4.7. TESTING OF FREE NITORUS ACID AS A MEANS FOR SULFIDE CONTROL IN FIELDS SITE

The testing aimed to verify the valuable results obtained from the UQ lab-scale studies in the field site. The key results showed that with a very short exposure time, long-term inhibition on sulfate reduction and methane production can be achieved. This means intermittent addition could be applied to achieve long-term sulfide and methane control, resulting in a key advantage of this chemical over many other chemicals, where continuous addition is typically required. Three free nitrous acid dose trials have been performed in the UC09. In these trials the addition of free nitrous acid was carried out manually due to practical and safety reasons.

4.7.1. UC09 NORMAL FUNCTIONING

As described in Section 3.2, UC09 rising main which is located on the Gold Coast was used for the free nitrous acid field testing. Figure 33 displays the typical pump events and HRT over a 24 hour of the UC09.

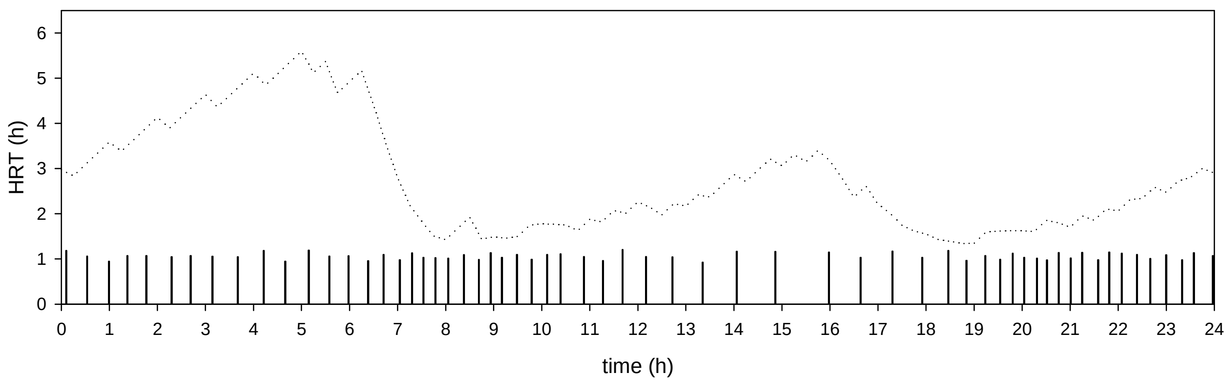

Figure 33. *UC09 normal functioning (....) Sewage Hydraulic Retention Time (HRT) and (___) pump events corresponding to UC09 rising main.*

Figure 34 displays a typical profile of sulfide concentration 828 m downstream of UC09 wetwell corresponding to the period prior to any dose. In this particular day, the average sulfide concentration was 4.9 mgS/L, with a variation range from 2.2 to 8.4 mgS/L depending of the HRT of the sewage in the pipe. The methane concentrations varied between 15 and 25 mgCH_4-COD/L with average concentrations around 20 mgCH_4-COD/L.

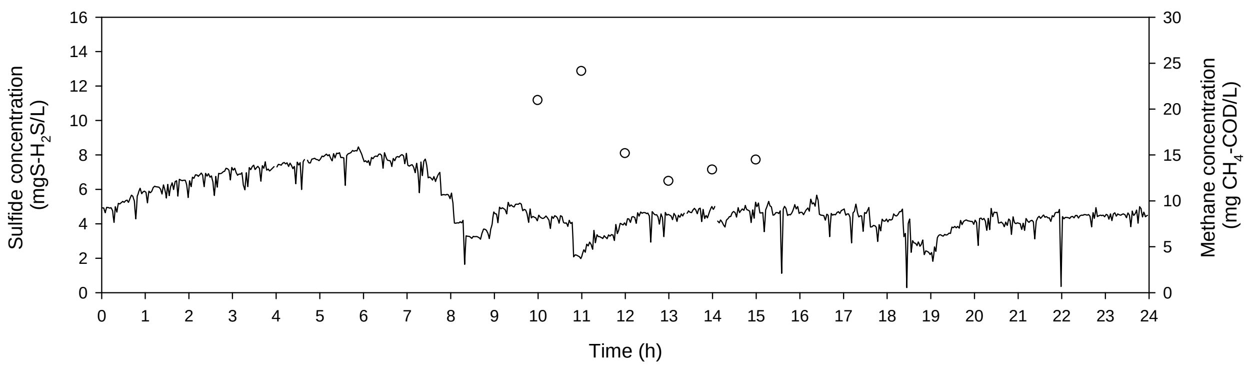

Figure 34. Typical 24h profile in UC09 rising main 828m downstream location for the background period. (——): Sulfide concentration measured by an on-line S::CAN sensor. (○): Methane data from offline sampling is also displayed.

4.7.2. FREE NITROUS ACID DOSE DESIGN

The SCORe-SP6 studies revealed the effectiveness of free nitrous acid in controlling sulfide and methane production. Three FNA dose trials have been performed in the UC09. The FNA solution was dosed to the UC09 pump station following a flow paced pattern. The target concentration of nitrite in sewage was 100 mgN-NO_2/L in the three trials.

- **Nitrite solution dose 1**: On the 17th of November, FNA was dosed overnight for 2 consecutive days, from 8:00 PM to 6:30 AM, to test FNA exposition during long HRT times in the UC09. It can be seen in Figure 35 that HRT was higher during overnight times due to the low flow in the pipe. In addition to usual pump events, extra short pump events (20 seconds) were manually performed to produce mixing conditions inside the pipe.

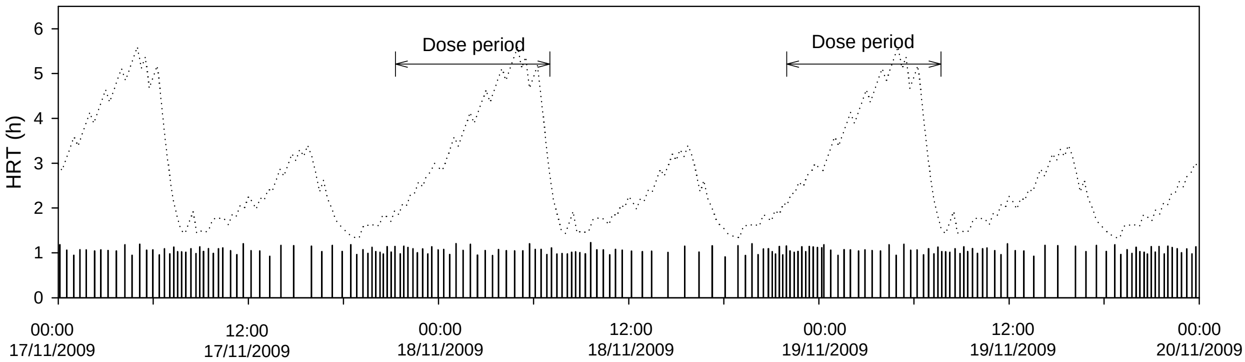

Figure 35. Nitrite solution addition period corresponding to the 1st dose trial. HRT and UC09 pump events are also presented.

- **Nitrite solution dose 2**. On the 16th of December, FNA was added on 3 consecutive days from 8:00 AM to 7:00 PM to test nitrite exposition during high flow periods in the UC09 (Fig. 36). No manual pump events were performed.

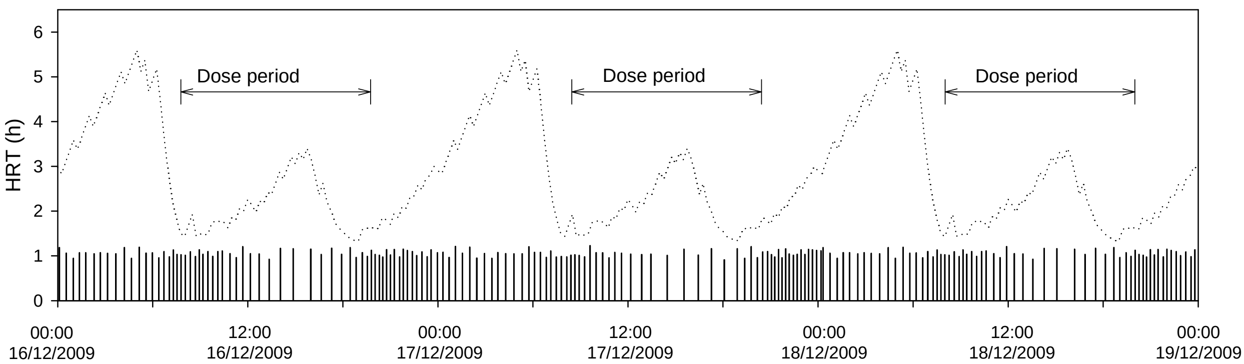

Figure 36. Nitrite solution addition period corresponding to the 2nd dose trial. HRT and UC09 pump events are also presented.

- **Nitrite solution dose 3:** The 3rd dosage trial was designed based on the observations from the previous field trials and lab studies that showed sewer anaerobic biofilms seemed to be more vulnerable to chemicals in the initial days after an exposition to FNA. Therefore, in order to extend the toxic effect of FNA, the trial was divided in two different applications:

- Initial dosage (100 mgN-NO_2/L): 20 hours (6:00 AM to 2:00 AM) of continuous flow pace addition of FNA solution at UC09 wet well, aiming to hit hard the biofilm. Figure 37 shows the initial dosage plan.
- Second dosage (100 mgN-NO_2/L): flow pace addition of FNA solution was performed for 4 days after the initial dosage for a period of 8 continuous hours (7:00 AM to 3:00 AM). The objective of the second dosage was to further shock the biofilms while they were still on the weak state. Figure 38 shows the second dosage plan.

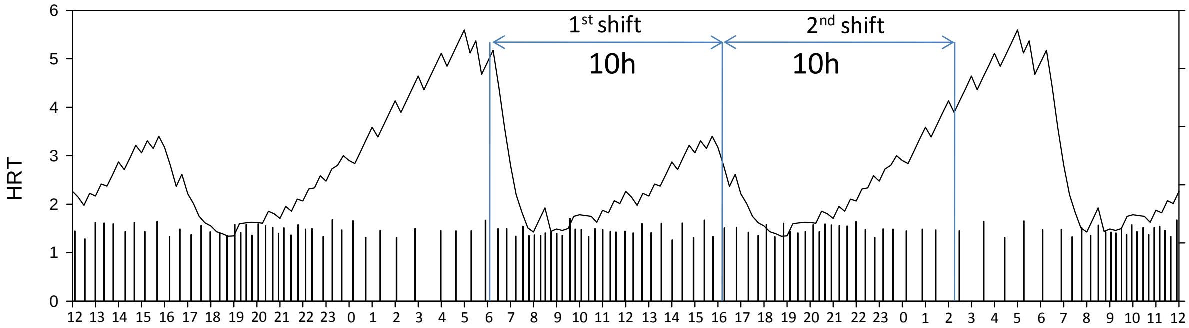

Figure 37. *Proposed periods corresponding to Dosage 1. UC09 HRT and Pump events are presented.*

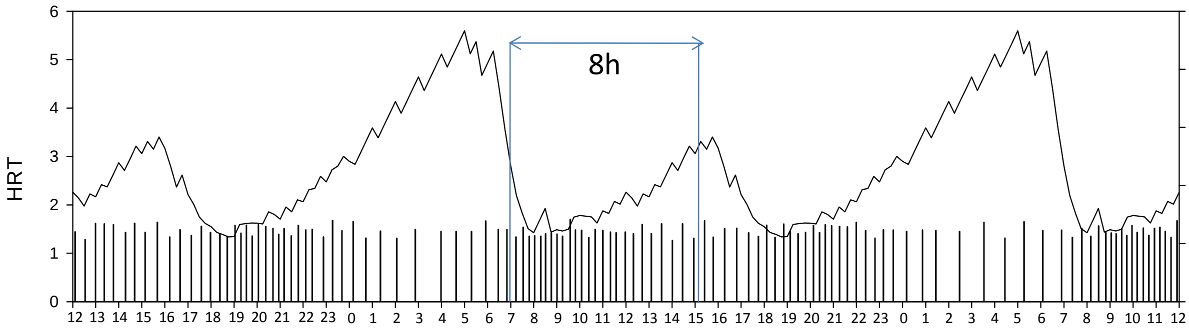

Figure 38. *Proposed period corresponding to Dosage 2. UC09 HRT and Pump events are presented.*

4.7.3. RESULTS OF FREE NITROUS ACID DOSE TRIAL 1

The free nitrous acid was added during the long HRT periods in the UC09. It was hypothesized that lower HRT in the pipe would significantly reduce the amount of FNA required to ensure sulfide control.

The findings of the first field FNA dosage trial are:

1. The addition of FNA prevented the sulfide production in UC09 (Day +1 profile in Figure 39, below). Unfortunately, the inhibitory effect did not last long and the sulfidogenic activity recovered steadily after the cessation of the FNA dose. Five days after the start of FNA dose the sulfide concentrations reached similar levels to prior to the chemical dose.

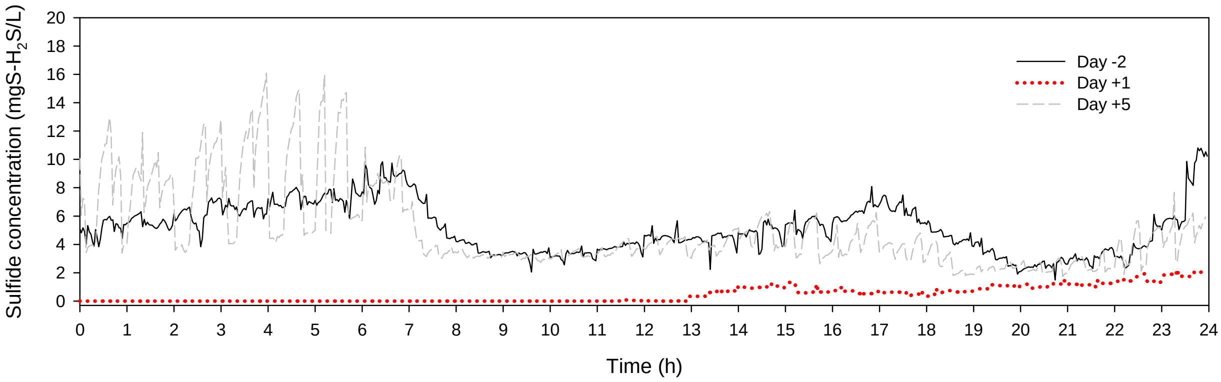

Figure 39. *24 hour online sulfide profiles corresponding to 1st trial of FNA addition in the UC09. Sulfide concentrations corresponding to 2 days before addition and 1 and 5 after special nitrite solution addition in the UC09 wetwell.*

2. The daily average values of sulfide detected at 828m downstream location corresponding to the first FNA dose trial is illustrates in Fig. 40. The baseline sulfide average concentration, around 5mgS-H_2S/L, was quickly reduced after the 2 days addition of FNA solution, down to 1mgS-H_2S/L. As described above, the SRB activity recovered steadily once FNA dose was stopped, reaching the initial baseline values 5 days after the first exposition to FNA.

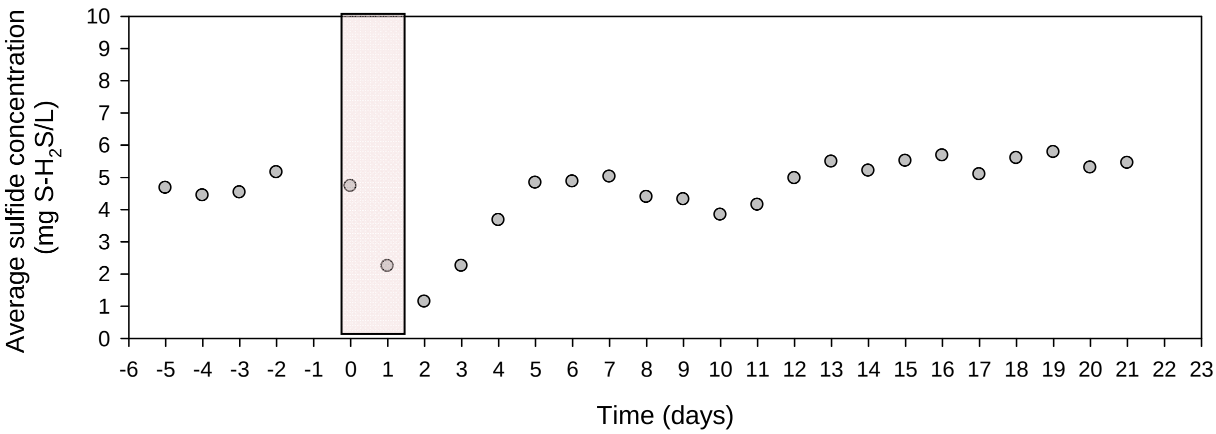

Figure 40. *Daily average sulfide concentrations corresponding to the 1st FNAtrial. Days -6 to 0: baseline period; Days 0 to 1: FNA solution dosing period; Days 2 to 21: recovery after stoppage of FNA dosing.*

3. The injection to FNA solution has drastically reduced the methane production in the pipe (Fig. 41). The net production of methane during the baseline period was 15.7 mgCH_4-COD. After the FNA first dose trial, the methane concentration was only 1.8 mgCH_4-COD, which corresponded to 90% reduction when compared to the baseline period. Opposite to the SRB, the toxic impact to MA lasted for a longer period of time. The MA activity did not show signs of recovery for a period up to 30 days.

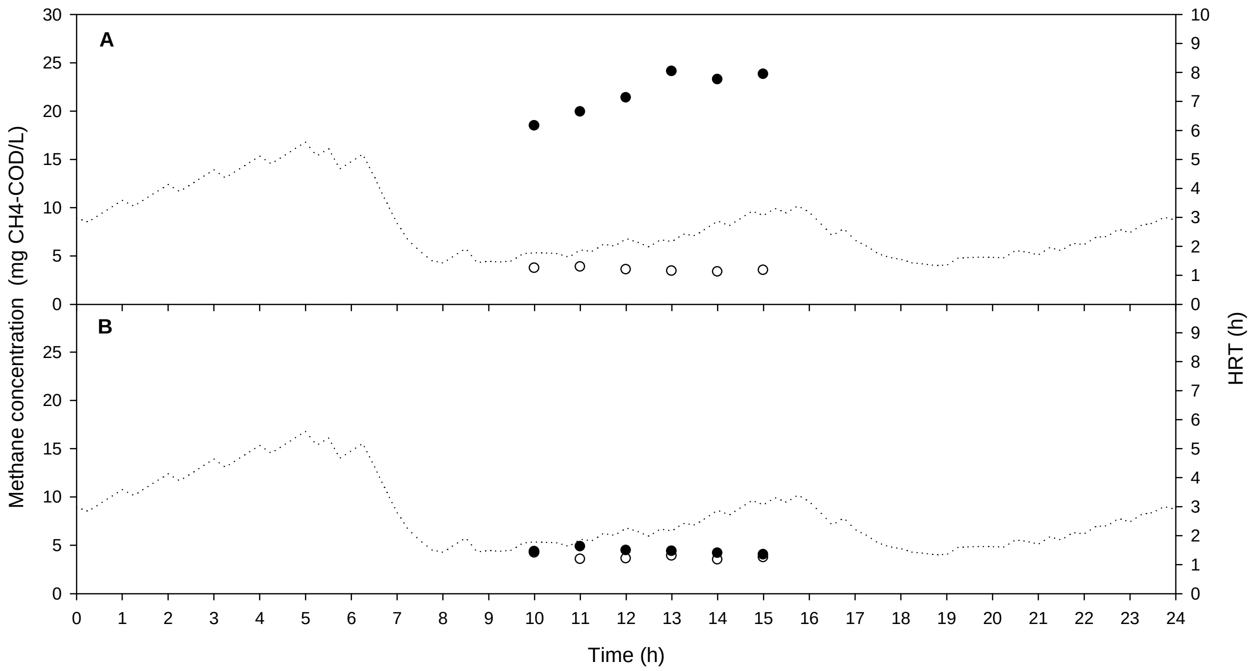

***Figure 41**. (○) Methane concentrations corresponding to the UC09 wetwell and (●) the UC09 828m downstream sampling point. (A): Baseline, 10 days prior to 1st nitrite solution addition; (B): 15 days after nitrite solution.*

4. Methanogens activity was highly reduced by FNA first dose. Moreover the inhibition lasted in time. This supports prior lab observations where methanogens have been more sensitive to nitrite solution toxicity than SRB and need more time to recover. While the recovery of the MA activity was slow, as previously revealed by laboratory studies, in the first trial, SRB recovered much more quickly than that observed in the lab. This could be explained by the insufficient mixing conditions inside the pipe provided by the short manual pump events. The volume of water displaced during the manual pump events most likely mixed the initial sections of the pipe. That means that the FNA was not sufficiently diffused into the biofilms, reducing the expected inhibitory effect. Mixing conditions inside the pipe was then identified as a crucial parameter to obtain higher degree of inhibition.

4.7.4. RESULTS OF FREE NITROUS ACID DOSE TRIAL 2

In the second trial, the FNA dosing time was shifted from night period (8:00PM to 6:30PM) to day period (8:00AM to 7:00AM). Higher flow was expected during daytime, therefore more pump events and more periods of turbulence regime that would increase the mixing conditions inside the pipe. It was expected that the FNA would penetrate deeper in to the sewer biofilms, producing a higher toxic effect.

Some outcomes from the second field FNA dosage test are:

1. The results of 24h sulfide profiles obtained in the FNA second trials are presented in Figure 42. Complete sulfide control was achieved directly after dosing, with no sulfide concentrations detected in the pipe (Day +1). The SRB activity gradually increased afterwards but in much slower than in the first trial. Seven days after the solution dose addition, the sulfide production was around half of that in the baseline. It took up to 22 days to reach similar sulfide concentrations as prior to the FNA addition.

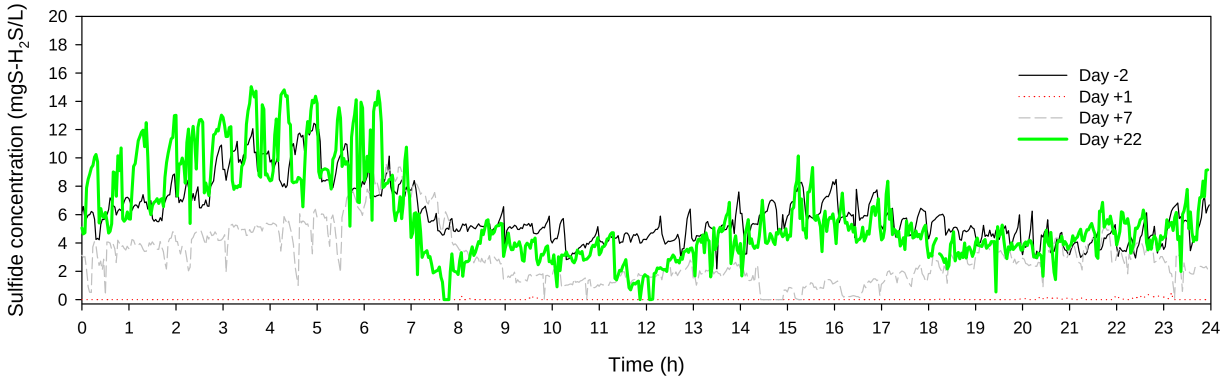

Figure 42. *24 hour online sulfide profiles corresponding to 2nd trial of FNA addition in the UC09. Sulfide concentrations corresponding to 2 days before addition and 1, 7 and 22 days after FNA addition.*

2. The recovery of the sulfide production capacity in the UC09 after the 2nd dosing was irregular through time. After the expected initial drop to zero due to the FNA exposition, a period of 10 days of constant SRB recovery occurred (Fig. 43). At this point, sulfide concentrations stopped its increase and stabilized at 3 mgS-H_2S/L day for period of 5 days. Surprisingly the SRB activity experienced then a second drop to zero without any further FNA solution addition. Once SRB touched ground, the sulfidogenic activity steadily increased again until reach the baseline levels of 6 mgS-H_2S/L 20 days after the nitrite solution was halted.

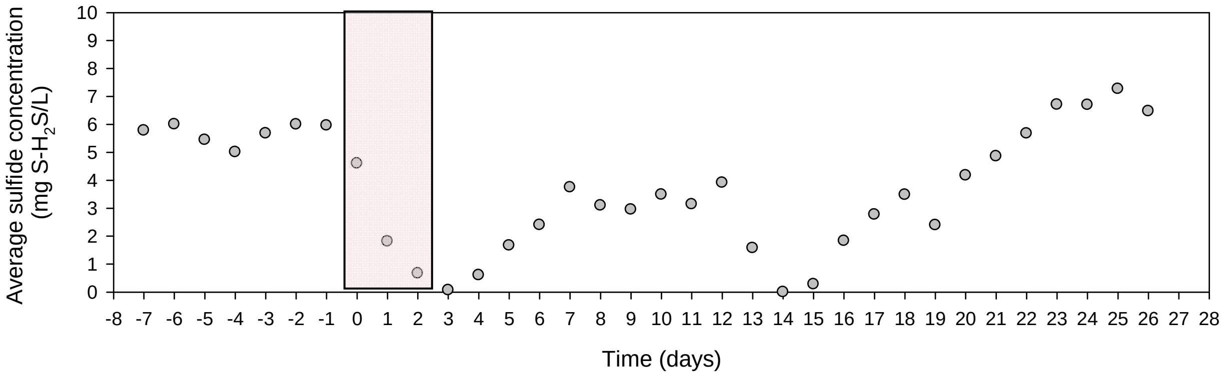

Figure 43*. Daily average sulfide concentrations corresponding to 2nd FNA trial. Days -8 to 0: baseline period; Days 0 to 2: FNA dosing period; Days 3 to 26: recovery after stoppage of FNA dosing.*

3. With regards to the methane production, the 2nd FNA addition confirmed the sensibility of methanogens to FNA. On day 36 after the 3 days addition, the MA activity was still reduced by 96% (Fig. 44). FNA dosing is confirmed as a very effective strategy to control methane emissions from rising main pipes.

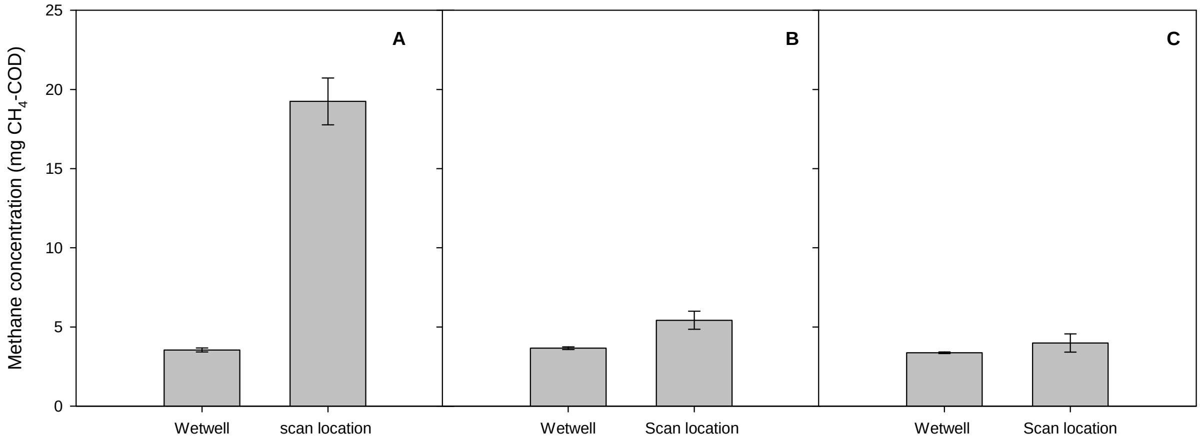

Figure 44. *Average methane concentrations in the UC09 wetwell and 828m downstream location. A: Baseline period, before FNA addition; B: 33 days after 1st FNA dose trial; C: 36 days after 2nd FNA trial.*

4. The dose of FNA during high flow periods substantially increased the inhibitory effect to SRB. The mixing conditions inside the pipe were crucial to enhance the toxic effect of FNA on sewer biofilms. For a period of 19 consecutive days, the dosing strategy applied was able to keep the sulfide concentrations levels below 50% of those of the baseline. The FNA toxic effect on methane control in field site conditions was very strong. A high degree of inhibition (>95%) was maintained for long periods of time (>35 days).

4.7.5. RESULTS OF FREE NITROUS ACID DOSE TRIAL 3

The third trial resulted in sulfidogenic activity in the UC09 inactivation for few days only. Figure 45 below presents the average sulfide concentration calculated from the online sulfide data recorded at 828m downstream of the rising main. As previously seen, the additions of nitrite solution produced an immediate reduction of the sulfide generated in the pipe. However the extent of the reduction was not lasting and recovery of sulfide concentrations was observed within the days after both additions. On day 8 after the first dosage, the sulfide average concentration was 90% similar to the average values recorded prior to the FNA dosage. In the third dosing trial, methane analysis was not performed. The reason is that the impact of the FNA dosing on methanogens was very conclusive as has been demonstrated in the previous trials.

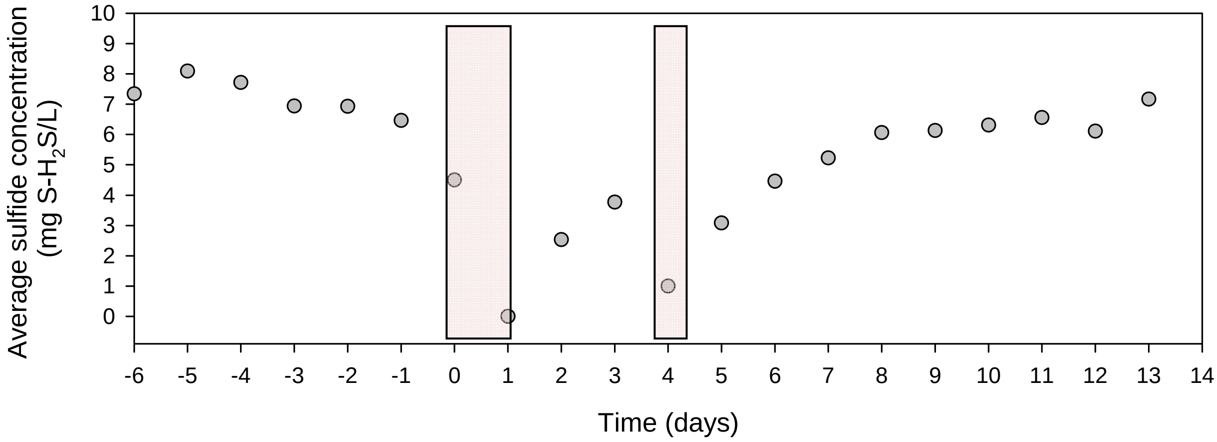

Figure 45. *24h average sulfide concentrations at the downstream section of the UC09 rising main. Dark sections indicate period of FNA dosage.*

From the study, FNA addition has shown as a competitive option in controlling anaerobic sewer biofilms. The intermittent FNA addition has the potential to achieve long-term sulfide and methane control. The trials also allowed the identification of crucial parameters for the improvement of the FNA effectiveness (hydraulic regime, dosing rates, etc.). For example, automatic continuous dose for more days, would definitely help to extend inhibitory effect. Unfortunately that has not been possible to date due to practical and safety issues.

4.7.6. CONCLUSIONS

The FNA dosage field study clearly confirmed that FNA addition into a sewer system had a toxic effect on both SRB and MA as also observed in the laboratory studies. The obtained results to date showed that FNA addition can be a competitive option when controlling anaerobic sewer biofilms to field site sewers. The intermittent FNA addition has the potential to achieve long-term sulfide and methane control. However, there is always room for optimisation and make FNA addition more effective, such as by combining it with other chemicals (H_2O_2, caustic, oxygen, etc.). The trials allowed the identification of crucial parameters for the improvement of the FNA effectiveness (hydraulic regime, dosing rates, etc.).