

FACTORS AFFECTING pH CHANGE IN ALKALINE WASTE WATER TREATMENT—I

L. LIJKLEMA

Twente University of Technology, The Netherlands

(Received 7 May 1969)

Abstract—The pH of wastewater in various stages of its purification depends mainly upon the equilibria of carbonic acid. Thus relations between pH and the concentrations of carbon dioxide, bicarbonate and carbonate can be formulated. Corrections for the non-ideal character of the sewage are necessary.

With some restrictions the concept of alkalinity can be used for these pH relations.

Several (bio)chemical and physical processes occurring in biological purification affect the concentrations of carbon dioxide and (bi)carbonate.

Processes studied are carbon dioxide desorption, oxidation of organic matter and nitrification.

Models are proposed for the calculation of the effluent pH and the values so obtained are compared with the available experimental results.

NOMENCLATURE

<i>p</i>	phenolphthalein alkalinity (mval l ⁻¹), i.e. mval of acid used per l to titrate to pH 8.3
<i>m</i>	methylred alkalinity (mval l ⁻¹), i.e. mval of acid used per l to titrate to pH 4.5
[<i>X</i>]	concentration of <i>x</i> (mol l ⁻¹)
<i>c</i>	concentration (mg l ⁻¹)
<i>c_s</i>	saturation concentration (mg l ⁻¹)
COD	chemical oxygen demand (mg O ₂ · l ⁻¹)
<i>α</i>	ratio of mol CO ₂ produced to mol COD removed
ppm	parts per million (ml m ⁻³)
<i>K_{1, 2}</i>	equilibrium constants for the ionization of carbonic acid
<i>t</i>	time (hr)
<i>K_LA</i>	desorption (absorption) rate coefficient (hr ⁻¹)
<i>Q</i>	inflow (l hr ⁻¹)
<i>φ</i>	air flow (m ³ hr ⁻¹)
<i>H</i>	Henry coefficient (mol l ⁻¹ at. ⁻¹)
<i>μ</i>	ionic strength (mol e ² l ⁻¹)
<i>z</i>	ionic charge (<i>e</i>)
<i>e</i>	charge of electron
<i>γ</i>	activity coefficient
subscript <i>i</i>	influent
subscript <i>e</i>	effluent

INTRODUCTION

BIOLOGICAL purification of waste water is generally accompanied by a change in pH. A comprehensive survey of the many factors affecting this change with their quantitative relationships has never been published.

Several authors, however, observed the significance of separate factors.

VIEHL (1932) noted qualitatively the contribution of carbon dioxide production and ammonia oxidation to the decrease in pH of alkaline waste waters in the activated sludge process. INGOLS and HEUKELEKIAN (1940) and SAWYER *et al.* (1955) were aware of the important buffering action of bicarbonate.

In accordance with previous authors Ingols and Heukelekian suggested a relation between the nitrate production and the drop in alkalinity.

They did not, however, establish the exact relation with respect to the change in pH.

The extensive properties of the influent (alkalinity, BOD) are more decisive for the ultimate H^+ concentration of the effluent than the intensive parameter pH of the influent.

REPLOH (1958) obviously applied this idea when stating that a greater quantity of alkali in waste water is acceptable if the reduction in BOD is complete within a relatively short time.

It is evident that the pH value of the influent by itself is of minor importance; essential for the biological processes is the pH of the mixed liquor resulting from the alkalinity of the influent and the bacterial activity (nitrification, BOD reduction). The importance of the buffer capacity in waste water chemistry was also emphasized by KLEYN (1965) and MCKINNEY (1967). A high pH value will be harmful to the various biochemical processes. According to a publication from "Das Institut für Siedlungswasserwirtschaft" of the Technical University of Hannover (1961), the upper limit for biological purification lies at pH 12. ECKENFELDER (1967) mentions approx. pH 11.5 as the upper limit and also draws attention to the advantages of an ideally mixed system.

SCOPE OF THIS RESEARCH PROJECT

The goal of this investigation is an assessment of the most relevant factors that influence the pH, and of their quantitative relationships. The results of this and further research may lead to prediction of the pH of the effluent and of the possibility of biological purification of strongly alkaline waste waters.

Models are proposed for the calculation of the probable pH of the effluent for weakly, moderately and strongly alkaline influents.

EXPERIMENTAL

Details of the experimental pilot plant, analytical methods and experimental results have been compiled in the appendix.

THEORETICAL CONSIDERATIONS

Equilibria

In effluent the main factors governing pH will be the equilibria of carbonic acid. Up to pH 8.3 the first ionization step is dominant; at 20°C

$$[H^+][HCO_3^-] = 4.15 \times 10^{-7} [CO_2]. \quad (1a)$$

(HARNED, 1943) In the pH region 8.3–10.5 the equilibrium

$$[H^+][CO_3^{2-}] = 4.20 \times 10^{-11} [HCO_3^-]. \quad (2a)$$

(HARNED, 1943) dominates and above pH 10.5 the concentration of free OH^- ions determines the pH.

Non-ideal solutions

Since sewage cannot be considered to behave as an ideal solution corrections will be necessary. The solubility of CO_2 is assumed to be unaffected by suspended and colloidal matter. The influence of electrolytes and of non-electrolytes must be ascertained. The depression of the solubility of CO_2 by 1500 mg l^{-1} of NaCl is less than 1 per cent, as can be calculated by the method of VAN KREVELEN and HOFTIJZER (1948).

In our investigation the salt concentration never reached so high a value, and therefore this effect has been neglected. The same authors evaluated the influence of non-electrolytes on the solubility of gases in water. This influence depends on the molecular weight of the substance added. Since on the whole the content of non-electrolytes in the effluent is very low, the same must be true for the mixed liquor from which the effluent originates. Thus the influence of non-electrolytes on the solubility of CO_2 can also be neglected. However, electrolytes influence the activity of the ions of the carbonic acid system, and this factor has to be taken into consideration.

Up to pH 8.3 the activity coefficient for monovalent ions may be reckoned to be about 0.82 (see Appendix). In the pH region 8.3–10.5 the activity coefficients for monovalent and bivalent ions are calculated to be about 0.80 and 0.41, respectively, in the sewage used (appendix).

The equations for the ionization equilibria become

$$\gamma[\text{H}^+] \times 0.82 [\text{HCO}_3^-] = 4.15 \times 10^{-7} [\text{CO}_2] \quad (1b)$$

and

$$\gamma[\text{H}^+] \times 0.41 [\text{CO}_3^{2-}] = 4.20 \times 10^{-11} \times 0.80 [\text{HCO}_3^-]. \quad (2b)$$

Since a glass electrode measures H^+ activity $\gamma[\text{H}^+]$ rather than concentration $[\text{H}^+]$, the pH according to the equations just mentioned will be:

$$\text{pH} = 6.30 + \log [\text{HCO}_3^-] - \log [\text{CO}_2] \quad (1c)$$

and

$$\text{pH} = 10.09 + \log [\text{CO}_3^{2-}] - \log [\text{HCO}_3^-]. \quad (2c)$$

(Bi)-carbonate and alkalinity

The analysis of bicarbonate and carbonate in water has always belonged to the province of drinking-water chemists. The importance of this branch of chemistry founded on the models of LANGELIER (1936), derives from the desirability to prevent scale formation by CaCO_3 and corrosion by free CO_2 .

The analysis instructions used in the determination of *p*- and *m*-alkalinity have been adopted by *Standard Methods for the Analysis of Sewage* (1965) and by the German equivalent (*Deutsche Einheitsverfahren*, 1968).

On principle one can calculate, from total CO_2 concentration and pH, the concentrations of carbonate and bicarbonate, taking the ionic strength into account (FREIER, 1964). Application of the *p*- and *m*-values as determined in practice appears more practicable. The two relations

$$10^{-3} p = [\text{CO}_3^{2-}] + [\text{OH}^-]$$

$$10^{-3} m = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-]$$

lead to a scheme for calculations as follows:

Result of titration	OH ⁻ -alkalinity mval. l ⁻¹	CO ₃ ²⁻ -alkalinity mval. l ⁻¹	HCO ₃ ⁻ -alkalinity mval. l ⁻¹
$p = 0$	0	0	m
$p < \frac{1}{2}m$	0	$2p$	$m - 2p$
$p = \frac{1}{2}m$	0	$2p$	0
$p > \frac{1}{2}m$	$2p - m$	$2(m - p)$	0
$p = m$	m	0	0

The basis for these calculations lies in two assumptions. Firstly, salts of weak acids other than carbonic acid are supposed to be absent. Particularly phosphate ions do contribute to the p - and m -values. Their influence has been checked in the investigations presented here and was found to be small in most cases and always less than 10 per cent of the p - and m -values. Other ions did not contribute demonstrably (see appendix). Secondly, hydroxide and bicarbonate are assumed to be incompatible with each other. This assumption, however, is not valid without any limitation. At pH 11 the OH⁻ concentration of 10⁻³ mol. l⁻¹ cannot be regarded as negligible when still 17 per cent of total CO₂ present occurs as bicarbonate.

Moreover, in principle it is wrong to determine concentrations of HCO₃⁻, CO₃²⁻ and OH⁻ with the aid of analytical methods for the determination of alkalities, because during the procedure the ionic strength of the solution changes perforce (HÖMIG, 1957). Hömig gives an analysis of the errors introduced. In the pH region 7-10.3, he shows the calculation of [HCO₃⁻] from alkalities to be fairly accurate; when total [CO₂] amounts to only 10⁻³ mol. l⁻¹ the error never exceeds 10 per cent. The relative error in CO₃²⁻ is larger. In the range where $2p \approx m$ errors of about 10 per cent can occur even when total [CO₂] is 10⁻² mol. l⁻¹.

Since the calculation scheme given above is simple, and a greater precision was unattainable in the present investigation because of inaccuracies in other parameters, we have used the scheme as outlined.

pH and alkalinity

When the bicarbonate and carbonate content are replaced by the p - and m -values described, equations (1c) and (2c) change into:

$$\text{pH} = 6.30 + \log(m - 2p \times 10^{-3}) - \log[\text{CO}_2] \quad (1d)$$

$$= 3.30 + \log(m - 2p) - \log[\text{CO}_2]$$

and

$$\text{pH} = 10.09 - \log p - \log(m - 2p). \quad (2d)$$

Equation (1d) is to be applied in the weakly alkaline region only, when p will generally equal zero.

FIGURE 1 shows a plot of effluent pH against $\log(m - 2p)$; the effluent is that of our pilot plant. The graph also indicates what the relation would have been, had the free CO₂ in the mixed liquor been in equilibrium with the air containing 360 ppm of CO₂.

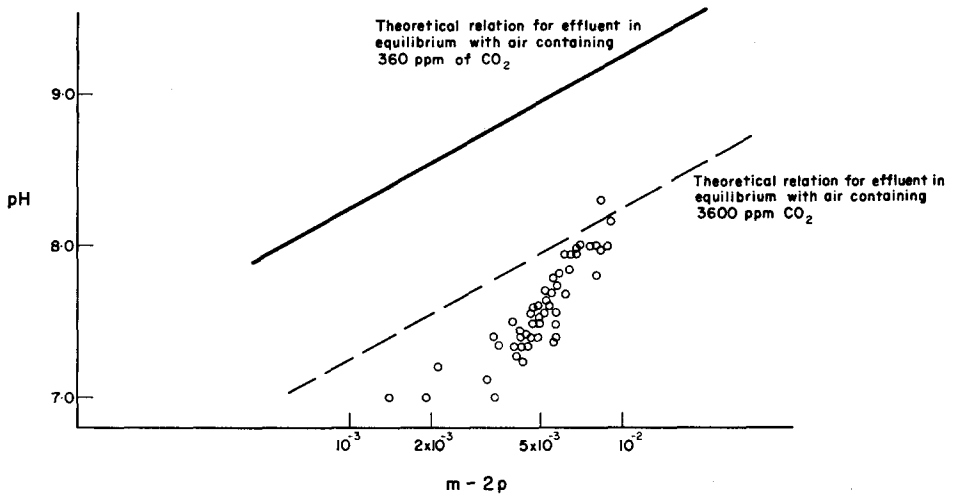


FIG. 1

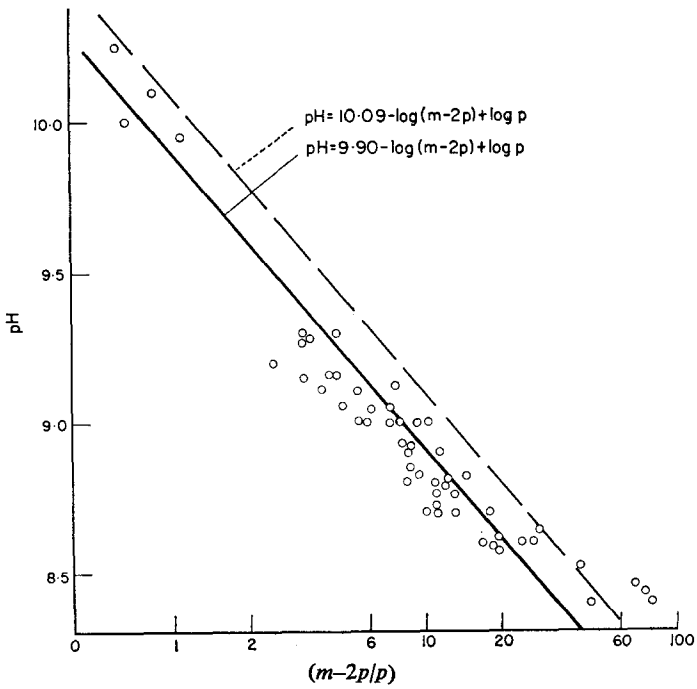


FIG. 2

Obviously the effluent is highly supersaturated with respect to free CO_2 . Hence the extent of CO_2 desorption will, for weakly alkaline sewage, bear heavily on the pH of the effluent. Equation (2d) is applicable in the moderately alkaline region. In FIG. 2 the mixed liquor pH has been plotted against $\log(m-2p/p)$ as determined in the effluent. (The reactor being ideally mixed, the m - and p -values will be identical in either liquid). At pH 8.5 consistency with (2d) is good, at higher pH values less good. The increasing concentration of especially bivalent ions (CO_3^{2-} , HPO_4^{2-}), leads to increasing ionic strength, this causes a lowering of the term 10.09 in equation (2d) and hence lower calculated pH values. The empirical relation used in the development of the calculation models and based on FIG. 2, is:

$$\text{pH} = 9.90 - \log(m - 2p) + \log p. \quad (2e)$$

FACTORS INFLUENCING EQUILIBRIA

The change in pH is controlled by two factors:

- (a) the production of acid or alkaline substances during the biological purification
- (b) the buffer capacity of the influent.

The buffer capacity, indicating the resistance against pH change through acids or bases, depends upon the influent alkalinity. The first factor, however, is dependent upon both influent properties and process parameters as detention time, aeration, sludge load, temperature. On the other hand, pH controls again the course of processes producing acids or bases; a high pH, e.g., can restrict the nitrification or the BOD reduction.

Various chemical and biochemical reactions may cause changes in p - or m -values; TABLE 1 gives the most important changes and also the changes in p - and m -values per millimole of substance turned over.

TABLE 1

Reaction	Δm (m val)	Δp (m val); pH > 8.3
$\text{NH}_4^+ + 1\frac{1}{2}\text{O}_2 \rightarrow 2\text{H}^+ + \text{NO}_2^- + \text{H}_2\text{O}$	-2	-2
$\text{NH}_4^+ + 2\text{O}_2 \rightarrow 2\text{H}^+ + \text{NO}_3^- + \text{H}_2\text{O}$	-2	-2
$\text{NO}_3^- + 5\text{H} + \text{H}^+ \rightarrow \frac{1}{2}\text{N}_2 + 3\text{H}_2\text{O}$	+1	+1
$\text{CO}(\text{NH}_2)_2 + 2\text{H}_2\text{O} \rightarrow 2\text{NH}_4^+ + \text{CO}_3^{2-}$	+2	+2
$\text{CO}_2 + \text{H}_2\text{O} + \text{CO}_3^{2-} \rightarrow 2\text{HCO}_3^-$	0	-1
$\text{CO}_2 + \text{OH}^- \rightarrow \text{HCO}_3^-$	0	-1
CO_2 desorption	0	
NH_3 desorption	-1	-1

The carbon dioxide mentioned in the table may be an oxidation product of organic matter; part of the ammonium also is a degradation product of organic nitrogen compounds.

In carbohydrate metabolism lactic acid and acetic acid have been identified as intermediates (ADAMSE, 1968), but will be completely oxidized under normal aerobic

conditions. The significance of nitrification and of the production, absorption and desorption of CO_2 have been the subject of closer investigation.

Desorption of carbon dioxide

The desorption of carbon dioxide from the mixed liquor is largely dominated by the pH value of this liquor (FIG. 3). Factors like temperature, suspended solids, concen-

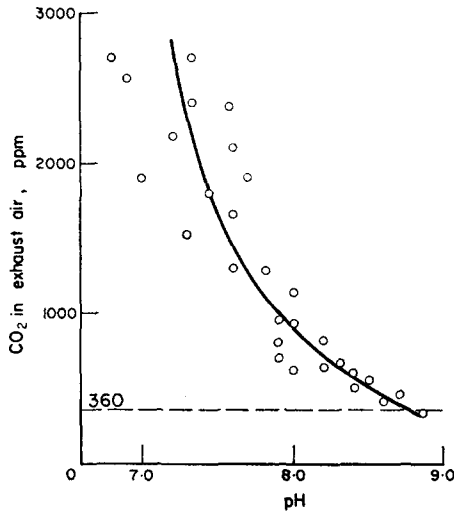


FIG. 3

tration of HCO_3^- , ionic strength and small fluctuations in hydrodynamic conditions caused by variations in the air flow contribute to the scatter in results.

SCHÄFER (1967) found first order kinetics for the desorption of CO_2 from pure water supersaturated with carbon dioxide

$$-\frac{d[\text{CO}_2]}{dt} = k' [\text{CO}_2].$$

He determined the free carbon dioxide content directly by potentiometric titration. In mixed liquor, however, the content of free carbon dioxide cannot be measured easily. The equilibrium $\text{H}^+ + \text{HCO}_3^- \rightleftharpoons \text{CO}_2 + \text{H}_2\text{O}$ offers a possibility to relate the quantity of CO_2 expelled to the CO_2 content of the liquid. In a laboratory experiment with a slow stream of separate air bubbles rising through a bicarbonate solution the relation

$$-\frac{d[\text{CO}_2]}{dt} = k'' [\text{H}^+]$$

was established for a constant HCO_3^- concentration of 0.01 mol. l^{-1} . Varying the HCO_3^- concentration at constant pH led to

$$-\frac{d[\text{CO}_2]}{dt} = k''' [\text{HCO}_3^-]$$

which is also in accordance with Schäfer's results. The desorption from the mixed liquor of the pilot plant, however, did not follow first order kinetics.

A better relation established empirically was (FIG. 4):

$$-\frac{d[\text{CO}_2]}{dt} = k[\text{H}^+]^{\frac{1}{2}} \cdot [\text{HCO}_3^-]^{\frac{1}{2}}$$

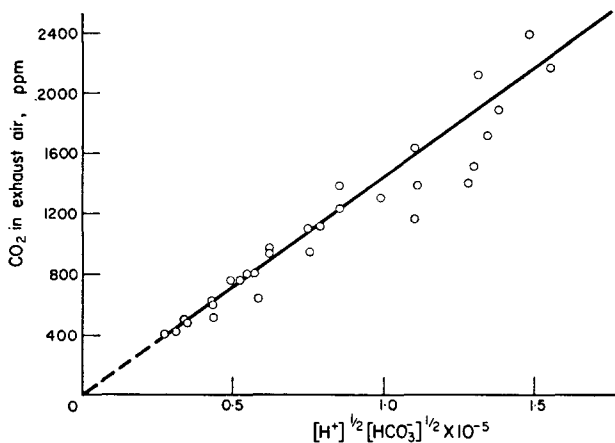
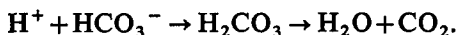
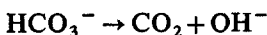


FIG. 4

Apparently the hydrodynamic conditions in the mixed liquor differ greatly from those in our laboratory experiment, and thereby the chemical transformations may determine the rate of CO_2 desorption.

The chemical reactions accompanying the physical desorption process are:



VAN KREVELEN (1953) calculated how the order with respect to OH^- varies between 0 and 1 for the reverse process, absorption of CO_2 by dilute alkali. This variation is a function of the ratio of (root reaction velocity constant) to (mass transfer coefficient for CO_2 in the liquid phase).

Hence the variation in order with respect to OH^- is connected with the fluctuating influence of turbulence.

Literature supplies only scanty data on CO_2 desorption. Therefore an indirect method was applied that might provide an impression of the promotion of desorption by the chemical reactions mentioned before. We compared the rate coefficients for absorption and desorption of CO_2 and O_2 in solutions with and without bicarbonate (see Appendix). The results have been compiled in TABLE 2.

Absorption and desorption of oxygen may be looked upon as purely physical processes without any concomitant chemical aspect. Schäfer, working with pure water, treated his process in this same way.

TABLE 2 demonstrates that the rate of absorption is about 1.5 times the rate of desorption for both O_2 and CO_2 if the hydrodynamic conditions remain identical. This generalization is valid for high turbulence (as in Schäfer's work), but also for very low turbulence (our bicarbonate solution). When 0.01 mol. l^{-1} of bicarbonate

has been added to the water, the rate of desorption of CO_2 increases with a factor of 10 when compared with both desorption and absorption of oxygen. In activated sludge suspensions the effect is smaller but still substantial. Probably the CO_2 desorption is strongly enhanced by accompanying chemical reactions; the difference in hydrodynamics between the mixed liquor (high turbulence) and the bicarbonate solution in our laboratory experiment (low turbulence) is undoubtedly responsible for

TABLE 2

	Schäfer experiment	Bicarbonate sol. (0.01 mole l^{-1})	Activated sludge
$\frac{K_L A \text{ abs. CO}_2}{K_L A \text{ des. CO}_2}$	1.3-1.7	—	—
$\frac{K_L A \text{ abs. O}_2}{K_L A \text{ des. O}_2}$	1.2-2.0	1.6	—
$\frac{K_L A \text{ des. CO}_2}{K_L A \text{ des. O}_2}$	0.1-0.3	2	—
$\frac{K_L A \text{ des. CO}_2}{K_L A \text{ abs. O}_2}$	0.08-0.15	1.2	0.5

the difference in desorption rate increase between the mixed liquor and the bicarbonate solution. Obviously the diffusion of H^+ ions from the mixed liquor bulk to the water-air interface is the limiting factor for a further increase in desorption rate. This can be inferred from the fact that the CO_2 desorption from the laboratory solution is hardly influenced by addition of a buffer solution that represents an extra pool of H^+ ions at the interface, whereas desorption from the mixed liquor tends to increase.

More research will be necessary for complete insight in the mechanism of CO_2 desorption.

Another aspect related with CO_2 desorption deserves attention. CO_2 is much more soluble in water than is O_2 ; the Henry coefficients are 4×10^{-2} and 10^{-3} mol. l^{-1} at. $^{-1}$ respectively. Moreover, the absorption rate coefficient of O_2 is about twice the desorption rate coefficient of CO_2 in mixed liquor (see TABLE 2). The aeration of the activated sludge process is always scheduled to provide a sufficient transfer of oxygen, and therefore will always be insufficient for a more or less complete desorption of CO_2 . Hence the effluent pH will be lower than is to be expected when CO_2 equilibrium with the ambient air exists. Adverse effects of the high CO_2 concentration have not been observed.

Trickling filters show a higher proportion of air supply to water supply so that a more complete CO_2 desorption may be expected resulting in a higher effluent pH than effluents of comparable activated sludge plants would yield.

Nitrification

Several authors have discussed the growth and the metabolism of *Nitrosomonas* and *Nitrobacter*. HOFMAN and LEES (1952), in studying the metabolism, found an

optimum pH of about 8.5 for *Nitrosomonas* with a steep decline of activity on the alkaline side. ENGEL and ALEXANDER (1958) found a wider plateau from pH 6.8–9.0 for the optimum activity of *Nitrosomonas*. *Nitrobacter* has its pH optimum in about the same region (BOON and LAUDELOUT, 1962).

In our experiments more or less complete nitrification was observed at pH 7.0–9.3. Detention times were 4 hr or more. At pH 9.4 the nitrification decreased sharply.

Important factors for our investigation, apart from the pH sensitivity of nitrifying bacteria, are their low growth rate and the strong dependence of growth rate on temperature.

Taking these factors into account along with other information, DOWNING *et al.* (1964) proposed a theoretical model for the calculation of the ammonium ion concentration in the effluent of an activated sludge plant. Their starting point is the idea that the fraction of nitrifying organisms must at least be constant. Hence the proportional increase of the growing nitrifiers must be equal to the proportional increase of the sludge mass as a whole. Since the proportional increase of sludge depends strongly on the load (kg of BOD per kg of sludge per day) (LINDNER, 1958) it will be evident that a slow sludge-load and hence a long detention time favour a good nitrification. Most experiments in our investigation were performed with long detention times thus allowing a good nitrification. An exact comparison with Downing's model is not possible as different definitions of the term "aeration time" have been used. The general trend, however, is the same.

The quantity of nitrite in the effluent compared with nitrate is usually negligible in our case, too.

Nitrification and alkalinity

An indication of the decrease in alkalinity during nitrate production is given by ECKENFELDER and O'CONNOR (1964). The predicted effect of nitrification on *m*-alkalinity of the influent (TABLE 1) has been confirmed by our experiments (FIG. 5). Denitrification was excluded as far as possible by maintenance of high oxygen concentrations and nearly complete BOD reduction in the mixed liquor. Even after standing for several days at room temperature the effluent lost little nitrate. Deviations from the theoretical relation $\Delta m = 2 \cdot \Delta[\text{NO}_3^-] \cdot 10^3$ could be ascribed to the presence of urea in the influent. Generally, however, the urea was completely hydrolysed before it could reach the aeration tank.

COD reduction and CO₂ production

ECKENFELDER (1967) suggests a production of about 0.9 kg of CO₂ per kg of COD removed (0.65 mole of CO₂ per mole of O₂). This value α depends on the composition of the sewage and on the degree of purification and sludge load. With lower sludge loads a larger proportion of the carbon compounds will be completely oxidized to CO₂. WASHINGTON and SYMONS (1962) report that 63–90 per cent of the incoming carbon is removed as CO₂, the higher percentage being reached at high sludge concentrations. In our investigation with low sludge loads and high COD reduction, α assumed values of approx. 0.8. Sewage with a high COD has a greater capacity for CO₂ production and hence for the neutralization of alkali. The COD reduction attainable is a function of sludge load, detention time, temperature and pH.

The influence of pH is of special interest in this investigation. Lower COD reductions will result in lower CO₂ production, thus in higher pH and in a further

decrease in the degree of purification. So a small increase in the alkali load of an activated sludge plant working at relatively high pH may cause the process to exceed the tolerance limit.

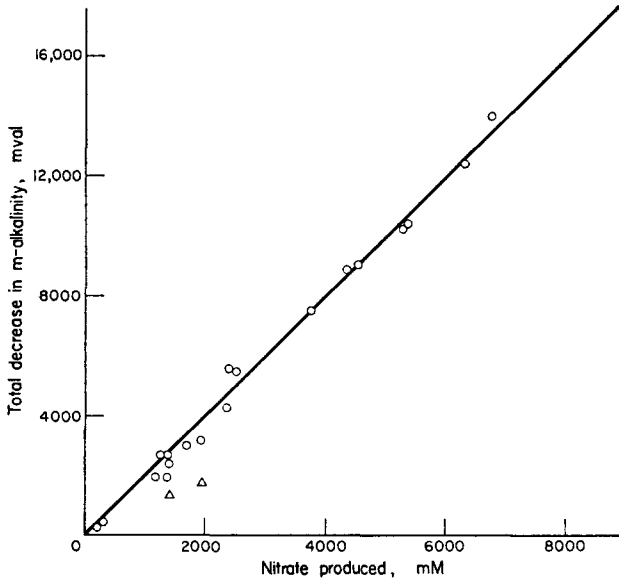


FIG. 5

The reduction in COD as a function of pH shows the same tendency as found by KEEFER and MEISEL (1951) and other authors (FIG. 6).

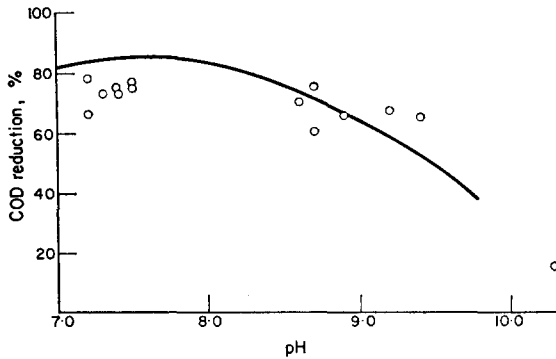


FIG. 6

MODELS FOR THE CALCULATION OF pH VALUES

Weakly alkaline region (pH < 8.3)

Starting point is the CO₂ mass balance:

CO₂ in influent: $Q(m_i - p_i)$ (m-mole hr⁻¹)

CO₂ in effluent: Qm_e (m-mole hr⁻¹)

CO₂ produced: $Q \frac{\alpha \cdot \Delta \text{COD}}{32}$ (m-mole hr⁻¹)

CO₂ expelled with air: $\phi \times \text{const.} [\text{H}^+]^{\ddagger} [\text{HCO}_3^-]^{\ddagger}$ (ml hr⁻¹)

CO₂ introduced with air: $\phi \times 360$ (ml hr⁻¹).

With $m_i - m_e = 2[\text{NO}_3^-]_e \cdot 10^3$ and some rearrangements a mass balance leads to:

$$Q \times \text{const.} \left(2[\text{NO}_3^-]_e \cdot 10^3 + \frac{\alpha \cdot \Delta \text{COD}}{32} - p_i + \frac{\phi}{Q} \cdot 15 \right) = [\text{H}^+]^{\ddagger} \cdot [m_i - 2[\text{NO}_3^-]_e \cdot 10^3]^{\ddagger}$$

or:

$$\text{pH} = C - 2 \log Q - 2 \log \left[2[\text{NO}_3^-]_e \cdot 10^3 + \frac{\alpha \cdot \Delta \text{COD}}{32} - p_i + \frac{\phi}{Q} \cdot 15 \right] + \log [m_i - 2[\text{NO}_3^-]_e \cdot 10^3]. \quad (4)$$

The value of C depends on air flow and temperature; at 15°C with an air flow of 8.45 m³ hr⁻¹ C was calculated to be 12.45. The term $\phi/Q \cdot 15$ originates from the correction necessitated by the fact that the incoming air contains about 360 ppm of CO₂. In most cases this term may be neglected.

The equation proposed has been checked in pilot plant experiments. TABLE 3 contains results for different experimental conditions with an air flow of approximately

TABLE 3. RESULTS UNDER DIFFERENT EXPERIMENTAL CONDITIONS WITH AN AIR FLOW OF APPROX. 8.45 m³ · hr⁻¹

Q (l hr ⁻¹)	COD _i (mg l ⁻¹)	COD _e (mg l ⁻¹)	m_i (mval l ⁻¹)	p_i (mval l ⁻¹)	NO ₃ ⁻ · 10 ³ (mol. l ⁻¹)	pH calculated	pH measured
120	199	68	9.08	—	1.17	7.63	7.66
120	151	76	3.20	—	1.14	6.98	7.20
120	322	90	7.20	0.25	0.58	7.45	7.60
132	330	90	9.37	1.84	0.27	7.81	7.80
60	162	62	9.20	—	2.08	7.86	7.68
120	140	92	3.21	—	1.13	7.12	7.20
90	140	80	3.21	—	1.37	6.87	6.90
126	180	80	7.04	—	1.90	7.19	7.30
126	236	88	6.45	0.70	1.16	7.43	7.20
110	348	105	14.88	8.42	1.73	8.88	8.75
111	348	94	8.29	0.53	1.72	7.18	7.25
120	255	65	12.39	7.79	1.68	9.13	8.95
120	255	56	7.31	0.84	1.38	7.31	7.20
86	248	65	6.70	1.56	1.57	7.52	7.40
82	370	90	6.56	1.04	1.43	7.30	7.50
192	261	97	7.36	0.95	1.16	7.18	7.20
198	320	111	7.37	0.40	0.95	7.03	7.20

8.45 m³ hr⁻¹. FIG. 7 provides a comparison of pH values calculated and estimated.

Substitution of the value 12.61 instead of the calculated value 12.45 for C in equation (4) yields pH values in reasonable agreement with experimental values.

Because of the low buffer capacity (KLEYN, 1965) of the mixed liquor around pH 8.3 there are no experimental values above pH 7.7. A small variation in nitrate production or in influent alkalinity already causes a relatively large change in pH. As

pointed out in a previous section, the desorption of CO₂ is relatively inefficient. Therefore variations in pH can only partly be counteracted by the increase or decrease of CO₂ desorption ensuing from these variations. The statement that mixed liquor tends to assume a pH value of about 8 (ECKENFELDER, 1967) will pertain only if negligible nitrification occurs.

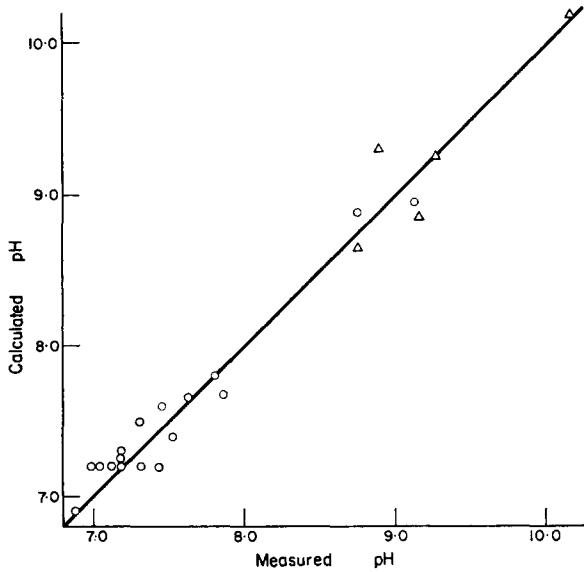


FIG. 7

The low buffer capacity at pH 8.3 also accounts for the low precision of predicted pH values in this pH region. This is evident mathematically from the relatively low value of the term

$$\left[2[\text{NO}_3^-]_e \cdot 10^3 + \frac{\alpha \cdot \Delta\text{COD}}{32} - p_i + \frac{\phi}{Q} \cdot 15 \right]$$

in equation (4). Small inaccuracies in COD or NO₃⁻ values lead to relatively great deviations in the values calculated.

Moderately alkaline region. (8.3 < pH < 10.5)

In this region the carbon dioxide absorption and desorption are neglected. The empirical relation (2e) leads, with

$$m_e = m_i - 2[\text{NO}_3^-]_e \cdot 10^3$$

and

$$p_e = p_i - 2[\text{NO}_3^-]_e \cdot 10^3 - \frac{\alpha \cdot \Delta\text{COD}}{32}$$

to:

$$\text{pH} = 9.90 + \log \left[p_i - 2[\text{NO}_3^-]_e \cdot 10^3 - \frac{\alpha \cdot \Delta\text{COD}}{32} \right] -$$

$$-\log \left[m_i + 2[\text{NO}_3^-]_e \cdot 10^3 - 2p_i + \frac{2\alpha \cdot \Delta\text{COD}}{32} \right]. \quad (5)$$

TABLE 4 shows the first experimental results. See also FIG. 7.

TABLE 4

m_i	p_i	$[\text{NO}_3^-]_e \cdot 10^3$	COD_i	COD_e	pH calculated	pH measured
14.90	7.30	1.50	235	93	8.75	8.65
15.64	9.09	1.45	273	93	9.16	8.85
16.76	10.96	1.95	305	107	9.28	9.27
17.00	9.93	1.38	370	130	8.89	9.32
24.50	12.70	1.67	261	220	10.17	10.20

The precision of the pH values calculated around 8.3 will be poor, as has been explained previously.

Mathematically the small value of the term

$$\left(p_i - 2[\text{NO}_3^-]_e \cdot 10^3 - \frac{\alpha \cdot \Delta\text{COD}}{32} \right)$$

is responsible for the greater deviations. The lack of precision occurring at pH around 10.5 has been discussed in previous sections.

Strongly alkaline region. (pH > 10.5)

At 15°C and without correction for ionic strength the following relations pertain:

$$\text{pH} = 14.3 + \log [\text{OH}^-]_e$$

or

$$\text{pH} = 11.30 + \log (2p_e - m_e) \quad (6)$$

with

$$p_e = p_i - 2[\text{NO}_3^-]_e \cdot 10^3 - \frac{\alpha \cdot \Delta\text{COD}}{32}$$

and

$$m_e = m_i - 2[\text{NO}_3^-]_e \cdot 10^3$$

this leads to

$$\text{pH} = 11.30 + \log \left[2p_i - m_i - 2[\text{NO}_3^-]_e \cdot 10^3 - \frac{2\alpha \cdot \Delta\text{COD}}{32} \right]. \quad (7)$$

Experimental results testifying to the applicability of this equation have not yet been obtained.

Acknowledgement—I am grateful to Dr. H. LAND for discussion of the text and to Mr. M. GOEDHART for technical assistance.

APPENDIX

Experimental

The pilot plant consisted of two identical parts, both comprising a 700 l. cylindrical PVC aeration tank and a 800 l. funnel-shaped PVC settling tank. Sludge recirculation (150–250 per cent of the inflow) was effected by a gas-lift pump. The aeration with compressed air was regulated through control valves and the quantity of air applied was measured with flowmeters that had been calibrated at the pressure required (slightly above 1 atm.). The aeration tank may be regarded as ideally mixed.

The sewage inflow was regulated through variable V-notch weirs in the wall of a small auxiliary tank in which a constant level was maintained. The influent used was preclarified sewage of the town of Enschede; this sewage has an alkaline character since it consists predominantly of textile-trade waste. Dosage of additional alkali in a number of experiments was achieved by means of a small pump that fed directly into the mixed liquor.

Sampling

Usually composite samples were taken over 24 hr periods. Since the inflow was kept constant no proportional sampling was necessary. In the continuous samples taken daily fluctuations in concentrations occurred. Further experiments in a laboratory equipment will provide results from an influent of constant composition.

Analytical procedures

Generally the standard methods were followed.

Whenever possible (brucine method for nitrate, COD) small samples were used as required by the automatic pipetting and dosing system available in our laboratory.

Determination of CO_2 was carried out according to the method of BLOM and EDELHAUSEN (1955): CO_2 is trapped in acetone in a small gas washing apparatus and subsequently titrated with sodium methylate in methanol. CO_2 in air was determined directly; total CO_2 in influent and effluent was first liberated by acidification and then swept into the titration vessel by a stream of nitrogen.

Contribution to p- and m-values by phosphate and other compounds

The mixed liquor usually contained 40–50 mg. l^{-1} of PO_4^{3-} which is equivalent to approximately 5×10^{-4} mol. l^{-1} . In FIG. 8 the *p*- and *m*-alkalities of a phosphate solution of this strength have been compared with total alkalities as usually encountered.

The phosphate contribution to alkalinity has been derived from the titration plot for phosphoric acid and turns out to be always less than 10 per cent of total alkalinity. Ions other than phosphate, bicarbonate and carbonate may contribute to the *p*- and *m*-values. SPLITTBERGER (1954) suggests how one can evaluate the contribution of non-carbonate ions. In our investigation the total CO_2 content of the effluent has been determined; subsequently the free CO_2 content derived from FIG. 1 has been subtracted from total CO_2 (FIG. 8). The HCO_3^- and CO_3^{2-} content thus obtained was compared with the content of these ions as calculated from the *p*- and *m*-values corrected for 5×10^{-4} mol. l^{-1} of phosphate (FIG. 9). In view of the good agreement

it is evident that substances other than phosphate can hardly be held responsible for more than a minor part of the p - and m -values. The difference occurring at low

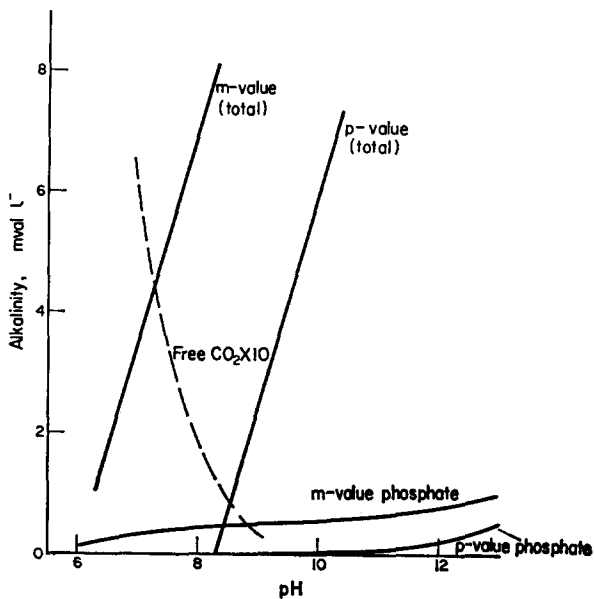


FIG. 8

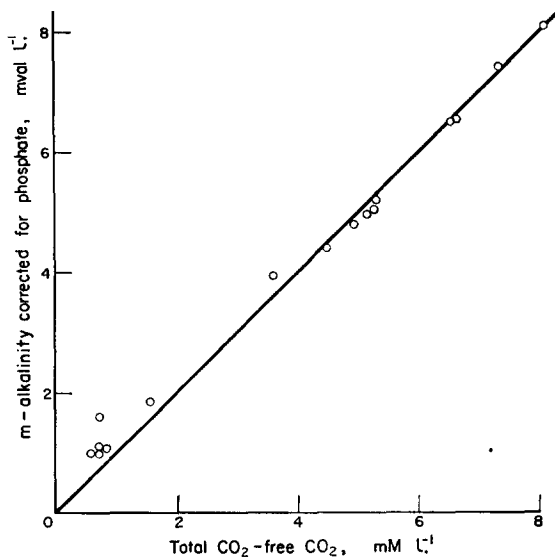


FIG. 9

values (FIG. 9) arises in all probability from loss of free CO_2 during transport. This is to be expected especially with low m -values because of the high supersaturation with respect to CO_2 (FIG. 1).

Activity coefficients

At pH values around 7.8 the sewage used in our experiments contains mainly the following ions:

Cl^- (0.02 mol. l^{-1}), HCO_3^- (0.006 mol. l^{-1}),
 HPO_4^{2-} (0.0005 mol. l^{-1}) and Na^+ (0.027 mol. l^{-1}).

Other ions are neglected. The ionic strength

$$\mu = \frac{1}{2} \sum c_i \cdot z_i^2$$

can be calculated to amount to 0.027. Since $\log \gamma = -0.51 z^2 \sqrt{\mu}$ the activity coefficient for monovalent ions is 0.82. In the moderately alkaline region the concentrations of chloride, bicarbonate, carbonate, hydrophosphate and sodium ions are approximately 0.02; 0.008; 0.002; 0.0005 and 0.034 mol. l^{-1} , respectively. From this it follows that $\mu = 0.036$. For monovalent ions ($z = 1$) this leads to $\gamma = 0.80$, for bivalent ions ($z = 2$) to $\gamma = 0.41$.

Determination of $K_L A$ values

The $K_L A$ -values for CO_2 desorption have been established by analysis of the CO_2 content of the gas stream leaving the solution. The value of $-d[\text{CO}_2]/dt$ for the mixed liquor incurred an inaccuracy of a few percents stemming from the contribution of CO_2 desorption in the gas-lift pump. In the bicarbonate solution the determination was more accurate.

$K_L A$ has been computed from $-d[\text{CO}_2]/dt = K_L A (c - c_s)$.

In this equation c represents the free CO_2 concentration in the bulk of the liquid; its value was calculated from pH and $[\text{HCO}_3^-]$ by means of equation (1c).

$K_L A$ -values for oxygen absorption and desorption have been determined from measurements of oxygen concentrations in the liquid phase by use of a membrane-covered Pb-Ag electrode. All measurements followed the method recommended by KAYSER (1967); a correction for salinity, however, proved indispensable when the membrane electrode was calibrated (LIJKLEMA, 1968).

REFERENCES

- ADAMSE A. D. (1968) Response of dairy waste activated sludge to experimental conditions affecting pH and dissolved oxygen concentration. *Water Research* **2**, 703-713.
- BLOM L. and EDELHAUSEN L. (1955) Direct titration of carbon dioxide. *Analyt. chim. Acta* **13**, 120-128.
- BOON B. and LANDELOUT H. (1962) Kinetics of nitrite oxidation by *Nitrobacter winogradskyi*. *Biochem. J.* **85**, 440-447.
- Deutsche Einheitsverfahren zur Wasseruntersuchung* (1968) Verlag Chemie, Weinheim.
- DOWNING L. A., PAINTER H. A. and KNOWLES G. (1964) Nitrification in the activated-sludge process. *J. Inst. sew. Purif.* **2**, 130-158.
- ECKENFELDER JR. W. W. (1967) Industrial waste treatment. *J. Wat. Pollut. Control Fed.* **39**, 240-250.
- ECKENFELDER JR. W. W. and O'CONNOR D. J. (1964) *Biological Waste Treatment* pp. 63, 64. Pergamon Press, Oxford.
- ENGEL M. S. and ALEXANDER M. (1958) Growth and autotrophic metabolism of *Nitrosomonas europaea*. *J. Bact.* **76**, 217-222.
- FREIER R. K. (1964) *Wasseranalyse* pp. 23-30. Walter de Gruyter, Berlin.

- HANNOVER (1961) Beitrag zur biologischen Reinigung der Abwässer der Textilveredlungsindustrie p. 71 Heft 7. Veröffentlichungen des Institutes für Siedlungswasserwirtschaft der Technischen Hochschule Hannover.
- HARNED H. S. and DAVIS JR. R. (1943) The ionization constants of carbonic acid in water and the solubility of carbon dioxide in water and aqueous salt solution from 0–50°C. *J. Am. chem. Soc.* **65**, 2030–2037.
- HOFMAN T. and LEES H. (1952) The biochemistry of the nitrifying organisms, part 4: the respiration and intermediary metabolism of *Nitrosomonas*. *Biochem. J.* **54**, 579–583.
- HÖMIG H. E. (1957) Ein Beitrag zur Theorie der *p*- und *m*-Werte. *Mitt. Verein. Grosskesselbesitzer* **48**, 170–177.
- INGOLS R. S. and HEUKELEKIAN H. (1940) Buffer values of sewage during purification. *Ind. Engng Chem.* **32**, 401–404.
- KAYSER R. (1967) Ermittlung der Sauerstoffzufuhr von Abwasserbelüftern unter Betriebsbedingungen. *Korrespondenz Abwasser* **14** [10], 7–9.
- KEEFER C. E. and MEISEL J. (1951) Activated sludge studies. Part III Effect of pH of sewage on the activated sludge process. *Sewage ind. Wastes* **23**, 982–991.
- KLEYN H. F. W. (1965) Buffer capacity in water chemistry. *Int. J. Air Wat. Pollut.* **9**, 401–413.
- KREVELEN D. W. VAN (1953) Kinetik und Transporterscheinungen bei Reaktionen in flüssig-gasförmigen Systemen. *Z. Elektrochem.* **57**, 502–512.
- KREVELEN D. W. VAN et HOFFLIZER P. J. (1948) Sur la solubilité des gaz dans les solutions aqueuses. *Chimie et Industrie, XXI^{ème} Congrès International de Chimie Industrielle* pp. 168–173.
- LANGELIER W. F. (1936) The analytical control of anti-corrosion water treatment. *J. Am. Wat. Wks Ass.* **28**, 1500–1521.
- LIJKLEMA L. (1968) Over de werking van zuurstof-membraan elektroden. *H₂O* **1** [21], 495.
- LINDNER W. (1958) Schlammproduktion und Schlammalter beim Belebungsverfahren in ein- und zweistufiger Betriebsweise. *Gesundh. Ing.* **79**, 271–273.
- MCKINNEY R. E. (1967) Biological treatment systems for refinery wastes. *J. Wat. Pollut. Control Fed.* **39**, 346–359.
- REPLOH H. und KÜSTERMANN H. (1958) Pufferungsgrad alkalischer Industrieabwässer und biologischer Abbau. *Gesundh. Ing.* **79**, 233–235.
- SAWYER C. N., FRAME J. D. and WOLD J. P. (1955) Revised concepts on biological treatment. *Sewage ind. Wastes* **27**, 929–938.
- SCHÄFER W. (1967) Untersuchungen zur Entsäuerung durch Belüftung. *Vom Wasser* Band XXXIV, pp. 443–458.
- SPLITTBERGER A. (1954) Die verschiedenen Arten der Darstellung von Wasseruntersuchungs-Ergebnissen. *Energietechnik* **4**, 203–208.
- Standard Methods for the Examination of Water and Wastewater* (1965) 12th edn. Am. Publ. Hlth Ass. New York.
- VIEHL K. (1932) Über den Einfluss der Wasserstoffionenkonzentration auf die Wirksamkeit und Biologie des Belebtschlammes. *Zentbl. Bakt. Parasitkde Abt. II* **86**, 34–43.
- WASHINGTON D. R. and SYMONS J. M. (1962) Volatile sludge accumulation in activated sludge systems. *J. Wat. Pollut. Control Fed.* **34**, 767–790.