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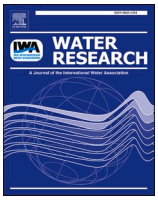

Integrated application of nanoscale zero-valent iron for sulfide and methane control in sewers and improved wastewater treatment

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ABSTRACT

Sewer systems are critical water infrastructures for sewage collection and transportation services but are frequently challenged by odour nuisance, corrosion and greenhouse gas emissions, primarily driven by sulfide and methane production. This study investigated the effectiveness of multifunctional nanoscale zero-valent iron (nZVI) in controlling sulfide and methane, along with its downstream impacts on wastewater treatment. Two continuous flow laboratory-scale reactor systems were used: sewer reactors and sequencing batch reactors (SBRs). Intermittent doses of 50 mg Fe/L of nZVI were introduced daily for a 6-h cycle in the experimental sewer reactors. Results indicated reduced sulfide (by 8.5±0.5 mg S/L during dosing; 4.2±0.6 mg S/L off-dosing) and methane (by 16.6±1.9 mg COD/L during dosing; 12.6±1.3 mg COD/L off-dosing) concentrations compared to the control. This reduction involved sulfide removal (0.12±0.01 g S/g Fe or 0.20±0.02 mol S/mol Fe) and the inhibition of microbial sulfate-reducing and methanogenic activities. Sulfate-reducing bacteria (SRB) and methanogenic archaea (MA) activities exhibited dynamic inhibition with long-term nZVI addition (SRB: 58 % after the first dose, 21 % after 3 months; MA: 27 % to 39 %). Additionally, the sewer-dosed nZVI improved downstream phosphorus removal (0.42±0.04 mg P/mg Fe or 0.76±0.07 mol P/mol Fe) and enhanced sludge settleability and dewaterability. These findings highlight the potential of intermittent nZVI dosing for effective sulfide and methane control in sewers while delivering downstream benefits for integrated urban wastewater management.

1. Introduction

Sewer systems are essential components of urban water infrastructure, consisting of underground pipelines, pumping stations, manholes, and channels that collect and transport sewage from households and industries to wastewater treatment plants (WWTPs) for treatment before environmental discharge (Gutierrez et al., 2016). These networks span approximately 117,000 km in Australia and 1190, 660 km in the US (Gutierrez et al., 2016; Sterling et al., 2010). However, globally, sewer systems face the challenge of corrosion, primarily driven by hydrogen sulfide (H_2S) produced by sulfate-reducing bacteria (SRB) under anaerobic conditions (Pikaar et al., 2014). This corrosion results in substantial economic losses, with an estimated annual cost reaching hundreds of millions of dollars in Australia and US$13.75 billion in the US (Koch et al., 2002; Taheri et al., 2020; Wells and Melchers, 2016). Additionally, H_2S emissions can cause severe odour nuisances and pose health risks (Jiang et al., 2017). Methane production by methanogenic archaea (MA) is another critical concern. Methane, a potent greenhouse gas (GHG), has a global warming potential approximately 84–86 times greater than that of carbon dioxide (CO_2) over a 20-year period (Song et al., 2023). Its release at venting points may contribute approximately 10–32 % of total GHG emissions from the wastewater sector and poses a significant safety hazard due to its explosive nature when exposed to air (Liu et al., 2024, 2015).

Chemical dosing approaches are commonly used for sulfide and methane control (Zhang et al., 2023). Their primary control mechanisms can be categorized into two groups: (1) reducing sulfide and methane production and (2) preventing the release of sulfide. The first approach

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involves using inhibitors to inactivate SRB and MA, such as caustic, free nitrous acid and ferrate (Gutierrez et al., 2014; Jiang et al., 2013; Yan et al., 2020). The second approaches include oxidizing sulfide with oxygen or nitrite/nitrate, precipitating sulfide with iron salts, and elevating sewage pH with magnesium hydroxide to limit H_2S transfer from liquid to air phases (Firer et al., 2008; Gutierrez et al., 2008, 2009; Jiang et al., 2009; Zuo et al., 2024).

Nanoscale zero-valent iron (nZVI) is a multifunction chemical agent, making it a promising solution for a broad range of applications, including water and soil remediation, drinking water filters, and disinfection (Fu et al., 2014; Kowalski and Søgaard, 2014; Liu et al., 2022; Yu et al., 2021; Zhou et al., 2025). It combines reduction, adsorption, precipitation, and inactivation mechanisms, potentially offering dual benefits by not only inactivating SRB and MA but also precipitating sulfide with Fe(II) and Fe(III) released by nZVI (Lefevre et al., 2016; Shi et al., 2021; Su et al., 2013). Studies have demonstrated that nZVI can inhibit SRB enriched from aquifer sediment at a dose of 8.9 mM (Kumar et al., 2014). However, these studies were conducted in batch tests, and it is essential to verify nZVI's potential for suppressing sulfate-reducing activity in continuous sewer systems. While Yang et al. (2013) showed that doses of $\geq$1 mM could reduce methane production by over 20 %, other studies have reported positive effects of nZVI addition on anaerobic digestion by enhancing methane production. This enhancement is due to the rapid release of hydrogen (H_2) from the chemical reaction between nZVI and water, promoting the hydrogenotrophic methanogenesis process (Barrena et al., 2021; Hu et al., 2015; Jia et al., 2017; Wang et al., 2024). These conflicting findings raise questions about the feasibility of implementing nZVI dosing for sulfide and methane control in sewer systems. Furthermore, the doses applied in these studies investigating the toxicity effect of nZVI on SRB and MA exceed the levels typically used for conventional iron salts in industrial sulfide control practice (3–47 mg Fe/L) (Ganigue et al., 2011). Such higher dosing requirement may limit the practicality of nZVI due to increased costs, potential impacts on downstream microorganisms in activated sludge, and the risk of introducing extra solids into wastewater treatment plants. Consequently, there is still a lack of study investigating the effectiveness of sulfide and methane control in sewers, as well as the changes in SRB and MA activities resulting from long-term nZVI addition.

The addition of chemicals changes the composition of liquid and/or sludge streams in wastewater and can impact downstream wastewater treatment plant (WWTP) performance (Cen et al., 2023b). These potential effects underscore the need for integrated management of sewer network and WWTPs, presenting an opportunity to cost-effectively enhance system-level performance with reduced chemical inputs (Cen et al., 2023a; Kulandaivelu et al., 2020; Rebosura et al., 2018). If nZVI is applied in sewers, the nZVI particles or their sulfidated forms entering wastewater treatment bioreactors are likely to be oxidized into iron oxide and iron oxyhydroxide under aerobic conditions (Jiang et al., 2015). These iron forms may serve as effective sources for phosphorus binding and act as coagulants, potentially improving phosphorus removal and sludge properties. However, downstream microorganisms in activated sludge could also be exposed to nZVI particles, possibly leading to cytotoxic effects (Wu et al., 2013). Therefore, it is imperative to investigate the long-term impact of sewer-dosed nZVI on downstream wastewater treatment processes to prevent unintended consequences.

This study aims to investigate the long-term effectiveness of the nZVI approach for sewer management from an integrated urban wastewater management perspective. To achieve this, freshly synthesized nZVI was used to identify the dosage required to inactivate sewer biofilms through viability tests. Subsequently, two parallel reactor systems, consisting of sewer reactors and sequencing batch reactors (SBRs) for biological carbon and nitrogen removal, were operated, one as the control and the other as the experimental system. After confirming comparable performance between the two systems, nZVI was dosed into the sewer reactors of the experimental system. By comparing the performance of two reactor systems, we investigated the effectiveness of nZVI on sulfide and methane control in sewers and evaluated the impact of sewer-dosed nZVI on downstream wastewater treatment processes.

2. Methods and materials

2.1. Reactor systems

Two continuously-flow reactor systems, including sewer reactors and SBRs, were used in this study, one as a control and the other as an experimental system (Fig. 1A). The reactor system received raw domestic wastewater feeding which was collected every 3 weeks from a sewer pumping station in a local residential area (Brisbane, Australia) and stored at 4 °C before use. The characteristics of wastewater are summarized in Table S1.

Each reactor system consisted of two air-tight sewer reactors in series, named sewer reactor A and sewer reactor B, both continuously mixing by magnetic stirrers (MIXdrive 1 eco). Each sewer reactor had a volume of 0.75 L, with a diameter of 80 mm and a height of 149 mm. The biofilm area developed on the reactor wall was 425 cm^2. Additionally, removable plastic carriers (K1 size of 1 cm diameter; surface area of 4.5 cm^2 for each) were clustered on four stainless-steel rods inside the sewer reactor A. The removable biofilm carriers were used for viability tests with the biocidal agent nZVI (see Section 2.3) and 16S rRNA gene amplicon sequencing analysis (see Text S1), without affecting the biofilm developed on the reactor wall.

Sewer reactors were fed with a 2.5-L batch of domestic wastewater every 6 h. The wastewater was pumped in over a 5-min period at the start of each 6-hour cycle, with a flow rate of 0.5 L/min. During this process, an equal volume of wastewater was simultaneously drained into a buffer tank, where it was temporarily held for sampling. After sampling, the entire 2.5 L of effluent from the sewer reactors was transferred to the SBR within 10 min, achieving a volume exchange rate of 29.4 %. The SBR was also operated with 6-hour cycles, with each cycle comprising 2 h of anoxic mixing (including 5 min for feeding), 3 h of aerobic mixing, 45 min of settling, and 15 min of decanting. Activated sludge was removed from the SBR at a rate of 708 mL per day, resulting in a solids retention time (SRT) of 12 days.

2.2. nZVI synthesis

Zero-valent iron nanoparticles with a hydrodynamic size range of 100–1000 nm, were synthesized by using the borohydride reduction method in a 250 mL three-neck flask with mechanical stirring and continuous N_2 sparging, following the same procedure previously established by the authors' group (Yu et al., 2022, 2021). Briefly, the dissolved sodium borohydride ($NaBH_4$) was added dropwise into $FeCl_3{\cdot}6H_2O$ solution, with a 4:1 molar ratio of $NaBH_4$ and $FeCl_3{\cdot}6H_2O$. An excess of $NaBH_4$ was used to ensure complete reduction of all iron species. After the $NaBH_4$ solution was added, the resulting slurries were stirred for another 90 min, then collected by centrifugation (3000 rpm, 5 min) and washed three times with deaerated Milli-Q water. The as-obtained particles were freshly prepared once a week and were stored in deaerated Milli-Q water in a 200 mL oxygen-free sealed bottle prior to the experimental sewer reactors dosing. All solutions were prepared by deaerated Milli-Q water (N_2 sparging for 30 min) before use.

2.3. Viability tests on the biocidal effect of nZVI

The effect of nZVI on cell viability was evaluated. A total of 14 biofilm carriers were transferred from the sewer reactors of two reactor systems into 120 mL of wastewater. The biofilm was detached from plastic carriers by vortexing for 30 s and, when necessary, scraped off using a small sterile brush. The mixture of biofilm and wastewater was then equally distributed into eighteen 12-mL vacuumed Exetainer vials, ensuring minimal exposure to air. Different volumes of nZVI slurry (prepared on the same day as the viability tests) were injected to each

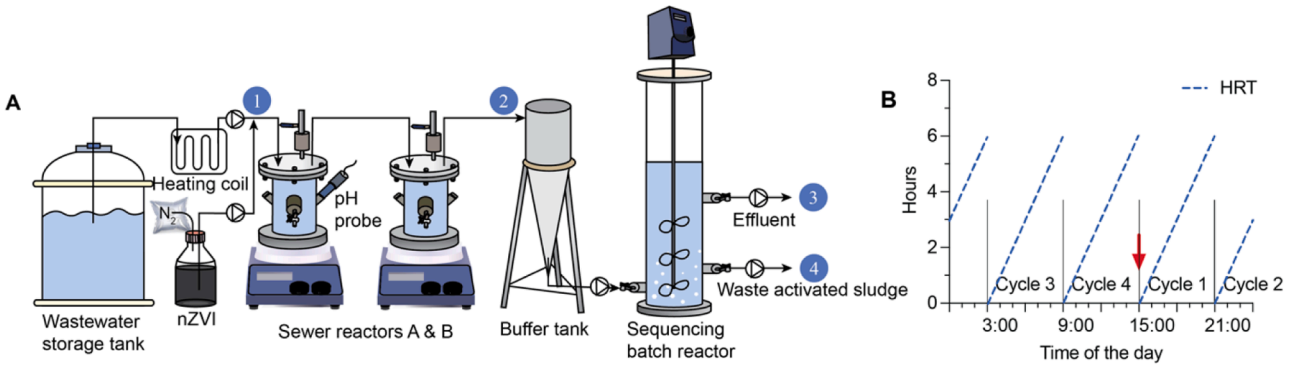

Fig. 1. Schematic of the experimental reactor system (A) and operation of the experimental sewer reactors (B). The control setup was identical but did not include the nZVI dosing unit. The vertical lines in the right plot indicate 5-min pumping events. The red "↓" indicates the injection of nZVI into the experimental sewer reactors (after Phase II commenced).

vial to achieve the designated nZVI concentrations of 0, 10, 20, 50, 100 and 150 mg Fe/L, in triplicate. The vials were then gently mixed by an orbital shaker at 60 rpm. After 12 h of exposure, the biomass was sampled for LIVE/DEAD staining, using the method described in Section 2.5.

2.4. Experimental design and monitoring protocol

2.4.1. Long-term monitoring of reactor systems

The experiment consisted of two phases. During Phase I, both the control and experimental reactor systems were operated identically. After they achieved comparable performance and completed the viability tests described above, Phase II commenced. In Phase II, the experimental sewer reactors were dosed with nZVI at 50 mg Fe/L for 6 h (one cycle, referred to as cycle 1). This dosing was achieved by adding 10 mL of stocked nZVI suspension (~12.5 g Fe/L) to the experimental sewer reactors during the final minute of the cycle 1 pumping event. nZVI dosing was suspended during the subsequent three cycles (referred to as cycles 2, 3 and 4) (Fig. 1B), corresponding to a daily dosage of 12.5 mg Fe/L/d.

A protocol to regularly evaluate reactor system long-term performance included measuring sulfur and dissolved methane concentrations in the sewer reactor influent and effluent, dissolved nitrogen and phosphorus concentrations in the SBR influent and effluent, mixed liquor suspended solids (MLSS) concentration of activated sludge in SBR, and other commonly used wastewater treatment parameters (details in Table S2). After achieving a pseudo-steady state, the total and dissolved iron concentration of sewer reactor effluent (i.e., SBR influent), SBR effluent and activated sludge, as well as sludge properties (i.e., settleability and dewaterability), were analysed and compared between the two reactor systems. Amplicon sequencing (16S rRNA) was conducted at the end of Phase II to assess microbial communities of both control and experimental sewer reactors (details in Text S1).

2.4.2. Biological activities of sewer biofilms with batch tests

Three types of batch tests were conducted to measure and compare the sulfate reduction and methane production capabilities of biofilms in both control and experimental sewer reactors. The Type I test was carried out during Phase I to confirm that the control and experimental sewer reactors had comparable sulfate-reducing and methanogenic activities. During Phase II, the Type II and Type III test were conducted at cycle 1 (with nZVI dosing) and 4 (without nZVI dosing), respectively, to measure the biological activities in the experimental sewer reactor after their initial exposure to nZVI, and again after two and three months of long-term nZVI addition. These results were then compared to the sulfate-reducing and methanogenic activities observed in the control reactors during the same periods.

The tests commenced by discharging the wastewater from the sewer reactors and pumping fresh wastewater into the reactors for at least 2 min to ensure they were fully filled with fresh sewage. 50 mg Fe/L of nZVI was added in experimental sewer reactor for the Type II test only. Wastewater samples were collected at 0, 15, 30, 45, 60, 120, 240, and 360 min after pumping for the analysis of dissolved inorganic sulfur (sulfide, sulfite, thiosulfate, and sulfate) and dissolved methane, as described in Section 2.6. The sulfate-reducing and methanogenic activities were calculated using linear regression of sulfate and methane concentrations during the first hour of hydraulic retention time (HRT) after pumping.

2.5. LIVE/DEAD staining

The viability of microbial cells was evaluated using the LIVE/DEAD® BacLight™ bacterial viability kit (Molecular Probes, L7012) in accordance with the manufacturer's instructions. This kit utilizes two nucleic acid stains: the green-fluorescent SYTO-9 and red-fluorescent Propidium Iodide (PI) dyes. SYTO-9 stains all live microorganisms, while PI selectively penetrates and labels those with damaged membranes. As a result, microorganisms with intact cell membranes (viable cells) fluoresce green, while those with damaged membranes (dead cells) fluoresce red.

To prepare the samples, 1 mL of biomass suspension collected from the nZVI toxicity tests (Section 2.3) was centrifuged at 18,000 × g for 5 min. After decanting the supernatant, the pellet was washed twice by resuspending it in a 0.8 % NaCl solution and centrifuging again at 18,000 × g for 5 min. The washed pellet was then resuspended in 1 mL of the NaCl solution, and 3 μL of a SYTO-9 and PI mixture (1:1 vol ratio) was added in 2 mL plastic centrifuge tubes. The tubes were incubated in the dark at room temperature for 15 min to allow the staining reactions to complete. After incubation, 5 μL of the stained suspension was transferred to microscope slides and imaged by using a confocal laser scanning microscope (Ziess LSM 710 BiG) equipped with a Krypton–Argon laser (488 nm) and two He–Ne lasers (561 and 633 nm) at 400 × magnification. At least three images were captured from randomly selected areas of each sample.

The quantification of live and dead microorganisms was carried out by analyzing the relative intensity of green and red pixels using ImageJ (National Institute of Health, USA). The percentage of green fluorescence relative to total fluorescence (red + green) was used as an estimate of the proportion of viable cells within the biomass.

2.6. Analytical methods for wastewater treatment performance

The analysis of dissolved inorganic sulfur species (sulfide, sulfate, sulfite and thiosulfate) was performed using ion chromatography (IC) equipped with an UV conductivity detector (Dionex ICS-2000). Before analysis, 1.5 mL samples were filtered through 0.45 μm filters (Millipore, Millex GP) into 0.5 mL of sulfide antioxidant buffer (SAOB) solu-

tion (Keller-lehmann et al., 2006). The dissolved methane content in the influent and effluent of the sewer reactors was measured according to the protocol outlined by Guisasola et al. (2008). A 6 mL liquid sample was injected into a 12 mL vacuumed Exetainer vial through a filter (0.45 μm, Millipore, Millex GP) and a hypodermic needle. The vial was then inverted and left overnight to allow an equilibration between the liquid and gas phases. The methane in the gas phase was analyzed by gas chromatography (Agilent GC7890A) using argon as the carrier gas. Concentrations of dissolved methane in wastewater were calculated using Henry's Law and expressed in COD units.

For the analysis of phosphate ($P—PO_4^{3-}$), ammonium ($N—NH_4^+$), nitrate ($N—NO_3^-$) and nitrite ($N—NO_2^-$), samples were filtered in a similar manner and analysed using a Flow Injection Analyzer (FIA) (Lachat QuickChem 8000, Milwaukee). Total and dissolved iron concentrations were measured using Inductive Column Plasma Optical Emission Spectroscopy (ICP-OES) (Perkin Elmer Optima 7300DV, Waltham, MA, USA). Total and soluble chemical oxygen demand (COD) were measured using a spectrophotometer Merck CSB spectroquant model SQ300 (10–150 mg COD/L and 25–1500 mg COD/L range). The pH was measured using a portable pH monitor and probe ($pH5^+$, Oakton). Total suspended solids (TSS), volatile suspended solids (VSS) and sludge volume index (SVI) were determined according to standard methods (APHA, 2005). Sludge dewaterability was assessed using procedures previously described by Rebosura et al. (2018).

2.7. Statistical analysis

During the nZVI dosing period, data from the experimental system were subtracted by the data from the control to calculate differences at all the sampling times. The mean difference and the associated standard error between two systems were then calculated. An unpaired *t*-test was performed to assess whether these differences were statistically significant, using a 95% confidence interval. A *p*-value of <0.05 was considered indicative of a significant difference.

3. Results

3.1. Biocidal effect of nZVI on sewer biofilms

There was a negative impact of nZVI on microbial viability, as shown in Fig. 2 and Figure S1. The confocal microscopy of the control group (i.e., 0 mg Fe/L) showed almost all live cells (green) with no obvious dead cells (red). However, the percentage of live cells significantly ($p < 0.001$) decreased to 56±5 % after a 12-h exposure to 50 mg Fe/L of nZVI. As depicted in Fig. 2C, some microorganisms within the enclosed matrix survived even in the adverse environment of nZVI dosing at 50 mg Fe/L, potentially due to limited chemical penetration. Notably, the percentage of viable cells did not decrease further when higher concentrations of nZVI were applied. This may be because higher nZVI concentrations are more prone to aggregation, driven by the low surface charge of nZVI in aqueous solution at near-neutral pH (pH 7.2±0.0 in this study) and the magnetic attraction between the particles (Phenrat et al., 2007; Wang et al., 2022). Collectively, these results indicate that the nZVI dosage of 50 mg Fe/L could cost-effectively achieve a partial inactivation effect on sewer biofilm. To optimize chemical consumption, an intermittent dosing strategy of 50 mg Fe/L for one 6-h cycle per day, equivalent to 12.5 mg Fe/L/d (see Fig. 1B), was employed in this study to explore its effectiveness in controlling sulfide and methane in sewer reactors.

3.2. Effectiveness of nZVI on sulfide and methane control

Phase I was operated over 81 days, during which the control and experimental sewer reactors were operated identically (Fig. 3). The average concentrations of sulfate, sulfide and dissolved methane in the influent were 15.7±0.6 mg S/L, 2.9±0.7 mg S/L and 6.2±1.2 mg COD/L, respectively. After a 6-h reaction period, the effluent from two lines showed similar concentrations of sulfate (4.5±0.4 mg S/L for the control vs. 4.6±0.4 mg S/L for the experiment), sulfide (13.7±0.7 mg S/L for the control vs. 13.6±0.7 mg S/L for the experiment) and dissolved methane

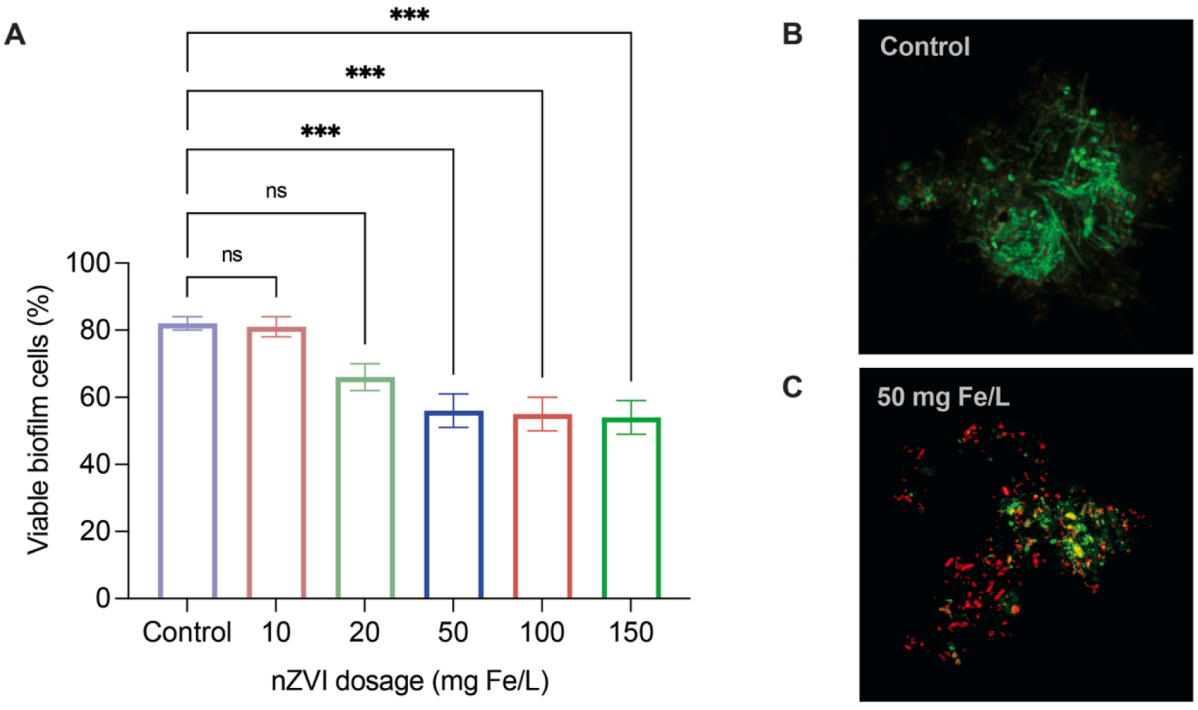

Fig. 2. Sewer microbial viability of before (Control) and after exposure to 10 mg Fe/L, 20 mg Fe/L, 50 mg Fe/L, 100 mg Fe/L and 150 mg Fe/L of nZVI for 12 h (A). The plot showed the mean of each group with error bars representing the standard error. The sample sizes were 11, 9, 12, 12, 10, and 10, respectively. Significant differences were determined using unpaired *t*-test: *** indicates $p < 0.001$, and "ns" indicates no significant difference ($p > 0.05$). Confocal laser scanning microscope images of LIVE/DEAD-stained (green/red) microbial cells exposed to 0 mg Fe/L (B) and 50 mg Fe/L (C) of nZVI.

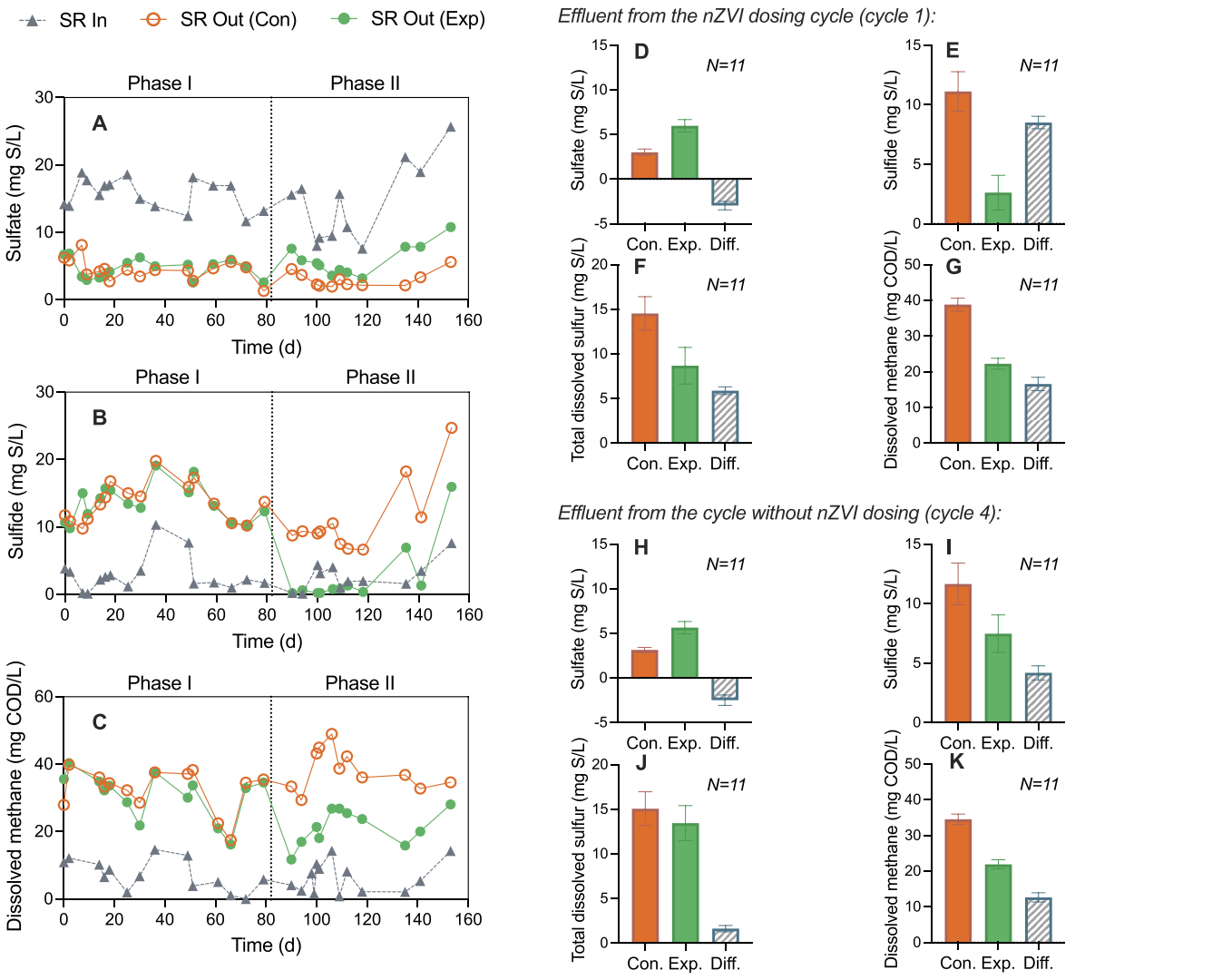

Fig. 3. Concentrations of sulfate (A), sulfide (B), and dissolved methane (C) in the influent and effluent of sewer cycle 1. Phase I shows the establishment of stable baseline conditions between the two reactors. The vertical dotted line marks the start of nZVI dosing in cycle 1 of the experimental sewer reactors. Effluent characteristics of sulfide (D, H), sulfate (E, I), total dissolved sulfur (i.e., sulfate + sulfide + sulfite + thiosulfate) (F, J) and dissolved methane (G, K), in the cycle 1 (D, E, F, G) and cycle 4 (H, I, J, K) of both control and experimental reactors during Phase II are summarized and compared in bar charts. The third bar in each plot represents the mean difference and the associated standard error calculated as described in Section 2.7.

(31.3±2.3 mg COD/L for the control vs. 30.9±1.5 mg COD/L for the experiment), with no significant difference ($p > 0.05$). This suggests that the sewer biofilms in both control and experimental sewer reactors had comparable capabilities in reducing sulfate to sulfide and producing methane. nZVI dosing on the experimental sewer reactors commenced on day 82, marking the beginning of Phase II. The long-term performance of the sewer reactors revealed that during the nZVI dosing cycle, the effluent from the experimental reactors contained a higher sulfate concentration by 3.0±0.5 mg S/L (105.0±19.4 %) and a lower dissolved methane concentration by 16.6±1.9 mg COD/L (42.2±4.1 %) compared to the control (Fig. 3A, 3C, 3D and 3G). This suggests that the long-term addition of nZVI reduced the sulfate-reducing and methanogenic activities of sewer biofilms, effectively suppressing methane discharge from the experimental sewer reactors. Even when nZVI addition was suspended on the subsequent sewer cycles (Fig. 3H and 3K), a higher sulfate concentration of 2.5±0.6 mg S/L (82.6±17.8 %) and a lower dissolved methane concentration of 12.6±1.3 mg COD/L (36.3±3.1 %) were still observed in the experimental line compared to the control, indicating that SRB and MA did not recover their activity immediately. Additionally, nZVI addition removed sulfide down to 2.6±1.5 mg S/L, whereas the sulfide concentration in the control line was 11.1±1.7 mg S/L (Fig. 3B and 3E). The overall 84.4±5.8 % reduction in sulfide was largely attributed to sulfide adsorption or precipitation by nZVI, as confirmed by the long-term results from the sewer cycle not receiving nZVI dosing (i.e., cycle 4), where only a 38.5±4.2 % sulfide reduction was observed (Fig. 3I and Figure S2). Since the sewer reactors were fully filled with wastewater, ensuring no headspace, there was no loss of sulfur as H_2S gas. The amount of sulfide adsorbed or precipitated in the experimental sewer reactors can be estimated by the difference in total dissolved sulfur (sulfate + sulfide + sulfite + thiosulfate) between the two reactors. The total dissolved sulfur concentrations in the control and experiment (intermittently dosed with 50 mg Fe/L of nZVI) were 14.5 ±1.9 mg S/L and 8.7±2.0 mg S/L, respectively, with a mean difference of 5.9±0.4 mg S/L (Fig. 3F). The calculated sulfide removal capacity of nZVI was 0.12±0.01 g S/g Fe (or 0.20±0.02 mol S/mol Fe), which is close to the capacity of sulfide uptake by nZVI (~0.18 mol S/mol Fe) determined through a reported kinetic study conducted in the dosed S/Fe molar ratio 0.224 (Fan et al., 2013).

3.3. Effect of long-term nZVI addition on sulfate-reducing and methanogenic activities

The biological activities of SRB and MA before and after nZVI addition are presented in Fig. 4 and Figure S3. In Phase I, the suflate reduction and methanogenic rates of the experimental sewer reactors were 7.6±1.2 mg S/L/h and 9.3±1.4 mg COD/L/h, respectively. These rates were comparable with those of the control, with a sulfate reduction rate of 7.6±1.3 mg S/L/h and a methane production rate of 10.5±0.7 mg COD/L/h. In Phase II, the control sewer reactors continued to be operated as was in Phase I, while the experimental sewer reactors received nZVI dosing of 50 mg Fe/L intermittently. Differences in the biological activities between Phases I and II in the control reactors were attributed to the changes in wastewater composition (e.g., COD) over time. Since both the control and experimental reactors received the same wastewater throughout the study period, any variations in biological activities due to wastewater composition changes were accounted for in the comparison between the two reactors.

When 50 mg Fe/L was added into the experimental sewer reactors for the first time on day 82 (cycle 1), the sulfate reduction rate of the experimental sewer biofilm dropped to 2.1±0.2 mg S/L/h, representing a 58 % reduction compared to the control (5.1±0.2 mg S/L/h). A partial inhibition effect of SRB activity was also observed during the batch tests (i.e., cycle 4) even in the absence of nZVI addition. This suggests that nZVI addition has an immediate inhibitory effect on sulfate reduction in anaerobic sewer biofilms, and SRB activity does not recover immediately. However, as shown in Fig. 4A, after prolonged nZVI addition, the sulfate reduction rate in the experimental sewer reactors was reduced by 21 % relative to the control. Specifically, during cycle 1 on day 140, the sulfate reduction rate was 6.5±0.5 mg S/L/h in the control, whereas it decreased to 5.1±0.4 mg S/L/h in the experimental reactors. This inhibitory effect remained stable until the end of phase II (day 167), suggesting that the biofilm adapted to nZVI and that of 50 mg Fe/L dosage did not have a lasting inhibitory or toxic effect on the sulfide production capability of sewer biofilm. Interestingly, the long-term effect of nZVI addition on methane suppression exhibited an opposite trend (Fig. 4B). Initially, nZVI addition did not substantially suppress methane production, with a relative difference of 27 % between the control (3.3±0.3 mg COD/L) and in the experimental reactors (2.4±0.2 mg COD/L). The suppression effect slightly increased to 33 % during subsequent cycles (cycle 4), when nZVI dosing was suspended. Over three months of nZVI exposure, the methane production rate of the experiment reached an inhibitory effect of 39 %, decreasing from 24.6 ±1.5 mg COD/L/h in the control to 15.0±1.5 mg COD/L/h in the experimental reactors.

Fig. 5 illustrates the changes in microbial community structure after three-months of nZVI dosing. The total relative abundance of methanogenic genera significantly decreased ($p < 0.05$) from 34.2 % in the control biofilms to 29.2 % in the experimental biofilms, consistent with the reduced methane production observed in experimental sewer reactors on day 167. Specifically, *Methanosaeta, Methanobacterium* and *Methanospirillum* dropped from 25.2 %, 3.3 % and 3.1 % to 23.6 %, 1.1 % and 0.9 %, respectively, while *Methanomethylovorans* increased from 1.9 % to 2.8 after long-term nZVI dosing. Meanwhile, the total relative abundance of SRB slightly declined from 6.2 % in the control biofilms to 5.3 % in the experimental biofilms, with individual SRB genera responding differently. For example, *Desulfobulbus, Desulfovibrio* and *Syntrophorhabdus* decreased, whereas *Desulfomicrobium* increased, and *Desulfomonile* along with SRB genera remained unchanged. This overall minimal shift in the SRB community corresponded to the recovery of the sulfate reduction rate in the experimental sewer reactors by the end of the experimental phase.

3.4. Impact of sewer-dosed nZVI on downstream wastewater treatment

The fate of iron from nZVI dosing throughout the reactor systems is

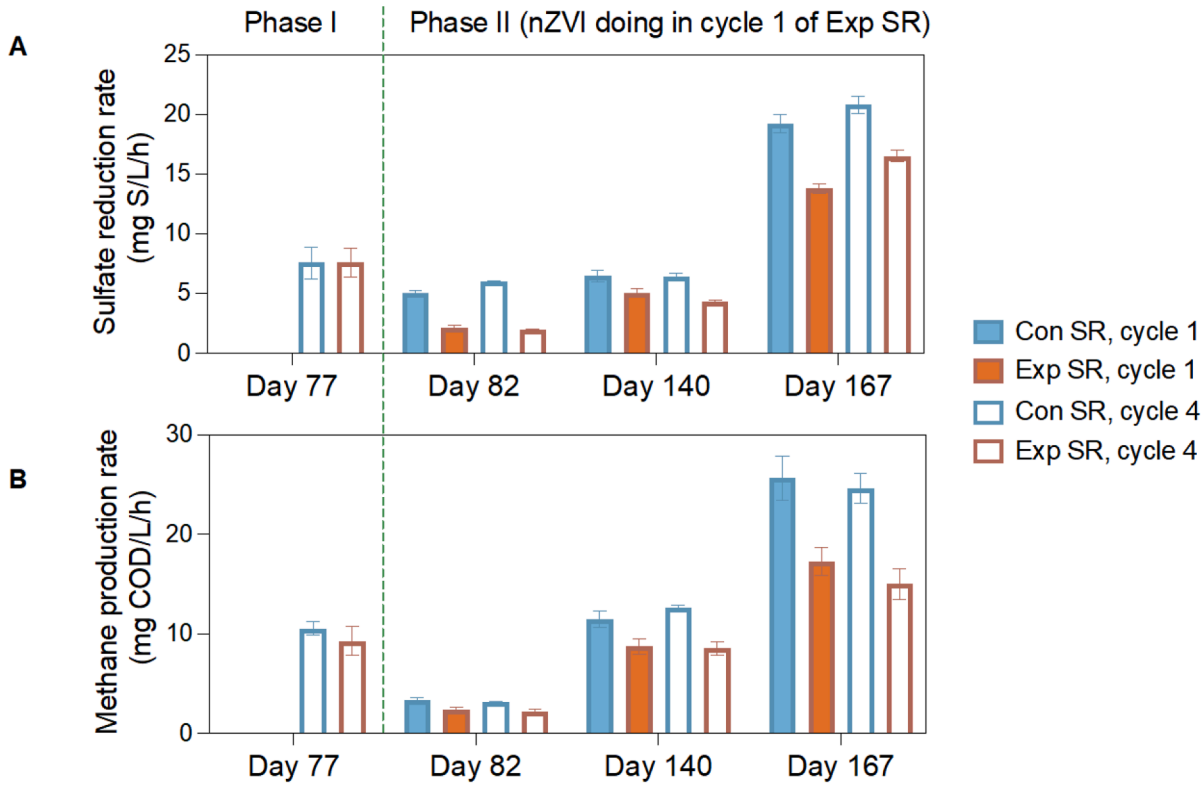

Fig. 4. Sulfate-reduction and methane production rates of the control and experimental sewer reactors on day 77 (baseline), 82 (the first day of nZVI addition), 140 (~two months of long-term nZVI addition) and day 167 (~three months of long-term nZVI addition). The value and standard errors represent the slopes of linear regression of sulfate and dissolved methane concentrations profiles during the first hour.

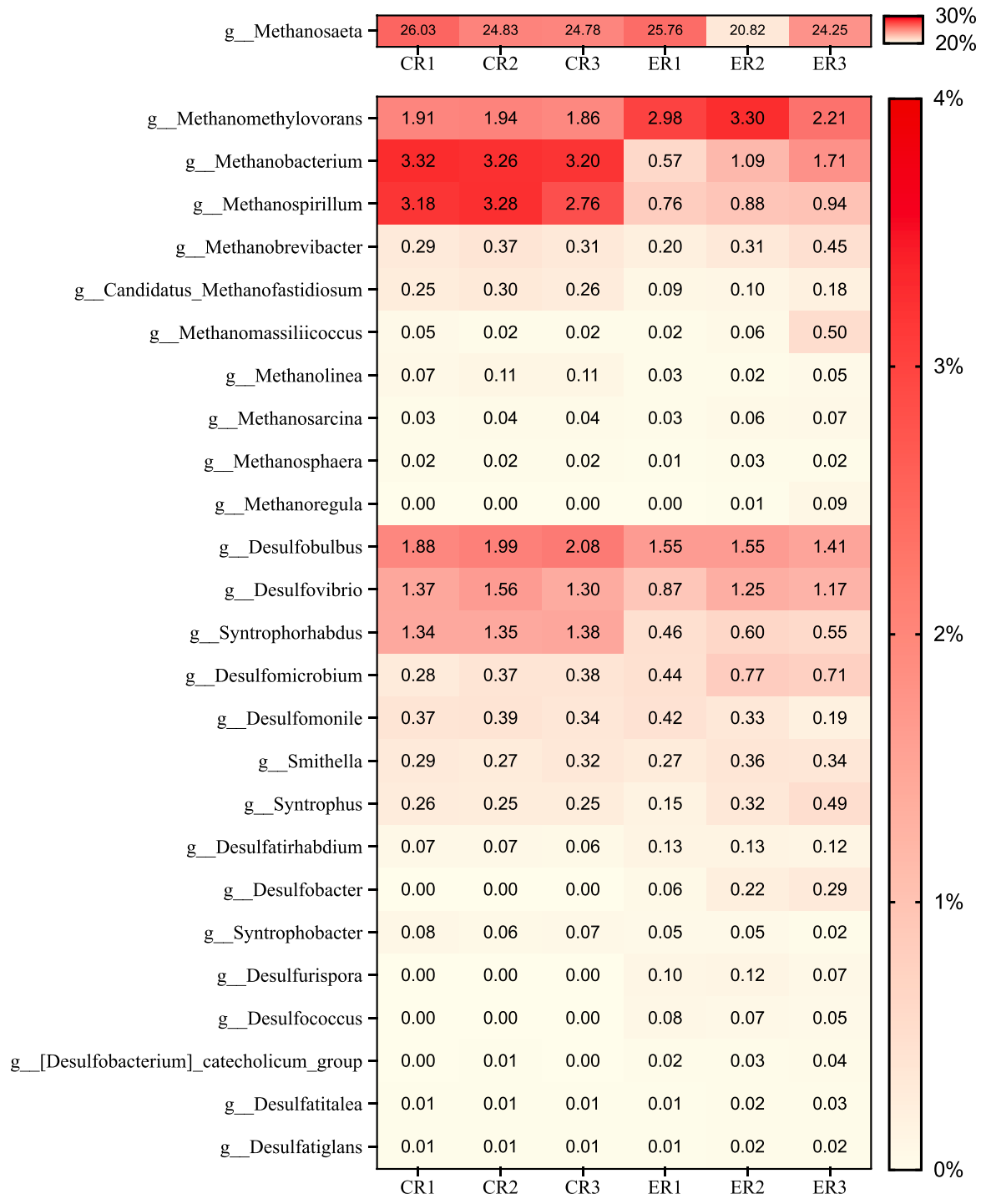

Fig. 5. Heatmap summarizing the sequencing results of MA and SRB in the biofilms of the control and experimental reactors at the end of Phase II.

illustrated in Fig. 6. The differences in total iron concentrations between the effluents of the two sewer reactors from cycle 1 and cycle 4 were 18.9±2.1 mg Fe/L (equivalent to iron mass of 47.3±5.3 mg) and 1.6 ±0.3 mg Fe/L (equivalent to iron mass of 3.9±0.8 mg), respectively. With a negligible iron loss in the SBR effluent (0.2±0.2 mg Fe/L), iron accumulated in the SBR WAS at a concentration of 67.9±8.8 mg Fe/L. Theoretically, if the iron dosed in sewers could run off into downstream WWTPs, it should accumulate in the downstream activated sludge at a concentration determined by the SBR HRT (0.85 d in this study) and SRT (12 d in this study), which is expected to be 14.1 times that in the sewer reactor effluent (i.e., SBR influent). Thus, by considering the total iron concentration in SBR effluent, the theoretical average iron concentration in sewer reactor effluent is 5.0±0.7 mg Fe/L (equivalent to 49.7±6.6 mg Fe/d), which is closed to the measured iron mass in the sewer reactor effluent from cycle 1. This suggests that, in the laboratory-scale reactor system, approximately 40 % of the dosed nZVI being transported downstream during cycle 1 (i.e., nZVI dosing cycle).

Before the additional iron transporting into the experimental SBR, the performance of the control and experimental SBR were comparable, having an insignificant mean difference of MLSS (5.3±46.7 mg/L) and the effluent of phosphate (0.10±0.20 mg P/L), ammonium (0.19±0.15 mg N/L) and total nitrogen (2.4±0.8 mg N/L) concentrations ($p > 0.05$) (Fig. 7). During Phase II, the additional iron in the experimental SBR resulted in MLSS concentration of 2061.4±145.1 mg/L, 16.9±6.2 %

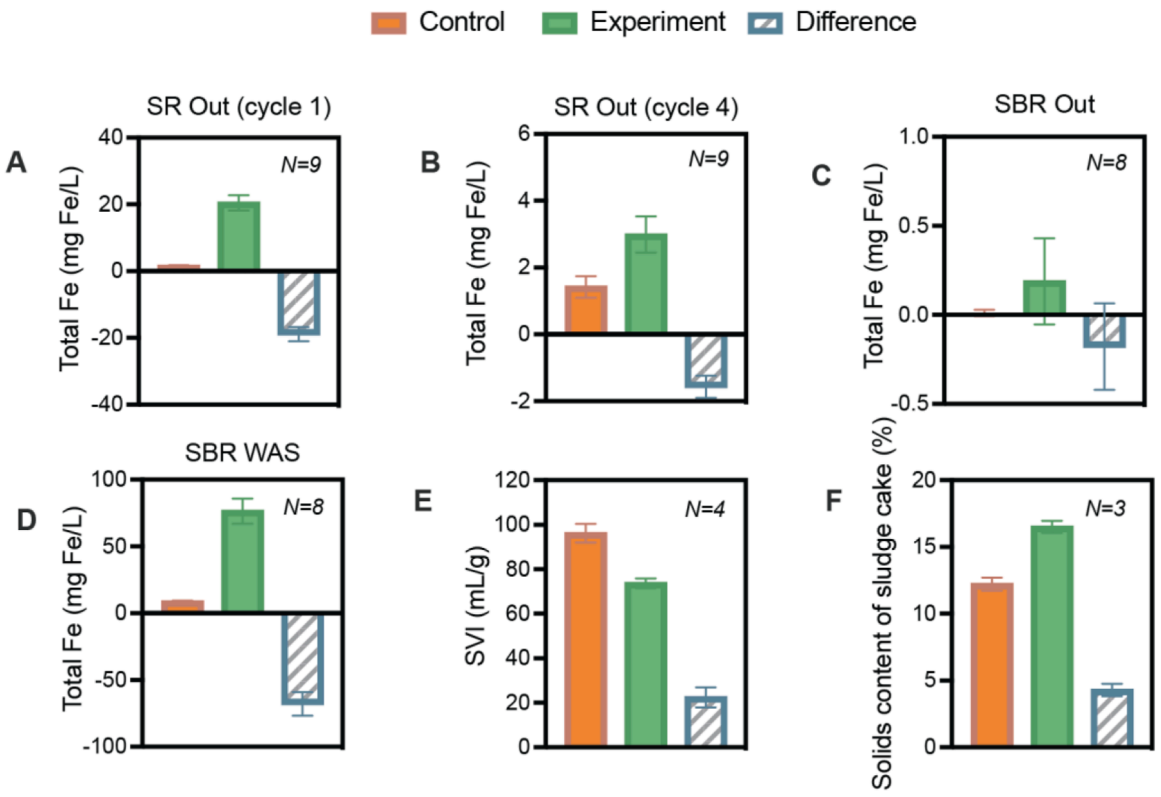

Fig. 6. Total iron concentrations in the control and experimental systems in Phase II: (A) sewer reactor out during cycle 1; (B) sewer reactor out during cycle 4; (C) SBR out and (D) waste activated sludge (WAS). Sludge properties of the WAS in Phase II: (E) sludge volume index (SVI) and (F) dewaterability. The third bar in each plot represents the mean difference and the associated standard error calculated as described in Section 2.7.

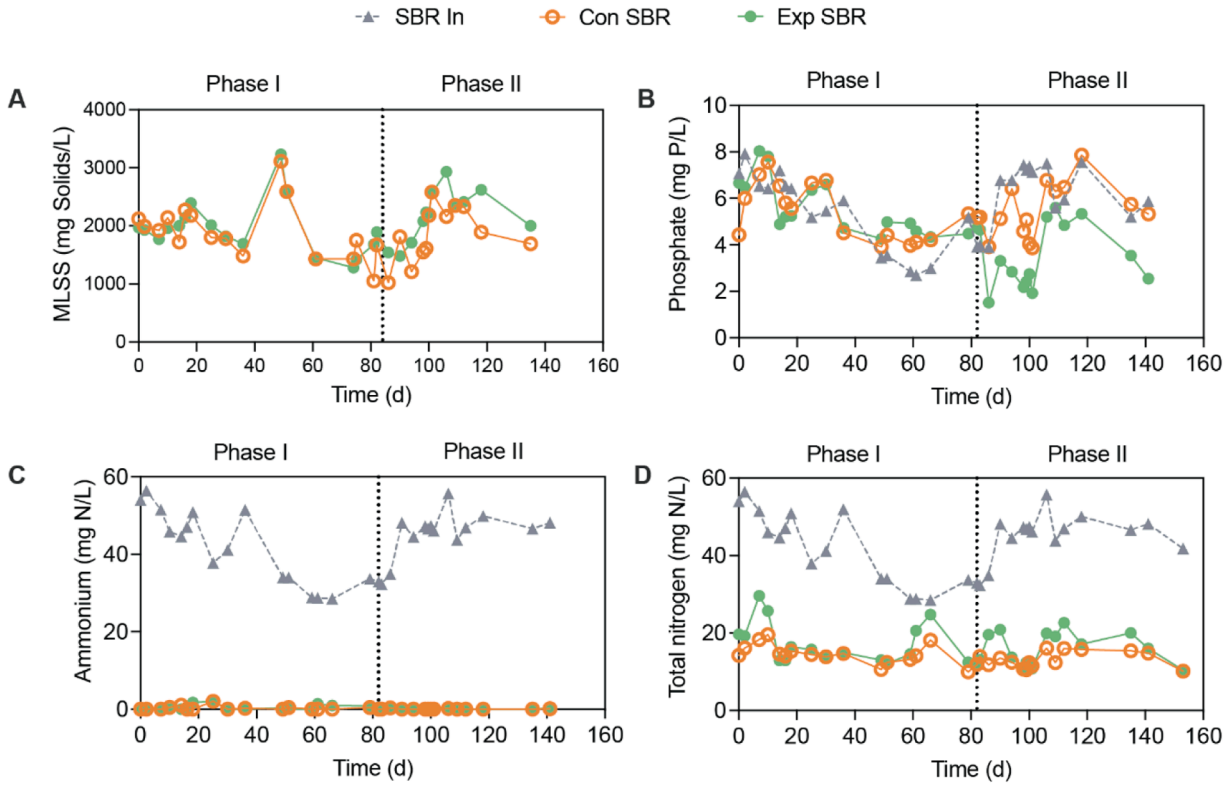

Fig. 7. Long-term monitoring SBR performance: (A) MLSS; (B) phosphate; (C) ammonium and (D) total nitrogen (ammonium + nitrite + nitrate).

higher than that of 1792.9±130.9 mg/L in the control. The sludge with accumulated iron, measured at 76.5±9.4 mg Fe/L compared to 8.7±0.7 mg Fe/L in the control, exhibited improved sludge settleability and dewaterability (Fig. 6e and 6f). The sludge settleability was improved by 22.9±4.0 % (22.5±4.5 mL/g), and dewaterability was improved by 35.3 ±4.6 % (4.3±0.5 %). These improvements could mitigate concerns about introducing more solids into WWTPs.

Consistent with previous comprehensive studies of the effects of sewer dosing with iron salts (Cen et al., 2025; Kulandaivelu et al., 2020; Rebosura et al., 2018), nZVI dosing in sewers did not negatively impact the downstream biological nitrogen removal process, while enhancing phosphorus removal (Fig. 7b, 7c and 7d). This was evident from the insignificant difference ($p > 0.05$) in ammonium (0.02±0.02 mg N/L) and total nitrogen concentrations (2.6±0.8 mg N/L) between two systems in the effluent. It was hypothesized that iron particles entering the SBR might aggregate, potentially mitigating their adverse impacts on downstream wastewater treatment performance while also regenerating iron to precipitate phosphates during aeration. The theoretical molar ratio of phosphorus removed (2.1±0.2 mg P/L) relative to the amount of iron (5.0±0.7 mg Fe/L) introduced to SBR was calculated to be 0.76 ±0.07 mol P/mol Fe (equivalent to 0.42±0.04 mg P/mg Fe).

4. Discussion

This study, for the first time, demonstrates the effectiveness of engineered nanomaterial nZVI in controlling both sulfide and methane in sewers and its flow-on impact on downstream wastewater treatment processes. Beyond the conventional precipitation and coagulation mechanisms of iron, commonly employed for sulfide and phosphorus removal as well as sludge settleability and dewaterability enhancement (Gutierrez et al., 2010; Rebosura et al., 2018), nZVI also functions as an inactivator, suppressing microbial activities in sewers due to its nano-scale properties. These combined chemical and biological actions of nZVI offer an integrated solution to addressing key environmental challenges in urban wastewater management. nZVI particles were freshly synthesized weekly to partially mitigate the loss of reactivity over time. By implementing an intermittent dosing strategy of nZVI (i.e., 50 mg Fe/L for 6 h every day), the response of SRB and MA activities to long-term nZVI dosing is distinctive. Although nZVI initially inhibits SRB activity, SRB activity tends to recover with prolonged dosing, which is commonly discovered in sewer biofilm studies with other biocidal additives, such as free ammonia (FA), ferrate and free nitrous acid (FNA) (Jiang et al., 2013; Yan et al., 2020; Zuo et al., 2020). Meanwhile, methanogenic activity exhibited a gradual and sustained inhibition, with no significant signs of recovery over three months of nZVI addition.

The microorganisms within these sewer biofilms are embedded in a slimy extracellular matrix (Yan et al., 2020), which limits the direct contact between nZVI and the microorganisms located in the inner layer of biofilms, a key requirement for nZVI to exert its toxic effects (Lefevre et al., 2016). SRB and MA occupy distinct zones within the stratified biofilms. Previous research has shown that SRB predominantly inhabit the upper surface of the biofilm, while MA are concentrated in the deeper layers (Liu et al., 2023; Sun et al., 2014). Consequently, SRB are more vulnerable to initial nZVI exposure, leading to a significant reduction in sulfate reduction rates compared to the control. In contrast, MA in the deeper zones are protected from nZVI exposure due to mass transfer limitations. With prolonged nZVI addition, SRB might migrate deeper within the biofilm, allowing their activity to persist. This hypothesis supports that SRB activity is not entirely inhibited despite long-term exposure to 50 mg Fe/L of nZVI. As expected, iron particles may deposit and accumulate on the biofilm surface (Kulandaivelu et al., 2019; Liu et al., 2023). This accumulation likely restricts the access of substrates, such as sulfate and organic carbon, to the microorganisms, potentially leading to inhibited biological activities. Given that the higher affinity of SRB to organic carbon compared to MA (Gutierrez et al., 2016), methanogenic activity might be more effectively suppressed under these conditions. In this regards, nZVI dosing strategy may be particularly effective in suppressing biological activities in thin sewer biofilms, such as in sewer pipelines with high flow rates and short HRT. It should be noted that the results were obtained in laboratory sewer reactors, where the shear force that might slough biofilm is significantly lower than that in real sewer systems. This difference likely results in biofilms with varying thickness and morphology. Consequently, adding nZVI in real sewer systems could potentially have better performance in reducing sewer biofilm activities but requires validation.

Additionally, nZVI chemically removed the formed sulfide at the molar ratio of 0.20±0.02 mol S/mol Fe (or 0.12±0.01 g S/g Fe) observed in this study, which closely aligns with the sulfide uptake capacity of nZVI (~0.18 mol S/mol Fe) reported in a kinetic study conducted at a dosed S/Fe molar ratio of 0.224 (Fan et al., 2013). Two stages have been postulated for the sulfidation of nZVI in the literature: a surface reaction between nZVI and sulfide (rapid reaction), and the transformation from nZVI to FeS (slow reaction) (Fan et al., 2013; Garcia et al., 2021; Xu et al., 2019). The first step involves the instantaneous sulfide adsorption onto the iron oxides (Fe_xO_y) and hydroxides ($Fe(OH)_x$) coating on nZVI, forming a surface complex of Fe(II)–HS^-. However, the formation of a passivating FeS_x layer limits further sulfur uptake, and thus only a limited amount of sulfur can be incorporated with nZVI surface. The second stage is the slower formation of FeS precipitates. Therefore, the deposited zero-valent iron particles on sewer biofilms are thus likely to further precipitate dissolved sulfur, but this process requires a longer reaction time. This may explain why, during the nZVI dosing cycle, the sulfide-to-nZVI ratio of 0.12±0.01 g S/g Fe is lower compared to other iron materials, such as magnetite nanoparticles (0.26 g S/g Fe), $FeCl_3$ (0.43 g S/g Fe) and $FeCO_3$ (0.58±0.05 g S/g Fe) (Cen et al., 2025; Lin et al., 2017; Rebosura et al., 2018). nZVI dosing in sewers slightly elevates sewage pH by 0.04 units (Figure S4). This effect mitigates the acidification caused by conventional iron salts (e.g., $FeCl_3$), which consume alkalinity and lower sewage pH, potentially influencing the iron dosage required for complete sulfide control. Moreover, nZVI offers notable benefits to downstream wastewater treatment plants (WWTPs), including phosphate removal and sludge settleability and dewaterability improvement. These downstream benefits were comparable to those achieved by $FeCl_3$ dosing in sewers (Rebosura et al., 2018). Additionally, by reducing sewer microbial activities, nZVI dosing in sewers preserved COD to some extent (Figure S5), which could be advantageous for WWTP receiving sewage with insufficient COD for complete denitrification (Cen et al., 2023a). Overall, the downstream benefits make nZVI dosing in sewers a more cost-effective option for both sewer management and WWTP operations. nZVI aggregation is a key factor to assess its integrated application in urban wastewater systems. As nZVI concentration increases, the aggregation rate also increases, leading to the formation of larger nanoparticle clusters that settle down more quickly (Phenrat et al., 2007; Wang et al., 2022). This limits their reuse in downstream wastewater treatment processes. However, the iron that accumulated in sewer biofilms or sediments presents an opportunity for advanced oxidation process through oxygen or air injection. This, approach, recently demonstrated by Liu et al. (2023), has been shown to further inhibit sulfidogenic activity and promote sulfide oxidation. Nevertheless, sewer systems are dynamic in flow and wastewater composition, and future studies in real conditions of sewer systems are necessary.

It should be acknowledged that the relatively high price of nZVI could raise concerns, particularly if there is no demand for methane control. Based on the long-term results presented in Section 3.2 and the chemical cost of nZVI provided by the supplier ($1.2/100 g), the cost of nZVI dosing to remove an average sulfide concentration of 5.3 ± 0.5 mg S/L was estimated at $28.5/kg S. This is higher than conventional iron dosing practices, which range from $5–8/kg S for $FeCl_3$ and $11.5/kg S for $FeCl_2$ (de Lis et al., 2007; Nielsen et al., 2005; Saracevic et al., 2007; Yan et al., 2020). However, this study is limited in examining a single dosing scheme. Given the higher reactivity of nZVI and its reported peak

contaminant removal capacity within the first 2 h of reaction, followed by a decline (Calderon and Fullana, 2015), there is potential to reduce chemical costs by minimizing the required exposure time for nZVI treatment in sewers. Therefore, further investigation is needed to optimize dosing strategies and investigate the underlying mechanisms.

5. Conclusion

The effectiveness of nZVI dosing in sewers for sulfide and methane control, as well as its flow-effects on downstream wastewater treatment processes were investigated through laboratory-scale reactor systems, consisting of sewer reactors and SBR. The main findings are summarized as follows:

- Intermittent dosing of nZVI at 50 mg Fe/L for 6 h every day effectively reduced sulfide and methane discharges in sewer reactors, leading to simultaneous reduction of microbial activities and sulfide removal.
- SRB and MA in sewer biofilms responded differently to nZVI. While the sulfate-reduction rate was initially inhibited but gradually recovered with prolonged exposure, methanogenic activity remained partially inhibited. Moreover, nZVI removed sulfide at a molar ratio of 0.20±0.02 mol S/mol Fe, enhancing sulfide control performance.
- nZVI dosing showed no adverse effects on downstream biological removal processes. Instead, it delivered multiple benefits, including phosphorous removal at a molar ratio of 0.76±0.07 mol P/mol Fe, and sludge settleability and dewaterability improvement.

This study explored the potential of integrating the use of nZVI in urban sewer and wastewater treatment systems. However, further research is required to optimize nZVI dosing strategies and elucidate the underlying mechanisms.

CRediT authorship contribution statement

Xiaotong Cen: Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Zhetai Hu:** Supervision, Resources, Investigation. **Zhigang Yu:** Methodology, Investigation. **Xin Huang:** Methodology, Investigation. **Zhiqiang Zuo:** Resources, Methodology. **Jianhua Guo:** Writing – review & editing, Resources. **Zhiguo Yuan:** Writing – review & editing, Validation, Supervision. **Min Zheng:** Writing – review & editing, Validation, Supervision, Resources, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.watres.2025.123248.

Data availability

Data will be made available on request.

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