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Biodegradability of organic matter associated with sewer sediments during first flush. Science of the Total Environment, 407 (8). pp. 2989-2995.

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1 **BIODEGRADABILITY OF ORGANIC MATTER ASSOCIATED WITH**
2 **SEWER SEDIMENTS DURING FIRST FLUSH**

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12
13
14 **ABSTRACT**

15 The high pollution load in wastewater at the beginning of a rain event is commonly
16 known to originate from the erosion of sewer sediments due to the increased flow rate
17 under storm weather conditions. It is essential to characterize the biodegradability of
18 organic matter during a storm event in order to quantify the effect it can have further
19 downstream to the receiving water via discharges from Combined Sewer Overflow
20 (CSO). The approach is to characterize the pollutograph during first flush. The
21 pollutograph shows the variation in COD and TSS during a first flush event. These
22 parameters measure the quantity of organic matter present. However these parameters do
23 not indicate detailed information on the biodegradability of the organic matter. Such
24 detailed knowledge can be obtained by dividing the total COD into fractions with
25 different microbial properties. To do so oxygen uptake rate (OUR) measurements on
26 batches of wastewater have shown itself to be a versatile technique. Together with a
27 conceptual understanding of the microbial transformation taking place, OUR
28 measurements lead to the desired fractionation of the COD. OUR results indicated that
29 the highest biodegradability is associated with the initial part of a storm event. The
30 information on physical and biological processes in the sewer can be used to better
31 manage sediment in sewers which can otherwise result in depletion of dissolved oxygen
32 in receiving waters via discharges from CSOs.

33
34 **KEYWORDS**

35 Biodegradability, first flushes, organic matter, watercourse, oxygen utilisation rate
36 (OUR), Combined Sewer Overflow (CSO)

37
38 **INTRODUCTION**

39
40 In times of high sewer flow, conditions can exist which enable previously deposited
41 material to be re-entrained into the body of the flow column. The expression first flush
42 denotes these pulses of highly polluted flow at the beginning of a rain event after a

43 period of dry weather flow (DWF) (Ashley *et al.*, 1993). It is important to know the
44 effect of the first flush through the combined sewer overflows (CSO) and its
45 downstream impact to the receiving water course. The effect of the first flush is usually
46 assessed by measuring parameters such as Chemical Oxygen Demand (COD), Total
47 Suspended Solids (TSS), Volatile Suspended Solids (VSS) and ammonia. COD, TSS
48 and VSS indicate pollutants released from the sediment bed, which is associated mainly
49 to the particulate phase while ammonia concentrations is associated to the dissolved
50 phase (McGregor *et al.*, 1996).

51

52 During rainfall events, CSOs can bring a substantial quantity of organic matter to the
53 receiving water, leading to an increased consumption of oxygen (Servais *et al.*, 1999).
54 Degradation of organic matter by heterotrophic bacteria is one of the primary processes
55 controlling the oxygen level of aquatic ecosystems and thereby their quality.

56

57 Such depletion of dissolved oxygen is typically the main impact of CSO events (Seidl *et*
58 *al.*, 1998). The degree of impact will be dependent on the sewer type, the rain intensity
59 and the sewage characteristics as well as the properties of the receiving waters
60 (Harremoes, 1988). In order to better understand and model the impact of the
61 discharged pollutants, it is essential to characterize all the aspects of the wet weather
62 discharge. In particular special attention should be paid to the biodegradability of
63 organic matter in addition to the usual conventional parameters such as COD, TSS and
64 ammonia. Attempts to rely on models for a better description of biodegradation
65 processes in rivers influenced by CSO discharges demonstrated the need to account for
66 bacterial biomass (Seidl *et al.*, 1998b).

67

68 Conventional quality parameters as COD, BOD (Biochemical Oxygen Demand), VSS
69 and ammonia give us the quantity of organic matter present in the wastewater. However
70 COD, TSS, VSS and ammonia do not give a clear indication on the biodegradability of
71 the released pollutants during a first flush event and consequently they only allow a
72 gross impact assessment to receiving waters.

73

74 To quantify the biodegradability of organic matter, it is essential to divide the total
75 COD into fractions with different microbial properties (Vollertsen and Hvitved-
76 Jacobsen, 2001). A conceptual model known as WATS (**W**astewater
77 **A**erobic/**A**naerobic **T**ransformations in **S**ewers) developed by Vollertsen and Hvitved-
78 Jacobsen (1998) using this COD fraction technique has used the oxygen uptake rate
79 (OUR) measurements on batches of wastewater to quantify its biodegradability.

80

81 In general research on sewers as part of the urban drainage has tended to focus on the
82 physical processes from an engineering point of view in order to alleviate and manage
83 problems such as sediment deposition which reduces conveyance, cause blockages,
84 accumulates pollutants and unsatisfactory operation of the Combined Sewer Overflows
85 (CSO) (e.g. Arthur & Ashley, 1998; Ashley & Crabtree, 1992; Ashley *et al.*, 1992;
86 Ashley *et al.*, 1993; Ahyerre *et al.*, 2001). CSO is a hydraulic device for the reduction of
87 flows downstream within a sewer system to reduce flooding and overloading. However
88 very little work has been published on assessment of the quality of the wastewater that
89 is discharged from the CSOs, in terms of its biochemical processes.

90

91 It is important to take into consideration the biochemical processes that occur in sewer
92 sediments as it influences the quality of the wastewater in sewers. OUR measurement

93 proves to be a way to quantify the biodegradability that occurs in the wastewater due to
94 the suspension of sediments into the water column. The management of the first foul
95 flush is important since when it is discharged via the CSOs to the receiving water
96 course, it can have detrimental effect on dissolved oxygen. The information gathered
97 from this work is important as it characterises the biodegradability of the wastewater
98 during foul flush of actual storm events. In addition the information obtained from this
99 research is also able to quantify the biodegradability of the wastewater for different
100 stages of a storm event. All these are valuable information which needs to be considered
101 when managing the release of discharges from CSOs to receiving waters.

102

103 The objective of this study is to quantify the transformations of organic matter in
104 sewage during wet weather conditions, via characterisation of the storm flush in terms
105 of biodegradability. Then based on this information it would be possible to foresee
106 impacts posed by the release of first flushes to the receiving waters. Characterisation of
107 the first flush in terms of biodegradability is the approach used in this study which is
108 based on the work published by Sakrabani (2004). This opens up a new dimension of
109 the effects of first flushes to the oxygen mass balance downstream of the CSO.

110

111 **STUDY SITE, MATERIAL & METHODS**

112

113 Wastewater was sampled in Frejlev, Denmark at the Frejlev Research and Monitoring
114 Station (Schaarup-Jensen *et al.*, 1998). Frejlev has a combined sewer system and 2000
115 inhabitants and without significant industries. In the Frejlev Research and Monitoring
116 Station, two autosamplers (ISCO Model No : 6712¹) (Figure 1) were connected to the

¹ Supplier address for ISCO : Isco Inc, 4700 Superior Street, Lincoln NE 68504 USA.

117 sewer to collect samples simultaneously during a storm event. The sampling
118 programme was carried out from August – November 2001.

119

120 One of the samplers was programmed to take samples for COD, TSS and VSS. Every
121 sample was a composite sample of 5 x 200 ml taken over a period of 10 minutes. The
122 other sampler was connected directly to the OUR instruments and was programmed to
123 fill 4 OUR instruments with a composite sample of 5 x 500 ml taken over 10 minutes,
124 i.e. the first OUR instrument contained a composite sample of the first 10 minutes of a
125 storm event and the second, third and fourth instrument contain a composite sample of
126 the subsequent 10-20, 20-30 and 30-40 minutes respectively of the same storm event.

127

128 TSS and VSS were determined using the APHA (1995) Standard Methods. COD was
129 determined using the Closed Reflux Colorimetric Method also in accordance with the
130 APHA (1995) Standard Methods.

131

132 The model concept put forward by Vollertsen and Hvitved-Jacobsen (1998) is briefly
133 depicted in Figure 2. The model proposes that the substrates present in the wastewater
134 can be divided into two COD fractions i.e. fast and slowly hydrolysable fractions. These
135 substrates are generally large molecules and need to be hydrolysed into readily
136 biodegradable substrate (S_s). During the hydrolysis process, microorganisms present in
137 the wastewater secrete enzymes to enable the larger molecules to disintegrate and form
138 readily biodegradable substrates. These readily biodegradable substrates are then easily
139 up taken by microorganisms to support its growth. During the growth process, dissolved
140 oxygen (DO) is utilised for respiration and carbon dioxide (CO_2) will be liberated as a
141 by-product of this process. Microorganisms that utilise the S_s and DO will proliferate

142 and form new biomass. This model concept varies from the concept applied in the
143 activated sludge processes in many ways. The microbial decay process is omitted as it
144 does not agree with experimental results and also because this process is of minor
145 importance in sewer systems (Vollertsen, 1998). A concept of maintenance energy
146 requirement of heterotrophic biomass has been introduced because experiments show
147 that DO is consumed when no net growth of heterotrophic biomass is seen (Vollertsen
148 and Hvitved-Jacobsen, 1998; 1999). Inert soluble and particulate organic matter are
149 omitted because processes related to these fractions are of minor importance in the
150 sewer system. In order to achieve the COD mass balance, these fractions are covered by
151 slowly hydrolysable substrate (Vollertsen and Hvitved-Jacobsen, 1999).

152

153 In order to determine the model parameters and components, experimental procedures
154 have been developed. The equations used to determine the model parameters will be
155 described very briefly as they are explained in detail by Vollertsen and Hvitved-
156 Jacobsen (1999; 2001).

157

158 Equations for all the components and processes are shown in Table 1, using a matrix
159 notation derived from the activated sludge modelling. Later in the OUR experiment, a
160 known concentration of substrate (Sodium Acetate Trihydrate is chosen in this case) is
161 added to the sample. Acetate is the dominating volatile fatty acid in wastewater and the
162 turnover of acetate is of major interest because its presence in the wastewater influences
163 biological nitrogen and phosphorus removal in wastewater treatment and the sulphide
164 production in pressure mains. Acetate and dissolved carbohydrate are the primary
165 compounds removed when dissolved organic matter is removed in gravity sewers
166 (Raunkjær et al. 1995). In the OUR experiment, acetate is added once the available

167 substrates get insufficient to support biomass growth. This is essential to determine the
168 yield constant, Y_H (g COD/g COD) and q_m maintenance energy rate constant (d^{-1})
169 (Vollertsen and Hvitved-Jacobsen, 1999). The various model parameters were
170 determined using the formulas described below and Figure 3 shows the various
171 parameters (such as dissolved oxygen associated with microbial growth denoted as
172 $\Delta S_{O,growth}$ (g O_2/m^3), readily biodegradable substrate associated with maintenance
173 energy denoted as $\Delta S_{S,maint}$ (g COD/ m^3), readily biodegradable substrate associated with
174 amount of added acetate denoted as $\Delta S_{S,added}$ (g COD/ m^3)) that can be obtained from a
175 typical OUR curve which are needed for the equations below. The symbols for
176 heterotrophic active biomass, hydrolysable substrate, fraction n and maximum specific
177 growth rate for heterotrophic biomass are denoted as X_B (g COD/ m^3), X_{Sn} (g COD/ m^3)
178 and μ_H (d^{-1}) respectively.

179

$$180 \quad Y_H = \frac{\Delta S_{S,added} - \Delta S_{O,growth}}{\Delta S_{S,added}} \quad (1)$$

181

$$182 \quad q_m = \frac{\Delta S_{O,maint} ((1 - Y_H) / Y_H) \mu_H}{\Delta S_{O,growth}} \quad (2)$$

183

$$184 \quad \ln \left(\frac{OUR(t)}{OUR(t_o)} \right) = \mu_H (t - t_o) \quad (3)$$

185

$$186 \quad X_B(t) = \frac{OUR(t)}{(1 - Y_H / Y_H) \mu_H + q_m} \quad (4)$$

187

188
$$S_s = \frac{S_{O1}}{1 - Y_H} \quad (5)$$

189

190
$$X_{S1} = \frac{S_{O2}}{1 - Y_H} \quad (6)$$

191

192
$$X_{S2} = COD_{total} - X_B - X_{S1} - S_s \quad (7)$$

193

194

195 **RESULTS AND DISCUSSION**

196

197 The results presented are based on triplicate measurements which were carried out to
198 ensure reproducibility. Standard deviations were calculated as shown in Table 2 and 3.

199

200 Figure 4 depicts OUR profiles for 4 storm events. These graphs show the time sequence
201 in which the OUR reactors were filled up by the ISCO sampler with wastewater. Hence
202 in Figure 4(a), the first out of four graphs indicate the OUR profile for the first 0-10
203 minutes of the storm event. The subsequent graphs indicate 10-20 minutes, 20-30
204 minutes and 30-40 minutes respectively after the start of the storm event. Generally
205 these graphs indicate depletion in the initially present S_s followed by a continuous
206 utilisation of $X_{s,fast}$ and finally the fraction $X_{s,slow}$. During the OUR experiment, acetate
207 was added to measure the values Y_H and q_m . Acetate was chosen as it is readily
208 degradable and represents a common substrate found in wastewater (Vollertsen, 1998).
209 The various values of Y_H , q_m and μ_h are tabulated in Tables 2 and 3. The general trend
210 observed is that there is a decrease in the Y_H values as we progress from start till the

211 end of the storm. This similar observation is noted for the various storm events during
212 the sampling programme.

213

214 However the maintenance energy requirement rate constant, q_m did not follow any
215 particular trend. The variation in the q_m values is probably because of the great diversity
216 in the micro organisms present in the wastewater and its various kinetics (Vollertsen,
217 1998). Hence q_m may vary with substrate concentration and time. The Y_H , q_m and u_h
218 values were not determined during 30-40 minutes of the experiment because of the
219 difficulty encountered in measuring these constants due to the OUR curve being at very
220 low value when most of the substrates were depleted.

221

222 Seidl *et al.*, 1998b demonstrated that a large proportion of the excess biomass in the
223 rivers which mostly came from a CSO is made up of large bacteria. Servais and Garnier
224 (1993) have also shown that large bacteria have 2 to 3x higher growth rates than small
225 bacteria. These bacteria and other microorganisms tend to have an association with the
226 resuspended particles and may favour settling (Servais and Garnier, 1993). Table 3
227 shows that values for μ_h as high as 7.1 d^{-1} and 6.33 d^{-1} were recorded during the storm
228 events.

229

230 In the OUR experiments, the duration for the added acetate to be consumed increased
231 from 0-10 to 30-40 minutes. Hence in the 0-10, 10-20 and 30-40 minute slot, the
232 duration for the added acetate to be consumed was 4, 7 and 15 hours respectively (data
233 not shown). This observation coincides well with the figures shown in e.g. Table 4 for
234 the storm event on 07/09/01 where the heterotrophic biomass (X_B) values decrease from
235 2.13 g COD/m^3 to 1.21 g COD/m^3 . Similar observations were also noted for the

236 subsequent storm events with a general decline in the values of X_B . When there is no
237 net increase in the heterotrophic biomass as observed in this case, bacteria may be
238 considered as grazed and respired by their predators (Seidl, *et al.*, 1998b).

239 Table 4 shows the various OUR coefficients depicting the composition of the
240 wastewater for 4 different storm events. Generally the S_S , X_B and X_{S1} values tend to be
241 high at the start of the storm event and deplete gradually towards the end. Resuspension
242 due to additional shear stress exerted on the sewer sediment bed causes release of
243 particulates into the bulk water column. Consequently there is an increased availability
244 of readily biodegradable substrate, S_S at the start of a storm event. The resuspension of
245 sediment bed also causes an increase in heterotrophic biomass, X_B which may be
246 inherently present as part of the particulates or X_B can also proliferate due to greater
247 availability of S_S . The surge in the availability of S_S causes an increase in bacterial
248 activity present in the sediment. The increased bacterial activity aids in the breakdown
249 of the complex substrates that are present in the resuspended particulates to form more
250 particulate substrates such as X_{S1} . The breakdown process by bacteria can be through
251 hydrolysis by extracellular enzymes and diffusion of the products into the cell (Hvitved-
252 Jacobsen, 2001).

253

254 Figure 5 shows OUR profiles for a set of three storm events from 01-02-1999 till 24-02-
255 1999. During these experiments acetate was not added which is indicated by the
256 absence of the second peak in the OUR curve. The graphs in Figure 5 also follow the
257 same trend as Figure 4. This demonstrates the reproducibility of the OUR technique to
258 characterise the biodegradability of organic matter released from sewer sediments.

259

260 Figure 6 shows the variation in the easily biodegradable substrate with the TSS and
261 Total COD during storm events, which occurred on 21/9/01, 15/09/01, 07/09/01 and
262 04/11/01. Easily biodegradable substrate is defined as a sum of readily biodegradable
263 substrate (S_S) and fast hydrolysible substrate (X_{S1}) whereas the slowly biodegradable
264 substrate is defined as the sum of heterotrophic biomass (X_B) and slowly hydrolysible
265 substrate (X_{S2}) (Hvitved-Jacobsen et al, 1998a; 1998b). The utilisation of the easily
266 biodegradable substrate gives an indication of the biodegradability of the organic matter
267 present in the wastewater. For example in Figure 6a, within 30 minutes of the storm
268 event, the easily biodegradable substrate has reduced from 140 gCOD/m³ to almost zero
269 whilst the Total COD and TSS values are much higher and continue to increase until 60
270 minutes after which there is a gradual decline. Similarly in Figure 6b, the easily
271 biodegradable substrate declines within 30 minutes, whilst TSS and Total COD are
272 much higher and reach a peak value at 75 minutes. In general Figure 6 shows that the
273 easily biodegradable substrate is highest at the start of the storm event and gradually
274 declines. Biodegradability does not follow the same trend as Total COD and TSS and
275 provides a good indication of the potential impact to receiving waters when wastewater
276 associated with initial part of a storm event is released. Easily biodegradable substrates
277 show that the negative impact of the initial part of a storm event occurs much earlier
278 than those shown by Total COD and TSS. Conventional parameters such as TSS and
279 Total COD do not provide accurate impact of the release of discharges from a storm
280 event and its effect further downstream. The focus of this work was to mainly determine
281 the impact of the biodegradability of easily biodegradable substrate via CSO discharges
282 on water course. However more work needs to be carried to investigate the impact of
283 the slowly biodegradable substrate. It is not very clear what the impact the slowly
284 biodegradable substrate may cause further downstream.

285

286 Figure 7 shows similar trends as Figure 6. In Figure 7, the easily biodegradable
287 substrates decline within the first 40 minutes. Total COD takes a longer time to deplete
288 and still much higher than easily biodegradable substrates.

289

290 The high biodegradability of the initial part of the storm event can exert high oxygen
291 demand on the receiving waters. Proper management of the release of the initial storm
292 event is important in order to minimise impacts on the receiving waters. Policy driver
293 such as the EU Water Framework Directive stipulates that all receiving waters should
294 be in good ecological status by 2015.

295

296 Degradation kinetics experiments (Mouchel *et al.*, 1997) showed that the degradability
297 of organic carbon was not the same during dry weather and storm event. During wet
298 weather, organic carbon was less degradable than during dry weather, roughly 65% of
299 organic carbon was degradable during the rain event contrary to 78% during the dry
300 weather. When a comparison was made between relative compositions of the biomass
301 during dry weather along a sewer network, there was a rise in the total biomass and in
302 large bacteria. This rise in total biomass and large bacteria during dry weather resulted
303 in greater degradability during dry compared to wet weather. Bacterial growth (in size
304 and biomass) is probably a function of residence time and abundance of appropriate
305 substrate. (Seidl *et al.*, 1998a).

306

307 One possible explanation for the results on higher biodegradability at the start of the
308 storm could be that during wet weather when there is resuspension of the sewer
309 sediment, high concentration of particulates occurs in the bulk water phase. These high

310 concentrations of particulates are broken down by the microbial population present in
311 the consolidated sediments via hydrolysis to produce fast hydrolysable fractions. The
312 greater availability of fast hydrolysable (X_{S1}) and readily biodegradable substrates (S_S)
313 causes the biodegradability to be high at the start of a storm event. Figures in Table 4
314 also show high values of S_S and X_{S1} at the start of the storm event which supports this
315 claim.

316

317 It is important to stress that the initial particulate loading in the wastewater entering the
318 sewer system is important to be considered. In this experiment the background
319 particulate loading has been addressed by measuring it during dry weather flow
320 conditions.

321

322 Bacteria transported during wet weather mostly originate from the in-sewer deposits
323 and have a long residence time in the system (Servais *et al.*, 1999). Hence these bacteria
324 are more adapted in the sewer environment and readily respond to availability of excess
325 substrates during a storm event. This could explain the corresponding high
326 biodegradability of organic matter at the start of a storm event.

327

328 **CONCLUSION**

329

330 OUR measurements provide useful information in addition to conventional parameters
331 such as TSS and Total COD. Information from OUR measurement provides
332 information on biodegradability of organic matter which is not reflected by TSS and
333 Total COD. Biodegradability is highest at the start of a storm event which directly
334 relates to the greater amount of oxygen utilised to breakdown the easily biodegradable

335 substrate. From this study it is now clear that the detrimental effect of first flushes to the
336 receiving waters is at the initial part of the storm event. Any further input in terms of
337 TSS and COD does not pose a greater detrimental effect due to the fact that the
338 biodegradability of these inputs is the greatest at the initial part of the storm. The high
339 biodegradability at the start of the storm event can be attributed to rapid breakdown of
340 substrates by microbial population which are well adapted in consolidated sediments
341 during dry weather flow. The high biodegradability of the initial part of the storm event
342 can exert high oxygen demand on the receiving waters. Proper management of the
343 release of the initial storm event is important in order to minimise impacts on the
344 receiving waters.

345

346

347 ***List of symbols***

348	BOD	Biochemical Oxygen Demand (mg/L)
349	COD	Chemical Oxygen Demand (mg/L)
350	OUR	Oxygen Utilisation Rate (mg/Lh)
351	q_m	maintenance energy requirement rate constant (d^{-1})
352	S_S	readily biodegradable substrate (g COD/ m^3)
353	S_O	dissolved oxygen (g O_2 / m^3)
354	X_B	heterotrophic active biomass (g COD/ m^3)
355	X_{Sn}	hydrolysable substrate, fraction n (g COD/ m^3)
356	Y_H	yield constant for X_B (g COD/g COD)
357	μ_H	maximum specific growth rate for X_B (d^{-1})

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