BufferSystem
User Manual v. 1.000

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Background

The buffer system in wastewater consists of several species,

- Dissolved Inorganic Carbon (DIC)
- Acetic acid (and other VFA's)
- Dissolved sulfide
- Phosphate
- Ammonia
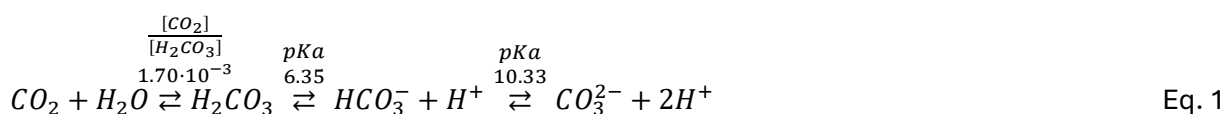- Amino groups
- Carboxyl groups/HSO_4^-

Dissolved inorganic carbon is typically the species that dominates the buffer system of wastewater, but other species cannot be ignored. Their importance depends partly on their concentration and partly on the pH at which the buffer effect is assessed.
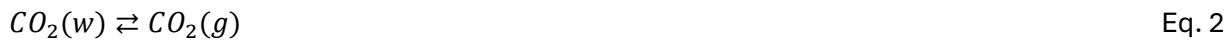
In Mega-WATS, the buffer system is solved as outlined in Anaerobic Digestion Model No.1 (ADM1), published by IWA (latest revision is 2005). Here the buffer system is calculated from the sum of cations and anions. For further details, see ADM1.

Buffer system compounds

Carbonates

In many aquatic systems, carbonates are a significant contributor to the buffer system. This also holds true for municipal wastewater where carbonates are formed by biological oxidation of organic matter (Hvitved-Jacobsen et al., 2013). Carbonates also originate from potable water and from infiltrating groundwater, both of which may be supersaturated with CO_2. Carbonic acid is in equilibrium with dissolved CO_2 and the dissolved inorganic carbon (DIC) concentration of wastewater is hence affected by liquid-gas mass transfer of CO_2. In other words, the exchange of CO_2 between wastewater and sewer headspace affects the wastewater buffer system (Eq. 1 and 2) and must hence be taken into account, as it must when addressing the carbonate in other aquatic systems (Carroll et al., 1991). Wastewater in sewers is typically supersaturated with CO_2 as the solubility of CO_2 in water is low compared to the CO_2 formed by biological oxidation of organic matter. As an example, a headspace CO_2 concentration of 400 ppm in equilibrium with CO_2 in wastewater at pH 7.5, results in a DIC concentration of about 0.2 mole m^{-3}. However, at aerobic conditions, typically some 5-20 g COD m^{-3} is oxidized per hour (Hvitved-Jacobsen et al., 2013), causing some 0.1-0.7 mole m^{-3} of carbonate to be formed every hour. Carbonates can also react with several cations to form insoluble precipitates. It is conceivable that salts of carbonate such as calcium carbonate play a role in some wastewaters (Eq. 3); however, little or no research has hitherto addressed this issue.

$$CO_2 + H_2O \overset{\frac{[CO_2]}{[H_2CO_3]}}{\underset{1.70\cdot10^{-3}}{\rightleftarrows}} H_2CO_3 \overset{pKa}{\underset{6.35}{\rightleftarrows}} HCO_3^- + H^+ \overset{pKa}{\underset{10.33}{\rightleftarrows}} CO_3^{2-} + 2H^+ \hspace{2cm} \text{Eq. 1}$$

$$CO_2(w) \rightleftarrows CO_2(g) \hspace{6cm} \text{Eq. 2}$$

$$Ca^{2+} + CO_3^{2-} \rightleftarrows CaCO_3 \hspace{5cm} \text{Eq. 3}$$
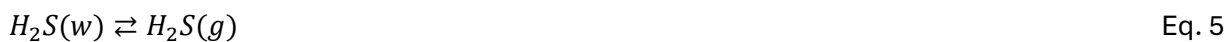
The formation of CO_2 causes a decrease of wastewater pH, while the release causes an increase.
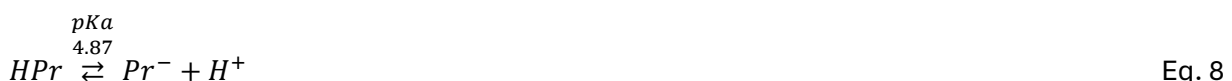
Sulfides

Hydrogen sulfide is seldom present at the wastewater source but is formed in the conveyance system by anaerobic reduction of sulfate. Under aerobic or anoxic conditions, it can be oxidized to for example sulfate or elemental sulfur (Nielsen et al., 2006). Like carbon dioxide, hydrogen sulfide has low water solubility and is readily transferred across the liquid-gas boundary (Eq. 5). It is only the molecular form that is transferred, and with a pK_a value around 7, the transfer hence depends strongly on pH at levels typically found in sewer systems (Eq. 4). Sulfide furthermore precipitates with various divalent heavy metal cations such as iron, copper, and zinc (Eq. 6), all of which are present in municipal wastewaters (Nielsen et al., 2005; 2006; 2008). At typical wastewater pH-levels, the formation as well as the precipitation of hydrogen sulfide causes a lowering of the pH, while the oxidation as well as the release to the sewer headspace causes an increase.

$$H_2S \overset{\substack{pKa \\ 7.05}}{\rightleftarrows} HS^- + H^+ \overset{\substack{pKa \\ 19}}{\rightleftarrows} S^{2-} + 2H^+ \hspace{3cm} \text{Eq. 4}$$

$$H_2S(w) \rightleftarrows H_2S(g) \hspace{5cm} \text{Eq. 5}$$

$$Me^{2+} + S^{2-} \rightleftarrows MeS \hspace{5cm} \text{Eq. 6}$$

Volatile fatty acids

Of the VFA's, it is especially acetic acid, and propionic acid which can be present in municipal wastewaters. They are formed under anaerobic conditions by fermentation processes (Hvitved-Jacobsen et al., 1995) and again oxidized under aerobic and anoxic conditions. They have pKa-values around 4.8 and hence contribute to the buffer strength at low pH only (Eq. 7 and 8). They are slightly volatile and can in their molecular form hence in principle be transferred from the wastewater to the sewer headspace. Their low pK_a-values and their high water solubility means, however, that this process in practice can be disregarded when addressing the buffer system of sewer wastewaters. The formation of VFA's causes pH to decrease while its oxidation causes the pH to increase.

$$HAc \overset{\substack{pKa \\ 4.76}}{\rightleftarrows} Ac^- + H^+ \hspace{5cm} \text{Eq. 7}$$

$$HPr \overset{\substack{pKa \\ 4.87}}{\rightleftarrows} Pr^- + H^+ \hspace{5cm} \text{Eq. 8}$$
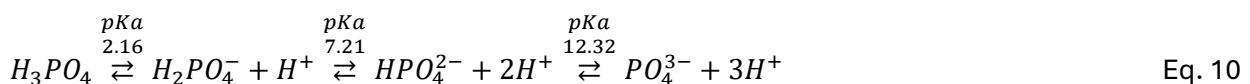
Ammonia

Ammonia can in principle can be transferred between liquid and gas. However, like the VFA's it is rather water soluble and hence tends to stay in the water. It furthermore has a pK_a value around 9.2 with the molecular form only being present at high pH (Eq. 9). Its liquid-gas transfer can hence be ignored under typical sewer conditions. A complicating factor is that ammonia originates from urea and hydrolysis of organic matter and seldom is present in the wastewater at its source. It is generally agreed upon that bacterial decomposition of urea to ammonia is a rapid process and that it is largely completed by the time the wastewater has reached the treatment works (Sattayatewa et al., 2010). However, the fate of urea in sewer systems has not been thoroughly studied, and no quantification of this process is hence available. It is in this context worthwhile to note that the decomposition of urea to ammonia at typical wastewater pH (7-8) consumes protons (Eq. 9) and hence causes pH to increase. Ammonia is not much affected by in-sewer processes as nitrification does not take place in sewers. The reason for the latter is that the comparative low growth rate of the nitrifiers restricts these to the sewer biofilm where they loose the competition for oxygen to the faster growing heterotrophs. Ammonia can hence be treated as conservative (not undergoing transformation) when addressing the buffer system of wastewater in sewers.

$$NH_4^+ \overset{\substack{pKa \\ 9.25}}{\rightleftarrows} NH_3 + H^+ \qquad \text{Eq. 9}$$

Phosphate

Mono-phosphates originate from the source of the wastewater but can also to some extent be formed by breakdown of organic molecules in the sewage (Eq. 10). Mono-phosphates can form precipitates with trivalent iron which may be present in the wastewater. At typical wastewater pH values, the phosphates can form complexes probably also containing calcium, hydroxide and carbonates. These processes have though not been thoroughly studied and for practical applications phosphates should be treated as conservative in sewer systems.

$$H_3PO_4 \overset{\substack{pKa \\ 2.16}}{\rightleftarrows} H_2PO_4^- + H^+ \overset{\substack{pKa \\ 7.21}}{\rightleftarrows} HPO_4^{2-} + 2H^+ \overset{\substack{pKa \\ 12.32}}{\rightleftarrows} PO_4^{3-} + 3H^+ \qquad \text{Eq. 10}$$

Amino groups

Organic compounds containing amino groups are weak bases of the form R-NH$_2$. Examples of such compounds present in high concentrations are proteins and amino acids. The NH$_2$-group can, like ammonia, take up a proton and become a NH$_3^+$ group (Eq. 11). The pK_a values of such bases vary but are often above 9.

$$R - NH_3^+ \overset{\substack{pKa \\ often>9}}{\rightleftarrows} R - NH_2 + H^+ \qquad \text{Eq. 11}$$

Bisulphate

Bisulfate (HSO_4^-) is a weak acid with sulfate (SO_4^{-2}) as its conjugate base. Sulfates in wastewater originate from the potable water source, from waste source, and from infiltrating groundwater. Bisulfate has a pK_a value around 2.0 and hence only plays a role in the wastewater buffer system at very low pH. The same is the case for the carboxyl groups of organic compounds, R-COOH. They have varying pKa values but typically at the lower end of the pH-scale.

Water

Finally, water self-ionizes with a pK_w value which at 25°C of 14.0, and hence acts as a week acid/base itself.

Modeling the buffer system of wastewater

The approach to solve the complex buffer system of an aquatic solution has been well-known since the beginnings of chemistry, and the approach is thoroughly described in many textbooks such as Atkins et al (2012). For a weak aquatic solution, it requires that the total concentrations of each buffer compound are known, that dissociation constants are known, and that the concentration of protons (pH) is known. Based here on a set of coupled equations can be formulated which can readily be solved.

The approach can be illustrated using carbonate as example, where Equation 12 defines the mass balance in inorganic dissolved carbonate. The mass balances for the other acids and their conjugate bases are formulated similarly.

$$T_{carb} = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] \qquad\qquad Eq.\ 12$$

For a specific compound the distribution between its species can be found from the mass balance together with the definition of the acid dissociation constants, K_a. Carbonic acid, for example, has two acid dissociation constants, K_{a1} and K_{a2}, as it is a diprotic acid. The constants are defined by Equations 13 and 14.

$$K_{a1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} \qquad\qquad Eq.\ 13$$

$$K_{a2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \qquad\qquad Eq.\ 14$$

Substituting Equations 13 and 14 into Equation 12 and isolating the three carbonate species results in Equations 15, 16 and 17 which determine the relative concentration of each species depending on the proton concentration.

$$[H_2CO_3] = T_{carb}\frac{[H^+]^2}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}} \qquad\qquad Eq.\ 15$$

$$[HCO_3^-] = T_{carb}\frac{K_{a1}[H^+]}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}} \qquad\qquad Eq.\ 16$$

$$[CO_3^{2-}] = T_{carb} \frac{K_{a1}K_{a2}}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}}$$

Eq. 17

The concentrations of other constituents of the buffer system can be set up similarly.

Calculating the pH for a change in the buffer system

The foundation of the calculation approach is the observation that for any aquatic solution, the sum of cations must equal the sum of anions.

$$\sum Cations = \sum Anions$$

Eq. 18

where

$$\sum Cations = [OH^-] + 2\left[CO_3^{2-}\right] + [HCO_3^-] + [R-COO^-] + 2\left[S^{2-}\right] + [HS^-] +$$
$$3\left[PO_4^{3-}\right] + 2\left[HPO_4^{2-}\right] + [H_2PO_4^-] + 2\left[SO_4^{2-}\right] + [HSO_4^-]$$

$$\sum Anions = [H^+] + [NH_4^+] + [R-NH_3^+]$$

BufferSystem – the model

BufferSystem simultaneously solving Equation **Error! Reference source not found.** together with the relevant mass balance equations of the type illustrated by Equation 12 and the species distribution equations of the type illustrated by Equations 15, 16 and 17 to calculate the pH of an aquatic solution of buffers. In praxis the set of algebraic equations are solved iteratively.

The software is stand-alone and does not require any other file than the exe-file. When running BufferSystem.exe, the program opens as shown Figure 1.

Comments to the buffer species:

- Dissolved Inorganic Carbon is often unknown and a calibration parameter.
- Acetic acid is used as surrogate for all VFAs as the VFAs have somewhat similar pKa values and because acetic acid typically is the dominating VFA.
- Dissolved sulfide is the sum of all dissolved sulfide species.
- Phosphate is the sum of all dissolved mono-phosphate (dissolved phosphate) species.
- Ammonia is the sum of ammonia and ammonium
- Amino groups is typically not known. As it relates to ammino acids and proteins, it can be assumed proportional to the COD of the wastewater, for example as [Amino groups] = 0.0042 [COD]
- Carboxyl groups are only relevant at very low pH (below 3-4), and can be set as [Carboxyl groups] = [sulfates]
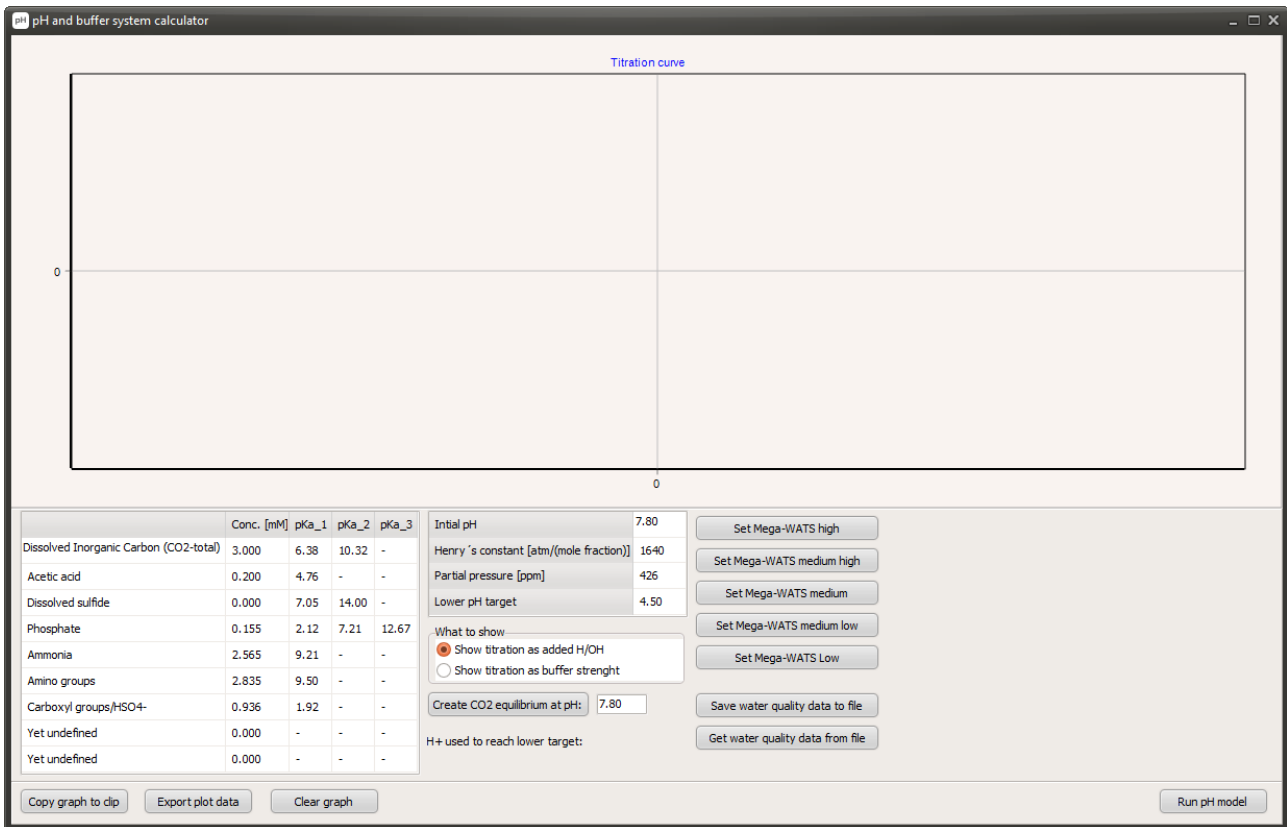
Figure 1. BufferSystem after opening the software

Running the pH model with the parameters set in Figure 1 yields the simulation shown in Figure 2. Note that the simulation begins at the initial pH and ends at the lower pH target.
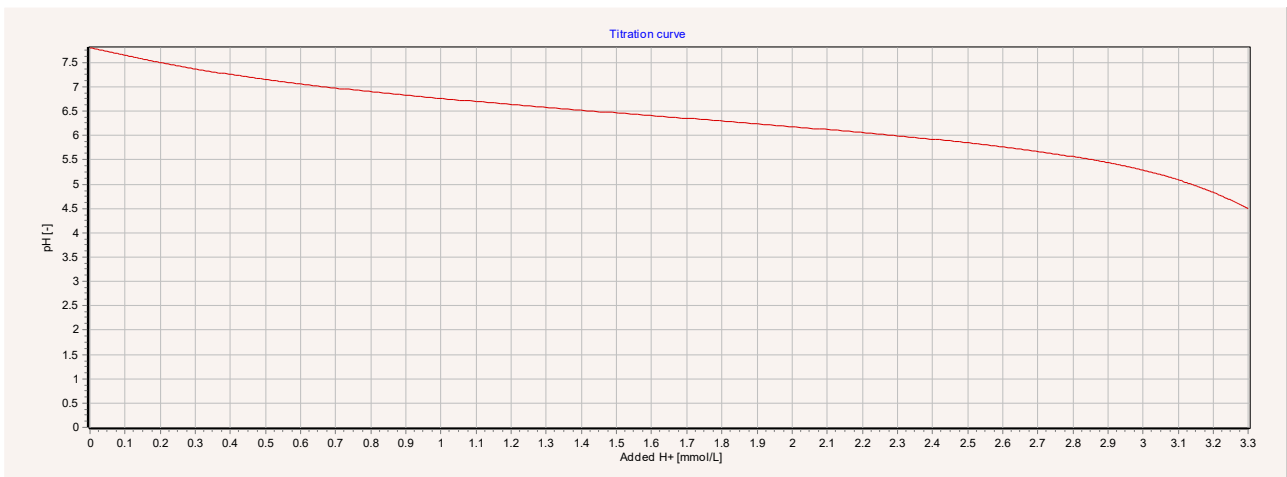

Figure 2. Simulation of titration according to the setup shown in Figure 1.

The buffer strength of the water can be shown by checking the radio button *Show titration as buffer strength*. The resulting graph is shown in Figure 3. Buffer strength tells how much acid must be added to reduce the pH, i.e. it is obtained as the slope of the curve in Figure 2. In this case it for example shows that it would require significant amounts of acid to reduce the pH much below 7.
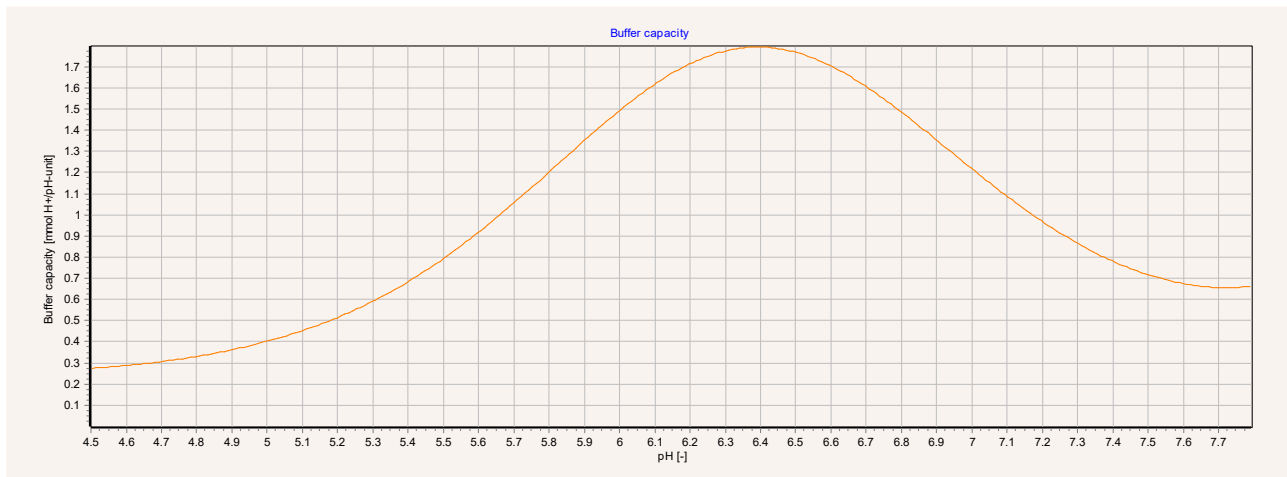
Figure 3. Simulation of buffer strength according to the setup shown in Figure 1.

Relating alkalinity to the titration curve

Alkalinity is a measure of the buffering capacity of a water, or alternatively 'the capacity of water to resist acidification '. It is defined as the amount of acid needed to titrate a water volume down to a certain pH. Often that pH is chosen as 4.5. There is however no clear endpoint of this titration, and some confusion can hence arise.

In the example shown in Figure 2, the titration endpoint was chosen as pH 4.5, i.e. the endpoint for an alkalinity titration. In the simulation, 3.30 mM of acid was needed. The alkalinity of the water hence was 3.30 milli-equivalents per L. (m-eq/L).

Alkalinity is often measured in the unit of $CaCO_3$. As calcium has the charge 2+, one mole of $CaCO_3$ is equal to 2 equivalents (eq). The alkalinity as measured in $CaCO_3$ equivalents hence is 3.3 × 50 = 165 mg/L of $CaCO_3$.

The approach can also be used to calculate the dissolved inorganic carbon from a measured alkalinity. Assume for example that the measured alkalinity is 300 mg/L of $CaCO_3$ measured at pH 7.5. The alkalinity in terms of m-eq/L is 300/50 = 6.0 m-eq/L. Adjusting the dissolved inorganic carbon till this value is reached, leads to 6.16 mg/L of dissolved inorganic carbon. If the same alkalinity had been measured at pH 7.0, then the dissolved inorganic carbon concentration would have been 7.25 m-eq/L. This illustrates that one must know the start pH of the alkalinity titration to interpret the measurement correctly.

Using the buffer system to predict alkaline dosing

BufferSystem can also be used to predict how much base is needed to reach a certain pH. Simply set the initial pH to the required value and the lower pH target to the actual pH of the wastewater. Then run the model. The outcome is how much acid is needed to lower the pH from the initial value to the end value. However, to go the other way, one must add the same amount of base. Note that of ammonia

and amino groups concentrations become quite important when increasing pH above approx. 8.5 (Figure 4)
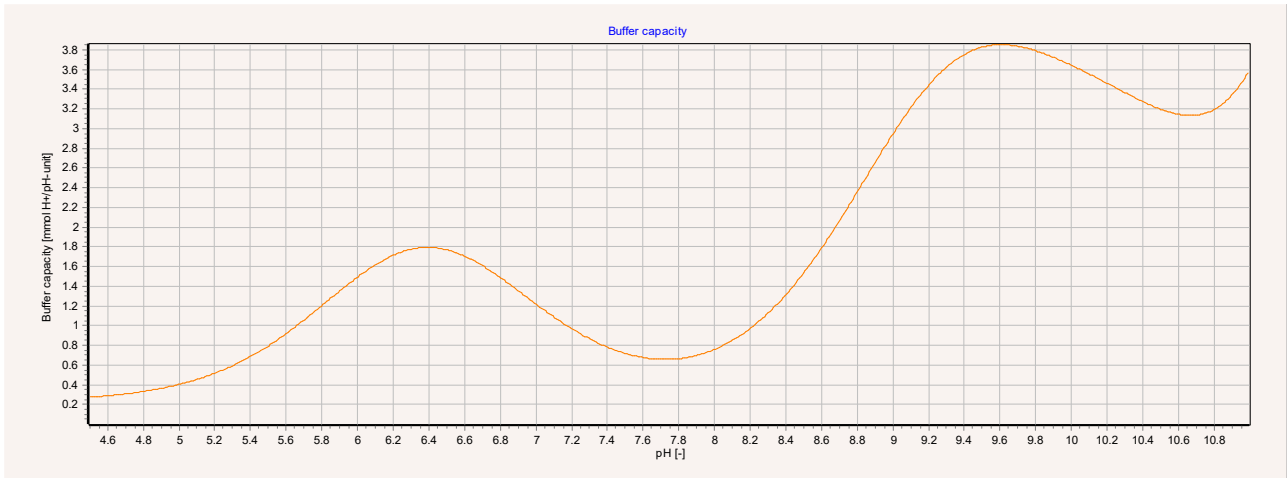

Figure 4. Simulation of buffer strength according to the setup shown in Figure 1.