

BIOLOGICALLY MEDIATED CHEMICAL CHANGES

IN THE FILTRATION OF AERATED GROUND WATERS

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Research on the process of filtration, until recently, has dealt only with the mechanical properties of the process. There are, however, chemical changes that occur, and this recent study attempts to discover and evaluate such changes.



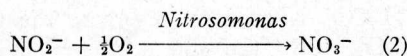
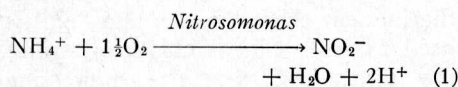
Aeration aids bacterial effects on waste chemicals.

FILTRATION has been acclaimed as the most significant engineering development of the 19th century in the field of public health. The process has been used since 1869, but without a complete understanding of the mechanisms involved in its effectiveness.¹ Starting with the early studies of the hydraulics of flow-through filters²⁻⁴ and the mechanism of removal of suspended matter,⁵ a great deal of effort has been spent in the study of filtration, as indicated by more recent literature.⁶⁻⁹ Most of the research emphasis has been placed on studies relating to the mechanisms of removal of suspended matter in the process of filtration. This tack is understandable because the primary objective in the process of filtration is the removal of suspended matter. However, concomitant with the removal of suspended matter (turbidity), other quality parameters may also change during filtration, notably the chemical properties of water. Changes in chemical properties may result from shifting equilibrium conditions from a chemical point of view, or they may be mediated by biologic activity. Precipitation of CaCO_3 is an example of the former, and nitrification is an example of the latter. A survey of literature shows that, in the case of rapid sand filtration in water supply, there is a general paucity of understanding of the role of bacterial activity. Most studies on filtration are done on a short-term basis, without regard to long-term effects. Since the growth and establishment of bacterial populations may take considerable time, changes in chemical properties may develop slowly. It is, therefore, necessary to study the process for many months to observe these changes. The chemical changes that may be brought about obviously are dictated by the characteristics of the water being filtered, and the nature of the bacterial populations sustained by the substances in the water.

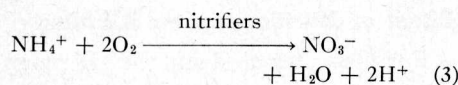
In iron-removal practice, the function of the filter is the removal of precipitated hydrated ferric oxide formed following aeration. In the absence of biological growths on filter beds, iron removal by this procedure has been observed to be efficient, even when the oxidation of ferrous iron present in the raw ground water has not been completed prior to filtration.^{10, 11}

When biological growths generate in filter beds, iron-removal efficiency may decrease markedly. An extreme case was observed during pilot-plant studies of iron removal when more ferrous iron was found in the filter effluent than was present in the filter influent.¹² The amount of organic matter naturally occurring in raw waters, though low in concentration, very often is adequate to support significant bacterial growth on the filter media. The large surface area of the filter media provides an interface for the growth of bacteria. In Illinois, the amount of organic matter in raw ground water, measured as COD, has been reported to be as high as 40 mg/l.^{12, 13} Ammonia may serve as the nitrogen source for bacterial growth in general and as the energy source for nitrifying bacteria. Since the complete oxidation of ammonia to nitrate exerts a theoretic oxygen demand of 4.54 mg/l of DO per mg/l of the ammonia's nitrogen (ammonia nitrogen) oxidized, less than 2 mg/l of ammonia nitrogen in the raw water source may bring about complete depletion of oxygen in oxygen-saturated water at room temperatures. As a result, when the growth of nitrifying bacteria occurs in a filter bed, the ammonia in the water being filtered may undergo biologic nitrification and anaerobic conditions may result.¹²

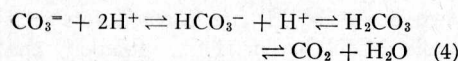
Nitrification is the aerobic biologic process of oxidation of ammonia to nitrite and nitrate by the autotrophic bacteria *Nitrosomonas* and *Nitrobacter*, respectively.



The overall reaction may be written as:



The form of ammonia in the above equations is taken as NH_4^+ in contrast with NH_3 because of the predominance of the former at neutral pH's. The H^+ liberated during nitrification alters the carbonate equilibria in water primarily buffered by carbonates.



Consequently, there will be a partial neutralization of alkalinity and a decrease in pH. In summary, the process of nitrification results in a depletion of

dissolved oxygen owing to the oxidation of ammonia to nitrite and nitrate, a reduction in alkalinity and a decrease in pH. The extent of change in each parameter can be calculated from the chemical reactions given. The purpose of the current study was to observe the chemical changes occurring as a result of the growth of nitrifiers in a sand filter, and to evaluate the agreement between the theoretically predicted values and the observed changes in quality parameter values from nitrification.

Pilot Plant Studies

The general layout of the units of the pilot plant used in this work is shown in Fig. 1. The pilot plant consisted of (a) an aerator; (b) settling tank; (c) eight filter units made from 4-in. ID plexiglass tubing; and (d) rate-of-flow control devices. All the units were supported on a Uni-strut steel frame. The system of rate-of-flow control devices was specially designed for this work and proved to be very successful.¹⁴

The raw water for the study was obtained from a 150-ft deep well drilled just outside the Sanitary Eng. Lab. of Univ. of Illinois, Urbana.

The raw well water was passed through a constant-head device to obtain a constant flow through the system. It was then aerated with compressed air passing through a diffuser stone. The aerated water was detained for about an hour before being applied to the filter. The units of the pilot plant were so arranged that flow took place by gravity, the water surface levels in the sedimentation tank and filter units differing by only the headloss in the connecting piping. The filter units were of open-top type with 30 in. of sand (0.55 mm effective size, 1.5 uniformity coefficient) atop a 12-in. bed of gravel ($\frac{1}{8}$ – $\frac{1}{4}$ in.). There was 5 ft of water over the top of the sand bed. Provision for surface wash was made because it was found necessary to keep mudball formation to a minimum. The conventional rate of flow, 2 gpm/sq ft, was employed in the studies. The pilot plant was operated continuously for 300 days during which time 157 experimental runs were made.

Figure 2 shows the plot of various parameters of settled water with respect to time. It may be seen that the natural level of ammonia in settled water was about 1 mg/l up to the 198th day. Thereafter, ammonium chloride

solution was added to augment the ammonia concentration until the 222nd day. The unusually high concentration of ammonia after the 196th day was due to faulty operation of the pump used for the addition of the ammonium chloride solution. Between the 222nd and 245th days, ferrous ammonium sulfate solution was added to increase the concentrations of ammonia and ferrous iron in the water. After the 245th day, ammonium chloride was used again for increasing ammonia levels.

Aeration was effective in bringing concentration to near saturation. The DO concentration between the 99th and 101st days, however, was lower than normal. This anomaly was caused by a lower rate of aeration, which also in turn produced a corresponding dip in the pH value—presumably due to less removal of carbon dioxide during the same period. The alkalinity of the water remained fairly constant, except during the period when ferrous ammonium sulfate solution was added. The decrease was due to the acid produced during the oxidation of ferrous iron. Hardness was fairly constant.

The filter unit was started with clean, washed sand. A length of filter run of about 48 hr was maintained, with terminal head loss of about 8 ft or less. At the end of each filter run, the filter unit was backwashed. The backwash consisted of a surface wash with a jet of water for 2 min followed by backwash for 5 min at 50 per cent bed expansion. The rates of application of wash water were 40 and 30 gpm/sq ft, respectively, for the surface and backwash operations. These rates are admittedly higher than those commonly used in practice, but were found necessary because of the size and geometry of the filter unit. The quality of filter influent and effluent was determined by analyzing respective water samples collected, either during the middle of a run or both at the beginning and end of a run. Samples of water were collected at the beginning and the end of 79 runs and during the middle of another 11 runs, thus creat-

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TABLE 1
Average* Characteristic of Filter
Influent and Effluent

Parameter	Filter Influent	Filter Effluent
Temperature—C	16.9	18.14
pH—units	7.80	7.58
DO—mg/l	8.6	3.22
Total Iron—mg/l	1.31	0.09
Total ferrous—mg/l	0.18	0.05
Filtrable ferrous—mg/l	0.06	
Ammonia-N—mg/l	1.67	0.51
Nitrite-N**—mg/l	0.02	0.33
Nitrate-N**—mg/l	0.35	1.77
Alkalinity—mg/l	331.6	322.58
Hardness—mg/l	245.5	244.88

* Average of 90 of the 157 runs during 300 days of operation, except as noted.

** Average of 25 of the 72 (86 through 157) runs during the last 130 days of operation.

ing a total of 169 ($2 \times 79 + 11$) sets of samples. The analysis of samples included measurement of temperature, pH, DO and ferrous iron immediately after collection, nitrite and nitrate nitrogen within 4 hr, ammonia nitrogen within 12 hr, and alkalinity, hardness and total iron within 24 hr of collection. Samples were kept refrigerated during the intervening period. Analyses were performed in accordance with *Standard Methods*¹⁵ except for the determination of ferrous iron, which was carried out using a modified bathophenanthroline method.¹⁴ The average values of the parameters measured during the 90 runs for the filter influent and effluent are shown in Table 1. The plot of the characteristics of filter effluent from filter unit No. 1 of the pilot plant is shown in Fig. 3. The ordinate values of ammonia, nitrite, and nitrate nitrogen in Fig. 3 show the difference between the influent and effluent concentrations. Figure 3 shows that the temperature and hardness values closely followed the influent values as shown in Fig. 2. The iron concentrations, both ferrous and total, were low in the filter effluent, indicating a satisfactory iron removal in the process of filtration.

The values of (Inf—Eff) for ammonia increased, indicating ammonia depletion. The concentrations of nitrite and nitrate (measured after the 170th day of operation) increased as seen from the values of (Eff—Inf), indicating that nitrification was taking place in the filter. As discussed earlier, accompanying the process of nitrification were changes in DO, alkalinity, and pH. These changes are reflected in Fig. 3. The average value of filter effluent characteristics are in Table 1.

Stoichiometric Correlation

The chemical changes taking place as a result of nitrification during filtration have been shown to be related by the chemical equilibrium and mass-balance equations given in Eq (1)–(4). For example, the oxidation of ammonia to nitrate would theoretically require 3.42 mg/l of oxygen per mg/l of ammonia N as seen from Eq (1). Similarly, 4.54 mg/l of oxygen will be theoretically required for the complete oxidation of 1 mg/l of ammonia N to nitrate, as per Eq (3). From these relationships, the mass-balance on oxygen (DO) can be written as:

$$\left[\begin{array}{c} \text{DO in} \\ \text{influent} \end{array} \right] - \left[\begin{array}{c} \text{DO demand of NO}_2^- \\ \text{and NO}_3^- \text{ formed} \end{array} \right] = \left[\begin{array}{c} \text{DO in} \\ \text{effluent} \end{array} \right]$$

In the above equation, DO in the influent and effluent are measured experimentally, and oxygen demand for NO_2^- and NO_3^- is calculated from the amount of NO_2^- and NO_3^- formed. The mass balance on nitrogen is made by comparing the total amount of nitrogen (ammonia, nitrite, and nitrate) in the influent and effluent.

Corrections to Equilibrium Constants

The calculations for effluent alkalinity and pH involve the equilibrium expression for the first protolysis of carbonic acid:

$$K_1 = \frac{(\text{H}^+)(\text{HCO}_3^-)}{(\text{H}_2\text{CO}_3)} = 10^{-6.3} \text{ at } 25\text{C} \quad (5)$$

Two types of correction for the equilibrium constant are necessary when dealing with natural water systems: a temperature correction and a correction for the ionic strength due to its influence on the activity coefficients. From a complete mineral analysis of the water used in the study, the ionic strength was calculated from the equation

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

and was found to be 0.0091 mole/l.¹⁴ The correction for ionic strength may be made by calculating the activity coefficients using the Debye-Hückel law, or it may be applied as a correction factor, given by Dye,¹⁶ as follows:

$$pK_1' = pK_1 - \frac{\sqrt{\mu}}{(1 + 1.4\sqrt{\mu})} \quad (6)$$

The latter method was adopted in these calculations. The temperature correc-

tion was applied using vant Hoff's equation:

$$\log (K_{1(T)}/K_{1'(25)}) = \frac{\Delta H_f}{2.3R} \left(\frac{1}{T + 273} - \frac{1}{298} \right) \quad (7)$$

where ΔH_f is the heat of reaction, R is the universal gas constant, and $K_{1(T)}$ is the equilibrium constant at any temperature T (C).

The pH value measured by the calomel-glass electrode system is presumed to include the effects of ionic strength. The temperature correction, in this case, the instrument correction, had to be applied. Even though the pH meter (Beckman expanded scale) did have a manual temperature compensator, the setting was left at 25C, at which point standardization was carried out, in order to avoid the difficulty in making fine adjustments on the instrument for temperature compensation for the temperatures of different samples. Therefore the instrument correction for temperature was made by calculation. Such an instrument correction was observed to be an increase of 0.03 pH unit for a change in the manual setting of the temperature compensator from 25 to 15C, the range of interest in this study. Hence a temperature correction was applied as follows:

$$\text{pH}_T = \text{pH}_{25} + 0.003(25 - T)$$

With the above corrections applied to the K_1 and pH, the following method of calculation of effluent pH and alkalinity was used for each set of reading. The subscript "in" is used to denote the influent characteristic, and "eff" is used for the effluent characteristic of the filter process. The expression H_2CO_3 is used to designate the total CO_2 , both free and combined, in the water.

Effect of Nitrification on Alkalinity

For the water used and the pH range encountered it is reasonable to assume that all of the alkalinity was present in the bicarbonate form. Therefore,

$$\text{HCO}_3^- \text{ in mole/l} = \frac{\text{Alkalinity}_{\text{in}} \text{ mg/l CaCO}_3}{50,000} \quad (8)$$

Recalling from Eq (1) and (3), that two moles of H^+ are formed for each mole of NO_2^- or NO_3^- formed, the amount of H^+ produced during nitrification is

$$\text{H}^+ \text{ moles/l} = 2 (\text{NO}_2^- + \text{NO}_3^-) \text{ moles/l formed} \quad (9)$$

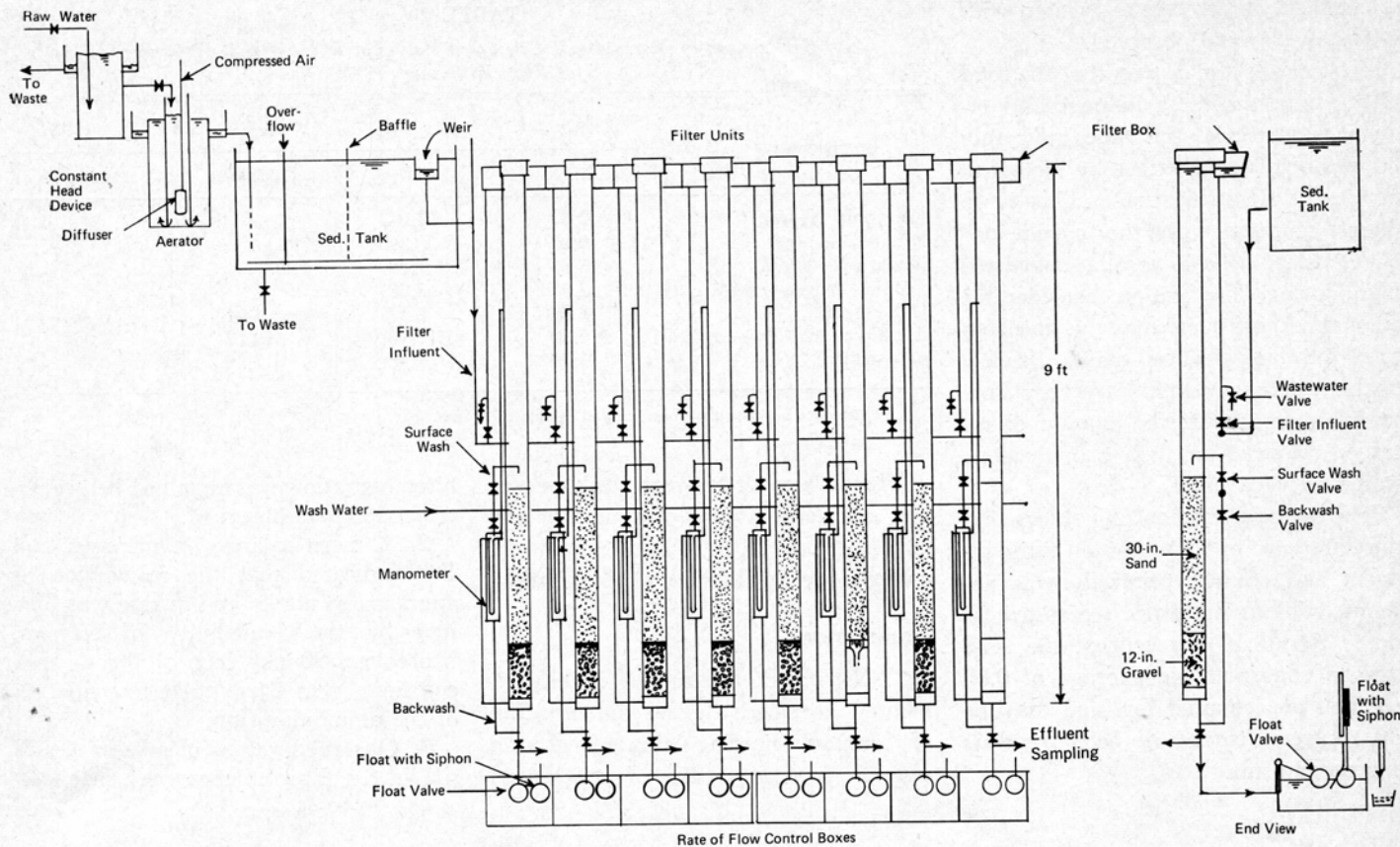


Fig. 1. Schematic Representation of Pilot Plant at Urbana

The pilot plant was supported on a Uni-strut steel frame. The filter units were open-top type with surface wash installations. The rate-of-flow control devices with double floats and siphon were very efficient.

The H^+ produced during nitrification will neutralize an equivalent quantity of bicarbonate alkalinity. The amount of HCO_3^- thus neutralized in terms of alkalinity is the amount of $CaCO_3$ neutralized in mg/l:

$$[2(NO_2^- + NO_3^-) \text{ moles/l formed}] \times 50,000 \quad (10)$$

The effluent alkalinity is then calculated as

$$\text{Computed } Alk_{eff} = Alk_{in} - \text{Alkalinity neutralized, mg/l } CaCO_3$$

On some occasions, there was a small change in the hardness between the influent and the effluent of the filter, which was of the order of 1 to 2 mg/l. Since all of the hardness was carbonate hardness, a change in hardness would also reflect a change in alkalinity. A correction was applied to the Alk_{eff} calculated above to take into consideration the changes in hardness. The value of computed Alk_{eff} was then compared with the observed Alk_{eff} .

Effect of Nitrification on pH

The HCO_3^- neutralized is converted into an equivalent amount of carbonic acid, H_2CO_3 , thereby increasing the carbonic-acid content of the water. The increased carbonic-acid content in turn decreases the pH. The following calculations show how the effluent pH was computed:

$$H_{in}^+ \text{ moles/l} = - \text{antilog}_{10} (pH_{T in}) \quad (11)$$

From Eq 5

$$H_2CO_{3in} \text{ moles/l} = \frac{(H_{in}^+)(HCO_3^-)_{in}}{K_{1T}} \text{ moles/l} \quad (12)$$

The amount of carbonic acid produced as a result of nitrification is equal to the amount of bicarbonate alkalinity neutralized on a molar basis, assuming no losses for a closed system. Thus,

$$H_2CO_3 \text{ moles/l produced} = HCO_3^- \text{ moles/l neutralized,} \quad (13)$$

and

$$H_2CO_3 \text{ eff} = H_2CO_{3in} + H_2CO_3 \text{ produced moles/l} \quad (14)$$

From Eq 5 again,

$$H^+_{eff} = H_2CO_{3eff} \times K_{1T}/HCO_3^-_{eff} \text{ moles/l} \quad (15)$$

Expressing the H^+ in terms of pH and including the instrument correction as before

$$\text{computed } pH_{eff} = - \log_{10} (H^+_{eff}) - 0.003(25 - T) \quad (16)$$

The computed effluent pH was then compared with the actual observed pH of filter effluent.

The above calculations for nitrogen balance, oxygen balance, alkalinity and pH changes between the influent and effluent of the filter were performed on the IBM 360 computer for each set of observations during runs 86 through 157. The average of these readings is given in Table 2.

Results and Discussion

Owing to nitrification, the filter bed during filtration can be considered to be a "biochemical reactor" where chemical changes in the quality of water takes place. All of the changes

in chemical parameters associated with nitrification were observed.

First of all, it may be seen that the total nitrogen in the filter influent and effluent is practically the same, indicating no loss of nitrogen either by biological uptake or denitrification. This is in direct contrast with the conclusions of Ghosh,¹² whose results suggested that during nitrification considerable amount of nitrogen may be incorporated into biological cell mass. In view of the fact that nitrifiers are very slow growing organisms, the amount of nitrogen required for their growth alone would be very small.

The mass balance on DO shows that the difference of DO between filter influent and effluent primarily was accounted for in the process of nitrification. About 10 per cent of the total oxygen consumed, an average of 0.88 mg/l is unaccounted for, and may be the oxygen demand of heterogeneous microorganisms.

TABLE 2
Comparison of Observed and Calculated Values of DO, pH and Alkalinity
for Runs 86 through 157

Parameter	Influent	Effluent		
	Observed	Observed	Calculated	Difference*
Ammonia N—mg/l	2.67	1.01		
Nitrite N—mg/l	0.02	0.31		
Nitrate N—mg/l	0.36	1.77		
Total Nitrogen—mg/l	3.05	3.09		
DO—mg/l	8.83	0.53	1.41	0.88
Alkalinity, CaCO ₃ —mg/l	330.88	317.70	318.17	0.47
pH—units	7.70	7.38	7.36	0.02

* Difference between the observed and calculated values.

The agreement between the observed and calculated values of alkalinity and pH is excellent, indicating again the changes are attributable to nitrification.

Conclusions

1. Nitrification occurred in experimental filter beds during the filtration of ammonia-bearing aerated ground water. Several weeks of continuous

filter operation was required before nitrification was observed.

2. A mass balance on nitrogen and DO indicated that the conversion of ammonia to nitrite and nitrate was limited by the availability of oxygen. Moreover, 90 per cent of the oxygen consumed was attributable to oxidation of the ammonium ion.

3. Observed values of alkalinity and pH in the filter effluent were in excel-

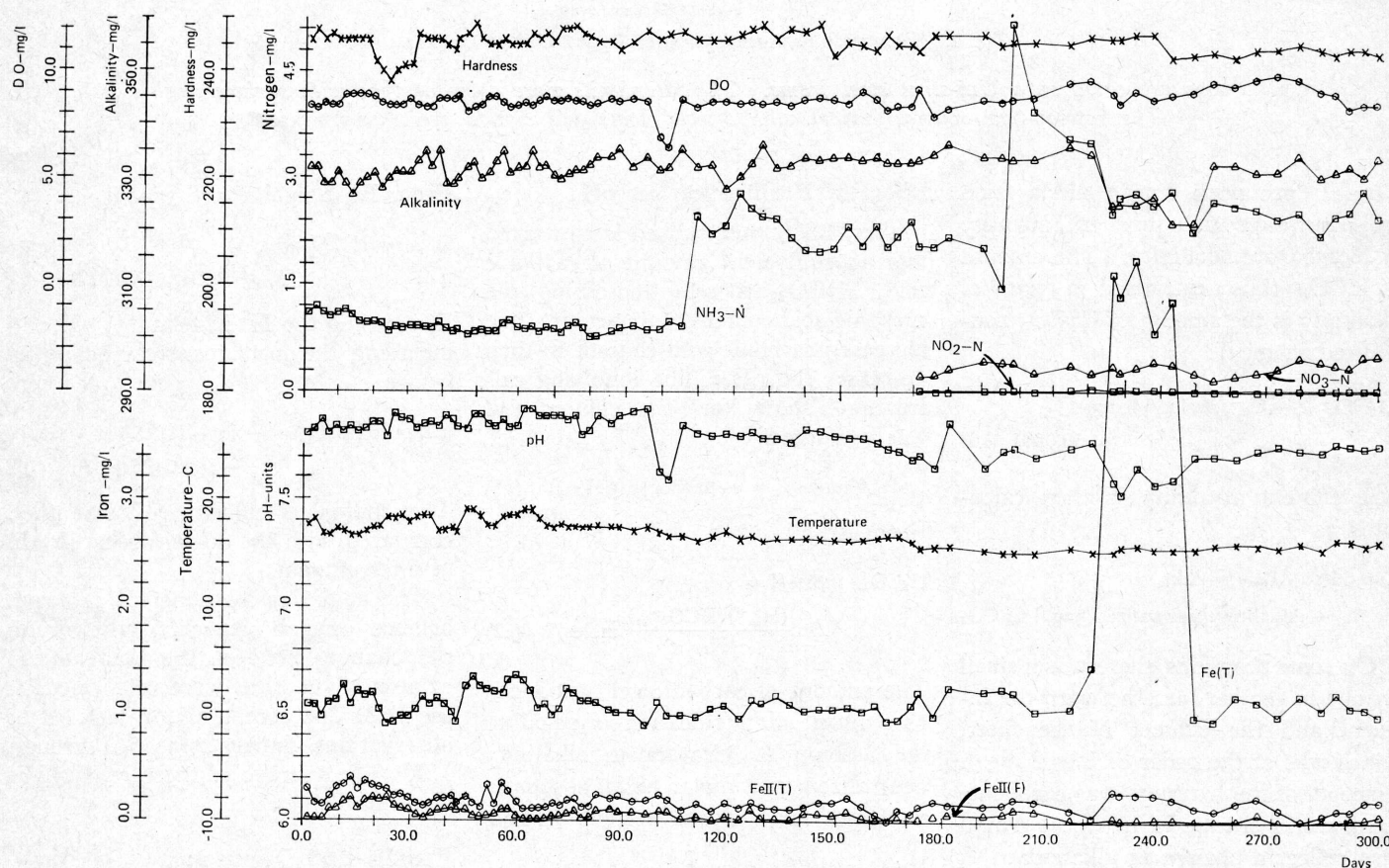


Fig. 2. Characteristics of Filter Influent

Quality parameters shown up to the 109th day represent the aerated and settled natural water pumped from the well. Between the 109th and 222nd days, ammonium chloride solution was added to the natural water to augment the ammonia N concentration. Between the 222nd and 245th days, ferrous ammonium sulfate solution was added to augment both ammonia N and iron concentrations in the water. After the 245th day, ammonium chloride solution was used again.

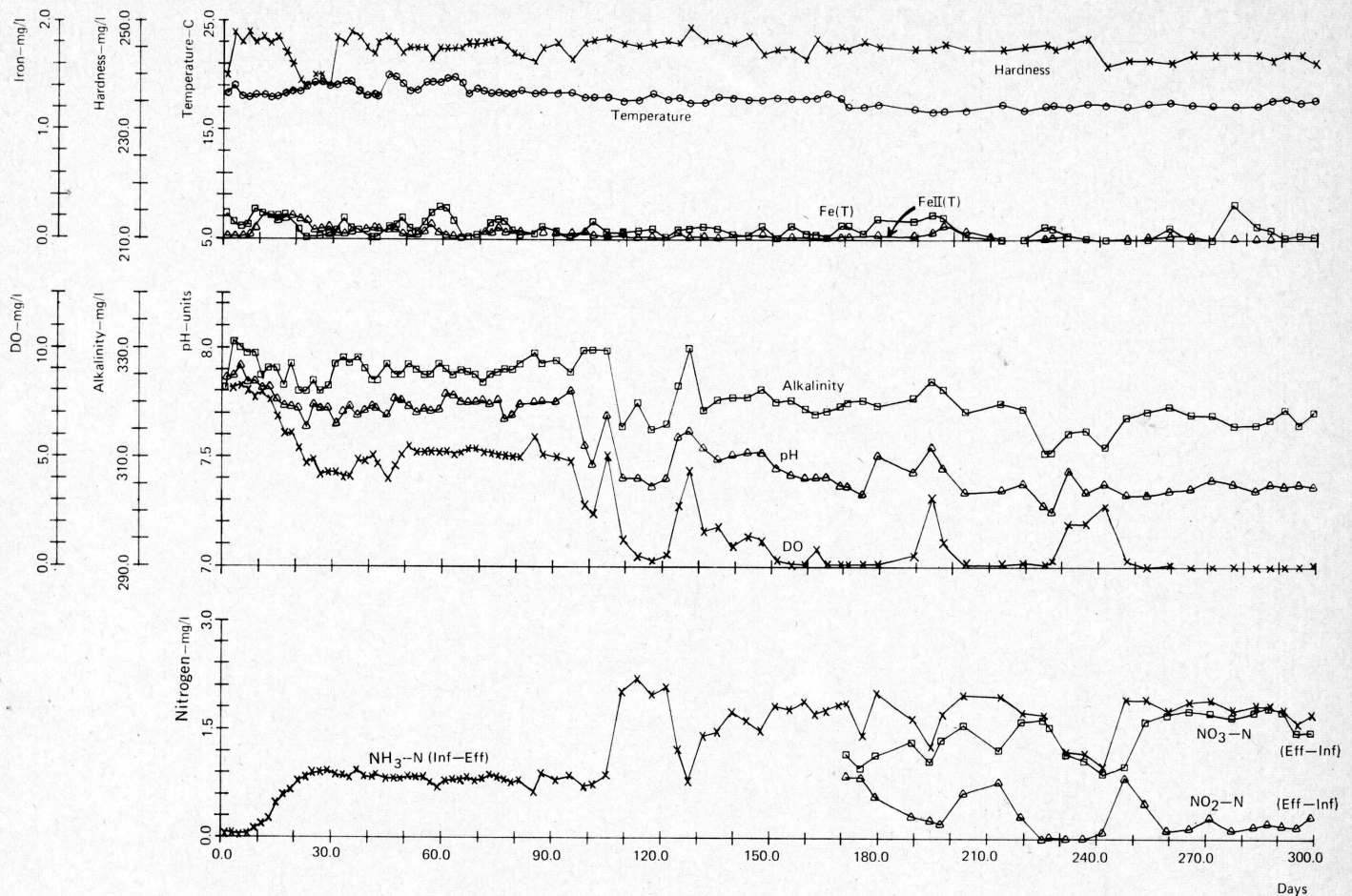


Fig. 3. Characteristics of Filter Effluent

Quality parameters of the filtered water showed good iron removal with small variations in hardness (HARDNS) and temperature. The process of nitrification during filtration is apparent from the increasing depletion of ammonia N, accompanied by decreasing values of DO, alkalinity (ALK) and pH. Formation of nitrite (NO_2) N and nitrate (NO_3) N showed that nitrification was in fact taking place.

lent agreement with the stoichiometrically predicted (calculated) values arrived at under the assumption that only nitrification was influencing these parameters, and the filter bed behaved as a closed system.

4. The results of this study suggest a method of calculating the quality of filter effluent for a given filter influent undergoing nitrification. This fact is particularly important with respect to establishing criteria relevant to the depletion of DO that may lead to potentially troublesome anaerobic conditions, and to increasing concentrations of nitrate, both of which may result in the deterioration of water quality.

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