pH dynamics in sewers and its modeling

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ABSTRACT

pH variation in sewers has a significant effect on hydrogen sulfide production and emissions, and hence its accurate prediction is critical for the optimization of mitigation strategies. In this study, the nature and dynamics of pH variation in a sewer system is examined. Three sewer systems collecting domestic wastewater were monitored, with pH in all cases showing large diurnal variations. pH in fresh sewage in all three cases had a very similar trend with maximum pH in the range of 8.5–8.7. pH variation in fresh sewage followed the same pattern as the sewage flow rate, suggesting that sewage pH is influenced by household water use. Nitrogen content of the wastewater was found to be the most influential factor causing pH variation in fresh sewage, with the total ammonium concentration variation well correlated with the pH variation. A methodology for predicting pH variation in sewers is developed and calibration protocols proposed. The methodology, which is based on the concept of charge balance, was validated using titration curves and field pH data. Measurement of the total ammonium concentration in fresh sewage was found necessary and adequate for the calibration of the charge balance-based pH model.

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1. Introduction

Anaerobic conditions in sewers, especially in forced mains, result in the generation of sulfide (Pomeroy, 1959; USEPA, 1974). In gravity sewer pipes and pumping stations, dissolved hydrogen sulfide is released to the sewer atmosphere due to the presence of free water surface, where it is absorbed on the moist concrete surface. The absorbed hydrogen sulfide is further oxidized to sulfuric acid, lowering the pH and hence causing corrosion of concrete and steelwork (Boon, 1995; Jensen et al., 2009). In addition, being a malodorous and toxic gas, the release of hydrogen sulfide to atmosphere causes serious odor problem and poses potential health risks (Boon and Lister, 1975).

Sewage pH is an important parameter affecting not only the transfer of hydrogen sulfide from sewage to sewer air

(Yongsiri et al., 2004) and the production rate of sulfide by sewer biofilms (Gutierrez et al., 2009), but also the effectiveness of various sulfide mitigation strategies:

- Dissolved sulfide is present in sewage primarily in two forms, the molecular hydrogen sulfide (H_2S_{aq}) and bisulfide (HS^-), with the exact fractionation depending on the sewage pH. At 25 °C and neutral pH, H_2S_{aq} and HS^- exist in similar proportions (Bjerrum, 1957). Shift of pH into the acidic range increases the proportion of H_2S_{aq}, while that into the alkaline range increases the proportion of HS^-. The odor and corrosion problems are directly related to the concentration of H_2S in the gas phase, which is the result of the liquid–gas transfer of dissolved H_2S_{aq}. Sewage pH influences the availability of H_2S_{aq}, and hence affects the rate of transfer of H_2S from liquid to gas phase.

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- The change in sewage pH also affects the rates of biochemical processes in the sewer biofilm and consequently the sulfide production rate. Gutierrez et al. (2009) have reported 30% and 50% reduction in sulfide generation rate by sewer biofilm at pH 8.6 and 9.0, respectively in comparison to biofilm operated at pH 7.6. Similarly a recent study by Sudarjanto and co-workers (Sudarjanto et al., 2011) has shown significant decrease in sulfate reduction rate by sewer biofilm grown with a mixed domestic and brewery wastewater under the pH of 6.0 as compared to the sewer biofilm that received domestic sewage with pH of 7.1. Understanding of the pH variation in sewers is therefore very important not only for understanding but also for mitigating odor and corrosion problems in sewers.
- Among the various methods currently employed for sulfide control in sewers, the addition of magnesium hydroxide to increase sewage pH, and hence control the release of H_2S to atmosphere, is widely used (Ganigué et al., 2011; WERF, 2007). The amount of magnesium hydroxide that is needed to raise pH to a desirable level would depend upon the wastewater pH and composition (buffering capacity). The current practice of dosing $Mg(OH)_2$ at a constant or in some cases flow-paced rate without taking into account the variation of pH does not give optimum results (Ganigué et al., 2011). In many other cases, iron salts are used to remove hydrogen sulfide through precipitation. pH is found to have a major impact on the efficiency of sulfide removal in such cases, with a lower pH leading to a higher iron demand to achieve the same level of sulfide control (Firer and Friedler, 2008). Significant savings in chemical costs could thus be achieved by considering the variation of pH (Ganigué et al., 2012). Increase of pH has also been observed in sewers where nitrate is dosed to control hydrogen sulfide production (Mohanakrishnan et al., 2008) further highlighting the need for pH consideration in chemical dosing.

pH variations in sewer systems have been reported in a number of studies. Nielsen and co-workers (Nielsen et al., 1998) observed that pH in two pressure mains receiving domestic sewage varied in the range of 7.0–8.5. Houhou et al. (2009) conducted several sampling campaigns in a sewer network in Greater Nancy (France), and found pH variation in the range from 7.7 to 9.8. The sewer network received wastewaters from residential, commercial as well as industrial sources. In another study, Pai et al. (2010) assessed the variation of sewage composition in a gravity sewer in Taiwan, and observed that the wastewater pH varied with time and space, in the range of 6.2–7.4.

Although all these studies confirmed significant pH variation in sewage, only the range of pH is reported and there is no report on the pattern of the variation and the underlying causes. Further, there has been no successful attempt reported in literature on the prediction of pH variation in sewers. The modeling of sulfide formation in sewers has attracted considerable attention in the last few decades since it provides strong support to water utilities to achieve cost-effective sulfide management for odor and corrosion control. The models range from earlier empirical models developed in 1970s (Boon and Lister, 1975; Pomeroy and Parkhurst, 1977; Thistlethwayte, 1972) to more detailed and structured models (Jiang et al., 2009; Sharma et al., 2008a, 2008b; Tanaka and Hvitved-Jacobsen, 2002). However, none of these models is able to predict pH variation in wastewater. As such, these models do not adequately support the optimization of mitigation strategies that rely on (e.g. the elevation of pH with $Mg(OH)_2$ or NaOH) or are sensitive to (e.g. iron salt addition) pH variation. Further, the lack of pH prediction resulted in the inability of these models to consider the effect of pH variation on the rates of biological (e.g. sulfate reduction), chemical (e.g. metal-sulfide precipitation) and physical (e.g. liquid–gas transfer of H_2S) processes (Gutierrez et al., 2009; Lahav et al., 2006; Nielsen et al., 2008), leading to inaccurate prediction of sulfide production and emission rates.

This study aims to develop a methodology to model the pH change during sewage transport in a sewer system. Towards this end, measurement campaigns were done at three pumping stations receiving freshly discharged sewage across two states in Australia, to reveal pH variations in fresh sewage, as model input. In addition to the monitoring of pH, grab samples were collected from one of the pumping stations for the full characterization of the sewage composition. The data were used to develop an understanding of the diurnal variation of pH in fresh sewage, and the underlying causes of such a variation. A methodology was then developed for modeling the pH change during the transportation of sewage in a sewer based on the cation balance approach that is commonly used for pH prediction in anaerobic sludge digester (Batstone et al., 2002) and activated sludge processes (Jones and Dold, 2005; Volcke, 2006). The model was validated using the data collected during the measurement campaign. Application of the methodology was demonstrated by investigating prediction of pH change during the sewage transport, based on sewage characteristics at the inlet and pipe hydraulics. In addition, minimum data requirement for accurate pH estimation was also established.

2. Materials and methods

2.1. Field measurements

2.1.1. Sewer systems
Field measurements were conducted in the three sewer systems, the details of which are summarized in Table 1. UC09 was the subject of a sampling campaign for sewage characterization and pH model validation, and is further described below.

UC09 rising main has a total length of 1084 m and a diameter of 150 mm. This sewer system receives fresh sewage, primarily from households in the vicinity, with an average dry weather flow of about 150 m^3/d. The sewer is operated with short pumping events (with approximate duration of 2 min), followed by the pump "OFF" period of variable lengths (10 min − 1 h).

2.1.2. Online pH monitoring
pH was measured using online sensors at the pumping station wet wells listed in Table 1. Each of these measurements lasted for several days. These pH data were collected to reveal the

Table 1 – Details of the sewer systems used for field measurements.

Sewer system	Location	Measurements	Sampling location
UC09	Gold Coast, Queensland, Australia	pH, flow, sewage composition	Wet well of pumping station and 828 m downstream of the pumping station
Ningi Sandstone	Moreton Bay Regional Council, Queensland, Australia	pH	Wet well
Clifton Springs	Geelong, Victoria, Australia	pH	Wet well

variation of pH in fresh sewage. Additionally, pH data was also measured 828 m downstream from the UC09 pumping station, and was used to validate the pH model to be developed.

2.1.3. Flow data

Sewage flow data were also collected from the UC09 sewage pumping station (SPS). Pump operation data, which included the duration and timing of the pumping events, was obtained from the supervisory control and data acquisition (SCADA) system. Based on the pump operation data and the wet well dimensions, the incoming flow into the wet well, which gives an indication of the household sewage discharge rate, was estimated for each pump cycle as follows:

$$Q_{\text{in}[t_0, t_2]} = Q_{\text{pump}} \cdot \frac{(t_2 - t_1)}{(t_2 - t_0)} \tag{1}$$

where $Q_{\text{in}[t_0, t_2]}$ is the average sewage flow rate into the wet well between t_0 and t_2; Q_{pump} is the constant pump flow rate when the pump is turned on; t_0 is the time when pump stopped during the previous pump cycle, t_1 is the time when the pump started in the current cycle, and t_2 is time when pump stopped during the current pump cycle.

2.1.4. Sewage characterization

Field samples were collected from the UC09 SPS wet well. Hourly sewage samples were collected from the wet well from 04:00 am to 02:00 pm, a 10 h period accounting for the major variability of pH. The collected sewage samples were filtered immediately using 0.20 μm filter (Millipore, USA) and then transferred to 5 separate vials for the analysis of soluble inorganic sulfur species, soluble nitrogen and phosphorus compounds, volatile fatty acids (VFA), chemical oxygen demand (COD) and soluble total inorganic carbon (TIC). Sample vials were stored in an icebox to prevent degradation and transported to an analytical laboratory at The University of Queensland. The samples were stored in a fridge at 4 °C until analyzed. Sewage characterization was done to examine the correlation between the pH and the sewage constituents. Total ammonium (sum of ammonia and ammonium concentrations), phosphate, sulfide and VFA data were used to estimate the concentration of charged species to be used in the pH calculation. TIC measurement in a sewage sample gives the sum of the concentrations of H_2CO_3, HCO^{3-} and CO_3^{2-}, and hence TIC concentration was taken as the total carbonate concentration after applying unit conversion.

2.1.4.1. Analytical methods.
Liquid samples for total dissolved sulfide analysis were preserved using a sulfide anti-oxidant buffer (SAOB) according to the procedure described by

Keller-Lehmann et al. (2006) and subsequently analyzed using an ion chromatograph equipped with an UV detector (Dionex ICS-2000). Total ammonium and phosphate concentrations in the samples were measured using a Lachat QuikChem8000 Flow Injection Analyzer (FIA, Lachat Instrument, Milwaukee, WI). Soluble Kjeldahl Nitrogen (SKN) was analyzed following the Kjeldahl method, 4500-Norg.B, using FIA (APHA, 1998). Total and Soluble COD was measured from unfiltered and filtered sewage samples respectively, following the closed reflux colorimetric method 5220D of standard methods (APHA, 1998) using a spectrophotometer Merck CSB spectroquant model SQ300 (25–1500 mg COD/L range). VFAs were measured by gas chromatography (GC) (PerkinElmer, Inc.). Filtered sample (0.9 mL) was transferred into a GC vial to which 0.1 mL of formic acid was added. Measured values were converted to COD using the theoretical chemical oxygen demands of each VFA. Dissolved Inorganic Carbon was analyzed using a multi N/C 2100 Total Organic Carbon (TOC) analyzer (Analytik Jena, Germany) equipped with a Focus Radiation NDIR-Detector.

2.1.4.2. Titration tests.
The hourly sewage samples collected from the UC09 pump station were titrated with 0.065 N NaOH solution in duplicates to obtain a titration curve up to pH 11.0. Titration was conducted using an automatic titration device, which consisted of a pH sensor and a micropump, which delivered 47.5 μL of NaOH solution per pump stroke. Initially, 30 mL of sewage sample was placed in the titration device, and the micropump was started for continuous addition of the NaOH solution. A computer, to which the pH sensor and the micropump were connected, controlled the progress of the titration and recorded both the volume of NaOH solution added and the pH. Titration curve was obtained by plotting the pH against the volume of added NaOH solution.

2.2. pH model and calibration

2.2.1. Model description
Models for predicting pH dynamics in wastewater have been developed and incorporated in a number of sewage treatment process models including the anaerobic sludge digestion models (Batstone et al., 2002) and the activated sludge models (Jones and Dold, 2005; Volcke, 2006). All these models use the concept of charge balance to calculate the hydrogen ion concentration as represented by the following expression:

$$\sum S_{C^+} - \sum S_{A^-} = 0 \tag{2}$$

where $\sum S_{C^+}$ and $\sum S_{A^-}$ are the total cation and anion concentrations, respectively, as calculated below.

$$\sum S_{C^+} = [NH_4^+] + [H^+] + \sum [\text{Other Cations}] \qquad (3)$$

$$\sum S_{A^-} = 3 \cdot [PO_4^{3-}] + 2 \cdot [HPO_4^{2-}] + [H_2PO_4^-]$$
$$+ 2[CO_3^{2-}] + [HCO_3^-] + 2 \cdot [S^{2-}] + [HS^-] \qquad (4)$$
$$+ [Ac^-] + [Pr^-] + [OH^-] + \sum [\text{Other Anions}]$$

Where $\sum [\text{Other Cations}]$ represents the total concentration of metallic ions such as Na^+ and K^+, while the term $\sum [\text{Other Anions}]$ represents the total concentration of negatively charged ions such as Cl^-. These cations and anions are considered inert and hence do not take part in any reactions (Volcke, 2006), and can be lumped in an artificial variable called T_{Cat}, which is the difference between the total concentrations of cations and anions not included in the charge balance equation. If a cation or an anion participates in any of the reactions, it needs to be explicitly included in the charge balance equation so that T_{Cat} is truly conserved.

The concentrations of the ionic species can be calculated from the respective lumped total concentrations (for example total phosphate in the case of phosphate species) and the pH, taking into account pKa values of the equilibrium reactions. The relationship between the concentration of charged specie and the pH is a non-linear one. Once all the known (or calculated) ionic concentrations are entered into the charge balance equation, the hydrogen ion (H^+) concentration becomes the only unknown. The charge balance equation can then be solved to obtain the H^+ ion concentration that satisfies the charge balance. Due to non-linearity of the charge balance equation, determining the H^+ concentration (and hence the pH) becomes an iterative process.

Based on the previously described concept of charge balance (Batstone et al., 2002; Volcke, 2006) a pH model was formulated for the determination of pH as a function of the sewage characteristics. The following weak acid and base systems were considered in the pH model for a sewer system: i) Carbonate system; ii) Phosphate system; iii) Ammonia system; iv) Volatile fatty acids (acetate and propionate); and v) Sulfide system.

The equilibriums of the above weak acids and bases were considered to calculate the concentration of charged species and expressed in terms of H^+ concentration from the corresponding total concentration and constant of the equilibrium reaction (Ka), as demonstrated for the phosphate system in the Supplementary Information, Table S1. $[OH^-]$ was calculated by considering the H^+ concentration and the water equilibrium reaction. The pH model (Eq. (5)) was then obtained based on the charge balance.

$$[H^+] = 3 \cdot [PO_4^{3-}] + 2 \cdot [HPO_4^{2-}] + H_2PO_4^- + 2 \cdot [CO_3^{2-}]$$
$$+ [HCO_3^-] + 2 \cdot [S^{2-}] + [HS^-] + [Ac^-] + [Pr^-] \qquad (5)$$
$$+ [OH^-] - [NH_4^+] - T_{Cat}$$

The effect of ionic activity on the concentration of the different species and the pH calculation was assumed to have a negligible contribution given the low ionic strength of sewage (Tait et al., 2012).

2.2.2. Model calibration

Solution of Eq. (5) for H^+ concentration requires the knowledge of T_{Cat}, which cannot be measured directly, but needs to be calibrated. T_{Cat} can be calculated for sewage with known composition and known pH through rearranging Eq. (5):

$$T_{Cat} = 3 \cdot [PO_4^{3-}] + 2 \cdot [HPO_4^{2-}] + H_2PO_4^- + 2 \cdot [CO_3^{2-}] + [HCO_3^-]$$
$$+ 2 \cdot [S^{2-}] + [HS^-] + [Ac^-] + [Pr^-] + [OH^-] - [H^+]$$
$$- [NH_4^+] \qquad (6)$$

As T_{Cat} does not participate in the reactions, T_{Cat} in a slug of sewage can be considered to remain constant during its transport. This implies that T_{Cat} can be calibrated by measuring total concentrations of phosphate, total ammonium, total dissolved sulfide, total acetate, total propionate, total inorganic carbon and pH in the fresh sewage. The calibrated T_{Cat} can then be used in Eq. (5) for predicting pH during sewage transport.

2.2.3. Model validation

Model validation was conducted in two stages:

Model validation (I): T_{Cat} was calibrated by measuring total concentrations of phosphate, total ammonium, total dissolved sulfide, total acetate, total propionate, total inorganic carbon and pH in a fresh sewage sample. The calibrated pH model was used to simulate the pH change during the titration of the sewage sample (addition of alkali to increase the pH). The predicted pH profile in response to NaOH addition was then compared with the experimentally observed pH profile during titration.

Model Validation (II): Sewage flows in the sewer pipe in a plug flow manner, during which a number of biological, chemical and physical reactions occur resulting in changes in the sewage composition. Any change in the concentration of the week acids and bases would change the equilibrium and hence the concentration of the charged species. pH variation in sewage is likely caused by: i) Changes in the sewage composition; ii) Biological and chemical reactions during transportation such as production and consumption of volatile fatty acids, production of hydrogen sulfide and CO_2, precipitation and oxidation of hydrogen sulfide, and ammonification; iii) Stripping of gases such as CO_2, H_2S and NH_3 and volatile fatty acids (VFA) due to turbulent conditions at the manholes, drop structures and in gravity sewers; and iv) Addition of chemicals such as $Mg(OH)_2$ which alter the sewage pH.

The sewer model developed at The University of Queensland (SeweX) describes biological, chemical and physical processes that occur in the sewer system (Sharma et al., 2008a, 2008b). The biological processes include the conversation of carbonaceous, sulfurous and nitrogenous compounds under anaerobic, aerobic and anoxic conditions, such as sulfate reduction, methanogenesis, aerobic carbon oxidation and denitrification as well as hydrolysis, fermentation and ammonification. The chemical processes include, among others, the reactions leading to precipitation and chemical sulfide oxidation, while the physical processes primarily consists of liquid/gas mass transfer of volatile compounds such as H_2S, O_2, CO_2 and CH_4. The model has previously been fully calibrated for the pressure main following the UC09 pumping station, and used to investigate temporal and spatial

variations of sulfide production in this pipe (Sharma et al., 2008b). pH calculation described in the previous section was built into the SeweX model, making the model capable of predicting pH changes in response to the change in sewage composition during sewage transport. pH was modeled using a set of algebraic equations representing acid/base equilibrium and charge balance instead of using kinetic rate expressions. The inclusion of the pH model into the dynamic SeweX model therefore did not affect the speed of simulation. It is worth mentioning that the modeling of pH based on reaction kinetics would increase the stiffness of the system of differential equations thereby substantially slowing down the simulation speed. The methodology employed for the calculation of pH in the sewer model is demonstrated in Fig. 1.

The pH component of the SeweX model was calibrated using the UC09 dynamic feed data. The calibrated model was then employed to predict the pH at 828 m downstream of the pumping station for which 24 h pH data was available. This was done to test the capability of the model in terms of predicting both the change in sewage composition and the change in pH during the transportation of sewage in the sewer pipe. Since the complete feed data were only available from 04:00 am to 2:00 pm, sewage composition for the period from midnight to 04:00 am and from 2:00 pm to midnight was generated from measured pH data by using the correlations between pH and the key water quality parameters that

affected the pH. For this purpose, a number of correlation curves between the pH and total ammonium, total phosphate and inorganic carbon were developed using the measured data collected from 4:00 am to 2:00 pm, as will be presented in detail in the Results and Discussion section.

An uncertainly analysis was carried out to investigate the impacts of errors in TCat estimation on pH prediction. The analysis involved pH simulation with ±10% change in the calibrated T_{Cat} values. The induced changes in the pH profiles are assessed by calculating the change in pH levels resulting from the change in T_{Cat} concentration and examining the range of the pH deviation.

3. Results and discussion

3.1. pH dynamics in sewer systems

With the aim of revealing the dynamics of pH in fresh sewage, the wet wells of the pumping stations of the UC09, Ningi Sandstone and Clifton Springs sewer systems were monitored for several days. These wet wells were close to the settlements and hence collected fresh household domestic sewage. Online data revealed a characteristic pH pattern that was repeated over-time on a daily basis. To illustrate this, the 24-h variation of sewage pH in the wet wells of all the monitored pumping stations for a representative day is presented in Fig. 2. All three monitored sites showed similar diurnal variations of pH. There were two distinct pH peaks, one in the morning and another in the afternoon in all the cases. pH in all the systems varied by about 1.5 units within 24 h. The lowest pH levels (7.2–7.5) were generally observed during the early morning hours and the hours before midnight. pH reached peak levels of 8.5–8.7 around 8:00 to 9:00 am in the morning. A second pH peak was observed around 4:00 to 5:00 pm. The second peak for the Ningi Sandstone system occurred earlier than the other two systems. In terms of the peak level, the second pH peak for the Ningi Sandstone system was similar to the first peak, while the other two systems showed lower peak levels as compared to the first one. The maximum pH level in all the three sewer systems was similar (8.5–8.8). The changes of pH from the lowest to the highest level was so significant that the rate of emission of dissolved sulfide from liquid to the headspace would vary in one to two orders, for the same level of total dissolved sulfide. Such a large variation in pH would certainly be a key contributing factor to the dynamic H_2S concentrations often observed in sewer air (Jiang et al., 2013). Such a variation should also be taken into consideration for mitigation operations. For example, the dosing of magnesium hydroxide should be substantially reduced during the period of high pH.

3.2. Variation of pH with sewage composition and flow

Diurnal variation of sewage flow is normally associated with the diurnal variation of the key sewage constituents (Metcalf and Eddy, 2003). A correlation between the pH and the concentration of the sewage constituents is expected. In order to investigate further the reasons for the large variation of pH in fresh sewage, a number of sewage constituents likely to have
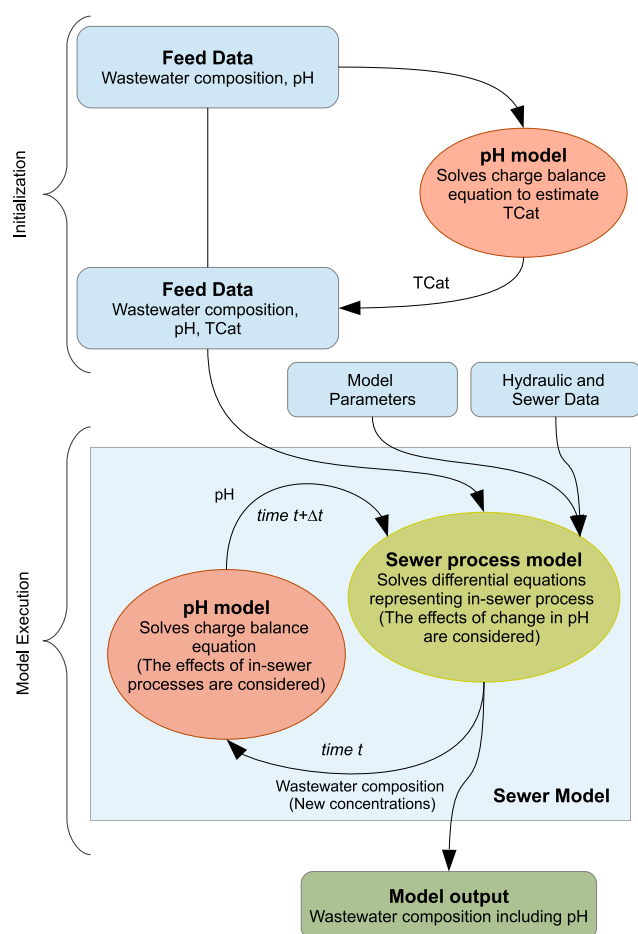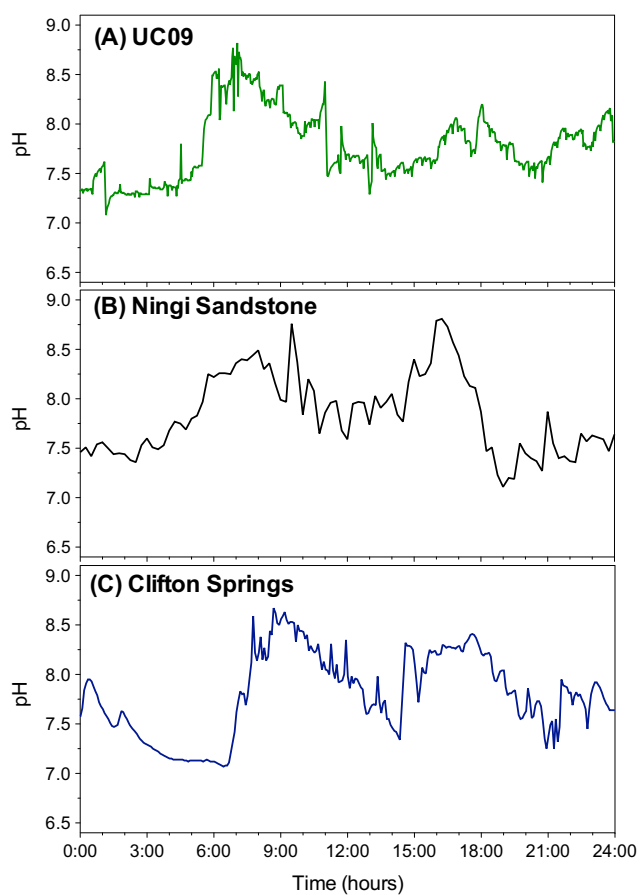

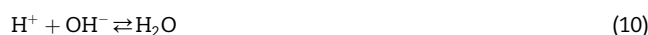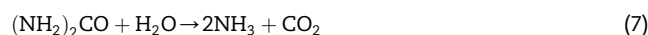**Fig. 1 – Methodology for calculating pH in the sewer model.**

Fig. 2 – Variation of pH at the wet wells at (A) UC09; (B) Ningi Sandstone; and (C) Clifton Springs.

some influence on sewage pH, were measured by collecting grab samples from the UC09 wet well for a period of 10 h (4:00 am to 2:00 pm). The time of sampling was so chosen to cover the period of morning pH peak as shown in Fig. 2A as well as the periods before and after the peak. The variations of the concentration of the key sewage constituents and their correlation with pH are shown in Fig. 3.

The results revealed significant changes in the sewage composition during the measurement period. Except for inorganic carbon and sulfate, which most likely come from the drinking water, the variation of the concentration of sewage constituents followed the same trend as the pH. Among the parameters studied, the total ammonium, total Kjeldahl nitrogen (TKN) and phosphate concentrations followed a similar profile as pH (Fig. 3A and B). Although the trends of VFAs and total COD (Fig. 3C and D) looked similar to pH, there was a slight time shift. Possible factors responsible for the time shift are the water use pattern at households such as the use of toilet, shower and kitchen and delayed transport of solids from household connectors to the wet well. On the contrary, pH did not seem to be affected by the change in inorganic carbon concentration and dissolved sulfide concentration. To further explore these relationships, correlation curves were developed for each of the parameters, and are presented in the Supplementary Information (Figure S1).

The sewage flow rate typically follows a diurnal pattern with minimum flow occurring during the early morning hours and peak flow in the late morning and early evening hours. In an attempt to gain a deeper understanding of the factors responsible for the sewage pH variation in sewers, the UC09 sewage flow rate (inflow into the wet well) was also measured and the variation of pH was compared with that of the sewage flow rate (Fig. 3F). A clear trend of increasing pH with increasing flow rate was observed (Figure S2, Supplementary Information). These variations are closely related to the pattern of household water consumption and hence domestic sewage discharge (Metcalf and Eddy, 2003). The increased sewage flow during the peak hours is likely associated with the toilet flushing, which carries both urine and faecal materials with higher concentrations of nitrogen (mainly in the form of urea), phosphorus and organic matter. Urea is subsequently converted into ammonium releasing hydroxyl and bicarbonate ions during hydrolysis (Eqs. (7)–(10)). Each mole of urea generates 2 mol of ammonium, 1 mol of OH^-, and 1 mol of HCO_3^-, contributing thereby to the increase of pH. These reactions are likely underlying the observed correlation between the total ammonium and TKN concentrations.

$$(NH_2)_2CO + H_2O \rightarrow 2NH_3 + CO_2 \qquad (7)$$

$$2NH_3 + 2H_2O \rightleftarrows 2NH_4^+ + 2OH^- \qquad (8)$$

$$CO_2 + H_2O \rightleftarrows HCO_3^- + H^+ \qquad (9)$$

$$H^+ + OH^- \rightleftarrows H_2O \qquad (10)$$

Concentration of phosphate was higher during the period of high sewage flow for the same reason as for total ammonium. Being a weak acid, any increase of phosphate concentration should result in a decrease in pH rather than the increase. The extent of pH decrease would however depend upon the buffering capacity of the sewage. Fig. 3A therefore indicates insignificant effect of phosphate in sewage pH. Increase in the VFA concentration should also result in pH decrease, which is opposite to what have been shown in Fig. 3C. Hence, the VFA also had very little impact on the sewage pH. The results and the above analysis suggest that the variation of pH was due to the variation in total nitrogen concentration.

3.3. pH modeling

3.3.1. Calibration of the pH model
The hourly samples collected at UC09 were analysed for water quality parameters as described in the Materials and Methods section. The pH of the sewage samples was obtained from the initial pH of the sample in the titration tests. The net total cation (T_{Cat}) concentration was calculated for each of the hourly samples collected based on the sewage composition data and measured pH using the charge balance equation (Eq. (6)), constituting the pH model. The calculated T_{Cat} for the collected samples is shown in Fig. 4.

The T_{Cat} concentration in general varied between 0.002 and 0.003 M except for the early morning sewage samples. Two sewage samples obtained at 4:00 am and 5:00 am during the period of low flow, and hence low household activity, showed lower T_{Cat} concentrations.
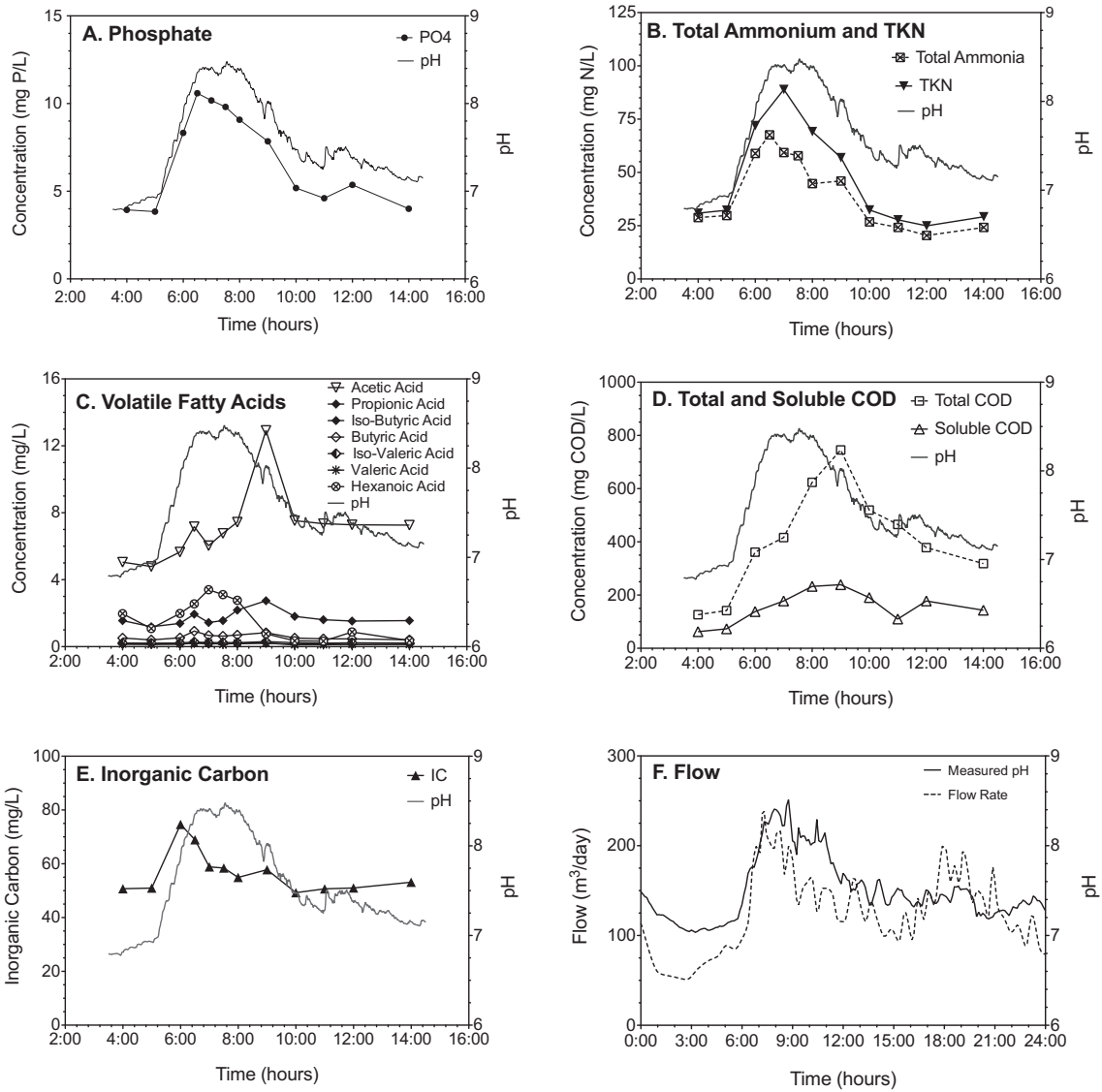
Fig. 3 − Changes in sewage composition and pH.

3.3.2. Validation of pH model using the titration curves

In order to validate the pH model, titration curves were acquired for a number of sewage samples collected during the

Fig. 4 − Calibration results showing the variation of T_{Cat}.

field sampling at UC09. Measured sewage characteristics and the T_{Cat} concentrations calculated in Section 3.3.1 were employed and the change in pH due to the addition of NaOH was predicted using the pH model (Eq. (5)). The correlation between the measured and model predicted pH for the all the titration curves is presented in Fig. 5. Comparison of the measured pH and the pH predicted by the model for each of the titration tests are shown in Figure S3 (Supplementary Information). The pH model was able to predict accurately the change of pH for all the titration cases. The results thus provide validation to the methodology used in pH modeling.
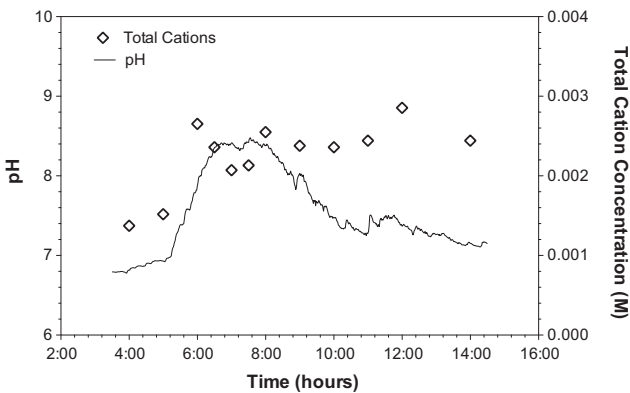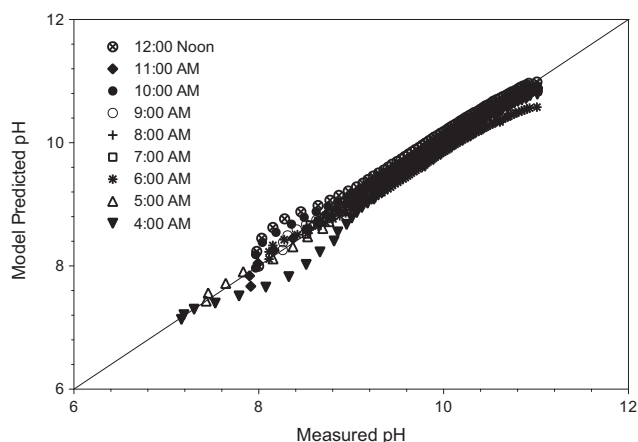
### 3.3.3. Validation of pH model − pH prediction for the UC09 pressure main

The most important application of pH modeling in sewers is the prediction of sewage pH variation during its transportation in sewers. In such a case, the calibrated pH model needs to be applied in conjunction with the sewer process model, which predicts the change in sewage composition,

Fig. 5 – Model predicted pH versus measured pH for the titration tests.

including changes in charged species, caused by the in-sewer physical, chemical and biological processes. In order to validate the methodology of pH modeling described previously, pH was measured at the wet well of the UC09 sewer system and at a location 828 m downstream of the wet well. The results of the measurement are presented in Fig. 6 pH profiles at the two locations show a similar trend. The two pH peaks are somewhat dampened and slightly shifted at the downstream location due to the sewage retention time in the pipe (ranging from 2 to 8 h in this case). As the sewage is transported along a sewer pipe under anaerobic conditions, fermentable COD is converted into VFA due to fermentation (Sharma et al., 2008b). During this process, H^+ ions are produced, hence driving the pH down as shown by the results.

The SeweX model enhanced with the pH model was applied to the UC09 main to validate its pH prediction
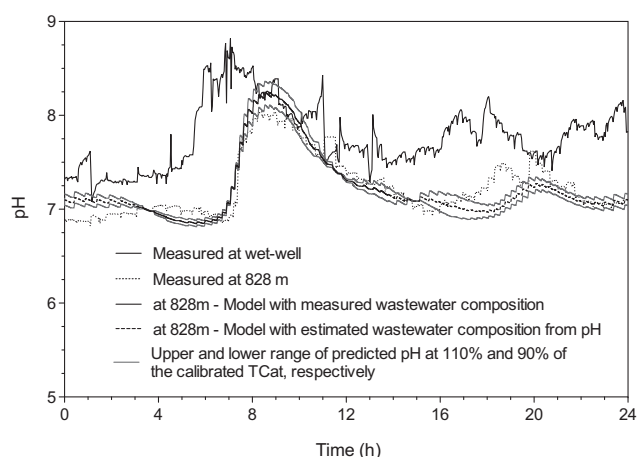
Fig. 6 – Comparison of model predictions with measured pH (0 h is midnight, model predicted results shown in solid line are with known sewage composition, while those shown in dotted line are based on estimated sewage composition. Faint solid lines represent upper and lower range of pH predicted using 110% and 90% of the calibrated T_{Cat} concentrations).

capabilities. Data characterizing the sewage in the wet well was available for the period between 4:00 am and 2:00 pm, as the hourly samples were collected and analysed during this period (see the previous section). For the period outside this range, only pH data was available and hence model input data (TIC, phosphate, VFA, Total ammonium and sulfide) for the pH model was inferred from the available pH data by using the correlations between pH and the key sewage quality parameters obtained from the data presented in Fig. 4. A correlation curve was developed for each of the parameters in Section 3.2 (shown in the Supplementary Information, Figure S1) and the relationship was used to estimate the parameter concentration from the measured pH.

A comparison of the measured and the model predicted pH data at 828 m of the UC09 sewer pipe is shown in Fig. 6 pH variation in the wet-well is caused by the variation in sewage characteristics with time, while the shift in pH peaks and valleys between the two locations is mainly caused by hydraulics as variation of flow with time caused variation in hydraulic residence time. The decrease in pH at the end of the pipe in comparison to that in the wet-well (with shift considered) is due to the biochemical reactions during the transport of sewage in the sewer pipe.

As shown in Fig. 6, the pH model implemented in the SeweX model was capable of predicting the pH at the downstream location. During the period when the sewage composition data were available (04:00 am and 2:00 pm), the pH prediction was accurate. For the remaining period, where the input data was generated from the pH measurement, pH prediction was still reasonably good and the model was able to predict the second pH peak at around 8:00 pm. The mismatch between the measured data and the model prediction during first 3 h was potentially due to discrepancies in wastewater characteristics data. This highlights the need for reliable sewage characteristics data for pH modeling. The good match between the data and the model results further validates the approach used for pH modeling in sewers. Once the feed characteristics are known, the SeweX model, enhanced with the pH model, is able to predict the change in pH during the transport of sewage in sewer accurately. This integration has made pH prediction in sewers possible.

Fig. 6 also shows the results of the uncertainty analysis (pH prediction using ±10% change in T_{Cat} concentrations). A quantitative analysis of the data shows that ±10% change in T_{Cat} concentration resulted in mean pH deviation of 0.04 units with a maximum of 0.14 units in both the cases. The results therefore suggest minor impacts of the error in the estimation of calibrated model parameter on pH prediction.

In order to visualize the impact of pH change on gas phase H_2S concentration at the point of discharge, a discharge manhole at the end of the rising main was added in the model. Simulation results show several fold decrease in gas phase H_2S concentration when pH changed from the lowest level to the highest level (Figure S4, Supplementary Information). This demonstrates the significance of pH on H_2S emission and the associated sewer odor and corrosion problems.

Although the validity of the pH model is demonstrated using data from a rising main sewer, it is expected to be applicable to gravity sewers so long as the biological and chemical processes contributing to the change in sewage

composition are properly modeled. It is acknowledged that the model is yet to be validated for gravity sewers.

The pH calculation is fundamentally based upon the concentrations of acid/base systems present in the sewage. While the model has been validated for domestic wastewater only in this study, it should be applicable to sewers receiving industrial wastewater discharges. Any changes to the acid/base concentrations brought by the discharge of industrial wastewaters will be automatically accounted for by the pH model through model calibration.

3.4. Data requirement for sewer pH modeling

As discussed above, the initial characterization of sewage is needed for pH modeling, which is a laborious and tedious task, involving intensive field sampling and chemical analysis. Although the measurement of pH at the wet well, which is required for T_{Cat} calibration, is easy and less time consuming due to the availability of online sensors, other characteristics (such as TIC, phosphate, VFA, total ammonium and sulfide) are not always available thereby limiting the use of the pH model. In order to work out alternative options for data collection and to establish minimum data requirement, pH prediction for the following four cases was examined using the model described in Section 3.3:

1. Dynamic profiles for TIC, total phosphate, total VFA, Total ammonium and total dissolved sulfide concentrations are all measured for the feed wastewater.

2. Only the dynamic profile for total ammonium concentration is measured for the feed wastewater. Constant values are used for all other parameters.
3. The dynamic profile for total ammonium concentration is estimated based upon the measured pH using the correlation shown in Eq. (11) (Figure S1A, Supplementary Information). Constant values are used for all other parameters.

$$pH = 0.0304 \times \text{Total Ammonium Concentration} + 6.472 \quad (11)$$

4. Typical values are used for all the parameters without considering the daily variation.

As discussed in Section 3.2, ammonium concentration appeared to be the most influential parameter and hence was used as the key variable in this analysis. Since the sewage characteristics data were available for 10 h from 4:00 am, simulation was performed only for this period. Feed data used in Section 3.4 were changed to accommodate the four cases above and used to predict the pH at 828 m of the UC09 sewer line. The simulation results are compared in Fig. 7. Different pH profiles were predicted in the four cases. However, the pH profiles for the first two cases are almost identical indicating that the total ammonium concentration is the single most influential parameter for pH model with other parameters having negligible impact. For the accurate prediction of pH in sewers, it is necessary to measure the initial total ammonium concentration. With the availability of online ammonium
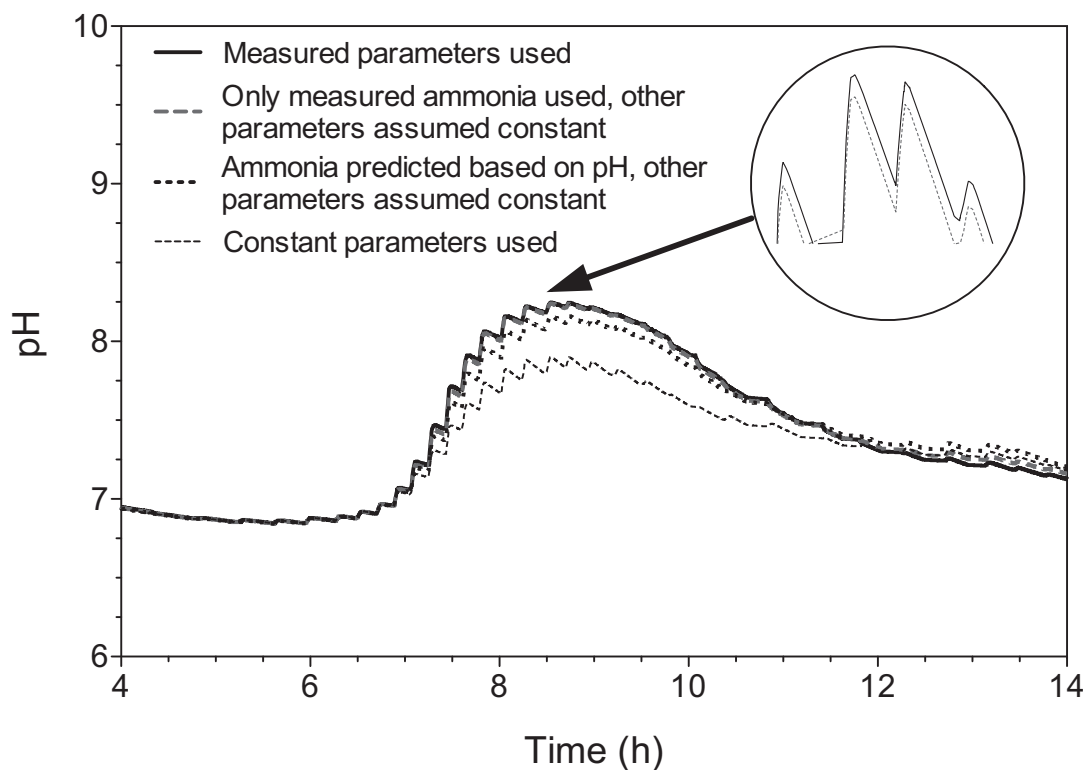

Fig. 7 — **Analysis of different scenarios with respect to the need for sewage composition data for pH modeling (the lines for two cases, all parameters measured used and only total ammonium measured, are overlapping as there are only small differences between the predicted pH profiles).**

sensors, the dynamic variation of ammonium could easily be obtained suggesting general applicability of the approach. In situations where this measurement is not possible, this can be predicted from pH measurement. Such an approach appears to produce pH prediction with relatively small errors (up to 0.1 unit in this case). In contrast, significant errors in pH prediction will result if constant values are used for all water quality parameters.

4. Conclusions

Based upon the findings of this study, the following can be concluded:

- Sewage pH in sewers varies significantly, caused by both the variation of wastewater composition and the in-sewer processes.
- Change of sewage pH during its transportation in a sewer could be predicted using the charge balance approach. This requires knowledge of net total cation concentration, which could be obtained from the composition and pH data of fresh sewage.
- Measurement of total ammonium in the feed is necessary for the accurate prediction of pH change during the transportation of sewage in sewer. Calculation of total ammonium concentration based on the initial pH measurement can be used for pH modeling with reasonable accuracy.
- Total ammonium in sewage is the most influential factor determining pH in fresh sewage. The pH variation in fresh sewage follows closely the variation in the total ammonium concentration. The pH model can be reasonably calibrated by measuring ammonium in fresh sewage.

Acknowledgments

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.watres.2013.07.027.

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