel concentration profiles of PFA was followed until 2h in the remaining sample.

2.4 Chemical analysis of CSO water
Conductivity, pH, and NH$_4^+$ were determined according to standard methods [15] and using standard operating procedures and control methods from the general water laboratory at Department of Environmental Engineering, Technical University of Denmark.

2.5 Microbiological analysis
Samples were processed within 2 h after collection. Residues of PFA were neutralized in laboratory experiments by adding 100 mg·L$^{-1}$ sodium thiosulphate followed by 50 mg·L$^{-1}$ catalase to destroy hydrogen peroxide [16]. Bottles in the auto sampler used to collect disinfected samples in the field experiments had 100 mg·L$^{-1}$ sodium thiosulphate pre-added followed by addition of 50 mg·L$^{-1}$ catalase immediately on arrival in the laboratory. *E. coli* and *Enterococcus* were enumerated using the Colilert and Enterolert methods from IDEXX (IDEXX laboratories, Maine, United States) as described by Chhetri et al. [14].

3. Results and discussion
3.1 Approval of field dosing experiments
The environmental safety of the release of the chemicals related to the treatment was evaluated and approved by the local authority, Gentofte Municipality, according to the Danish statutory order 1022 of 25th August 2010 [17]. Both the potential pH drop in water in the area around the outlet due to the acidity of the disinfectant mixture (sulfuric and formic acid) as well as the potential toxic effects of PFA, formic acid and hydrogen peroxide concentrations in the receiving water were initially considered. The toxicity evaluation was based on an initial dilution zone with a 50 m radius around the end of the pipe in which the CSO is instantaneously diluted 75-fold according to a standard model used by the Danish environmental authorities. The permit was finally based on that PFA degraded very fast and therefore hydrogen peroxide was the limiting factor. The permit allows that the undiluted treated effluent contains 7.5 mg·L$^{-1}$ hydrogen peroxide and 10 mg·L$^{-1}$ formic acid, that the treatment can be performed for up to 8 h and that the quality criteria of 0.1 mg·L$^{-1}$ hydrogen peroxide cannot be exceeded in the dilution zone. The criterion for hydrogen peroxide was derived from the dataset on eco-toxicity to aquatic organisms by JACC [18].

3.2 Characterization of CSO events
The two studied CSO events occurred on 28 October 2013 (first CSO event) and 7 May 2014 (second CSO event). The first CSO event lasted 5 h 40 min (12:40 pm to 6:20 pm) and the second CSO event lasted for 5 h 15 min (10:15am to 3:30 pm). From the first CSO event 16 samples (CSO fraction) were collected from sampler 1 (non-disinfected) and 17 samples were collected from sampler 2 (disinfected); from the second CSO event 16 non-disinfected samples were collected but only 12 disinfected samples were collected due to repeated clogging of the flexible polyethylene pipe
collecting disinfected samples. All samples were analyzed for conductivity, $\text{NH}_4^+$, and pH, as is illustrated in Figure 2. The conductivity and $\text{NH}_4^+$ of the non-disinfected and onsite disinfected samples from both CSO events showed the variation of the CSO composition over time (Figure 2, Table S1-S2). The conductivity and $\text{NH}_4^+$ peaked during the first hour of both events and decreased to reach a minimum during the second hour and remained constant. At the end of both CSO events conductivity increased progressively which was also observed by Passerat et al. [19]. The difference in conductivity between non-disinfected and disinfected samples is constant through both CSO events as it is due to the pre addition of sodium thiosulphate in bottles collecting disinfected samples to destroy residual PFA. The pH of non-disinfected and disinfected samples showed variation but no trend was observed in both events which were due to the variation of CSO composition over time. This shows that the acidity in the PFA mixture is insignificant, compared to the alkalinity in the water and its variation. The matching trend in the parameters between the influent and effluent of the disinfection system prove that the retention time of 20 min is correct.

![Overflow event 28th Oct 2013](image1)

![Overflow event 7th May 2014](image2)

Figure 2: Conductivity, ammonium and pH of non-disinfected and disinfected CSO fractions from the CSO event occurred on the 28th October 2013 (top) and 07th May 2014 (Bottom).

### 3.3 Field disinfection

Disinfection effectiveness was derived by comparing concentrations of indicator organisms measured in fractions of the CSO event collected in the two auto samplers with adjustment for the 20 min delay in the tube reactor to simulate the hydraulic retention time in the outfall-pipe. Results are shown as connected points in Figure 3 and in Table S3-S4 and S6-S7 for the two CSO events and two indicator organisms. The maximum initial start concentration of $\text{E. coli}$ and $\text{Enterococcus}$ was $10^{5.6}$ and $10^{5.9}$ MPN and minimum was $10^{3.6}$ and $10^{3.9}$ MPN per 100 mL respectively in the October 2013 CSO event. In the May 2014 CSO event the maximum initial start concentration of $\text{E. coli}$ and $\text{Enterococcus}$ was $10^{5.9}$ and $10^{6.0}$ MPN and the minimum was $10^{3.9}$ and $10^{3.2}$ MPN per 100 mL, respectively.

In the October 2013 CSO event the Disinfix unit was set to deliver 0.08 kg·min$^{-1}$ performic acid which would give a minimum delivered concentration of 2 mg·L$^{-1}$ PFA if the flow in the sea outfall-pipe was at the maximal hydraulic capacity of 2500 m$^3$·h$^{-1}$. The first 3 CSO fractions collected were not disinfected due to a failure in the automated start of the Disinfix unit. The remaining CSO fractions were disinfected with a variable PFA dose, detailed in Figure 3 with dotted line resulting from the constant dose from the Disinfix unit but variable flow in the sea-outfall pipe. The removal of $\text{E. coli}$ increased from 2.5 to 3.0 log units in CSO fractions 4 to 8 when the PFA dosing changed from 2.5 mg·L$^{-1}$ to 8 mg·L$^{-1}$ and remained constant for the remaining CSO. Similarly, removal of $\text{Enterococcus}$ changed from 1.0 to 2.3 log units in CSO fractions 4-8 treated with 2.5 mg·L$^{-1}$ to 8 mg·L$^{-1}$ PFA and remained constant for the remaining CSO. The average $\text{E. coli}$ and $\text{Enterococcus}$ concentration after full scale disinfection was $10^{3.1}$ MPN $\text{E. coli}$ and $10^{3.6}$ MPN $\text{Enterococcus}$ per 100 mL of CSO fraction. The CSO water is diluted a minimum of 75 times around the discharge point which means the concentration will be below the 500 MPN $\text{E. coli}$ and 200 $\text{Enterococcus}$ per 100 mL limits mentioned in the European Union directive 2006/7/EC for the good quality of bathing water.

In the May 2014 CSO event the Disinfix unit was set to deliver half the dose of that was used in the first overflow event i.e. 0.04 kg·min$^{-1}$ PFA. The PFA dose was changed to observe the variation in disinfection efficiency on indicator
organisms. The observed removal of *E. coli* was 1.0 to 3.5 log units in CSO fractions treated with 1 to 4 mg L$^{-1}$ PFA. The removal of *E. coli* decreased to 0.9 log unit at the end of the overflow event. This is believed to be due to clogging of the inlet to the tube reactor that simulated the retention time before the second automatic sampler. The removal of *Enterococcus* was 1.0 to 2.44 log units in this CSO event while the system was running properly but in the last fractions it was observed to decrease to 0.5 log unit while the tube reactor wasn’t functioning properly. It is believed that this is a sampling artifact and that the disinfection in the full system remained higher towards the end of overflow event. The average *E. coli* and *Enterococcus* concentration after full scale disinfection was $10^{4.9}$ MPN *E. coli* and $10^{4.8}$ MPN *Enterococcus* per 100 mL of CSO fraction. Considering the 75-fold dilution into the surface water the *E. coli* and *Enterococcus* concentrations will be higher than that allowed for bathing water in the European Union directive 2006/7/EC. In both events it was evident that *Enterococcus* is more difficult to disinfect with PFA than *E. coli* which was also observed by Chhetri et al. [14] and Ragazzo et al. [12].

![Figure 3: Dose (minus sign, right axis) and disinfection effect in laboratory and field (symbols, left axis) of PFA on *E. coli* and *Enterococcus* in two CSO events from 28th October 2013 (two graph from left) and 07th May 2014 (two graph from right). T-bars indicate 95% confidence interval of experimentally observed disinfection effectiveness.](image)

3.4 Laboratory disinfection

Based on ammonium concentration and conductivity, three non-disinfected CSO fractions were selected to match the quality of overflow to the first flush, typical overflow and extended overflow during rain event as described in Chhetri et al. [14]. These samples were disinfected with 3 (or 4) different concentration of PFA in the first and second CSO events to verify the onsite disinfection efficiency towards *E. coli* and *Enterococcus* (Figure 3, Table S5, S8). For *E. coli* and *Enterococcus* enumeration residual PFA was quenched by adding sodium thiosulphate and catalase to the samples after 20 min and in parallel concentration profiles were measured for 2 h to determine the degradation kinetic of PFA in CSO water as shown in Figure 4.

The disinfection effect with varied doses of PFA added in the laboratory to the selected CSO fractions is plotted in Figure 3 and complete data is shown in Table S5 and S8. The removals obtained for *E. coli* and *Enterococcus* with low PFA doses were similar with onsite disinfection removal in both CSO events. The removal obtained from laboratory disinfection for *Enterococcus* was lower than those observed for *E. coli* which was also evident from onsite disinfection. The laboratory removal of *E. coli* and *Enterococcus* increased in both CSO events when higher disinfection doses were used, but the same effect was not observed in the full scale experiments when onsite disinfection doses were increased. Some dissimilarity in removal of indicator bacteria between laboratory and field-scale is expected as laboratory experiments are conducted in controlled condition whereas onsite disinfection of a real CSO event occurs under highly variable operational conditions and are affected by numerous factors.

3.5 Concentration profiles

Three selected fractions of each of the CSO events were used for investigating the concentration curves with time of different PFA at different initial concentrations as seen in Figure 4. The degradation appears to be slower in water from the first CSO event with residual concentration of 0.5-1 mg L$^{-1}$ from 2.7, 3.7 and 7.5 mg L$^{-1}$ PFA remaining after 120 min, while initial concentrations of 4 mg L$^{-1}$ PFA were degraded in all fractions from the 2nd CSO event.
3.6 Dose dependency of disinfection effectiveness

Generally, chemical disinfection design and control is based on the concept that the disinfection is proportional with the exposure of the organism to the disinfectant, expressed as the product of concentration and time (Chick-Watson model). However, this has been difficult to demonstrate in previous work with PFA in wastewater [12] and CSO water [14] where both used the nominal dose as predictor.

Our laboratory disinfection and concentration profile provides data to compare this in 20 combinations of PFA doses and different CSO water samples but with the same exposure time. The correlation between disinfection with either the product of the exposure time and concentration (Ct) or nominal concentration of PFA (C0) is plotted in Figure 5. Calculation of Ct was done by integrating the actual concentration (C) of the disinfectant from the addition until the contact time (t) (area under the curve) of each concentration profiles in Figure 4.

For both the product of the exposure time and concentration and the nominal concentration of PFA the observed correlation with the disinfection appears to be continuous and positive but far from linear. The minimum Ct of 8 mg·L⁻¹·min removed 1.96 log units of E. coli whereas the highest Ct of 102 mg·L⁻¹·min removed 4.38 log units of E. coli. Similarly, the minimum Ct of 8 mg·L⁻¹·min removed 1.33 log units of Enterococcus and Ct of 102 mg·L⁻¹·min removed 3.31 log units of Enterococcus. Thus increasing the Ct 13-fold only increased disinfection by 2.2-fold and 2.5-fold of E. coli and Enterococcus, respectively. Thus, it appears that the disinfection is far more efficient at lower doses than at
higher doses

3.7 Considerations of experimental installation
The constructed full scale test system is far from perfect and many improvements could be envisioned. The most obvious is that the dosing of PFA from the Desinfix unit should be adjustable, so that the PFA dose will change proportionally to the CSO flow giving a constant treatment concentration. A further improvement would be to dose based on the water quality, e.g., the first 60 min of an overflow could be treated with a higher concentration of PFA as the bacteria and matrix concentrations are higher in the beginning of CSO events [14]. A much more reliable evaluation of the achieved disinfection could be achieved if the pump that draws water into the retention tube was also regulated according to the flow, so that the retention before the second auto sampler matched the retention time in the sea-outfall pipe rather than just delivering the minimum retention time before the PFA is quenched.

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