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BIODEGRADABILITY OF ORGANIC MATTER ASSOCIATED WITH SEWER SEDIMENTS DURING FIRST FLUSH

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ABSTRACT

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

KEYWORDS

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

INTRODUCTION

In times of high sewer flow, conditions can exist which enable previously deposited material to be re-entrained into the body of the flow column. The expression first flush denotes these pulses of highly polluted flow at the beginning of a rain event after a period of dry weather flow (DWF) (Ashley *et al*., 1993). It is important to know the effect of the first flush through the combined sewer overflows (CSO) and its downstream impact to the receiving water course. The effect of the first flush is usually assessed by measuring parameters such as Chemical Oxygen Demand (COD), Total Suspended Solids (TSS), Volatile Suspended Solids (VSS) and ammonia. COD, TSS and VSS indicate pollutants released from the sediment bed, which is associated mainly to the particulate phase while ammonia concentrations is associated to the dissolved phase (McGregor et al., 1996).

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

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

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

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

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

It is important to take into consideration the biochemical processes that occur in sewer sediments as it influences the quality of the wastewater in sewers. OUR measurement proves to be a way to quantify the biodegradability that occurs in the wastewater due to the suspension of sediments into the water column. The management of the first foul flush is important since when it is discharged via the CSOs to the receiving water course, it can have detrimental effect on dissolved oxygen. The information gathered from this work is important as it characterises the biodegradability of the wastewater during foul flush of actual storm events. In addition the information obtained from this research is also able to quantify the biodegradability of the wastewater for different stages of a storm event. All these are valuable information which needs to be considered when managing the release of discharges from CSOs to receiving waters.

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

STUDY SITE, MATERIAL & METHODS

Wastewater was sampled in Frejlev, Denmark at the Frejlev Research and Monitoring Station (Schaarup-Jensen *et al.*,1998). Frejlev has a combined sewer system and 2000 inhabitants and without significant industries. In the Frejlev Research and Monitoring Station, two autosamplers (ISCO Model No : 6712[1]) (Figure 1) were connected to the

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

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

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

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

The model concept put forward by Vollertsen and Hvitved-Jacobsen (1998) is briefly depicted in Figure 2. The model proposes that the substrates present in the wastewater can be divided into two COD fractions i.e. fast and slowly hydrolysable fractions. These substrates are generally large molecules and need to be hydrolysed into readily biodegradable substrate (S_S). During the hydrolysis process, microorganisms present in the wastewater secrete enzymes to enable the larger molecules to disintegrate and form readily biodegradable substrates. These readily biodegradable substrates are then easily up taken by microorganisms to support its growth. During the growth process, dissolved oxygen (DO) is utilised for respiration and carbon dioxide (CO_2) will be liberated as a by-product of this process. Microorganisms that utilise the S_S and DO will proliferate and form new biomass. This model concept varies from the concept applied in the activated sludge processes in many ways. The microbial decay process is omitted as it does not agree with experimental results and also because this process is of minor importance in sewer systems (Vollertsen, 1998). A concept of maintenance energy requirement of heterotrophic biomass has been introduced because experiments show that DO is consumed when no net growth of heterotrophic biomass is seen (Vollertsen and Hvitved-Jacobsen, 1998; 1999). Inert soluble and particulate organic matter are omitted because processes related to these fractions are of minor importance in the sewer system. In order to achieve the COD mass balance, these fractions are covered by slowly hydrolysable substrate (Vollertsen and Hvitved-Jacobsen, 1999).

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

Equations for all the components and processes are shown in Table 1, using a matrix notation derived from the activated sludge modelling. Later in the OUR experiment, a known concentration of substrate (Sodium Acetate Trihydrate is chosen in this case) is added to the sample. Acetate is the dominating volatile fatty acid in wastewater and the turnover of acetate is of major interest because its presence in the wastewater influences biological nitrogen and phosphorus removal in wastewater treatment and the sulphide production in pressure mains. Acetate and dissolved carbohydrate are the primary compounds removed when dissolved organic matter is removed in gravity sewers (Raunkjær et al. 1995). In the OUR experiment, acetate is added once the available substrates get insufficient to support biomass growth. This is essential to determine the yield constant, Y_H (g COD/g COD) and q_m maintenance energy rate constant (d^{-1}) (Vollertsen and Hvitved-Jacobsen, 1999). The various model parameters were determined using the formulas described below and Figure 3 shows the various parameters (such as dissolved oxygen associated with microbial growth denoted as $\Delta S_{O,growth}$ (g O_2/m^3), readily biodegradable substrate associated with maintenance energy denoted as $\Delta S_{S,maint}$ (g COD/m^3), readily biodegradable substrate associated with amount of added acetate denoted as $\Delta S_{S,added}$ (g COD/m^3)) that can be obtained from a typical OUR curve which are needed for the equations below. The symbols for heterotrophic active biomass, hydrolysable substrate, fraction n and maximum specific growth rate for heterotrophic biomass are denoted as X_B (g COD/m^3), X_{Sn} (g COD/m^3) and μ_H (d^{-1}) respectively.

$$Y_H = \frac{\Delta S_{S,added} - \Delta S_{O,growth}}{\Delta S_{S,added}} \tag{1}$$

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

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

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

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

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

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

RESULTS AND DISCUSSION

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

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

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

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

In the OUR experiments, the duration for the added acetate to be consumed increased from 0-10 to 30-40 minutes. Hence in the 0-10, 10-20 and 30-40 minute slot, the duration for the added acetate to be consumed was 4, 7 and 15 hours respectively (data not shown). This observation coincides well with the figures shown in e.g. Table 4 for the storm event on 07/09/01 where the heterotrophic biomass (X_B) values decrease from 2.13 g COD/m^3 to 1.21 g COD/m^3. Similar observations were also noted for the subsequent storm events with a general decline in the values of X_B. When there is no net increase in the heterotrophic biomass as observed in this case, bacteria may be considered as grazed and respired by their predators (Seidl, *et al*., 1998b).

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

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

Figure 6 shows the variation in the easily biodegradable substrate with the TSS and Total COD during storm events, which occurred on 21/9/01, 15/09/01, 07/09/01 and 04/11/01. Easily biodegradable substrate is defined as a sum of readily biodegradable substrate (S_S) and fast hydrolysible substrate (X_{S1}) whereas the slowly biodegradable substrate is defined as the sum of heterotrophic biomass (X_B) and slowly hydrolysible substrate (X_{S2}) (Hvitved-Jacobsen et al, 1998a; 1998b). The utilisation of the easily biodegradable substrate gives an indication of the biodegradability of the organic matter present in the wastewater. For example in Figure 6a, within 30 minutes of the storm event, the easily biodegradable substrate has reduced from 140 gCOD/m^3 to almost zero whilst the Total COD and TSS values are much higher and continue to increase until 60 minutes after which there is a gradual decline. Similarly in Figure 6b, the easily biodegradable substrate declines within 30 minutes, whilst TSS and Total COD are much higher and reach a peak value at 75 minutes. In general Figure 6 shows that the easily biodegradable substrate is highest at the start of the storm event and gradually declines. Biodegradability does not follow the same trend as Total COD and TSS and provides a good indication of the potential impact to receiving waters when wastewater associated with initial part of a storm event is released. Easily biodegradable substrates show that the negative impact of the initial part of a storm event occurs much earlier than those shown by Total COD and TSS. Conventional parameters such as TSS and Total COD do not provide accurate impact of the release of discharges from a storm event and its effect further downstream. The focus of this work was to mainly determine the impact of the biodegradability of easily biodegradable substrate via CSO discharges on water course. However more work needs to be carried to investigate the impact of the slowly biodegradable substrate. It is not very clear what the impact the slowly biodegradable substrate may cause further downstream.

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

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

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

One possible explanation for the results on higher biodegradability at the start of the storm could be that during wet weather when there is resuspension of the sewer sediment, high concentration of particulates occurs in the bulk water phase. These high concentrations of particulates are broken down by the microbial population present in the consolidated sediments via hydrolysis to produce fast hydrolysable fractions. The greater availability of fast hydrolysable (X_{S1}) and readily biodegradable substrates (S_S) causes the biodegradability to be high at the start of a storm event. Figures in Table 4 also show high values of S_S and X_{S1} at the start of the storm event which supports this claim.

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

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

CONCLUSION

OUR measurements provide useful information in addition to conventional parameters such as TSS and Total COD. Information from OUR measurement provides information on biodegradability of organic matter which is not reflected by TSS and Total COD. Biodegradability is highest at the start of a storm event which directly relates to the greater amount of oxygen utilised to breakdown the easily biodegradable substrate. From this study it is now clear that the detrimental effect of first flushes to the receiving waters is at the initial part of the storm event. Any further input in terms of TSS and COD does not pose a greater detrimental effect due to the fact that the biodegradability of these inputs is the greatest at the initial part of the storm. The high biodegradability at the start of the storm event can be attributed to rapid breakdown of substrates by microbial population which are well adapted in consolidated sediments during dry weather flow. The high biodegradability of the initial part of the storm event can exert high oxygen demand on the receiving waters. Proper management of the release of the initial storm event is important in order to minimise impacts on the receiving waters.

List of symbols

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

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