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Removal of Pharmaceuticals and Illicit Drugs from Wastewater Due to Ferric Dosing in Sewers

Abstract

Ferric (Fe^{3+}) salt dosing is an efficient sulfide control strategy in the sewer network, with potential for multiple benefits including phosphorus removal in the biological reactors and sulfide emission control in the anaerobic digesters of wastewater treatment plant (WWTP). This paper extends the knowledge on the benefit of iron dosing by exploring its impact on the fate of organic micropollutants (MPs) in the wastewater using sewer reactors simulating a rising main sewer pipe. The sulfide produced by the sewer biofilms reacted with Fe^{3+} forming black colored iron sulfide (FeS). Among the selected MPs, morphine, methadone, and atenolol had >90% initial rapid removal within 5 min of ferric dosing in the sewer reactor. The ultimate removal after 6 h of retention time in the reactor reached 93-97%. Other compounds, ketamine, codeine, carbamazepine, and acesulfame had 30-70% concentration decrease. The ultimate removal varied between 35 and 70% depending on the biodegradability of those MPs. In contrast, paracetamol had no initial removal. The rapid removal of MPs was likely due to adsorption to the FeS surface, which is further confirmed by batch tests with different FeS concentrations. The results showed a direct relationship between the removal of MPs and FeS concentration. The transformation kinetics of these compounds in the reactor without Fe^{3+} dosing is in good agreement with biodegradation associated with the sewer biofilms in the reactor. This study revealed a significant additional benefit of dosing ferric salts in sewers, that is, the removal of MPs before the sewage enters the WWTP.

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Removal of pharmaceuticals and illicit drugs from wastewater due to ferric dosing in sewers

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KEYWORDS. Micropollutants, adsorption, iron sulfide, biodegradation, sewer, ferric dosing

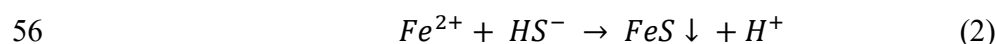
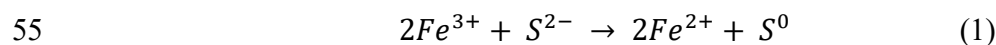
ABSTRACT. Ferric (Fe^{3+}) salt dosing is an efficient sulfide control strategy in the sewer network, with potential for multiple benefits including phosphorus removal in the biological reactors and sulfide emission control in the anaerobic digesters of wastewater treatment plant (WWTP). This

18 paper extends the knowledge on the benefit of iron dosing by exploring its impact on the fate of
19 organic micropollutants (MPs) in the wastewater using sewer reactors simulating a rising main
20 sewer pipe. The sulfide produced by the sewer biofilms reacted with Fe^{3+} forming black coloured
21 iron sulfide (FeS). Among the selected MPs, morphine, methadone and atenolol had >90% initial
22 rapid removal within five minutes of ferric dosing in the sewer reactor. The ultimate removal after
23 6 h of retention time in the reactor reached 93-97%. Other compounds, ketamine, codeine,
24 carbamazepine and acesulfame had 30-70% concentration decrease. The ultimate removal varied
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26 had no initial removal. The rapid removal of MPs was likely due to adsorption to the FeS surface,
27 which is further confirmed by batch tests with different FeS concentrations. The results showed a
28 direct relationship between the removal of MPs and FeS concentration. The transformation kinetics
29 of these compounds in the reactor without Fe^{3+} dosing is in good agreement with biodegradation
30 associated with the sewer biofilms in the reactor. This study revealed a significant additional
31 benefit of dosing ferric salts in sewers, that is the removal of MPs before the sewage enters the
32 WWTP.

33 **INTRODUCTION.** Hydrogen sulfide in sewers causes serious cracking and failure of the
34 concrete structure, malodor and human health problems ^{1,2}. Billions of dollars are expended every
35 year due to the need for rehabilitation or replacement of the corroded sewer pipes ³. The anaerobic
36 condition in the rising main induces the growth of stratified biofilms comprising of sulfate-
37 reducing bacteria (SRB) and methanogenic archaea (MA)⁴. The SRB reduce sulfate in the
38 wastewater and produce sulfide that subsequently transfers to the gas phase in the gravity sewers.
39 The H_2S gas induces sewer corrosion by forming sulfuric acid on the concrete surface ⁵.

40 Chemicals are commonly used for the control of sulfide, including i) chemical oxidation of
41 sulfide by the injection/addition of air, pure oxygen, nitrate salts ^{1, 6-8}, ozone, hydrogen peroxide,
42 hypochlorites, chlorine and potassium permanganate ^{9, 10} ii) pH elevation by the addition of alkali
43 such as Mg(OH)₂ and iii) precipitation of sulfide by forming insoluble metal particles through the
44 addition of metal salts such as iron, zinc, lead and copper salts ². Among the various metal salts
45 used, iron based salts were shown to be most efficient because of its specificity to H₂S ¹¹. In
46 Australia iron salts accounted for 66% of the sewage flow dosed with chemicals for sulfide control
47 ¹².

48 The iron salt dosing in the sewers is effective in the control of dissolved sulfide by the formation
49 of iron sulfide particles ^{2, 13-15}. These studies showed that the mechanism responsible for the
50 removal of sulfide includes the precipitation reaction of Fe²⁺ ions with sulfide forming ferrous
51 sulfide (FeS), while Fe³⁺ ions oxidizes sulfide chemically to elemental sulfur, with itself being
52 reduced to Fe²⁺, which subsequently precipitates sulfide (Equation 1&2). The continuous dosing
53 of iron salts for two months significantly inhibits the SRB and MA production in the long run,
54 leading to reduced demand for iron salts ².



57 Further studies found that FeS particles formed in the sewer network can be oxidized in the
58 aerobic activated sludge reactor. This enables phosphorus removal at a ratio of 0.44 and 0.37
59 mg P/mg of Fe²⁺ and Fe³⁺ added to the sewer network ¹³. The iron dosing (e.g. 5–20 mg-Fe/L) to
60 the sewer network was also demonstrated to provide iron for H₂S emission control in the anaerobic
61 digester by forming iron sulfide particles ¹⁶. Previous studies have demonstrated the multiple
62 benefits of iron salts dosed into sewers, including sewer corrosion and odour control, phosphorus
63 removal and biogas desulfurization ¹⁷.

64 Iron salt was shown to be an effective coagulant for the removal of MPs such as pharmaceuticals
65 and personal care products (PPCPs) in the drinking water treatment systems and WWTPs¹⁸⁻²⁰.
66 Organic MPs are ubiquitous in wastewater, and are recalcitrant to the traditional secondary
67 treatment processes. The MPs thus find their way in the aquatic environment and can have adverse
68 effects on aquatic organisms^{21,22}. Before entering the WWTP, MPs go through the sewers with
69 sewage flow and there is very limited understanding about their fate and transformation in the
70 sewers. Some recent studies focused on the biological transformation of organic MPs in the sewer
71 network due to the presence of biofilms²³⁻²⁵. Also, there are a couple of studies focused on the
72 biodegradation of pharmaceuticals and illicit drugs in the sewer network^{26,27}.

73 However, no study has systematically investigated the impact of iron salt dosing on the removal
74 of MPs in the sewer network. Considering the coagulating nature of iron salt and the adsorbing
75 nature of iron sulfide particles²⁸, it is hypothesized that there can be additional removal of some
76 MPs due to iron dosing on top of in-sewer biodegradation.

77 Collectively speaking, ferric dosing is one of the most widely used strategy to control sewer odor
78 corrosion and odor, with additional beneficial effects on the downstream WWTP. The main
79 objective of this study is to investigate the fate and removal of selected organic MPs from
80 wastewater due to ferric dosing and biological processes in the sewer network. Experiments using
81 laboratory-scale rising main sewer reactors were carried out with selected MPs, including
82 pharmaceuticals and illicit drugs in the wastewater. To understand the removal mechanisms of
83 MPs, batch tests were conducted with different levels of iron sulfide precipitate that was identified
84 and characterized with advanced electron microscopic analysis.

85 **2. MATERIALS AND METHODS**

86 **2.1. CHEMICALS.** The reagent grade ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) was purchased from Sigma
87 Aldrich (NSW, Australia). All the drugs and pharmaceuticals were purchased from Cerilliant
88 (Texas, US) and Sigma Aldrich (NSW, Australia). The selected MPs include ketamine,
89 methadone, morphine, codeine, carbamazepine, atenolol, paracetamol and acesulfame and their
90 properties are presented in Table S1. The compounds were selected to represent the hydrophobic
91 and hydrophilic MPs in the wastewater. The octanol-water partition coefficient is arranged in the
92 ascending order in table S1 (Acesulfame being hydrophilic and methadone hydrophobic). Spiking
93 solutions were prepared in Milli-Q water before being spiked in to the reactors. Liquid
94 Chromatography grade methanol was purchased from Merck, Germany. Deionized water was
95 produced by a Milli-Q system (Millipore, $0.22 \mu\text{m}$ filter, $18.2 \text{ m}\Omega \cdot \text{cm}^{-1}$).

96 **2.2. WASTEWATER CHARACTERISTICS.** The wastewater used in this study was collected
97 from a local sewer wet well (St. Lucia, Brisbane, Queensland) every week and was stored in the
98 cold room at $-4 \text{ }^\circ\text{C}$. The sewage typically contained sulfate at concentrations of 10-25 mg-S/L,
99 sulfide at $<3 \text{ mg-S/L}$, soluble chemical oxygen demand (sCOD) at 200-300 mg/L, volatile fatty
100 acids at 50 - 120 mg-COD/L and ammonium at approximately 50 mg-N/L. Negligible amounts of
101 sulfite, thiosulfate ($<1 \text{ mg-S/L}$), nitrate and nitrite ($<1 \text{ mg-N/L}$) were present. The background
102 micropollutant concentration in the feed wastewater includes methadone ($<0.1 \mu\text{g/L}$), morphine
103 ($0.15\text{-}2 \mu\text{g/L}$), atenolol ($0.8\text{-}1 \mu\text{g/L}$), ketamine ($<0.1 \mu\text{g/L}$), codeine ($0.6\text{-}2 \mu\text{g/L}$), carbamazepine
104 ($0.5 \mu\text{g/L}$), acesulfame ($10\text{-}12 \mu\text{g/L}$), paracetamol ($75\text{-}130 \mu\text{g/L}$). The paracetamol was not spiked
105 into the reactor considering its high background concentration.

106 **2.3. LABORATORY-SCALE SEWER REACTORS.** Two parallel lines, one control and one
107 experimental, of laboratory-scale sewer reactors were designed and set up to simulate rising main
108 sewers (Figure S1). The reactors were made of PerspexTM with a volume of 0.75 L (diameter 80

109 mm and height 149 mm) and an A/V ratio of 70.9 m^{-1} . Mixing was continuously provided by a
110 magnetic stirrer (Heidolph MR3000) at 250 rpm.

111 The wastewater described in section 2.2 was heated to 20°C using the heating coil before being
112 pumped into the reactor. The feed pumping event occurred for 2 min at a flow rate of 350 mL/min
113 for every 6-hr. The reactors were operated continuously for more than a year allowing for the
114 development of biofilms. The biological activities of the reactors were monitored by the dissolved
115 sulfide and methane production. Baseline monitoring of the systems showed consistent sulfide,
116 sulfate, and methane profiles over days for four months, suggesting that the pseudo-steady state
117 conditions were established in the systems.

118 The experimental line was dosed with FeCl_3 in the sewer reactor to study its impacts on the
119 sulfide and methane production in sewers. From this point, the experiment reactor will be
120 represented as ferric dosed reactor. The addition of FeCl_3 was initiated upon the establishment of
121 pseudo-steady state of the reactors. Fe^{3+} was added from a stock solution prepared from reagent-
122 grade ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$). The stock solution was prepared weekly by dissolving
123 appropriate amounts of ferric salts in deoxygenated water containing 0.01M HCl (to prevent ferric
124 hydroxide precipitation). The deoxygenated water was prepared by bubbling purified N_2 in
125 Milli-Q water for 1-hr. The Fe^{3+} stock solution was added into experimental rising main reactor
126 during each pumping event resulting in a theoretical Fe^{3+} concentration of 10 mg-Fe/L.

127 **2.4. EXPERIMENTS OF MICROPOLLUTANTS REMOVAL IN SEWER REACTORS.**

128 Cycle experiments (6-hr) were conducted in the two lines of sewer reactors to investigate the
129 impact of ferric dosing on the selected MPs (Figure S1). Fresh wastewater was used for each
130 experiment. After the pumping event, the targeted MP compounds were spiked separately in both
131 the control and experimental reactors and a thorough mixing was provided. The background

132 concentration of the spiked compounds was also analysed to quantify the exact concentrations
133 spiked. Wastewater samples were taken at a time interval of 1-hr throughout the cycle time of the
134 reactor (6-hr) after the experiment started. For each time point, 2 mL of sample was filtered into a
135 vial using 0.22 μm PES membrane syringe filter (Tullagreen, Ireland) and 20 μL of 2M HCl was
136 added to adjust each of the samples to pH 2. The acidified samples were then frozen at -20°C
137 until analysis. Hourly samples were taken for the analysis of sulfur compounds (sulfate, sulfide,
138 thiosulfate and sulfite) and dissolved methane. The total metal concentration of the samples was
139 also taken on an hourly basis. Duplicate experiments were performed for each cycle test.

140 **2.5. BATCH TESTS WITH DIFFERENT FeS CONCENTRATIONS.** The scope of the batch
141 tests is to reduce the complexity by avoiding biodegradation due to sewer biofilms and to find out
142 the sorption behavior of selected MPs on the suspended iron sulfide particles. The batch
143 experiments were conducted with serum bottles enclosed tightly with a rubber stopper to maintain
144 the anaerobic condition. Before the experiment, the wastewaters were flushed with N_2 until the
145 dissolved oxygen becomes negligible.

146 The wastewater containing iron sulfide particles formed in the ferric dosed sewer reactor was
147 taken and mixed with fresh sewage, either filtered or unfiltered, at three different ratios (1:2, 1:10
148 and 1:50). The filtration was done with 5 micron water cartridge filter, to remove suspended solids.
149 Selected MPs were then spiked in the wastewater mixture in the serum bottles. The bottles were
150 mixed in an orbital shaker (Lab-line instruments model 3520 and at 150 rpm) covered with
151 aluminum foil to avoid potential photo-transformation process. The batch tests were carried out
152 for 1-hr with the sampling interval of 15 min. Wastewater samples were taken as described in 2.4
153 for the analysis of selected MPs.

154 **2.6. CHEMICAL ANALYSIS.** The analysis of organic MPs in this study was based on a
155 previously developed analytical method ²⁴. Briefly, analysis was performed using liquid
156 chromatography (Shimadzu Prominence) coupled to a tandem mass spectrometer (AB-SCIEX
157 5500® QTrap) with electrospray ionization source in positive mode. Chemical separation was
158 achieved on a Kinetex Biphenyl column (Phenomenex, 50 × 2.1 mm, 2.6 μm) using the mobile
159 phase of (A) 1% methanol and 99% Milli-Q water and (B) 95% methanol and 5% Milli-Q water;
160 both with 0.1% acetic acid, at the gradient: 5% B, 0–1 min; 100% B at 7.5 min for 3 min; 5% B at
161 9.6 min for 3.4 min. The flow rate was set at 0.3 mL/min and the injection volume was 8 μL. The
162 MS was operated in multiple reaction monitoring (MRM) mode for data acquisition ²³. The matrix
163 spike samples were used in the analytical batch and the recovery % ranged between 90-105%.

164 Dissolved inorganic sulfur species (i.e. sulfide, sulfate, sulfite, and thiosulfate) were measured
165 using ion chromatography (IC) coupled with a UV and conductivity detector (Dionex ICS-2000).
166 The methane analysis was performed using BD vacuum tubes. The samples were allowed to reach
167 gas/liquid equilibrium overnight and the gas phase methane was analysed using a Shimadzu GC-
168 9A gas chromatography equipped with flame ionization detector. The concentrations of methane
169 in the wastewater were calculated using mass balance and Henry's law. The metal concentration
170 of the samples were analysed using Inductively Coupled Plasma- Optical Emission Spectroscopy
171 (ICP-OES optima 7300 DV). The samples were digested using 10% nitric acid before being
172 analysed.

173 **2.7. CHARACTERIZATION OF PARTICLES FORMED BY FERRIC DOSING.** To
174 characterize the suspended particles in the ferric dosed sewer reactors, wastewater was sampled
175 with a syringe and filtered immediately using a vacuum filter to avoid the interference of oxygen
176 during the sample preparation. The precipitate samples were dried overnight in a vacuum oven

177 (SEM/SA OVEN 718). These particles were then tested for its properties using scanning electron
178 microscopy-Energy dispersive X-ray spectrometry (SEM-EDS). The chemical composition of the
179 particles was further analysed using X-ray diffraction technique (XRD).

180 The vacuum dried particles were coated twice by the carbon coater (Quorum Q150T, UK),
181 following the three heavy-burst model to obtain the carbon thickness of 30-40 nm. The
182 microstructure and elemental composition of the particles were examined by SEM (JEOL JSM-
183 6610, America) equipped with a detector (Oxford 50 mm² X-Max SDD x-ray) that enables
184 simultaneous imaging and elemental analysis at high count rates with 125 eV energy resolutions.
185 The EDAX software (EDAX, AMETEK Inc.) was utilized, at a frame resolution of 1024×800,
186 with a dwell time of 200 s/frame, to collect 16 frames for each region of interest. The locations for
187 spot analyses were chosen by examining features of the back scattered electron image. The mineral
188 compositions of the particles were tested by XRD (Bruker D8 Advance MKII). X-rays were
189 generated at 40 kV and 40 mA, with a scanning speed of 2.0 deg/min, and a scanning range of 10–
190 100°. The composition identifications were carried out using Jade software (version 5) and pdf-2
191 crystal structure database.

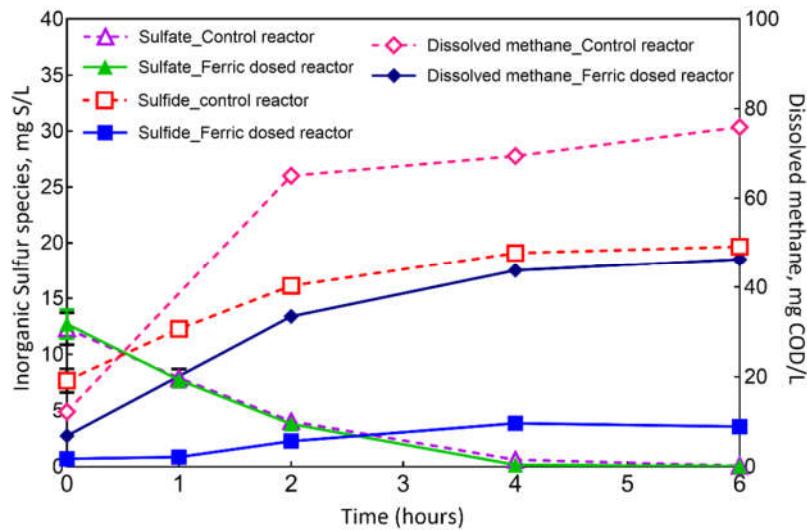
192 **2.8. TRANSFORMATION MODEL.** First-order kinetics (equation 3) was used to simulate the
193 transformation of the investigated compounds in the sewer reactors. For control reactor, simulation
194 starts at the time right after spiking (t_0). For the ferric dosed reactor, simulation starts at 5 min
195 after spiking (t_5), due to the rapid initial removal of some investigated compounds.

$$196 \quad C_t = C_0 \cdot e^{-k_{bio} \cdot t} \quad (3)$$

197 where C_t is concentration (ppb) at time t , C_0 is initial concentration (ppb), k_{bio} (h^{-1}) represents the
198 overall biomarker transformation in control and ferric dosed reactor with anaerobic condition and
199 biofilm. Determinations of k_{bio} use the Bayesian statistic method ²⁹

200 3. RESULTS AND DISCUSSION

201 **3.1 EFFECT OF FERRIC DOSING ON THE BIOLOGICAL PERFORMANCE OF THE**
202 **SEWER REACTORS.** Typical concentration profiles of dissolved sulfide, sulfate and methane
203 during a 6-hr batch test are shown in Figure 1. The wastewater in the reactors had a pH around 6.7
204 – 6.9. The sulfate reduction rates were 1.6 ± 0.7 and 1.7 ± 0.7 mg-S L⁻¹ h⁻¹ for the control and
205 ferric dosed reactor, respectively. The dissolved sulfide concentration in the ferric dosed reactor
206 was notably lower than the control reactor, with effluent concentration at 3.6 ± 0.1 compared to
207 19.7 ± 0.2 mg-S L⁻¹ h⁻¹ for the control reactor without ferric dosing. Considering similar sulfate
208 reduction in both reactors, the sulfide removal due to the dosing of FeCl₃ happened simultaneously
209 with sulfide production in the ferric dosed sewer reactor. The methane production rates were 12.3
210 ± 3.4 and 7.3 ± 1.5 mg-COD L⁻¹ h⁻¹ for the control and ferric dosed reactor, respectively. The
211 methane production in the ferric-dosed reactor had been reduced by 38%. The microbial
212 community analysis of the sewer biofilms also emphasize the reduction in the relative abundance
213 of MA in the ferric dosed reactor compared to the control reactor. The SRB community was not
214 affected by the ferric dosing (Section S4). The sulfate reduction and methanogenesis in the control
215 reactor are comparable to the previous reported values^{23, 25, 30-32}.



216

217 **Figure 1.** Concentration profiles of sulfur compounds and dissolved methane in the control and
 218 ferric dosed rising main sewer reactors (error bars are the error calculated from triplicates. For
 219 some points, the error bars are shorter than the height of the symbol and thus are not shown)

220 The ferric dosing in the rising main sewer reactor leads to the removal of dissolved sulfide,
 221 forming iron sulfide particles². The total suspended solids in the ferric dosed reactor were $550 \pm$
 222 90 mg/L, which is about 4 times higher than the control reactor due to the formation of particles.
 223 Zhang, et al.² observed the inhibition of methanogenic activity of the rising main reactor by about
 224 52-80% after two months of Fe^{3+} addition. Utgikar, et al.³³ hypothesized the deposition of metal
 225 sulfides on the surface of SRB and MA could cause the inhibition of these cells. The ferrous sulfide
 226 particles in close vicinity to the cells may reduce the access of reactants such as volatile fatty acids
 227 to the necessary enzymes. This could be the likely cause for the reduced methane production in
 228 the ferric-dosed reactor. In contrast, the SRB activity of the ferric dosed reactor in this study was
 229 not affected, contrary to what reported by Zhang, et al.² which may due to the high ferric dosing
 230 concentration (21 mg Fe^{3+} /L) used in the previous study.

231 **3.2 IRON SULFIDE PARTICLES.** The EDS elemental mapping analysis was performed on
232 particles collected from ferric-dosed sewer reactor to find the composition of the particles (Figure
233 S2a). The atomic % and the atomic ratio was calculated between iron and sulfide. The atomic ratio
234 between 0.8 – 1.1 (Table S4) suggests the speciation of the particles as FeS. Analysis of the
235 wastewater samples in the ferric-dosed reactor with ICP-OES also identified a molar ratio of Fe:S
236 to be around 1 (Table S5).

237 The SEM images (Figure S3) of the particles showed intergranular porous structure, likely due
238 to the formation of nanocrystalline mackinawite (FeS) particles that stacked irregularly^{34, 35}. To
239 further confirm this, XRD was used to identify the mineral forms of iron sulfide particles. Clearly,
240 theta-angle positions of the peaks from 10° to 100° as depicted in Figure S2b corroborate
241 mackinawite (FeS) as the main form of iron sulfide particles. The precipitation of mackinawite
242 might be a result of the reaction between Fe²⁺ and HS⁻, owing to the reduction of Fe³⁺ and sulfate
243 in the ferric dosed reactor, as shown in equation (1) & (2)

244 **3.3. REMOVAL OF ORGANIC MPS BY FERRIC DOSING IN THE SEWER REACTORS.**

245 The concentration profiles of selected organic MPs over the 6-hr cycle time in the control and
246 ferric-dosed sewer reactors are shown in Figure 2-Figure 4. For most MPs, a fast initial removal
247 was observed immediately after the spiking in the ferric dosed reactors followed by slower
248 biodegradation. The behavior and removal patterns of different compounds were thus discussed in
249 three groups distinguished by the different levels of initial removal. Group 1-3 organic MPs
250 showed high (>90%), medium (30-70%) and low (0%) levels of initial removal.

251 **3.3.1. GROUP 1. METHADONE, MORPHINE AND ATENOLOL.** The group 1 compounds
252 are classified as biodegradable organic MPs and also highly susceptible to the ferric dosing in

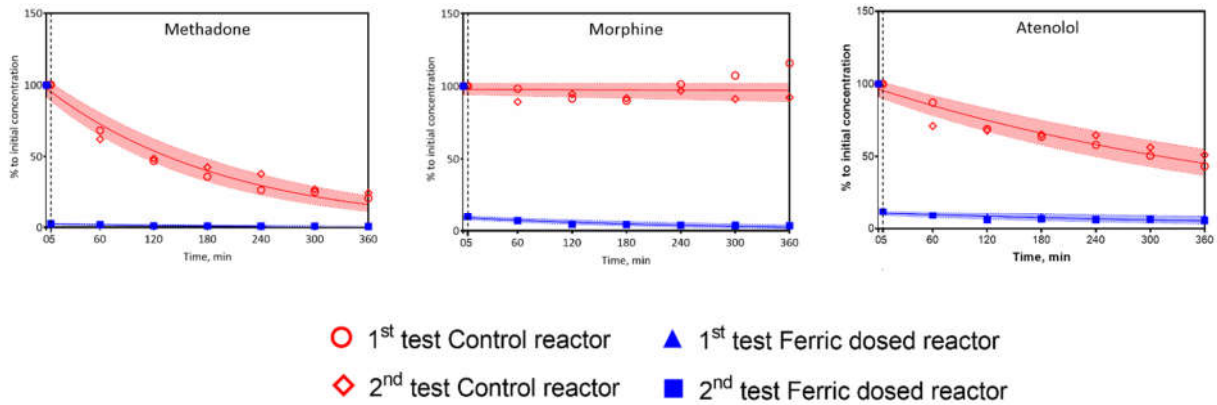
253 wastewater. The removal of methadone in the control reactor was 77 ± 3 % at the end of 6-hr
254 retention time. In the ferric dosed reactor, the removal of methadone within five minutes was 97.5
255 ± 0.1 % and after 6-hr it reached 99 ± 0.1 %. The removal obtained in control reactor is similar to
256 a previously reported removal of 76 ± 9 % in the rising main reactor over 12-hr²³. This removal
257 has been attributed to the biological degradation due to sewer biofilms, as confirmed by the
258 simulated biological transformation (Figure 2) with coefficients shown in Table S7. Formation of
259 2-ethylidene-1, 5-dimethyl-3, 3-diphenylpyrrolidine (EDDP), the human metabolite of methadone
260 was not observed in the control reactor, suggesting the complete degradation of methadone. The
261 in-sewer transformation pathway of methadone could also be different to human metabolism
262 ending up with different transformation product^{23,36}.

263 For morphine and atenolol, the initial removal was $90 \pm 0.3\%$ and $87.8 \pm 0.3\%$ within five
264 minutes of spiking the compounds respectively in the ferric dosed reactor. At the end of the 6-hr
265 cycle, the overall removal reached $97 \pm 0.2\%$ and $93.4 \pm 0.8\%$ for these two compounds. The
266 further removal was well simulated by the first order kinetics. Morphine might be formed from its
267 glucuronides as it increased with time in the control reactor, as shown before²³. The atenolol
268 removal after 6-hr in control reactor was 52.7 ± 5.5 %, which is higher than a previous report (i.e.
269 20% transformation within 24-hr)²⁶. This might be due to the high A/V ratio of the sewer reactors
270 (8 times higher) used in this study.

271 The removal of these group-1 compounds in the ferric dosed reactor after the initial rapid
272 adsorption has been shown in Figure S4. The removal % was plotted against the concentration of
273 these compounds left after the adsorption. The removal trend of methadone and atenolol remains
274 the same as the control reactor suggesting the biological degradation after adsorption. But, in the
275 case of morphine the removal trend after the initial rapid removal was also higher compared to the

276 control. This could be due to the adsorption of morphine glucuronides avoiding its back
277 transformations or could be due to the adsorption of codeine. About 30% of codeine was observed
278 to be transformed to morphine in the rising main sewer condition²³

279



280

281 **Figure 2.** Stability of Group – 1 compounds in the ferric dosed and control sewer reactors. 1st and
282 2nd test represents the experiment performed at two different days. The middle line represents the
283 simulated transformation with 95% confidence bounds (upper and lower lines).

284 3.3.2. GROUP 2. KETAMINE, CARBAMAZEPINE, ACESULFAME AND CODEINE. The

285 group-2 organic MPs are classified as slightly biodegradable and less susceptible to iron sulfide
286 particles. For ketamine up to $72.8 \pm 0.5\%$ was removed rapidly in the ferric dosed reactor within
287 five min after spiking the compound. At the end of 6-hr retention time, the accumulated removal
288 due to biological degradation and the fast initial removal reached $90.8 \pm 0.2\%$. Although ketamine
289 was also found to be biodegradable in the control sewer reactor, the removal was only $51.9 \pm 0.6\%$
290 at the end of 6-hr. This biological removal of ketamine by sewer biofilms was similar to previous
291 studies, e.g. $63 \pm 10\%$ for 12-hr retention time ²³. The removal in the raw wastewater was about

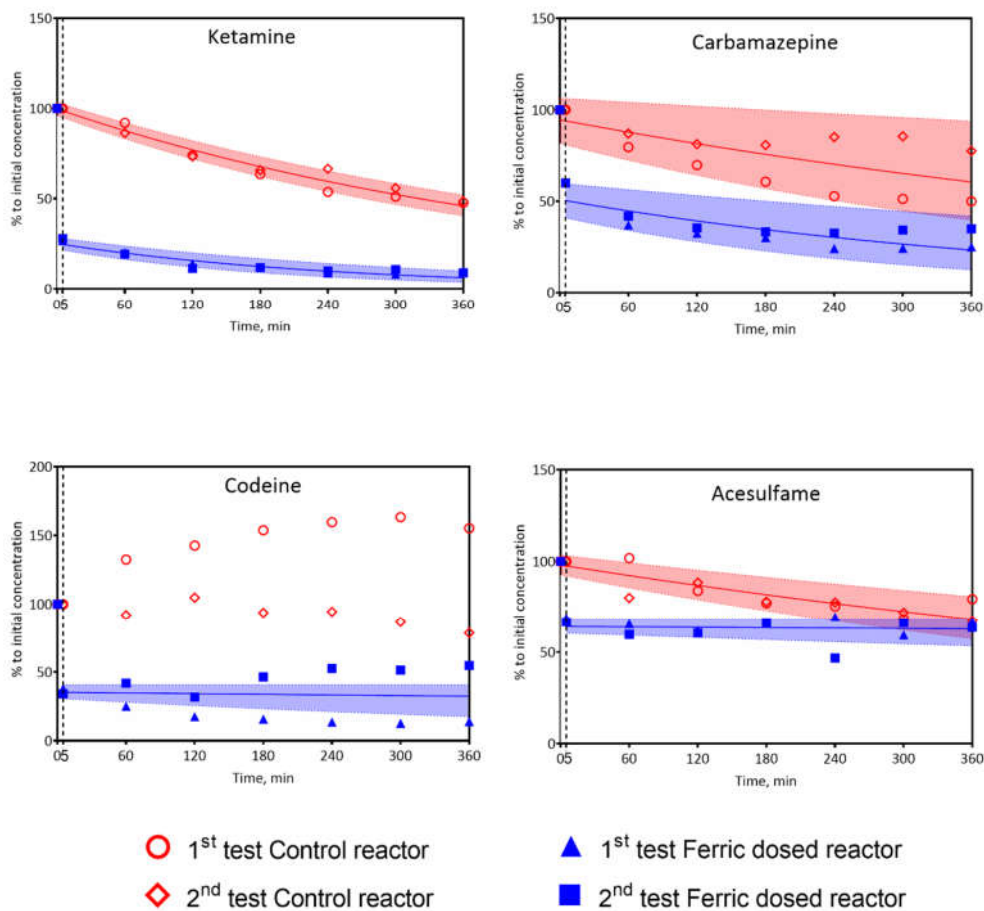
292 11% up to 72-hr without biofilm^{37, 38}. Norketamine, a major metabolite of ketamine, was not
293 observed in both reactors.

294 Carbamazepine is the most prominent drugs with a long history of clinical usage and it is
295 frequently found in the environment³⁹. The carbamazepine removal was $40 \pm 0.2\%$ within five
296 minutes of spiking the compound and at the end of 6-hr, the removal was $70 \pm 3.5\%$. In
297 comparison, the ultimate carbamazepine removal in control reactor was $36 \pm 19\%$. However,
298 carbamazepine was reported to be relatively stable in sewers and wastewater treatment plants^{23, 40}.

299 Similar to carbamazepine, acesulfame has been found to be one of the most stable and
300 hydrophilic compound and has been suggested as a suitable biomarker in the population estimation
301^{24, 41}. The initial removal of acesulfame was $32.1 \pm 0.9\%$ within five minutes and ultimately
302 reached $34.7 \pm 1.2\%$. Interestingly, the removal in the control reactor was $26.6 \pm 8.4\%$, likely due
303 to the diversity of microorganisms in the sewer biofilms (Section S4) as a recent study found some
304 species are capable of biodegrading acesulfame⁴².

305 The initial and ultimate removal of codeine was $64 \pm 1.4\%$ and $70 \pm 10\%$ in the ferric dosed
306 reactor. In contrast, the control reactor showed negative removal at the end of 6-hr. This may due
307 to the back-transformation from its glucuronides or morphine to its original form. The codeine
308 glucuronides was highly unstable in rising main sewers²³.

309 The better demonstration of biological degradation of these compounds in the ferric dosed
310 reactor after rapid initial adsorption has been shown in Figure S4. The comparison of biological
311 degradation in both the reactors has been discussed in section 3.4.

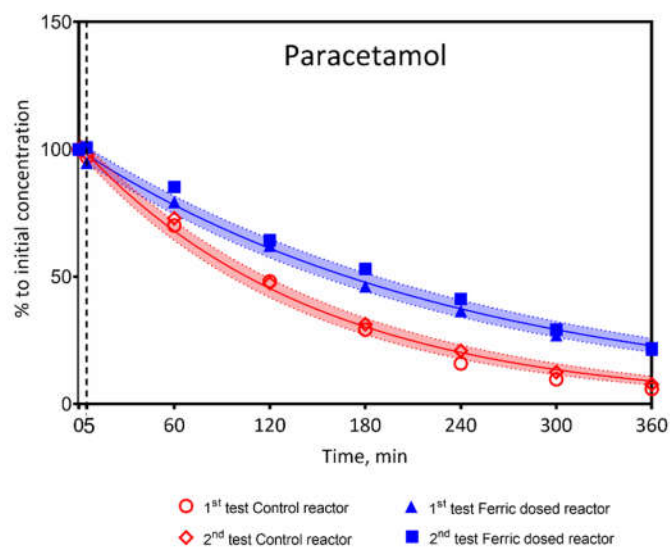


312

313 **Figure 3.** Stability of Group – 2 compounds in the ferric dosed and control sewer reactors. 1st
 314 and 2nd test represents the experiments performed at two different days. The middle line represents
 315 the simulated transformation coefficient with 95% confidence bounds (upper and lower lines)

316 **3.3.3 GROUP 3. PARACETAMOL.** As a singular case, ferric dosing did not induce an initial
 317 removal to paracetamol in the ferric dosed reactor. Considering the high paracetamol concentration
 318 of the wastewater (section 2.2), the surface of FeS particles might have reached its adsorption
 319 equilibrium for this specific compound. The biological degradation in both control and ferric dosed
 320 reactor was comparable, leading to the ultimate removal around $93.1 \pm 1.3\%$ and $78.4 \pm 0.2\%$ in
 321 the control and ferric dosed reactor, respectively. The relatively lower biodegradation in the ferric-

322 dosed reactor could be due to the decreased biofilm activity, e.g. methanogenesis (Figure 1 &
323 Section S4). The co-metabolism of methanogenesis was reported to account for the removal of
324 organic MPs such as the antibiotics (sulfamethaxazole, trimethoprim), neuro-drug (fluoxetine),
325 endocrine-disrupting compounds (4-octyl phenol, 4-nonyl-phenol, 17 α -ethinylestradiol, triclosan),
326 anti-inflammatory drug (naproxen) and the musk fragrances (galaxolide, tonalide, celestolide)⁴³.



327

328 **Figure 4.** Stability of Group – 3 compounds in the ferric dosed and control sewer reactors. 1st and
329 2nd test represents the experiment performed at two different days. The middle line represents the
330 simulated transformation coefficient with 95% confidence bounds (upper and lower lines)

331 It was clear that biological transformation can lead to different ultimate removal of MPs after 6-
332 hr in the control reactor, and on top of the initial removal in the ferric-dosed reactor. The complete
333 removal of compounds from the wastewater for group 1 can be achieved (methadone, morphine,
334 atenolol). Without ferric dosing, the ultimate removal is limited (ketamine, carbamazepine) due to
335 biological transformation alone or even formation (morphine, codeine) through back-

336 transformation from glucuronides forms. The removal of these MPs in the sewer reactors were
337 compared with previous studies and is shown in Table S5. The removal of methadone, ketamine
338 and codeine in control reactor of this study are comparable to other studies and is due to the
339 biological degradation. The difference in removal % observed could be due to change in microbial
340 composition of the sewer biofilms grown in different sewer environments (Section S4).

341 **3.4 ADSORPTION AND BIODEGRADATION OF MICROPOLLUTANTS.** The majority of
342 MP removal in the control reactor is mainly due to the biological transformations by
343 microorganisms in the biofilms. On top of biological degradation, this study found a fast removal
344 within minutes due to ferric dosing. Group 1 MPs are highly sensitive to the ferric dosing with an
345 initial removal >90% within 5 minutes. In contrast, limited (30-70%) and no (0%) removal
346 immediately after the dosing was observed for group 2 and 3 MPs, respectively. This fast initial
347 removal was likely due to adsorption, whose kinetics is much faster than the chemical or biological
348 degradation. For example, it was found that the sorption of methadone to the suspended solids in
349 the wastewater accounted for 11% of the total removal ³⁷. In this study, the nearly complete
350 removal within minutes for methadone could be due to the quick adsorption on to the surface of
351 the FeS particles, which can be formed in the ferric dosed reactor. Quick removal of these MPs
352 were not observed when iron was dosed into the sewer reactor without any preformed sulfides.
353 This shows that any other iron species formed due to the hydrolysis of Fe³⁺ is not contributing to
354 the removal of these MPs (Section S5). Batch tests with different ferric concentration (10, 5 and 1
355 mgFe/L) in the filtered wastewater also showed the negligible impact of other iron species on the
356 MPs removal (Section S.5.2.2). Further, the Fourier transform infrared-Attenuated Total
357 reflectance spectroscopy (FTIR-ATR) analysis of FeS particles before and after treating with MPs
358 showed some shift in the characteristic peaks of FeS particles (Section S3). The stretching of both

359 normal 'polymeric' –OH and aliphatic primary amine –NH functional groups showed a shift to
360 lower numbers. The symmetric vibration of aryl sulfides and polysulfides shifted to lower wave
361 numbers probably an indicative of hydrogen bonding. This further suggests that the initial fast
362 removal of these MPs could be due to the adsorption on the suspended FeS particles. For instance,
363 in group-1 compounds methadone ($\log K_{ow}=3.93$) being the non-polar compound, the sorption
364 could be due to the physical processes. In the case of morphine ($\log K_{ow}=0.89$) and atenolol (\log
365 $K_{ow}=0.16$) which are polar compounds, the quick removal could attribute to the chemisorption on
366 to the surface of FeS particles.

367 It is also important to note that, the metal ions such as zinc, copper (Cu) and iron in the
368 wastewater could lead to the formation and accumulation of metal sulfides such as FeS or CuS on
369 the sewer biofilms⁴⁴. But, in the control reactor and in additional experiment with iron dosing
370 (section S5), no rapid initial removal similar to ferric dosed reactor was observed. This indicates
371 that the freshly formed FeS, in the form of suspended particles, was responsible for the adsorption
372 of micropollutants. FeS precipitates accumulated in sewer biofilm was not as active likely due to
373 the interaction and coverage by bacteria and extra cellular polymeric substances.

374 The degradation kinetics of these compounds in the control and ferric dosed reactor were well
375 simulated using the first order kinetics²⁷. Although both SRB's and MA's in sewer biofilms are
376 capable of degrading the MPs it is still unclear how the change in microbial community due to
377 ferric dosing (section S4) will specifically impact the removal of each MPs. The simulated
378 transformation coefficients are shown in Table S6. The k_{bio} coefficients of some compounds like
379 methadone and atenolol, are almost the same in the control and ferric dosed reactors. This implies
380 that the microbes responsible for the biodegradation of those compounds were not impacted by the
381 ferric dosing. The k_{bio} coefficient of acesulfame & paracetamol are lower in the ferric dosed reactor

382 comparing to the control reactor which might be due to the co-metabolism of these compounds by
383 methanogens were inhibited, as discussed in the previous section.

384 For other compounds (morphine, ketamine, carbamazepine, codeine), the k_{bio} coefficient in the
385 ferric dosed reactor is higher than the control reactor. The iron sulfide with the adsorbed MPs can
386 precipitate inside the biofilm matrix or deposit on its surface (Figure S8). The MPs were thus in a
387 close vicinity and readily available for microbial biodegradation. This might be the reason for
388 higher k_{bio} coefficient in ferric dosed reactor. The change of microbial community structure due to
389 ferric dosing could be another potential reason for the enhanced biological degradation of MPs.

390 **3.5 EFFECTS OF FeS CONCENTRATION ON THE MICROPOLLUTANTS REMOVAL.**

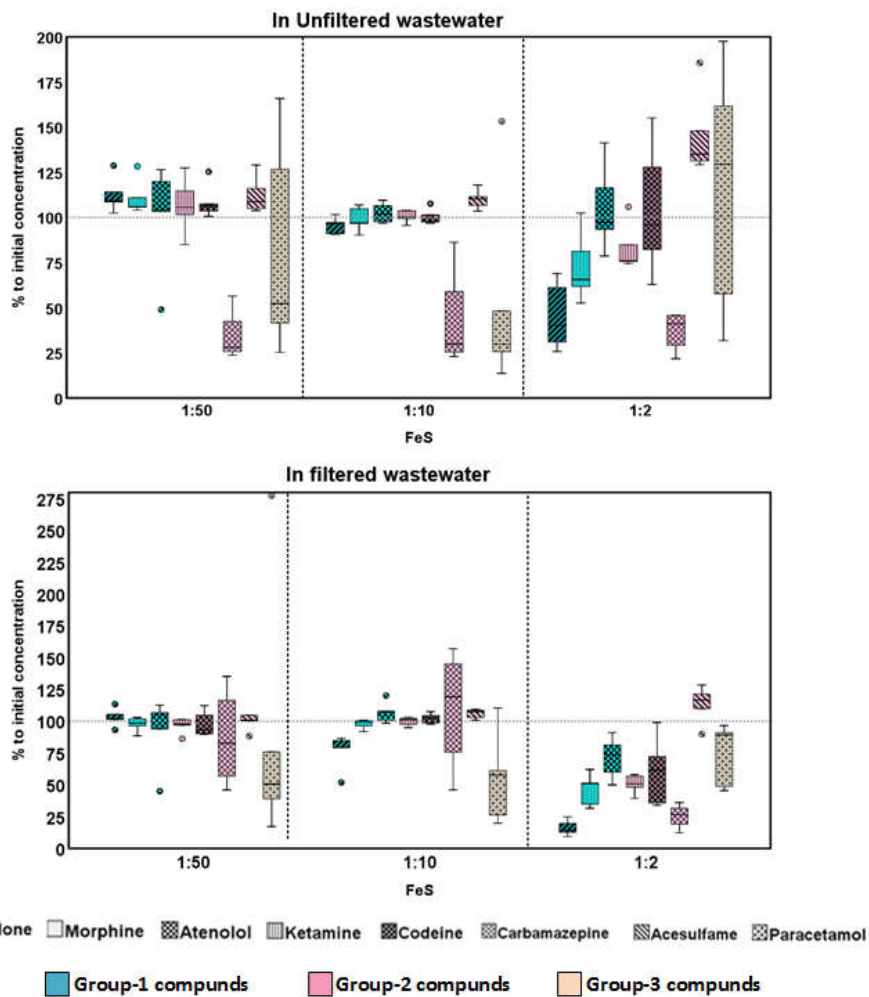
391 Batch tests were conducted with different FeS concentration to further confirm the fast initial
392 removal of MPs was due to the adsorption to suspended FeS particles. As shown in Figure 5,
393 comparing the median, it is observed that the removal of Group-1 compounds was high at high
394 concentration of FeS (1:2) in both unfiltered (methadone-59.7%, morphine-34.36% & atenolol –
395 2.7%) and filtered wastewater (methadone-85.79%, morphine-48.86% & atenolol – 26.21%).
396 However, the removal in the unfiltered wastewater is comparatively lower than the filtered
397 wastewater. This could be due to the interference of suspended particles for the adsorption sites on
398 the FeS particles. The methadone removal in unfiltered and filtered WW is c.a. 18 times and 4
399 times lower at 1:10 dilution ratio compared with a with 1:2 dilution ratio and no removal was
400 observed at lower FeS concentration (1:50 dilution ratio). Similar results were obtained in the case
401 of morphine and atenolol at lower FeS concentrations.

402 These results clearly emphasize that the removal obtained is mainly correlated to the amount of
403 iron sulfide particles and the result of rapid adsorption. There is no biofilm present in these batch
404 experiments. The removal of these compounds due to presence of suspended particles in

405 wastewater is negligible³⁷. The metabolites due to their biological transformation such as EDDP
406 were also not observed in this study.

407 Similar to group – 1, the group-2 compounds also showed less removal at lower FeS
408 concentration (1:50 and 1:10) in comparison to the higher FeS concentration (1:2), with different
409 ultimate removal of ketamine (23.91%, 49.18%), codeine (4.14%, 38.38%) and carbamazepine
410 (58.85%,73.44%) observed in unfiltered and filtered WW respectively. In the case of codeine, the
411 big variation of the data could be due to the abiotic backformation from its metabolites⁴⁵. In
412 contrast, the removal of carbamazepine was higher in the unfiltered wastewater than filtered
413 wastewater, suggesting the mediating role of suspended solids in wastewater for the adsorption of
414 carbamazepine to iron sulfide. Acesulfame, the more hydrophilic compound, showed no
415 adsorption at all FeS concentrations while comparing the medians and ultimately, no removal was
416 observed at the end of 1 hr.

417 Interestingly, we observed some removal of paracetamol in both unfiltered and filtered
418 wastewater at all FeS dilutions. These results were different from the sewer reactors. It could be
419 due to the continuous exposure of FeS particles with background wastewater paracetamol
420 concentration in the sewer reactors as discussed in section 3.2.3. Comparing the medians, the
421 highest removal of paracetamol was 48% and 49% at 1:50 FeS dilution ratio in unfiltered and
422 filtered wastewater.



423

424 **Figure 5.** Box and whiskers plot showing the removal of MPs at different FeS concentrations
 425 (Middle line of the box represents the median, the upper and lower lines represents the 25th and
 426 75th percentile, the whiskers extending the box and the outliers represents the data outside the inter
 427 quartile range. The data represents different measurements during the 1hr test)

428 **4. IMPLICATIONS FOR WASTEWATER TREATMENT.** This study showed that the
 429 biological degradation of MPs is limited in sewers. Due to their recalcitrant nature, the typical
 430 wastewater treatment process is also incapable of removing MPs from wastewater unless using the
 431 advanced treatment technologies. For the first time, the data supported that the removal of MPs in

432 the sewer network due to ferric dosing could significantly reduce the MPs load in the liquid phase
433 of the WWTPs. For nearly all the selected illicit drugs and pharmaceuticals, ferric dosing
434 significantly enhanced the removal from wastewater in a time scale of minutes. As a popular
435 chemical dosing strategy in rising main sewers, the dosing concentration required to remove
436 sulfide is higher than that required to achieve a reasonable removal of MPs. Therefore, the ferric
437 dosing in sewers is adding value to the downstream WWTP by removing the MPs from the influent
438 wastewater.

439 Previous studies have shown that iron sulfide formed in sewers can be reactivated in the
440 treatment plant for the phosphorus removal and the hydrogen sulfide emission control in the
441 anaerobic digester. This study demonstrated another additional benefit of ferric dosing in the
442 sewers. However, future research should focus on the diverse compounds of MPs and the
443 mechanism behind the adsorption of these compounds with the FeS particles. Also, it is essential
444 to understand the fate and transformation of FeS attached MPs when entering the WWTPs.

445 The usage of iron salts in drinking water treatment systems produces a huge amount of sludge
446 as a by-product. The iron content in the sludge varies from 133 – 268 g Fe/kg of sludge⁴⁶⁻⁴⁸. The
447 iron-rich drinking water treatment sludge has been used successfully to control the sulfide in the
448 sewer reactor⁴⁸. In addition, the complexing nature of natural organic matter (120 – 400 g/kg as
449 organic carbon) presented in drinking water sludge might enhance the removal of MPs from
450 wastewater^{49,50}. Future studies should further delineate the fate of MPs in sewers dosed with iron-
451 rich drinking water sludge.

452 SUPPORTING INFORMATION

453 Rising main sewer setup. Properties of selected organic MPs. Chemical spiking in batch tests.
454 Characteristics of particles formed in ferric dosed reactor. Atomic ratio of iron and sulfide based
455 on weight % obtained from EDS and ICP-OES. Biodegradation of compounds in the control and
456 ferric dosed reactor. Comparison of biodegradation results with previous studies. Simulated
457 transformation coefficients of the investigated compounds with/without iron dosage. FTIR-ATR
458 analysis depicting adsorption of MPs on the FeS particles.

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463 **Author Contributions**

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