pH buffer capacity based monitoring of algal wastewater treatment

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Abstract

A pH buffer capacity based method for multivariate monitoring of tertiary algal wastewater treatment systems is presented. A pilot plant with algal biomass receiving the effluent of a carbon removing activated sludge municipal wastewater treatment plant was used for the experimental work. Two types of buffer capacity profiles are considered, first resulting from a titration from the actual pH to pH 2.5 (down titration), and second as a result of a titration from pH 2.5 to pH 11 (up titration). The experiments were conducted with a laboratory titrator and the buffer capacity profiles were processed by fitting mathematical models of buffer systems to them. This allowed to quantify the inorganic carbon (IC) buffer from the down titration profiles. IC is of major importance, because it is the only carbon source used by algae. It is shown that the IC concentration derived from the buffer capacity profile gives different process information than a standard alkalinity measurement. The up titration profiles were successfully used for the quantification of NH_4^+ and o-PO_4, although an exact comparison of the laboratory results and the buffer capacity based results is difficult, because of the filtration step preceding laboratory analyses and possible interferences caused by unmodeled buffer systems. No filter device was used, which makes it possible to implement this measurement method in a robust and field applicable sensor. The complete measurement cycle (down titration followed by up titration and data interpretation) can be performed in less than 1 hour, with little manipulation, that could easily be automated.

Keywords

pH buffer capacity, algal wastewater treatment, alkalinity, on-line monitoring, mathematical modeling

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Introduction

Algal wastewater treatment: Traditionally, the aims of wastewater treatment have been to reduce the concentration of organic matter and the number of pathogens. However, in many treatment plants typical primary and secondary treatments cannot meet the increasingly stringent requirements of water pollution control. Although secondary effluents may contain low levels of BOD_5 and COD, they still contain high levels of inorganic nutrients (NH_4^+, NO_3^-, PO_4^{3-}). These nutrients are primarily responsible for eutrophication of the receiving waters [19] [27].

Nowadays more and more plants adapt and / or extend their secondary treatment facilities towards "nutrient removal capacity" [2] [17] [25], but even effluents with low concentrations of these pollutants can have a negative impact on the environment if they are discharged in high volume, especially if the receiving water is a rather small river. Tertiary treatment is becoming a necessity to minimize the harmful impact of effluents on the environment.

Besides biological nitrogen and phosphorus removal, numerous physico-chemical treatments such as chemical coagulation, breakpoint chlorination, NH_3-stripping, reverse osmosis and filtration have been proposed for removing nitrogen and phosphorus. However, due to costs and operational practices, these technologies are not implementable for municipal wastewater treatment of small communities [20].

As an alternative, tertiary treatment involving micro-algae or cyanobacteria is shown to be effective in nitrogen and phosphorus removal [20] [19]. The process is quite attractive because of its capacity to transform wastes into useful biomass using sunlight as an energy source. However these algal treatment systems also have some drawbacks: The generation time of the organisms involved is long compared to bacteria; there is a necessity for sunlight; the active part of the biomass is small and harvesting of biomass is difficult [27] [7].

In recent years, research has been conducted to overcome the problems related to algal tertiary wastewater treatment, and to optimize the treatment process [20] [18] [34] [38] [8]. The harvesting problem of the algal biomass has been solved by using organisms like the cyanobacterium *Phormidium bohneri*, which has the ability to form flocks that settle, thus facilitating harvest [30].

Algal wastewater treatment processes often are discontinuous, of SBR (sequencing batch reactor) type, where one treatment cycle consists of a filling phase, an aeration phase, a settling phase and an effluent discharge phase. Such processes need continuous monitoring of the most important process variables, in order to obtain an optimal nutrient removal capacity at minimal costs. Especially when one realizes that nutrient removal processes are often related to phases of luxury uptake (e.g. phosphates) and phases of nutrient release,

the usefulness of on-line measurements is obvious.

Alkalinity related to algal processes: The alkalinity of a water sample is defined as the amount of acid necessary to decrease the pH to a predefined end value. Two end values are considered [14]:

1. End value 8.3 (only relevant if the sample pH is higher than 8.3): this is called the phenolphtalein or carbonate alkalinity (symbol C), and is a measure of the amount of strong bases, carbonates and alkali present in the sample.

2. End value 4.5 (only relevant if the sample pH is higher than 4.5): this is called the total alkalinity (symbol T), and is a measure of the amount of strong and weak bases (like bicarbonates).

The alkalinity can be measured in the laboratory using a recipient of known volume of sample and a burette containing a strong acid (e.g. HCl 0.02 N). It can be expressed in $meq\, l^{-1}$ or in $mg\ CaCO_3\, l^{-1}$.

Alkalinity is a popular measurement used in the process control of diverse water treatment processes, e.g. in activated sludge treatment [28] [40] [29] or in anaerobic wastewater treatment [9] [5]. In practice alkalinity is often used as a practical measure of the amount of carbonates and bicarbonates in the water. There are some particular remarks concerning the use of alkalinity as "(bi)carbonate" estimator:

- In cases the sample is loaded with weak acid buffering systems other than the CO_2 subsystem (like ammonium, phosphates and VFA's), these components will be included in the alkalinity and will suggest that more (bi)carbonates are present than in reality [6].

- For the pH meter method, it is advised to choose the end value in function of the alkalinity (end-value ranging from pH 4.3 to pH 4.9 for high to low alkalinity respectively) [39]. For color indicator methods, like the bromcresol method, the pH value 4.5 corresponds with the inflection point on the titration curve where the color indicator will switch to its other state. In case the inflection point is not so sharp, or the solution contains strong coloring substances, the color switch will be difficult to observe. For this reasons, the pH meter method is mostly preferred above the older color indicator methods.

In the application area of wastewater treatment, modified or extended methods of the alkalinity measurement have been developed. Examples of extended methods where more than 1 end value in the titration profile are considered are a three-point method [1] and a five-point method [22] for the determination of bicarbonate and VFA. Methods using more than 5 points for bicarbonate and VFA estimation have also been developed

[3] [26]. To eliminate the effect of interfering pH buffers when one is only interested in bicarbonate content, a method was developed where the CO_2 is stripped from the sample by addition of strong acid. The stripped CO_2 can be directly measured by the volumetric [16] [15] or pressure [9] build-up of CO_2. The described methods have been used in the application area of anaerobic treatment, where high concentrations of both bicarbonate and VFA's are present [5] [6]. An overview of measurement methods for CO_2 and bicarbonate is given in [10] [24].

Alkalinity related techniques for bicarbonate estimation are well developed in applications where CO_2 is continuously generated by micro-organisms degrading organics. In these areas possible interferences with other pH buffering components are negligible. In the area of algal treatment, on the other hand, CO_2 is consumed by the algae, resulting in relatively low or even limiting concentrations of bicarbonate in the water samples. Inorganic carbon (IC) is of major importance, because it is the only carbon source used by algae. Among the different forms of IC ($CO_{2(aq)}$, HCO_3^- and CO_3^{2-}), only the two first ones are taken up by the algal biomass, and thus useful as a carbon substrate [11] [13] [36]. The preference for $CO_{2(aq)}$ or HCO_3^- uptake is pH dependent [42] and an adaptation period to switch between the $CO_{2(aq)}$ and HCO_3^- transport system may be required [11]. The importance of the IC buffer system in relation to photosynthetic algal growth is widely described in literature [31] [35] [23] [37]. Therefore, the usefulness of quantifying the IC buffer for algal wastewater treatment is twofold. First, a precise knowledge of the inorganic carbon content can indicate whether the IC becomes limiting [23], and whether IC supply is needed [31] [37]. Second, because IC is the only carbon source used by the algae, the rate of IC consumption under light conditions can be used as a process and control variable, e.g. indicating a possible reactor failure if the IC consumption is too low.

Theoretical Model for pH Buffer Capacity Curves

In general the pH buffer action of a system is defined by its resistance against pH changes when acid (C_A) or base (C_B) are added. The symbol for buffer capacity is β or π (buffer index) [33], and its unit is $meq\, l^{-1}\, pH^{-1}$.

$$\beta = \frac{dC_B}{dpH} = -\frac{dC_A}{dpH} \tag{i}$$

The origin of the buffer capacity are conjugated acid / base systems. A weak monoprotic acid ($C_a\ mol\, l^{-1}$) dissolved in water will dissociate until an equilibrium between the acid (HA) and the base (A^-) form is established:

$$HA \rightleftharpoons H^+ + A^- \tag{ii}$$

A mathematical representation of this chemical equilibrium is based on three equations: a mass balance, a dissociation equation and an electro-neutrality equation. First, a mass balance for HA can be written:

$$C_a = [HA] + [A^-] \tag{iii}$$

Second, the equilibrium is driven by its dissociation constant K_a or dissociation exponent pK_a [33]:

$$K_a = \frac{[H^+][A^-]}{[HA]} \text{ and } pK_a = -\log K_a \tag{iv}$$

The pK_a value is a function of the thermodynamic pK_a^0, the temperature and the ionic strength [10] [32]. Water itself can be considered to be a weak monoprotic acid, with concentration C_w = 55.5 $mol\ l^{-1}$ and pK_w = 15.74 (at T = 25 ^oC), thus a similar mass balance and equilibrium equation can be written:

$$C_w = [H_2O] + [OH^-] \tag{v}$$

$$K_w = \frac{[H^+][OH^-]}{[H_2O]} \text{ and } pK_w = -\log K_w \tag{vi}$$

The influence of the water buffer on the experimental buffer capacity curve is only significant at $pH < 5$ or $pH > 9$ [43]. In a water sample containing several buffering components, one can write that the total buffer capacity β is equal to the buffer capacity of the water itself β_w summed with the buffer capacity β_i of the different components i in the sample:

$$\beta = \beta_w + \sum_{i=1}^{n} \beta_i \tag{vii}$$

Consider a water sample with 1 monoprotic buffering component (HA) at low pH, to which a small volume of strong base (e.g. NaOH) with a concentration C_B ($mol\ l^{-1}$) is added. Third, the electro-neutrality has to be maintained:

$$[Na^+] + [H^+] = [OH^-] + [A^-] \tag{viii}$$

Based on this electro-neutrality equation one can write for an infinitesimal addition of C_B:

$$dC_B = -d[H^+] + d[OH^-] + d[A^-] \tag{ix}$$

or in terms of buffer capacity β:

$$\beta = \frac{dC_B}{dpH} = -\frac{d[H^+]}{dpH} + \frac{d[OH^-]}{dpH} + \frac{d[A^-]}{dpH} \tag{x}$$

After substitution of pH by $-\log[H^+]$, followed by differentiation (using $d(\log u) = \frac{1}{u}\log e\ du$) and using the mass balances (iii) and (v), together with the equilibrium equations (iv) and (vi), one can rewrite (x):

$$\beta = 2.303\left([H^+] + C_w K_w \frac{[H^+]}{([H^+] + K_w)^2} + C_a K_a \frac{[H^+]}{([H^+] + K_a)^2}\right) \tag{xi}$$

If different monoprotic weak acids are present in the sample, the equation for β can be extended with similar additional terms. For polyprotonic acids the additional terms are somewhat more complex. For a diprotic acid with concentration C_b in water:

$$\beta = 2.303 \left([H^+] + C_w K_w \frac{[H^+]}{([H^+] + K_w)^2} + C_b K_{b1} \frac{[H^+]^2 + 4K_{b2}[H^+] + K_{b1}K_{b2}}{([H^+]^2 + K_{b1}[H^+] + K_{b1}K_{b2})^2} \right) \quad \text{(xii)}$$

And for a triprotic acid with concentration C_c in water:

$$\beta = 2.303 \left([H^+] + C_w K_w \frac{[H^+]}{([H^+] + K_w)^2} \right.$$

$$\left. + C_c K_{c1} \frac{[H^+]^4 + 4K_{c2}[H^+]^3 + (K_{c1} + 9K_{c3})K_{c2}[H^+]^2 + (4[H^+] + K_{c2})K_{c1}K_{c2}K_{c3}}{([H^+]^3 + K_{c1}[H^+]^2 + K_{c1}K_{c2}[H^+] + K_{c1}K_{c2}K_{c3})^2} \right) \quad \text{(xiii)}$$

A general equation can be written for the buffer capacity of a sample containing l monoprotic, m diprotic and n triprotic weak acids:

$$\beta = 2.303 \left([H^+] + C_w K_w \frac{[H^+]}{([H^+] + K_w)^2} + \sum_i^l (term1)_i + \sum_j^m (term2)_j + \sum_k^n (term3)_k \right) \quad \text{(xiv)}$$

The objective of this paper is to develop a pH buffer capacity based sensor, capable of extracting concentrations of pH buffering components from on-line measured titration curves coming from the influent, effluent and reactor content of an algal pilot plant. The information that can be extracted from the buffer capacity profiles using mathematical modeling is evaluated towards its usefulness related to tertiary algal treatment processes. The relationship between the alkalinity and the IC buffer capacity will be discussed, as well as the ammonium and ortho-phosphate assessment from the buffer capacity profile. In the latter case, IC, NH_4^+ and o-PO_4 will be incorporated in equation (xiv) as diprotic, monoprotic and triprotic weak acids respectively. The results obtained with the buffer capacity sensor seem promising as input to develop a control strategy, although this is not the objective of this paper.

Materials and Methods

The algal pilot plant: A pilot reactor with algal biomass, installed at the outlet of the activated sludge plant Valcartier near Quebec city (Canada), was used for the sample collection between July 22 and August 12, 1997. The activated sludge plant was treating domestic wastewater of the military base Valcartier, and received an influent flow of around 2500 $m^3 d^{-1}$. The plant was operating in partially nitrifying mode and the secondary effluent nitrogen was present in two forms, NH_4^+ and NO_3^-.

The algal bioreactor with a triangular cross-section had a volume of 6 m^3 and combined aeration and mixing was obtained by means of a perforated flexible tube at the bottom of the reactor. This pilot reactor was in use for 2 years and its function was to further decrease the nutrient concentrations of the secondary effluent. The reactor was used in batch mode, in cycles of 1 or 2 days. A cycle consisted of a filling phase (in the morning), an aeration phase of 12 or 36 hours, a sedimentation phase (at night) to allow the algae to settle down, and a decantation phase (in the morning) to remove an upper liquid layer of around 75 % of the total reactor volume. The biomass concentration in the reactor was kept between 100 and 600 $mg\ DW\ l^{-1}$.

Sampling and laboratory measurements: Light, pH, DO and temperature were monitored continuously in the algal pilot plant. Three different kinds of samples were taken for further analysis in the laboratory:

- The Effluent of the ValCartier plant (sample code EVC), being the influent of the algal pilot reactor;
- The content of the Algal Pilot (sample code AP), 3 hours after the reactor was filled and completely mixed by the aeration;
- The Effluent of the Algal Pilot plant (sample code EAP).

The EVC and EAP samples were taken with a peristaltic pump in the inlet and outlet of the pilot plant during filling and decantation phases respectively. The AP samples were taken as manual grab samples. All samples were stored immediately in the fridge ($4\,^oC$) and processed in the laboratory within 1 day.

Prior to the laboratory analyses (NH_4^+, NO_3^-, o-PO_4), all samples were filtered on a Whatman 934 AH filter, with a pore size of 1.5 μm. The analyses were conducted according to Standard Methods [14]. For the total alkalinity measurements in the laboratory, the pH meter method was used [14].

Titration curves: Titrations were performed with a Titrino 716 titrator (Metrohm, Switzerland). Data acquisition was performed with a 386 PC connected to the titrator. The titrated sample volume was 100 ml, and titration took place in a completely closed magnetically stirred titration vessel containing a CO_2 scrubber (bowed glass tube with soda lime pellets) to prevent entrance of CO_2 from the air. The headspace of the titration vessel was 150 ml. Prior to titration, the refrigerated samples were equilibrated to $25\,^oC$ with a warm water bath, and they were immediately titrated at room temperature, which varied between 20 and 25^oC. Two different types of titration profiles were collected:

1. *Down titration profile*: The sample as such was titrated with 0.1 N HCl from the actual pH to pH 2.5 using a monotonic endpoint titration (MET) method [21], with fixed steps of 0.05 ml. This type of titration was

used for the determination of the IC buffer.

2. *Up titration profile*: The down titrated sample was strongly agitated with a magnetic stirrer for 15 minutes to remove all CO_2, while the titration vessel was open to the air. Next, the vessel was closed and the sample was titrated with 0.1 N NaOH to pH 11 using a dynamic endpoint titration (DET) method [21]. The difference with the MET method is that the DET method does not take fixed volume steps, but variable volume steps (small versus big steps when the buffer capacity is low or high respectively). This type of titration was used for the determination of ammonium and ortho-phosphate.

Data processing software: Software developed in C++ was used for the calculation of the buffer capacity profiles. Such a profile is the inverse of the first derivative of the titration profile. The calculation of the derivative was performed using a parabolic regression in a moving window of 5 experimental data points of the titration curve. No further smoothing algorithms were necessary to obtain a smooth buffer capacity profile. The same software was used to fit several mathematical models to the calculated buffer capacity curve. For the parameter optimization, the PRAXIS algorithm [4], which is freely available on the internet, was implemented in the software. The mathematical model specifications were defined in a special input file, read by the program. The software was running on an INDIGO workstation (Silicon Graphics, U.S.) and the data processing of 1 experimental data file needed approximately 1 minute.

Mathematical models: The mathematical models used were all based on the general buffer capacity equation (xiv). For each model used, the following considerations were taken into account:

1. What is the pH interval used for data processing.
2. Which pH buffering components have to be included in the model.
3. What are the initial guesses for the concentrations and pK_a values of the different buffering components.
4. Which concentrations and pK_a values are to be adjusted in order to fit the simulation model to the experimental data. The parameters that are to be estimated are specified with a lower and upper limit (constrained optimization). The reason for optimizing pK_a values instead of keeping them fixed at the pK_a^0 or another value is to take into account the residual effects of temperature, ionic strength and possible electrode errors on the position of the pK_a values in the experimental buffer capacity curve.

For the down titrations a simulation interval between pH 4 and pH 7.3 was taken. Even if the initial pH of the sample was much higher than 7.3, it was not worthwhile to extend the simulation interval and incorporate ortho-phosphate or ammonium in the model, because the magnitude of the IC buffer would interfere with the other smaller buffer systems. For the up titrations, a simulation interval between pH 4 and pH 10 was chosen. In the software, concentrations can be specified in $mol\ l^{-1}$ or $mg\ l^{-1}$. More detailed model specifications for the down and up titrations are shown in Table 1 and Table 2 respectively.

[Table 1 about here.]

[Table 2 about here.]

The "soap" term in the models stands for a range of components that all have a buffer capacity in the range of pH 4 to 5.5, e.g. numerous organic acids. The "blank1" term stands for an unknown buffering component around pH 10, found to be present in almost all samples analyzed. The reason for incorporating the "carbon" component in the up titration model, despite the fact that the sample is priorly made CO_2 free, is that during up titration the CO_2 initially present in the headspace above the vessel can enter the sample and typically accounts for 0.07 $meq\ IC\ l^{-1}$.

Furthermore, once the total concentration C_{IC} (which is $[CO_3^{2-}]+[HCO_3^-]+[CO_{2(aq)}]$) is determined using the simulation model, the partitioning of these 3 forms can be calculated as function of the actual pH [39]. Using the mass balance and the 3 equilibrium equations for IC, the concentrations $[CO_{2(aq)}]$, $[HCO_3^-]$ and $[CO_3^{2-}]$ are given by equations (xv), (xvi) and (xvii) respectively. Details on obtaining these equations can be found in [33] [39].

$$[CO_{2(aq)}] = \frac{10^{-2pH}}{10^{-2pH} + 10^{-(pH+pK_{a1})} + 10^{-(pK_{a1}+pK_{a2})}} C_{IC} \tag{xv}$$

$$[HCO_3^-] = \left(1 - \frac{10^{-2pH} + 10^{-(pK_{a1}+pK_{a2})}}{10^{-2pH} + 10^{-(pH+pK_{a1})} + 10^{-(pK_{a1}+pK_{a2})}}\right) C_{IC} \tag{xvi}$$

$$[CO_3^{2-}] = \left(1 - \frac{10^{-2pH} + 10^{-(pH+pK_{a1})}}{10^{-2pH} + 10^{-(pH+pK_{a1})} + 10^{-(pK_{a1}+pK_{a2})}}\right) C_{IC} \tag{xvii}$$

Important to remark is that the latter 3 equations are only valid in a completely closed and equilibrated system. As the algal reactor is an open system, the concentration of $CO_{2(aq)}$ is also driven by Henry's law [32]:

$$[CO_{2(aq)}] = K_H \times pCO_{2(air)} \tag{xviii}$$

With $K_H = 3.4\ 10^{-2} atm^{-1} M$ (at $T = 25\ ^oC$) and $pCO_{2(air)} = 3\ 10^{-2} atm$, equation (xviii) leads to an air / liquid equilibrium concentration of $[CO_{2(aq)}] = 1.2\ 10^{-5} M$ or 0.012 $meq\ l^{-1}$, which is a very low value. Furthermore,

one has to take into account that a biological active system like and algal system is quite seldom in equilibrium with the atmosphere, so careful use of equation (xviii) is advised.

Results and Discussion

Alkalinity and IC buffer capacity: A random sample from the algal pilot reactor AP, taken in the morning of a sunny day was analyzed with the titrator and in the laboratory. A filtered and an unfiltered sample were titrated from the actual pH to pH 2.5 (Figure 1). Both samples were also analyzed on the total alkalinity with two standard methods.

[Figure 1 about here.]

From the titration curves, the corresponding buffer capacity curves (Figure 2) were calculated and the simulation model (equation (xiv) and Table 1) was used to quantify the concentration of the IC buffer. The best fit simulation result for the unfiltered and filtered sample is given in Figure 2.

[Figure 2 about here.]

For the total alkalinity determination, the end-point pH value for the pH meter method was set at pH 4.5, according to the standard method [14]. This method was also applied to the titration curves of Figure 1, where an interpolation between 2 successive data points was used to make a reading of the amount of acid necessary to bring the pH to 8.3 and 4.5 respectively. For comparison reasons, the simulation results to quantify the IC buffer were also expressed as $meq\,l^{-1}$.

The results of the alkalinity measurements and the simulation results for IC are presented in Table 3.

[Table 3 about here.]

The precision of the total alkalinity measurements (both the pH meter method and from the titration curve), expressed as relative standard deviation (r.s.d.), was between 1 and 2 %. The r.s.d. of the simulated IC concentration based on down titration profiles was 2 %. One can notice that the results for the filtered sample are only about 7 % lower than the unfiltered sample. This means that the alkalinity or IC buffer capacity is mainly related to the soluble phase and not to the algal biomass phase. The total alkalinity with the standard pH meter method was not significantly different from the total alkalinity calculated from the titration curves in Figure 1 (t-test; α = 5 %). An interesting feature of this experiment is found when comparing the IC content found with

the modeled buffer capacity curves and the alkalinity calculated from the same experimental titration curve. From Table 3, it can be seen that the total alkalinity is about 40 % higher than the corresponding simulated IC concentration and that the (T-C) alkalinity is still more than 20 % higher than the simulated IC concentration. This is the case in both the filtered and unfiltered sample. This indicates that the alkalinity of the sample is mainly, but not completely determined by the amount of IC.

To make a further interpretation of the different results in Table 3, a summarizing table with the buffers that are included in these results is presented in Table 4. None of the measurements in Table 4 exactly represents the amount of $CO_{2(aq)}$ or HCO_3^- in the water, which are the only two IC species that are available to the algae.

[Table 4 about here.]

The IC obtained with the simulation model will be the closest to the real amount of IC because interferences in the pH range 7 or higher (ammonium, ortho-phosphate) and in the pH range of 5.5 and lower (organic acids, detergents) are excluded in the simulation method. For the sample studied, the initial pH was 9.1, and the partitioning between the 3 different carbon species was 0.2 % $CO_{2(aq)}$, 93.9 % HCO_3^- and 5.9 % CO_3^{2-}, calculated with equations (xv), (xvi) and (xvii) respectively. From this, it is concluded that the algal available carbon was mainly in the bicarbonate form. From Table 4, it can be concluded, that in case the only buffer in the sample is the IC buffer, then both (T-2C) and the simulated $[HCO_3^-]$ represent exactly the bicarbonate content. If also other buffer systems (ammonium, ortho-phosphate, organic acids, ...) are present in the sample, the situation is different. On the one hand, the simulated $[HCO_3^-]$ will overestimate the real bicarbonate content when extra buffers with the same $pK_{a.}$ as the pK_{a1} of IC are present. On the other hand, the bicarbonate assessment from the (T-2C) measurement will be influenced by a much wider range of buffers. All extra buffers between pH 8.3 and pH 4.5 (e.g. ortho-phosphate, organic acids) will lead to an overestimation of the bicarbonate content, and all extra buffers between the actual pH and pH 8.3 (e.g. ammonium) will lead to an underestimation of the bicarbonate content. Practically, in this example, when comparing the (T-2C) to the simulated $[HCO_3^-]$ for bicarbonate estimation, an overestimation of the real amount of bicarbonate by (T-2C) is minimal 8 and 12 % for the filtered and unfiltered samples respectively (concluded from Tables 3 and 4 together). From 36 unfiltered samples (pH between 7.1 and 9.1) taken at various times in the algal reactor, it was found that the (T-2C) measurement always gave 4 to 22 % overestimation of the bicarbonate content compared to the $[HCO_3^-]$ from the simulation method. In case the IC would become more limiting in the algal reactor, or the interfering buffers would become more pronounced, the simulation method is to be preferred by far for the determination of available bicarbonate for the algae. Besides, the result of the simulation method

does not depend on the choice of the endpoint (pH 4.3 to 4.9, depending on the method and alkalinity range).

For this particular case-study, an automated alkalinity measurement possibly would reveal similar process information as the IC determination with the buffer capacity sensor. However, because the hardware and the hardware related practical difficulties (maintenance, calibration, ...) of an automated alkalinity measurement are very similar to this buffer capacity sensor, the main advantage of the buffer capacity sensor is that more parameters are obtained with a single measurement device.

NH_4^+ and o-PO_4 evaluation in grab samples: During a period of 14 days, samples were taken in the influent of the algal pilot reactor (EVC), in the reactor itself (AP) and in the effluent of the algal pilot plant (EAP). These samples were analyzed in the laboratory for NH_4^+ and o-PO_4. Subsamples of 100 ml were used to perform up titrations to obtain the buffer capacity profiles. For the AP samples, containing algal biomass, 2 different titration experiments were performed:

1. Titration of the raw sample as such (including 100 to 600 $mg\ DW\ l^{-1}$ of the algae);

2. Titration of the supernatant after the algae were settled to the bottom of the sampling vessel.

After the titration data were collected, the data processing was performed. The reproducibility for repeated sampling, titrating and optimization, expressed as relative standard deviation (r.s.d.), was less than 2 % for the ammonium concentration and less than 5 % for the ortho-phosphate concentration. The results of the AP samples with or without biomass were comparable for the ammonium prediction but different for the ortho-phosphate prediction. For the o-PO_4, the samples with biomass gave 50 to 100 % higher values than the samples without the biomass. This might indicate that a considerable amount of phosphate is related to the biomass fraction, or that this biomass fraction contains other weak acid buffering systems that interfere with the titrimetric ortho-phosphate determination. The validity range of the measurements using this approach is case dependent (e.g. presence or absence of interfering buffers) and depends on the titration conditions (e.g. sample volume, titrans normality, measurement point density). Based on the experience for this particular case, the minimum validity values are considered around 1 $mg\ N\ l^{-1}$ and 1 $mg\ P\ l^{-1}$.

Using the mathematical model (equation (xiv) and Table 2), a perfect fit between the experimental and simulated buffer capacity curves was obtained for all experimental data. An illustration of the experimental data and the model fitting for 3 selected EAP samples taken at different days is illustrated in Figure 3.

[Figure 3 about here.]

On the graph, one can easily distinguish the profiles of samples that are high or low in ammonium and/or phosphate concentration. For the samples shown in Figure 3, together with the other grab samples, the laboratory measurements (LAB) of NH_4^+ and o-PO_4 and the concentrations estimated with the model (titrator) are presented in Table 5.

[Table 5 about here.]

For the AP samples, only the results of the titration experiments without the algal biomass are shown, because they correspond most closely to the laboratory procedure where all samples were filtered prior to analysis. Overall, the linear relationship between laboratory and titrator results is shown in Figures 4 and 5.

[Figure 4 about here.]

[Figure 5 about here.]

The constructed linear regression lines with their 95 % confidence intervals are comparable to previous results obtained on secondary effluents with a similar buffer capacity sensor [43].

Dynamic NH_4^+, o-PO_4 and IC evolution in a 48 hours batch experiment: A 48 hours batch experiment was set up to monitor the nutrient removal in the algal pilot plant. The experiment started with a filling phase with EVC water at 8.00h in the morning. In the first 36 hours of the experiment, the aeration was activated, ensuring a completely mixed reactor. During the last 12 hours, the aeration was stopped. An automatic time-proportional sampler was used to obtain combined samples every 3 hours. During this experiment, 19 samples were titrated, among which the first 11 were samples from a completely mixed system (when aeration was activated). The last 8 samples were taken during the second night of the experiment, when the aeration was stopped and the algae had settled to the bottom of the reactor (4 samples close to the surface and 4 samples at the bottom). Based on the results of the grab samples mentioned above, it was decided to take titration curves of samples without algae only (titration of the supernatant after the algae were settled to the bottom of the sampling vessel).

[Figure 6 about here.]

For each sample, a down titration was performed to estimate the IC buffer capacity, followed by a 15 minutes stirring at pH 2.5 to remove the IC. Subsequently an up titration to pH 11 was performed to estimate

the ortho-phosphate and ammonium. The specifications of the buffer capacity model in equation (xiv) for the down and up titrations are given in Tables 1 and 2 respectively. In Figure 6 the results are given for the laboratory and titrator analyses of NH_4^+ and o-PO_4, and for the laboratory measurements of pH and NO_3^-.

Ammonium was mainly removed in the first day, dropping from around 9 to less than 1 $mg\ N\ l^{-1}$ during the first 24 hours. The fit between the experimental and simulated buffer capacity was very good for all samples, indicating that an adequate model was used. The ammonium concentrations determined in the laboratory showed good correspondence with the titrator results in the first 18 hours, but from 18 hours on, the concentrations resulting from the titrator showed an overestimation with 0 to 1.5 $mg\ N\ l^{-1}$. This can possibly be explained by the fact that a rather strong buffer is present between pH 9.8 and pH 10.3 in all samples, possibly giving some interference with the ammonium buffer only. This extra unknown buffer was modeled and its concentration was estimated at 0.3 $mmol\ l^{-1}$. If this buffer was ignored in the model, the fit between experimental and simulated buffer capacity profiles was poor, and the estimation of the ammonium concentration was 2 $mg\ N\ l^{-1}$ higher than the laboratory result. The nature of the interfering compound remains, however, unknown.

The ortho-phosphate concentration did not change very much during this 48 hours batch experiment, and both the laboratory results and the titrator results varied between 2 and 3 $mg\ P\ l^{-1}$. Again, a small systematic deviation between the results of the 2 measurement methods was observed. This time, the titration results were lower than the laboratory results. A possible explanation can be found in the complex equilibria that exist between the different forms of phosphorus [41]. These different forms of phosphorus play the role of 'PO_4 reservoir' through chemical exchanges. It is reported [41] that standard methods, like the molybdate method used here, can give a significant overestimation of the PO_4-ion under such conditions.

The results show that o-PO_4 is not removed from the secondary effluent by this pilot reactor. On the other hand NH_4^+ is almost completely removed after 1 day of treatment. From the viewpoint of nutrient removal process control, the batch cycle time could have been shortened to 1 day. An exact comparison of the laboratory results and the titrator results is difficult, because the titrator used the samples as such (or in case algae were present, only the upper part without the algal biomass), while the laboratory analyses were preceded by a filtration.

In Figure 7 the results are shown for the titrator based determinations of the IC present in the AP samples. As discussed in an earlier paragraph the estimated IC concentration with the titration system corresponds most closely to the amount of carbon available to the algal biomass. The IC concentration at the beginning of

the experiment was around 1.6 $meq\,l^{-1}$. During day 1, this concentration decreased to 0.9 $meq\,l^{-1}$. During night 1 the concentration of IC increased a bit, pointing to algal respiration. During day 2, the IC further decreased to around 0.7 $meq\,l^{-1}$. During night 2, in the upper part of the reactor, where no algae were present, no further decrease in concentration could be observed. At the bottom of the reactor, where the algae were settled, one notices a higher IC concentration in the first 3 hours, decreasing to the same level as the upper part of the reactor. An explanation for this can be found when looking at the oxygen concentration at the bottom of the reactor during night 2. In the first 3 hours after the aeration was stopped, the concentrated algal biomass consumed all oxygen for their respiration, resulting in a high IC concentration. In the remaining part of night 2, under anoxic conditions, an equilibrium in IC concentration between the upper and lower part of the reactor was established.

[Figure 7 about here.]

In order to make an interpretation of the changes in NH_4^+, o-PO_4 and IC, at least 2 different biological processes may be considered to be responsible for the observed phenomena. First, there is algal photosynthesis and respiration, with a consumption and release of inorganic carbon respectively. During photosynthesis nitrogen (NH_4^+ or NO_3^-) and phosphorus are taken up together with inorganic carbon (CO_2 or HCO_3^-) in the proportion $C : N : P \approx 106 : 16 : 1$ [33]. Second, there is the bacterial autotrophic nitrification, with a transformation of NH_4^+ into NO_3^- with a small consumption of IC, in the proportion NH_4^+-N : NO_3^--N : $C \approx 1 : 1 : 0.08$ [12]. The IC consumed for the formation of new nitrifying biomass is too low to be used to quantify the nitrification rate accurately. This nitrification process is in accordance with the NO_3^- evolution measured with off-line laboratory analysis, where an increase in NO_3^- from 10 to 16 $mg\,N\,l^{-1}$ was observed in the first 24 hours of the experiment. The next 48 hours, almost no further changes in NO_3^- occurred because NH_4^+ became limiting. Besides the biological consumption of the inorganic carbon for assimilation into new biomass, the decrease of the IC buffer can also be partially explained by the H^+ production by both biological processes, resulting in an alkalinity decrease [33]. At the other hand, the algal uptake of dissolved CO_2 during daytime, resulted in a net pH increase from pH 7.3 to pH 8.7, as observed during the first 12 hours. The pH of all samples was between pH 7.1 and pH 8.7, meaning that the bio-available carbon was always higher than 95 % of the quantified IC buffer system (equations (xv) and (xvi)). In this case study, the IC never dropped below 0.7 $meq\,l^{-1}$, which is a rather safe value compared to the 0.5 $meq\,l^{-1}$ reported to be needed [23] for normal operation. From an industrial point of view, this algal wastewater treatment appears to be a viable alternative for small communities [20]. However, the pilot-plant experiments in this study have shown that

especially for the phosphate removal, the % P removed (by precipitation and/or biologically) is lower than previous, smaller-scale studies [18] [27]. In the viewpoint of possible eutrophication of the receiving waters, further insights in the phosphorus removal mechanisms and further process optimization are necessary.

As the results of the titration method can be influenced by interfering buffering components, this measurement method cannot be considered to be an analytical device, replacing the standard laboratory methods. As illustrated above, the application of this titration method has to be seen in a process monitoring and alarm generation context. An innovative aspect of the presented buffer capacity sensor, is that it gives a multivariate response (IC, NH_4^+, o-PO_4) supplemented with extra information, e.g. the appearance or disappearance of extra buffer systems, that are useful for process monitoring.

Further research will focus on the implementation of a fully automatic sensor, including automatic buffer model selection to accommodate for (dis)appearing buffer systems. Further, an appropriate control strategy will be developed in which this device is providing the necessary data in due time. The time needed to perform a full measurement cycle was approximately 1 hour (down titration, up titration and data interpretation). Further optimization of the titration parameters can reduce this cycle time with 10-20 minutes. The cycle time can be further decreased to 20-25 minutes if the down and up titrations are performed in parallel titration vessels. Electrode problems were never observed during the performed experiments. The maintenance of the titration vessel and electrode is comparable to the maintenance of a pH meter.

Conclusions

The proposed methodology of a pH buffer capacity based measurement system was evaluated for its usefulness for multivariate monitoring of tertiary wastewater treatment with algae. In waters which are low or even limiting in IC buffer capacity (like in algal treatment plants), standard alkalinity measurements can give an overestimation of the IC buffer system, because the alkalinity is a general composite measurement, including all pH buffering components in the considered pH interval. For the samples analyzed, the (T-C) alkalinity was around 20 % higher than the IC concentration obtained with the buffer capacity sensor, explaining that other buffering components than IC are included in the (T-C) alkalinity (o-PO_4, NH_4^+, organic acids, ...). It is concluded that the HCO_3^- concentration assessed with the simulation method is preferred, rather than the (T-2C) alkalinity, when one wants to quantify the available bicarbonate.

The NH_4^+ and o-PO_4 assessment from the up titration profiles were comparable with the laboratory measurements. An exact comparison of the laboratory results and titration results was difficult, because of the

filtration step preceding laboratory analyses, and possible interferences by buffer systems not accounted for in the model.

During a 48 hours batch experiment, the measured IC concentration reflected the day / night difference in activity of the algal biomass fairly well. The data of the titrimetric sensor showed that there was no carbon limitation and that the treatment cycle could have been halved to 24 hours, still allowing complete NH_4^+-removal. The IC reduction rate during daytime was an indicator of the biological activity.

The application of the sensor developed here has to be seen in process monitoring and alarm generation contexts. The developed methodology can be realistically implemented in an on-line automatic measurement system. The sensor does not need any sample filtration, a major advantage for field use. The chemicals used are environmental friendly and inexpensive.

Acknowledgments

Financial support for the work was partly granted by the Belgian Fund for Scientific Research (F.W.O.) and by the Flemish minister of Science and Technology through and international scientific and technological cooperation project between Flanders and Quebec. The authors would also like to thank the staff of the GREREBA (Groupe de Recherche En Recyclage Biologique et Aquiculture) research group, in particular Mr. Daniel Proulx for his help and advice in the experimental work. Finally, Prof. Duchesne and Mr. Jean Frenette from the Department of Geology (Université Laval) are thanked for their cooperation and loan of the titrator.

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List of Figures

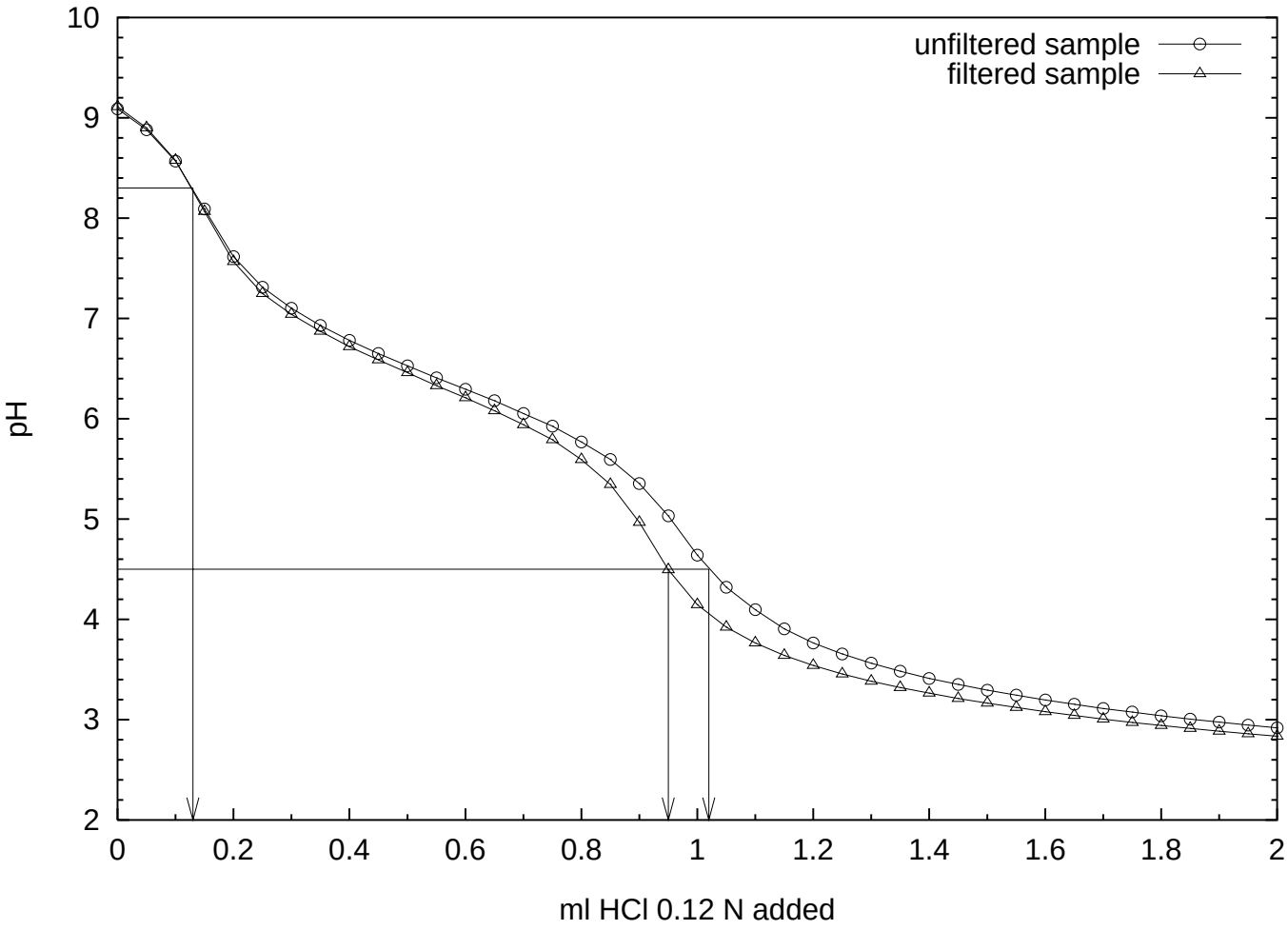

Figure 1: Titration curves of an unfiltered and filtered AP sample

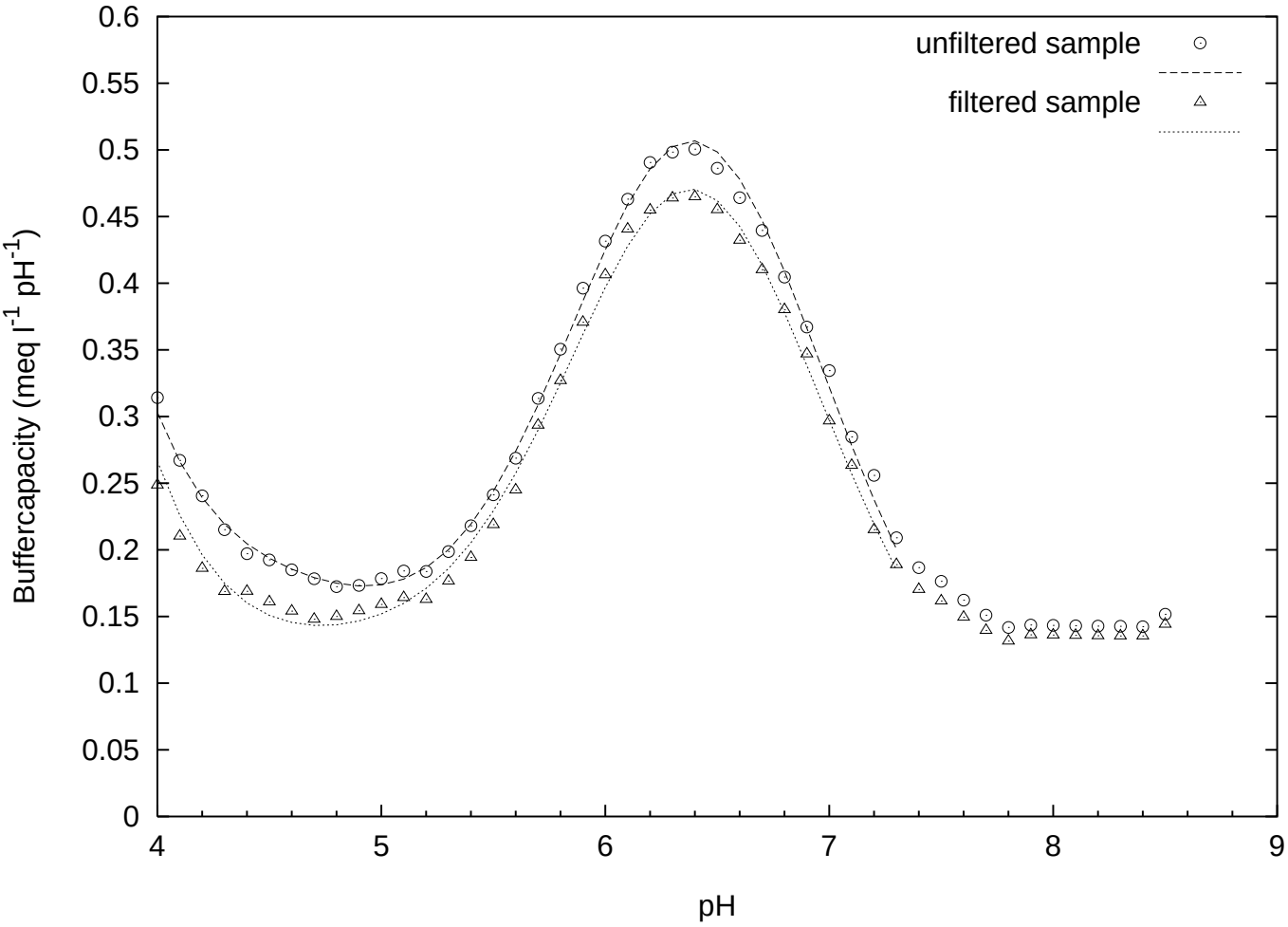

Figure 2: Measured (points) and simulated (lines) buffer capacity curves of an unfiltered and filtered AP sample

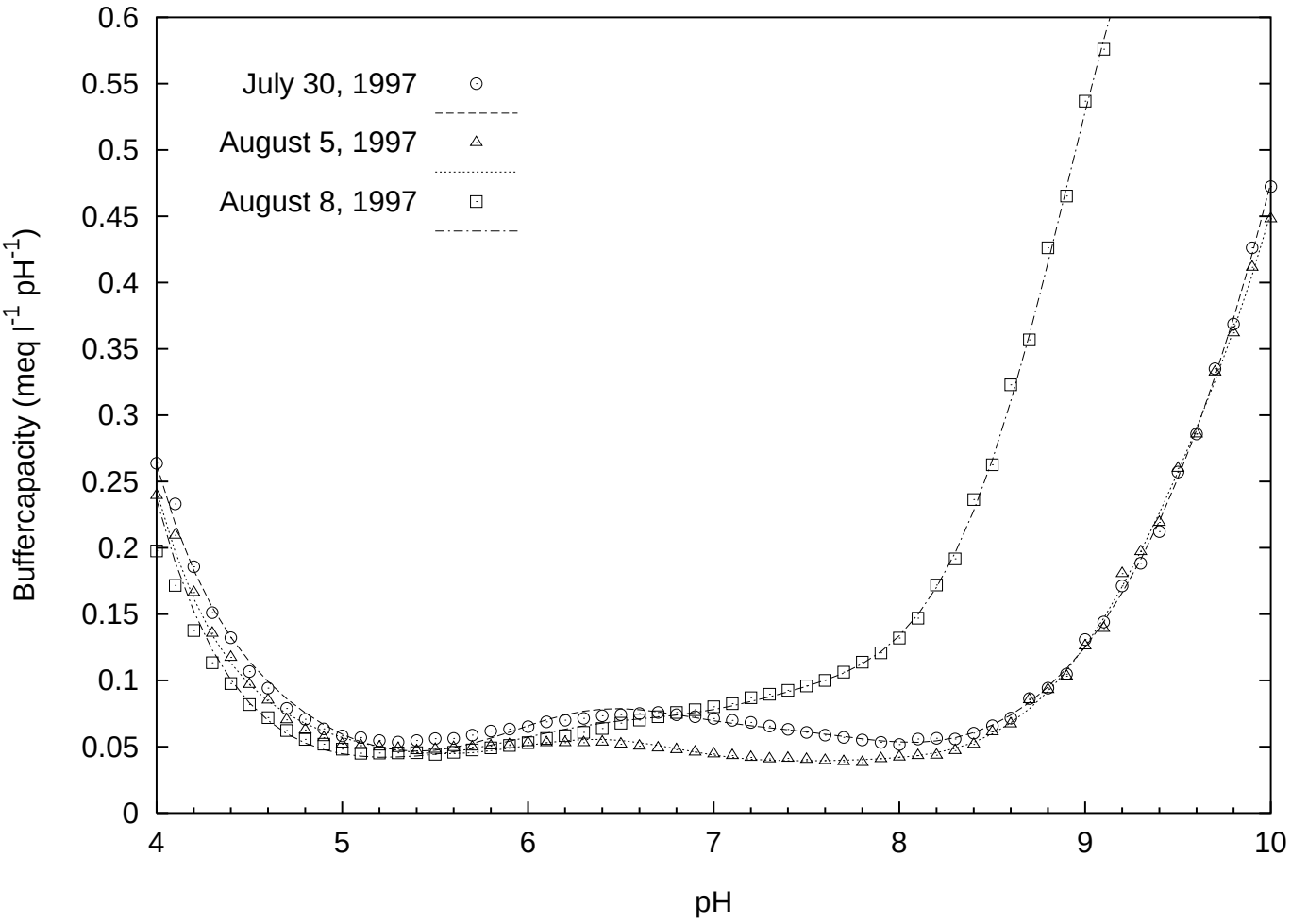

Figure 3: Measured (points) and simulated (lines) buffer capacity curves for 3 selected EAP samples

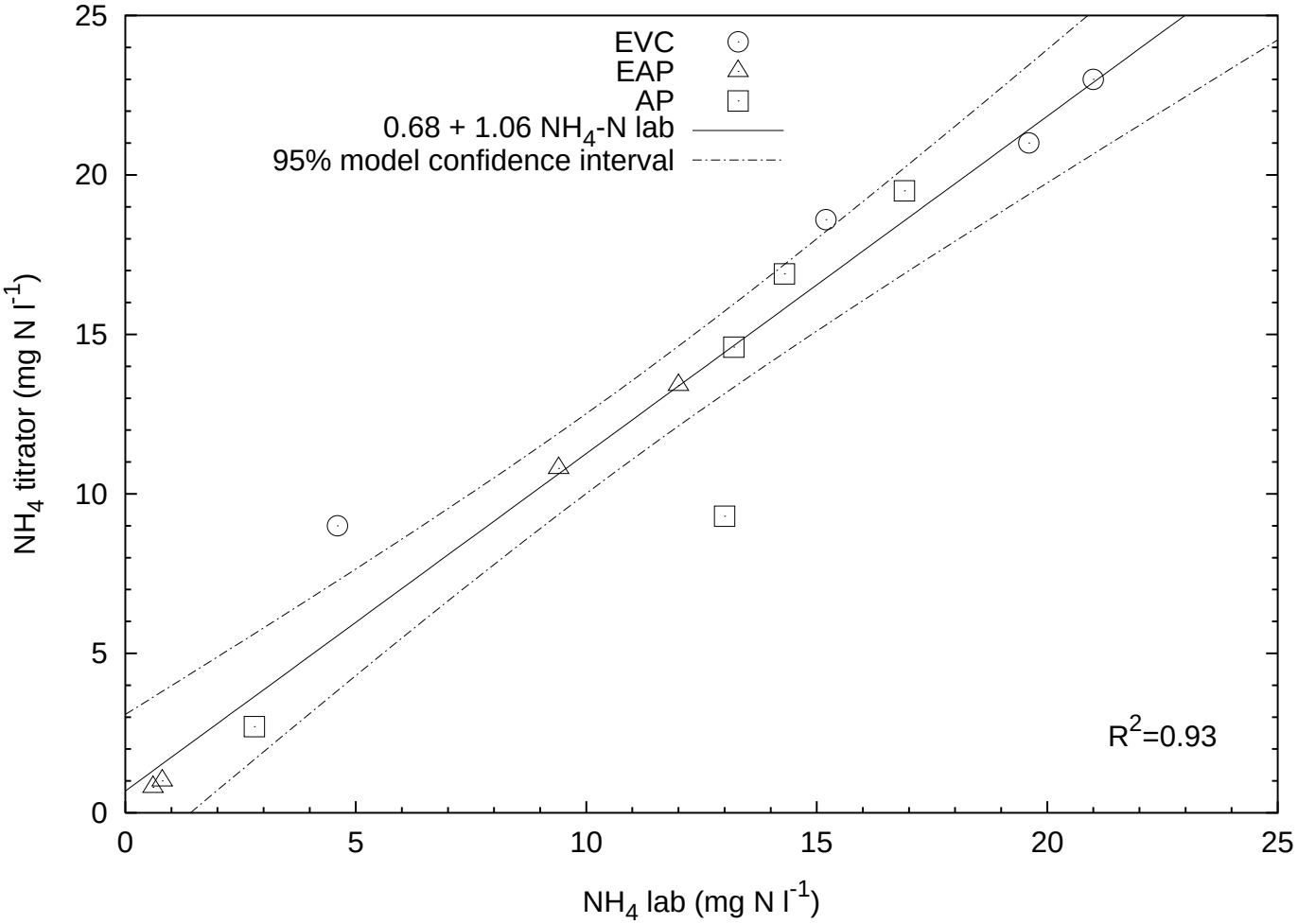

Figure 4: Scatterplot of laboratory and titrator ammonium results for all grab samples

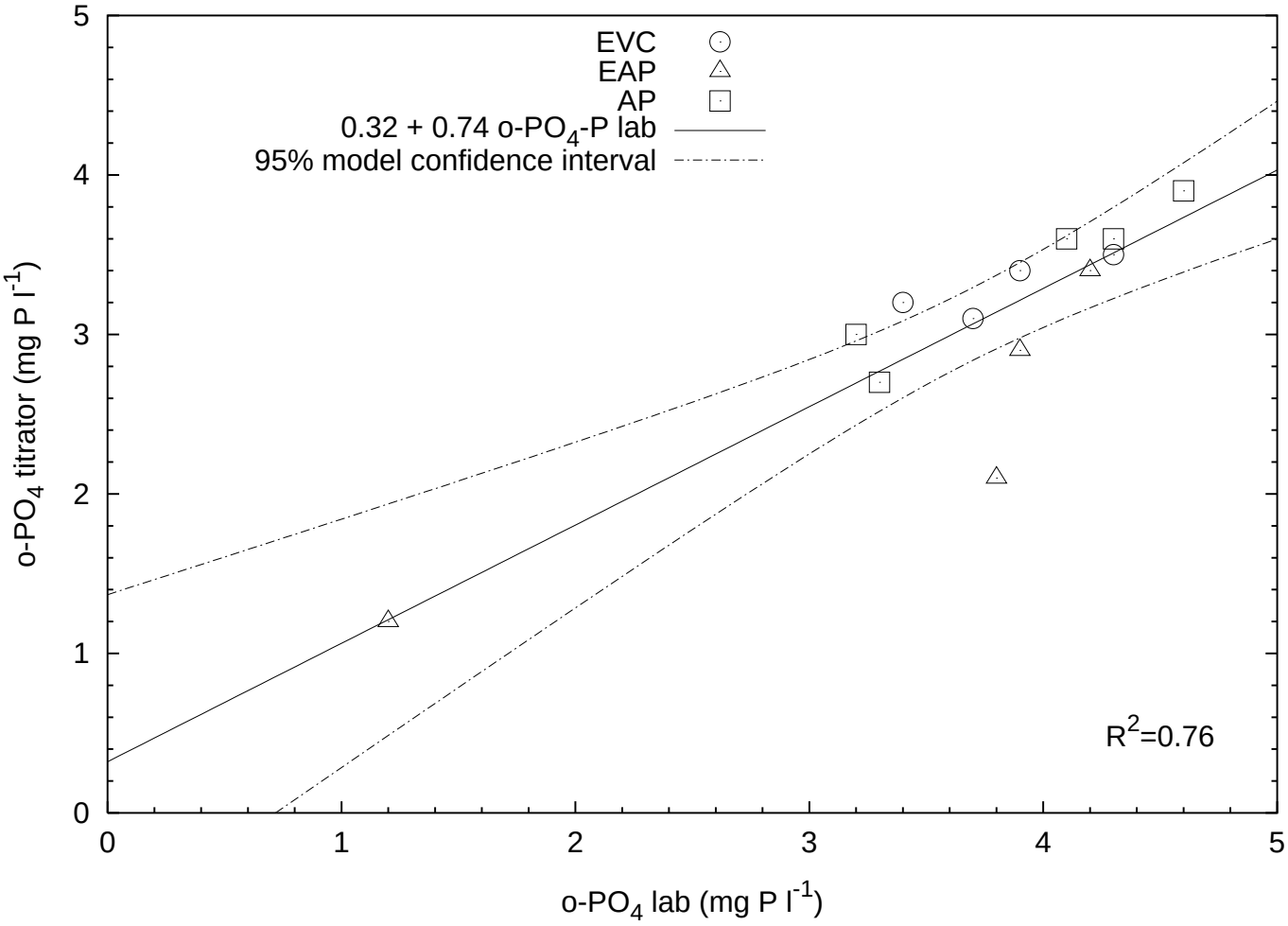

Figure 5: Scatterplot of laboratory and titrator ortho-phosphate results for all grab samples

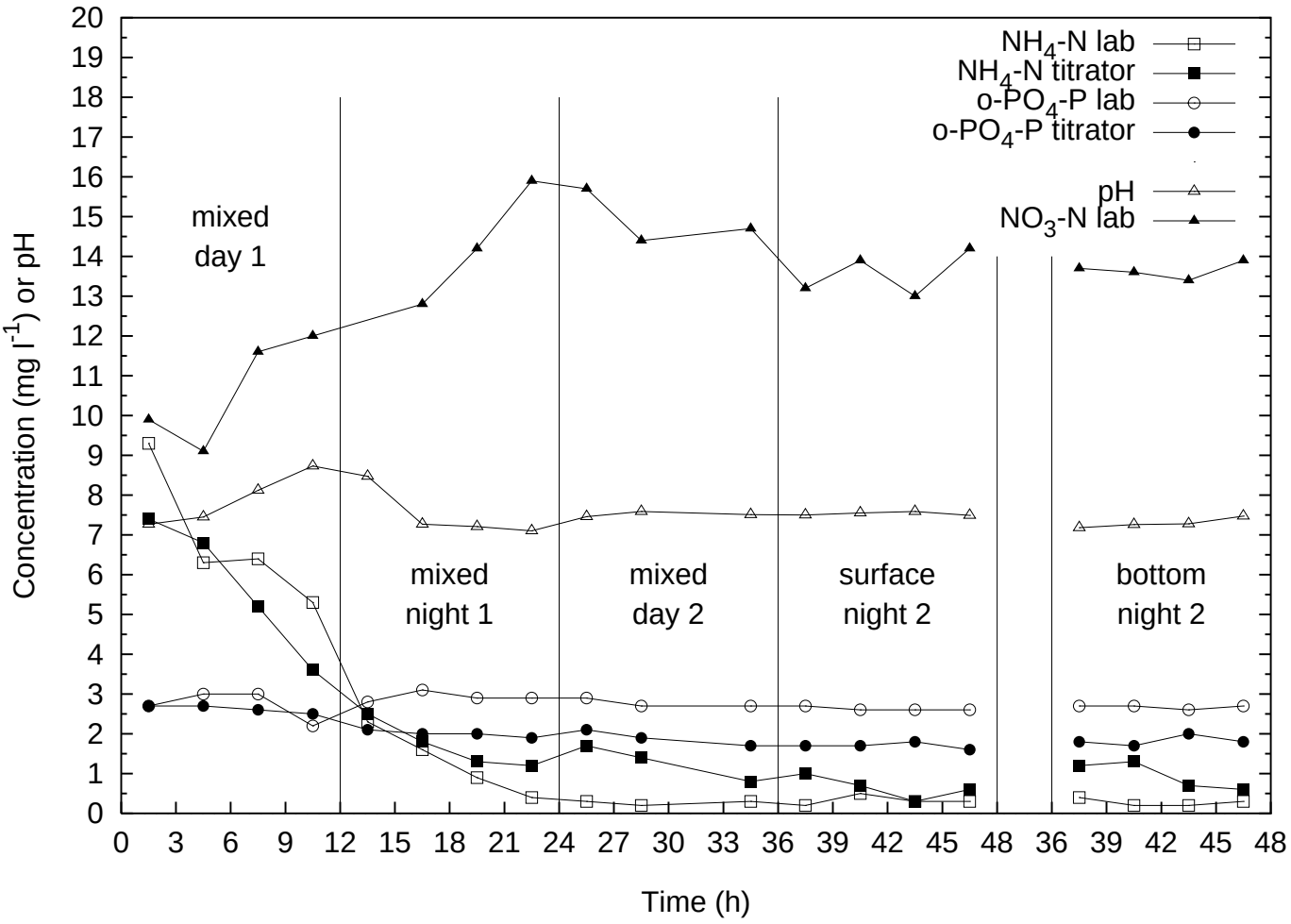

Figure 6: Laboratory and titrator concentrations for ammonium and ortho-phosphate; laboratory measurements of pH and nitrate

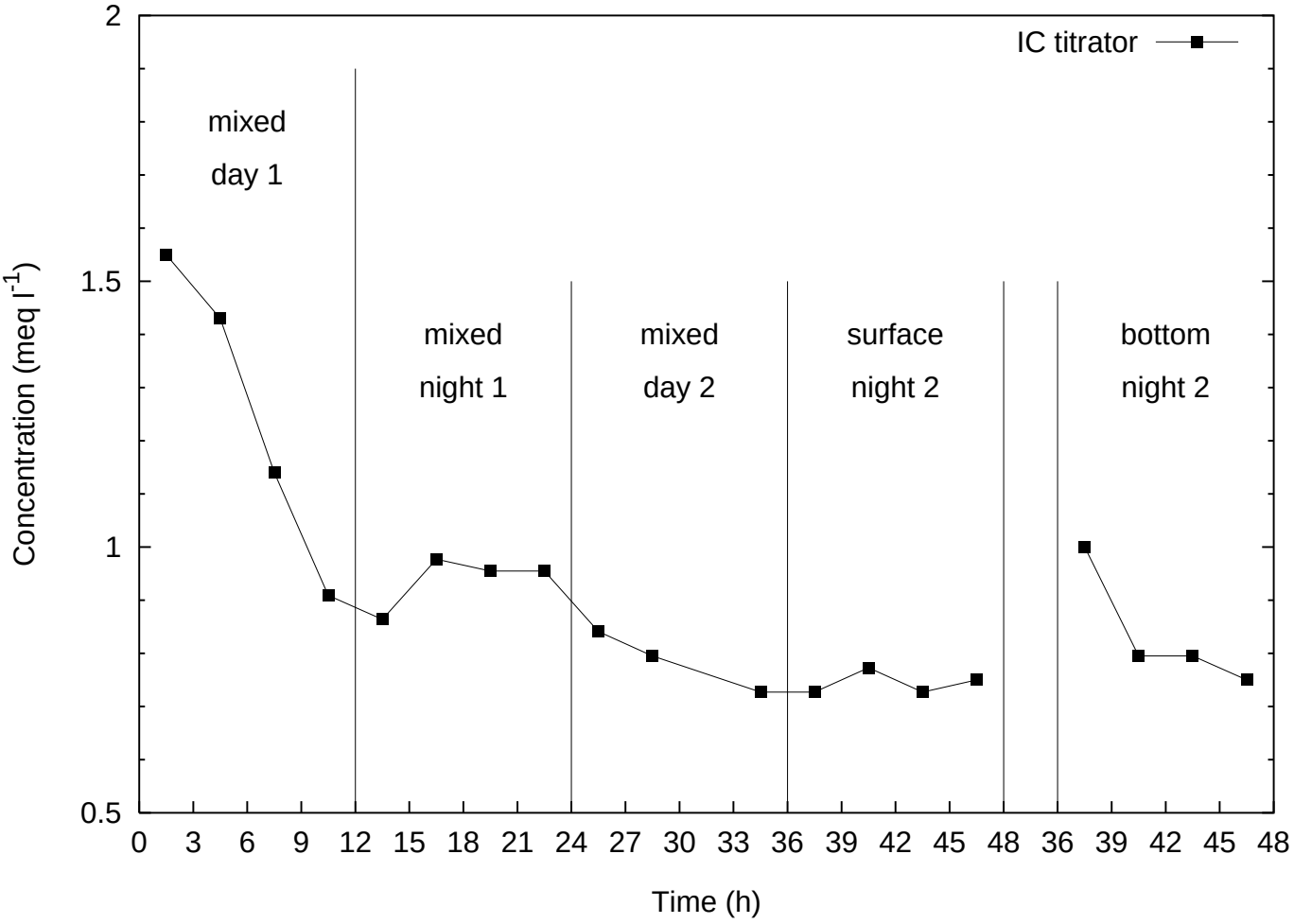

Figure 7: Titrator concentrations for inorganic carbon

List of Tables

Table 1: Model specifications for the down titrations using a simulation interval from pH 7.3 to pH 4

Buffer	Variable	Initial guess or value	Estimated?	Lower limit	Upper limit
Water	pka_water	15.74	No		
	conc_water	55.5 $mol\ l^{-1}$	No		
Carbon	pka1_carbon	6.37	Yes	6	7
	pka2_carbon	10.25	No		
	conc_carbon	1 $meq\ IC\ l^{-1}$	Yes	0	2.5
Soap	pka_soap	4.8	Yes	4	5.5
	conc_soap	$5\ 10^{-5}\ mol\ l^{-1}$	Yes	0	$1\ 10^{-3}$

Table 2: Model specifications for the up titrations using a simulation interval from pH 4 to pH 10

Buffer	Variable	Initial guess or value	Estimated?	Lower limit	Upper limit
Water	pka_water	15.74	No		
	conc_water	55.5 $mol\ l^{-1}$	No		
Carbon	pka1_carbon	6.37	No		
	pka2_carbon	10.25	No		
	conc_carbon	0.07 $meq\ IC\ l^{-1}$	Yes	0	0.25
o-Phosphate	pka1_phos	2.12	No		
	pka2_phos	7.21	Yes	7	7.8
	pka3_phos	12.67	No		
	conc_phos	3 $mg\ P\ l^{-1}$	Yes	0	20
Ammonium	pka_ammon	9.25	Yes	9	9.5
	conc_ammon	2 $mg\ N\ l^{-1}$	Yes	0	20
Soap	pka_soap	4.8	Yes	4	5.5
	conc_soap	$5\ 10^{-5}\ mol\ l^{-1}$	Yes	0	$1\ 10^{-3}$
Blank1	pka_blank1	9.6	Yes	9.4	11.5
	conc_blank1	$5\ 10^{-5}\ mol\ l^{-1}$	Yes	0	$4\ 10^{-4}$

Table 3: Alkalinity measurements and IC simulation results

	Filtered sample $meq\,l^{-1}$	Unfiltered sample $meq\,l^{-1}$
Total alkalinity (pH meter method [14])	1.09	1.17
Total alkalinity from titration curve (T)	1.11	1.20
Carbonate alkalinity from titration curve (C)	0.15	0.15
(T-C) alkalinity from titration curve	0.96	1.05
(T-2C) alkalinity from titration curve	0.81	0.90
Simulated C_{IC} from titration curve	0.80	0.85
Simulated $[HCO_3^-]$ using equation (xvi)	0.75	0.80

Table 4: Different buffers that are included in the alkalinity measurements and IC simulation results (assuming actual pH of sample $>$ 8.3)

Measurement	Buffers that are included in the measurement
Total alkalinity (T)	$2CO_3^{2-} + HCO_3^-$ + other buffers between actual pH and pH 4.5
Carbonate alkalinity (C)	CO_3^{2-} + other buffers between actual pH and pH 8.3
(T-C) alkalinity	$CO_3^{2-} + HCO_3^-$ + other buffers between pH 8.3 and pH 4.5
(T-2C) alkalinity	HCO_3^- + other buffers between pH 8.3 and pH 4.5 $-$ other buffers between actual pH and pH 8.3
Simulated C_{IC}	$CO_3^{2-} + HCO_3^- + CO_{2(aq)}$ + other buffers with $pK_{a.} \approx pK_{a.}$ of IC
Simulated $[HCO_3^-]$	HCO_3^- + other buffers with $pK_{a.} \approx pK_{a1}$ of IC

Table 5: Laboratory measurements and simulation results for all grab samples

Sample	Date	NH_4^+ ($mg\ N\ l^{-1}$)		o-PO_4 ($mg\ P\ l^{-1}$)	
		laboratory	titrator	laboratory	titrator
EVC	July 30, 1997	4.6	9.0	3.4	3.2
	August 5, 1997	21	23	3.7	3.1
	August 6, 1997	19.6	21	3.9	3.4
	August 8, 1997	15.2	18.6	4.3	3.5
EAP	July 30, 1997	0.6	0.8	3.8	2.1
	August 5, 1997	0.8	1.0	1.2	1.2
	August 6, 1997	9.4	10.8	4.2	3.4
	August 8, 1997	12	13.4	3.9	2.9
AP	August 4, 1997	2.8	2.7	3.3	2.7
	August 5, 1997	13.2	14.6	4.6	3.9
	August 6, 1997	16.9	19.5	4.3	3.6
	August 8, 1997	14.3	16.9	4.1	3.6
	August 12, 1997	13	9.3	3.2	3.0