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BIOLOGICALLY MEDIATED CHEMICAL CHANGES IN THE FILTRATION OF AERATED GROUND WATERS



By K. Y. BALIGA

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BIOLOGICALLY MEDIATED CHEMICAL CHANGES IN THE FILTRATION OF AERATED GROUND WATERS

ΒY

KALYANPUR YESHAVANTHA BALIGA B.E., University of Madras, (India), 1958 M.S., University of Illinois, 1964

THESIS

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BIOLOGICALLY MEDIATED CHEMICAL CHANGES IN THE FILTRATION OF AERATED GROUND WATERS

Kalyanpur Yeshavantha Baliga, Ph.D. Department of Civil Engineering University of Illinois, 1969

Many ground water supplies include treatment for iron removal by aeration, settling and filtration. Failure to produce an effluent to meet the U.S.P.H.S. Drinking Water Standards with respect to concentration of iron has led to many studies dealing with the problem of breakthrough of iron in filters. Biologic activity, particularly of nitrifying bacteria, has been suggested to be responsible for the chemical reduction of ferric iron to ferrous iron in the filter.

The current studies were undertaken to evaluate the chemical changes taking place in the water during filtration due to biologic activity and also to evaluate practical methods of controlling the bacterial growths in filters. Pilot plant studies were carried out for nearly five months at Rantoul and for ten months at Urbana, Illinois, in the treatment of aerated ground water for removal of iron. Raw water both at Rantoul and Urbana contained ferrous iron (1-2 mg/l) and ammonia (1-2 mg/l). Aeration introduced oxygen to oxidize most of the ferrous iron and bring the dissolved oxygen concentration to near saturation. In three to eight weeks of operation of the pilot plant, the ammonia in the filter influent was found to be oxidized to nitrite and nitrate, depleting the dissolved oxygen concentration to near zero in the process. The hydrogen ions liberated in the oxidation of ammonia were found to neutralize part of the alkalinity of the water resulting in a decrease in pH during filtration. The mean observed chemical changes in alkalinity and

pH were found to be in excellent agreement with the stoichiometrically predicted values, based on the process of nitrification.

In spite of evidence of mitrification in the filters, the iron removal was good, with an average concentration of iron being 0.10 mg/l or less. This is in contrast with the earlier belief that nitrification can cause breakthrough of iron in filters. It now appears that nitrification may be a necessary, but not a sufficient condition for breakthrough of iron in sand filters.

Because of the nature of hydrated ferric hydroxide floc as the suspended matter in the water being filtered, a filter cake was observed at the end of filter run. A simple backwash was found to result in the formation of mudballs from the filter cake. A surface wash prior to backwash was found to be effective in preventing mudball formation. Air scour was also found to be a satisfactory aid to backwash to prevent mudball formation. Presence of mudballs, when allowed to accumulate in the filter was found to have no effect on the filtered water quality with respect to iron, even when nitrification was taking place. Air scour and surface wash though effective in preventing mudball formation from the filter cake, did not prevent bacterial growth in the filter medium. Potassium permanganate and chlorine were evaluated as potential chemical agents of control for the bacterial growth in filters. A solution of potassium permanganate of concentration 5000 mg/l at pH 10.5 and contact time of three hours was found to be effective in inhibiting nitrification for about three weeks. A chlorine solution, 1000 mg/l at pH 4 and a contact time of seven hours was found to be effective in inhibiting nitrification for about a week. However, the estimated chemical cost per week for chlorine treatment was found to be less than that for potassium permanganate treatment.

I. INTRODUCTION

Ground Waters as Sources of Water Supply

less than three percent of the fluid fresh water available at any given moment on our planet earth occurs in streams and lakes. The other more than 97 percent - an estimated eight trillion acrefeet - is underground (1). However, not all the water beneath the earth's surface can be economically recovered from the water bearing formations in which it is found. Among the reasons for such limitations are prohibitive pumping costs for aquifers lying very deep, and poor yielding capacity of some aquifers. In spite of these limitations, the economically available supply of ground water is many times greater than the available supply of surface water. Because of the replenishment of the ground water by rainfall and seepage, successful management of withdrawal could perpetuate the ground water resources. A review of natural resources has shown that the current rate of depletion of ground water resources is many times less than the rate of depletion of most other natural resources, so much so that the nation at the current rate of consumption will deplete every other nonrenewable resource thousands of years before it will exhaust ground water (2). Of the total water withdrawn in United States (including domestic self-supplied, municipal, industrial and irrigation) only about one-sixth comes from ground water resources, and about fivesixths comes from surface water resources. However, among the total number of separate water supply installations in this nation (U.S.), there are 1500 ground water installations for every one surface water installation (2). The paradox arises from the tremendously greater daily production of typical surface water installation as compared with that of a typical ground water installation.

Some of the favourable arguments for the use of ground water are (2):

- "(a) ground water is more generally available at the point of use eliminating transmission;
- (b) it exists for the most part as an underground reservoir eliminating the need for impoundment;
- (c) it is less subject to pollution through human activity;
- (d) it is more constant in composition than surface water;
- (e) it is generally cooler than surface water, and of a more constant temperature throughout the season;
- (f) ground water installations are less vulnerable to various physical hazards such as floods, sabotage and enemy attack;
- (g) ground water occurrence is more widespread than surface water; and
- (h) ground water is economical even when produced in small quantities, and thus can foster decentralization of population, whereas surface water economics tends to foster the megalopolis."

The 1952 USPHS Summary of Municipal Water Facilities in communities of 25,000 or more reported that of the 905 facilities serving 781 communities, 382 facilities or 42 percent used ground water (3). An additional 8.5 percent used a combination of ground and surface water sources. These values were higher than those reported for 1960 when the percentages were 34.5 and 7.9 respectively (4). This is an upward trend for communities of 25,000 or more. The proportion of communities of smaller sizes using ground water would be much greater indeed.

.hen successful management of ground water is made, 'good economical ground water is a commodity that will never go out of style' (5). Greater attention is being given recently to the development and uses of ground water (6). A general depiction of the role of ground water in the overall uses of water in United States has been given by McKichan (7, 8). The fact that the full potential of use of ground water has not been realized, has prompted Geraghty to remark that ground water at the present time is a neglected resource (9).

When ground water is used for a municipal supply, the treatment needed may vary generally from disinfection only to softening and/or iron removal followed by disinfection. Half the water utilities in United States using ground water or 7,350 systems serving about twelve million people do not treat their well water supplies (10). This speaks for the better bacteriological quality of some of the ground water supplies compared with the surface water supplies, though disinfection would be highly desirable even in those cases to take care of post contamination.

Characteristics of Ground Water

The chemical formula H₂O represents water, but water in nature is never just H20. Ground water is no exception. Rain water, as it precipitates and falls to earth, dissolves impurities from the atmosphere, chiefly carbon dioxide. The water that percolates through the earth's crust comes in contact with the mineral deposits. The relatively slow movement of water affords intimate and prolonged contact with the minerals. Depending on the composition of the minerals and the acidic or alkaline nature of water, dissolution of mineral constituents takes place. The overall mineral content of water is thus determined by the chemical processes of solution. Ground water is relatively free from biological forms. This is partly because of lack of light and oxygen. Natural filtration of water through aquifers is also partly responsible. However some bacteria, particularly the sulfate-reducing bacteria, iron bacteria, etc., can be found. Some changes in chemical composition may also be brought about by the bacterial species present. Gases such as carbon dioxide, methane and hydrogen sulfide usually result from bacterial action. The relationship of the chemical constituents of ground water to the chemical composition of rocks and minerals is summarized below.

The five most abundant elements of the earth's crust are, in order of decreasing amounts, oxygen, silicon, aluminum, iron and calcium. The first three usually occur together as aluminum silicates in most rocks and clays. The fourth most abundant element of the earth's crust, iron, occurs in aesthetically objectionable quantities in many ground water supplies. The fifth most abundant element, calcium, is also undesirable beyond a certain limit, because it imparts 'hardness' to the water by its presence. Other divalent cations such as magnesium also contributes to the hardness of the water. The geochemical origin of some of the more common constituents of ground water are described below.

Iron in ground water is generally derived from magnetite (Fe301,), hematite (Fe₂0₃), limonite (Fe₂0₃.xH₂0), siderite (FeCO₃), pyrite (FeS), arsenopyrite (FeAsS) and iron aluminum silicates in rocks. Calcium is derived from limestone (CaCO3), and igneous rocks (feldspars, chiefly the calcium-aluminum-silicates), gypsum (CaSO₄), phosphorite $(Ca_3(PO_4)_2)$, apatite $(Ca_3(PO_4)_2)$ plus CaF_2 , dolomite $(CaCO_3.MgCO_3)$. The other major hardness-producing element, magnesium, is found in magnesite (MgCO3), and dolomite as well as in limestone and igneous rocks. Manganese is another element that is troublesome when found in water supplies. Manganese may be derived from pyrolusite (MnO2), or alabandite (MnS). The other predominant ions, sodium and potassium are chiefly derived from the feldspars. Sodium is also plentiful in sea water and salt deposits. Most other metals present in ground water are generally derived from the respective sulfides, e.g., copper from chalcocite (Cu₂S), or chalcopyrite (CuFeS); lead from galenite (PbS); cadmium from greenchite (CdS); selenium from selenite (SeS); silver from argentite (Ag2S); zinc from sphalerite (ZnS); and arsenic from realgar (AsS). Barium is derived from barite (BaSO_{μ}), and boron is derived

from borates such as rasorite $(Na_2B_4O_7\cdot L_4B_2O)$, or colemanite $(Ca_2B_6O_{11}\cdot 5^{H_2O})$ and also sassolite (boric acid, H_3BO_3).

During the dissolution of the minerals yielding the cations as described above, the associated anions also enter the solution. The list of minerals above show that the associated anions are, carbonates, sulfates, sulfides, fluorides. The oxides in dissolving generally yield hydroxide ions or hydrogen ions upon hydrolysis, depending on the environmental conditions. Chlorides are generally derived from salt deposits or sea water intrusion; or from a source of pollution. It is interesting to note that nitrogen is not derived from any minerals. On the other hand, the nitrates in ground water are derived from the bacterial action on the atmospheric nitrogen in top soil or on the ammonia either artifically added on farm land for purposes of fertilization or derived from the naturally occurring organic matter. The nitrate ions being very mobile in ground water, move along with water as it seeps down and joins the ground water reservoir.

The amount of each chemical constituent in ground water is limited by the respective solubility and oxidation-reduction equilibria which apply to the minerals in contact with the water. The role of dissolved carbon dioxide in water in affecting the solubility equilibria is also well recognized. Thether a true equilibrium exists between the mineral and the surrounding water or not may be decided by the extent of contact and the kinetics of solution. The chemical equilibria will change with changes in temperature and pressure. Cultural pollution may add a variety of other constituents to ground water, but this would depend on the locality and nature of pollution.

Ground Water Treatment

Treatment of ground water, as surface water, will be dictated by the composition of the raw water and the desired quality of the finished water.

Host commonly, ground waters are treated for reduction of hardness and removal of iron and manganese. Hardness is removed either by ion exchange or chemical softening processes. Iron and manganese, though they do not constitute a health hazard in drinking water, are objectionable for aesthetic reasons, in that iron-bearing water stains laundry and plumbing fixtures. In addition, industries may have more stringent requirement as to iron content of process waters. Because iron is found more frequently and in greater amounts than manganese in ground water, its removal from water supplies has been the subject of discussion and research for almost a century. Numerous methods have been proposed for the treatment of ground water for removal of iron.

The most common method for the removal of iron involves the aeration of raw water to oxidize the ferrous iron to ferric iron, and filtration for the removal of the precipitated ferric floc. This method, though conceptually simple, is beset with many practical problems. Difficulties are sometimes encountered with the oxidation and precipitation of iron from ground waters. Studies on synthetic systems have shown that the oxidation of ferrous iron is a first-order reaction with respect to ferrous iron concentration (11-13).

$$- \frac{d(\text{FeII})}{dt} = k (\text{FeII}) (p0_2) (OH^-)^2$$
(I-1)

The above equation predicts higher oxidation rate at higher pH. The oxidation of ferrous iron in natural systems has not always conformed to the above prediction (14). Among the reasons for the observed deviations are probably the fact that iron may be complexed by organic chelates or with inorganic addends. Moreover, waters high in alkalinity may promote the precipitation of carbonates (14) and the presence or absence of trace metals may catalyze or inhibit the reaction. The suggestion that ferrous carbonate precipitation may occur has been criticized (15) and partly supported by others (16). In any case,

generally, most of the iron in solution is precipitated by aeration in waters at neutral pH. However, because of the very poor agglomeration and settling characteristics of the iron floc thus formed, very little is removed from suspension even in an hour's time of settling. Longley (17) and Engelbrecht <u>et al.</u> (18) reported that the iron removal efficiencies of synthetic and natural waters by aeration and sedimentation (without filtration) were in the range of 2 to 56 percent, with most of the removal occurring in the aerator and only about 0-12 percent occurring in the sedimentation tank. The collcidal suspension of iron floc must therefore be removed from the water by filtration.

Filtration in Iron Removal

Filtration in general has been used since 1869, without a complete understanding of the mechanisms involved in its effectiveness (19). As a matter of fact, filtration has been acclaimed as the most significant engineering development of the 19th century in the field of public health.

Theories explaining the effectiveness of filtration have been slow in developing. Only recently have attempts been made to construct mathematical models for the theory of filtration. Hydraulic studies of flow through filters have preceded studies on the mechanism of removal of suspended matter (20, 21). Earliest among the studies of the latter type was by Iwasaki (22) who utilized discrete suspended particles (potter's clay) in the study of slow sand filtration for a period of about 150 minutes. Later studies by Ives (23) and Camp (24) are particularly noteworthy. Ives modified Iwasaki's equations to take into account the variations in the removal characteristics as the filter clogging proceeded. Camp advanced the hydraulic studies of flow through filters by considering the variation in Reynold's number and friction factor during filtration. Fox and Cleasby (25) have recently shown

that Ives' equations are not valid for iron floc, even though the equations have been shown to be valid for algae as suspended matter. The physical aspects of the removal of suspended matter by filtration are receiving considerable attention from researchers at the present time (26-29).

A conventional filtration rate of 2 gpm/sq ft has been established by experience and has become almost traditional, being handed down from the past (30), and commonly accepted by many. However, studies on the feasibility of higher rates of filtration recently reported would be sufficient to inspire those who are lulled into security by the spurious sanctity of 2 gpm/sq ft rate (31-33).

The penetration of suspended matter in the filter and the process of clogging of the pores of the filter bed have been described by many workers (24, 34-36). One or more of the following mechanisms has been thought to be responsible for the physical removal of suspended matter: sedimentation, coagulation-sedimentation, absorption, VanderWaal's forces, Brownian motion, inertial forces and ion-exchange. The predominant mechanism in a given case will depend on the filter medium and the size and nature of suspended matter. When clogging proceeds to such an extent as to cause a terminal headloss, particle breakthrough may take place due to shear forces on the suspended matter already deposited in the filter medium. Backwashing of the filter becomes imperative to return the bed to operating condition.

Hydraulics and methods of backwashing of filters have been reported by a number of investigators (20, 21, 23, 24, 37, 38). Ideally, the backwash should restore the filter bed to its original condition. Usually, the practice of filter backwash involves a 50 percent expansion of the filter bed (38). The necessity of a surface wash has not been emphasized in cases where the flocculent nature of suspended matter results in surface filtration forming
a filter cake in contrast to depth filtration of discrete suspended particles (31).

Physio-Chemical Changes Due to Filtration

The primary objective in filtration is the removal of suspended matter. In iron removal, the function of the filter is the removal of hydrated ferric oxide floc formed as a result of aeration, and flocculation during sedimentation. In this respect sand filters have been observed to be efficient in iron removal as long as the filter bed is free from significant biological growth (17, 18, 39-41). Nearly complete removals are obtained in spite of incomplete oxidation of ferrous iron. As a matter of fact, for many natural ground waters in Illinois, the oxidation of FeII was found to be incomplete even 60 minutes following aeration (17, 18, 41, 42). This was attributed either to some inhibitor or to the precipitation of ferrous carbonate. In either case, under optimum operation, all iron will be removed, providing a filter effluent which will meet the USPHS recommended Drinking Water Standards (43).

It has long been thought that when ferrous iron is present in the filter influent, it could be removed by 'catalytic oxidation' within the filter. Considering the fact that the oxidation of ferrous iron is slow in some natural systems, the oxidation of ferrous iron within a filter bed during a relatively short time may not be taking place. However, removal of precipitated ferrous iron is possible. In this connection, Boorsma suggested that other mechanisms such as adsorption on filter media may be responsible (13).

The oxidation of ferrous iron in the filter, if it does take place, is an example of a chemical change during filtration. Still more significant are chemical changes brought about by bacteria in filters. Ground waters, though generally considered to be free of organic matter, often contain organic matter in small quantities (44). The chemical oxygen demand of ground

waters in Illinois has been observed to be as high as 40 mg/l (41, 45). Considering the large amount of water filtered by a filter, the organic matter together with the dissolved oxygen in water may be able to support a heterotrophic bacterial population. The autotrophic bacteria, on the other hand, can thrive on the carbonates and carbon dioxide as carbon sources. These microorganisms will attach to the filter medium because of the large amount of surface area available. Depending on the environmental conditions within the filter, bacterial growths can flourish to such an extent as to impair the quality of filtered water. In addition, by exerting an oxygen demand, the bacteria could lower the dissolved oxygen concentration in the water being filtered to near zero. This in turn could initiate undesirable secondary effects arising from the resultant anaerobic conditions. Dissolved oxygen depletion during filtration has been reported at many plants in Illinois (41, 45).

Nitrification is the oxidation of ammonium ion to nitrite and nitrate. The autotrophic bacteria belonging to genera, <u>Nitrosomonas</u> and <u>Nitrobacter</u>, commonly referred to as 'nitrifiers', are the most important bacteria in the biological nitrification in nature. Other nitrifying bacteria are also known, e.g., <u>Nitrosococcus</u> and <u>Nitrosospira</u>. "All in all, <u>Nitrosomonas</u> and <u>Nitrobacter</u> are the only well-defined and active nitrifiers" (46). Because ammonium ion is found in many ground waters and because the filter medium provides a large surface to which attached growths can adhere, filters employed in the treatment of such ground waters can become a favorable site for the growth of nitrifiers. The aeration of ground water provides a source of oxygen while carbonates and carbon dioxide serve as a carbon source for autotrophic bacteria that use ammonia also as a nitrogen source. These organisms derive the energy needed for metabolism from the oxidation of ammonia. The biochemistry of

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nitrification has been studied in soil in relation to its significance in agriculture (47-50). Several investigators have reported observing nitrification in filters (13, 41, 51).

In view of the fact that a substantial amount of oxygen is required for the complete oxidation of ammonia to nitrates (theoretically, 4.55 mg/l of oxygen per mg/l of ammonia-nitrogen), ground waters containing armonia nitrogen may exert a high oxygen demand when nitrification takes place. When the ammonia concentration is high enough to cause a total depletion of dissolved oxygen in water being filtered, anaerobic conditions will result in part of the filter bed. Such conditions have been blamed for the observed breakthrough of iron in a study carried out at Clinton, Illinois (41). In that study, more ferrous iron was observed in the filter effluent during active nitrification, than was present in the filter influent. This led to the hypothesis that the anaerobic condition was responsible for the chemical reduction of iron from ferric to ferrous. Field surveys in Illinois have shown that poor plant performance in iron removal was concomitant with nitrification and oxygen depletion in filters (42, 45).

Scope of Present Work

In the conventional theory of filtration, four phenomena are considered to be responsible for the effectiveness of filtration (52): (a) mechanical straining; (b) sedimentation and adsorption; (c) electrolytic attraction and (d) biological activity. While the importance of biological activity is recognized in the filtration of waste waters and in slow sand filtration of water, little attention has been paid to this effect in rapid sand filters. However, rapid sand filters are known to have good efficiencies for coliform removal. In such filters bacteria are removed from the water and deposited in the filter media or, alternately, they may grow on the filter media from the

nutrients in the water being filtered. Since bacteria are known to accumulate in rapid sand filter beds used in the filtration of ground waters, it is the purpose of this study to investigate the chemical changes in water quality brought about by bacteria during filtration.

The growth of nitrifying organisms in filters can result in a marked depletion of dissolved oxygen. The chemical reactions in the process of nitrification may be represented as follows:

$$\operatorname{NH}_{l_{1}}^{+} + \operatorname{l}_{2}^{l_{2}} \operatorname{O}_{2} \xrightarrow{\operatorname{Nitrosomonas}} \operatorname{NO}_{2}^{-} + \operatorname{H}_{2}^{0} + \operatorname{2H}^{+}$$
(I-2a)

$$NH_{3} + 1\frac{1}{2}O_{2} \xrightarrow{\text{Nitrosomonas}} NO_{2}^{-} + H_{2}O + H^{+} \quad (I-2b)$$

$$NO_{2}^{-} + \frac{1}{2}O_{2} \xrightarrow{\text{Nitrobacter}} NO_{3}^{-} \quad (I-3)$$

The overall reactions may be written as:

$$\operatorname{NH}_{4}^{+} + \operatorname{2O}_{2} \xrightarrow{\text{nitrifiers}} \operatorname{NO}_{3}^{-} + \operatorname{H}_{2}^{0} + \operatorname{2H}^{+}$$
 (I-4a)

$$\operatorname{NH}_3 + \operatorname{2O}_2 \xrightarrow{\text{nitrifiers}} \operatorname{NO}_3^- + \operatorname{H}_2^- + \operatorname{H}^+$$
 (I-4b)

From the above equations, it can be seen that the overall process of nitrification results in oxygen consumption and release of hydrogen ions. The hydrogen ions are liberated as a result of the conversion of ammonianitrogen to nitrite, the amount depending on whether ammonia-nitrogen is present as NH_{4}^{+} or NH_{3} . For a given amount of total ammonia-nitrogen, the fraction of each form is determined by the pH of the solution. At neutral pH, the predominant form is the ammonium ion. In this connection, some workers believe that nitrosomonas bacteria prefer ammonium ions to free ammonia (47). In either case, the oxygen demand is the same for complete oxidation, namely, two moles of oxygen per mole of ammonia-nitrogen. The number of hydrogen ions liberated will depend on the form of the ammonia-

nitrogen: one mole of hydrogen ion produced per mole of NH_3 , or two moles of hydrogen ions produced per mole of NH_4^+ . Since ammonium ion predominates, at neutral pH reactions, usually two moles of hydrogen ions are produced per mole of ammonia-nitrogen undergoing nitrification.

The hydrogen ions liberated during nitrification may lower the pH in the absence of alkalinity or neutralize part of the alkalinity. In the latter case, a slight lowering of pH will result due to the liberation of carbon dioxide from neutralization of alkalinity, according to the following reactions:

$$CO_3^- + 2H^+ \longrightarrow CO_2^+ H_2^0$$
 (I-5a)

$$HCO_3^- + H^+ \longrightarrow CO_2^- + H_2^-$$
 (I-5b)

At the near-neutral pH's of natural waters, the alkalinity is predominantly in the form of HCO_3^- . Therefore, one mole of hydrogen ions will neutralize one mole of bicarbonate to produce one mole of carbon dioxide, as shown in Equation I-5b above. The carbon dioxide produced will disturb the following equilibria

$$CO_2 + H_2O \iff H_2CO_3 \iff H^+ + HCO_3^- \iff 2H^+ + CO_3^-$$

and consequently lower the pH. The change in pH can be calculated knowing the first dissociation constant of carbonic acid, the total alkalinity, and the initial pH.

From the above discussion, it is apparent that the nitrite and nitrate formation by nitrification, the oxygen consumption, the neutralization of a part of the alkalinity and the lowering of the pH are all stoichiometrically interrelated. Thus it is the purpose of this study to compare the theoretically calculated values with the experimentally observed values. From a

knowledge of these relationships, it will be possible to predict such changes for a given system.

Biologic activity in rapid sand filters has been implicated in other observed changes, e.g., breakthrough of iron (41, 53). A study of filtration of ground water at Clinton, Illinois, showed that the breakthrough of iron, mostly in ferrous form, was concomitant with active nitrification in filter bed (41). Chemical reduction of ferric iron to ferrous iron has been hypothesized, though without conclusive evidence. Soluble iron breakthrough has also been reported in other studies to be due to precipitated higher oxides of manganese (53). Because iron breakthrough is a real problem in many plants in Illinois, an evaluation of some of the environmental factors that may influence this phenomenon is included in this study.

In summary, the proliferation of any bacterial growth in sand filters may cause changes in filter performance and promote chemical changes which are biologically mediated. The bacterial growths are not only aesthetically objectionable, but may create undesirable anaerobic conditions resulting in the deterioration of filtered water quality. This study includes evaluation of some practical methods of physical and chemical control of excessive bacterial growth in rapid sand filters.

II. CHARACTERISTICS OF GROUND WATERS AT URBANA, AND RANTOUL, ILLINOIS

General

When water in contact with minerals in an aquifer is brought to the surface and comes in contact with the atmosphere, some chemical changes will occur. The chemical equilibrium that may have existed between the water and the minerals, and among the various constituents themselves, is perturbed. New equilibrium conditions, governed by the atmospheric conditions, will prevail. Important among the changes usually observed are, release of dissolved gases from the ground water, and oxygenation. The release of carbon dioxide from the ground water results in an increased pH with a concomitant change in the carbonate and bicarbonate ion concentrations. Often, dissolved gases such as methane and H_2S are also released. The increase in carbonate and ferrous carbonate, leading to subsequent precipitation. Dissolution of atmospheric oxygen will result in the oxidation of ferrous iron.

The characteristics of the ground waters used in this investigation are described as to their chemical nature, ionic strength, the activities of the ions present and the degree of saturation of calcium and ferrous carbonate. Ground water at Rantoul, Illinois was used in the studies conducted from June, 1967 to November, 1967. Ground water at Urbana, Illinois was used from June, 1968 to April, 1969.

Four wells supply the raw water to the Water Softening Plant at Rantoul, Illinois. Well No. 2 is 293 feet deep, drawing its water from the Kansan formation. Well Nos. 3, 4 and 5 are each 140 feet deep, drawing water from the Illinoisan formation. Because of poor yield, Well No. 4 is not always pumped. All of the wells are located within about 250 yards of each other.

The raw water pipe to the treatment plant at Rantoul was tapped for the studies at Rantoul.

Because of the difficulties of transportation of samples and materials to and from the laboratory where analysis were made, a well was drilled just outside the University's Civil Engineering Building in Urbana. Drilled in the spring of 1968, this well is 152 feet deep, and draws its water from the Illinoisan formation. From the samples of drilled material collected during the drilling of the well, the physical and mineralogic characteristics of the water bearing formation for this well has been described by the Illinois State Geological Survey, Urbana, as:

> "Brownish gray very fine to very coarse sand (70%) with granule to fine gravel (20%), some silt and clay (10%). (May be thin till bed within interval), rounded to subangular; Very fine to medium sand principally quartz (90-95%); coarse sand to fine gravel; 40% quartz, 20% limestone and dolomite, 15% siltstone and shale, 20% igneous and metamorphic rock fragments, 5% chert, sandstone, etc."

Table 1 summarizes the raw water characteristics of water at Rantoul and Urbana, Illinois. Urbana and Rantoul are about 17 miles apart geographically. The water yielding formation is the same at both places, namely, the Illinoisan formation, except for one well at Rantoul. The water characteristics of these wells is very nearly the same as can be seen from the Table. Both waters are hard and alkaline, with iron and ammonia present. Low chlorides and sulfates are typical of these waters.

Table 2 presents the observed average and range of values of some of the characteristics of the waters at Rantoul, Illinois during the study period.

The observed values for Rantoul, Illinois show some variations from the reported values. This may be because of the fact that the raw water at

TABLE 1

Constitutent	Expressed	Concentrat	ions at
	as	Urbana, Illinois [*]	Rantoul, _{***} Illinois
Iron	Fe, mg/l	1.1	2.8
Manganese	Mn, mg/l	0.02	0.1
Anmonium	NH ₄ , mg/l	1.1	2.8
Sodium	Na, mg/l	37	1)*
Calcium	Ca, mg/l	59.6	59.8
Magnesium	Mg, mg/l	23.7	36.6
Silica	SiO ₂ , mg/l	19.6	17
Boron	B, mg/l	1.0	-
Fluoride	F, mg/l	0.3	0.3
Nitrate	No3, mg/l	0.0	0.1
Chloride	Cl, mg/1	0.0	2
Sulfate	SO ₁₄ , mg/l	1.2	3
pH	units	-	7.3
Temperature	o _F	-	54
Alkalinity	CaCO3, mg/l	324	332
Hardness	CaCO3, mg/l	246	300
Total dissolved solids	mg/l	349	322
Methane & H ₂ S		Present	Present

REPORTED RAW WATER CHARACTERISTICS AT URBANA AND RANTOUL, ILLINOIS

*As reported by Illinois State Water Survey, Urbana, Illinois **From Reference (54)

TABIE 2

Constituent			Concentrati	on	
	Expressed	×	Observ	ed**	
	as	Reported	Average	Range	
Iron	Fe, mg/l	2.8	1.48	0.98-1.85	
Ammonium	NH ₄ , mg/l	2.8	2.11	1.1-3.16	
Alkalinity	CaCO3, mg/l	332	3 66	344-389	
Hardness	CaCO3, mg/l	300	299	242-328	
Temperature	°C	12.2	13.23	13.0-13.5	
pH	Units	7.3	7.54	7.4-7.6	

OBSERVED RAW WATER CHARACTERISTICS AT RANTOUL, ILLINOIS

*See Table 1

***Average of about 15 samples

Rantoul is a mixture of water from two different formations, the overall characteristics being a function of the fraction pumped from each formation at any given time. In addition, only ferrous iron was measured in the raw water at Rantoul, because of the interest in the phenomenon of iron breakthrough at the time.

Observed Characteristics of Raw Water at Urbana

The average values of raw water characteristics during 90 runs (about 170 samples) are tabulated in Table A-2 of Appendix. Figure 1 shows the plot of these data for the 300 days of operation of the pilot plant. It may be seen from the figure that the variations in the chemical and physical characteristics were small. It should be noted that of the three forms of iron determined - total ferrous, filtrable ferrous and total iron - the ferrous iron was determined by the bathophenanthroline method, and the total iron





was determined by the orthophenanthroline method. Because of the different sensitivities of the two methods, the total iron value was sometimes found to be less than the total ferrous iron. This is considered to be due to analytical error. Table 3 below shows the mean, minimum, maximum and standard deviation of the observed values for the various parameters:

TABLE 3

		· · ·		
Parameter	Mean	Minimum	Maximum	Std. Deviation
Temperature, °C	15.6	14.2	17.7	0.88
pH, units	7.17	7.07	7.39	0.05
Total Iron, mg/l	1.20	1.01	1.62	0.11
Total ferrous, mg/l	1.28	1.02	1.60	0.10
Filtrable ferrous mg/l	1.15	0.88	1.41	0.09
Ammonia-N, mg/l	1.04	0.94	1.33	0.08
Alkalinity, mg/l	333.8	326.5	338.5	2.2
Hardness, mg/1	245.7	239.5	249.5	2.0

MEAN, MINIMUM, MAXIMUM & STANDARD DEVIATION OF OBSERVED RAW WATER CHARACTERISTICS AT URBANA, ILLINOIS

The small values of the standard deviation indicate that the values were close together, with occasional values at the extremes of the range given as minimum and maximum in the above table. The mean observed values of total iron ammonia-N, alkalinity and hardness in Table 3 are found to agree well with respective reported values in Table 1.

Table 4 shows the results of gas and trace metal analysis carried out on raw water samples from the Urbana well by the Illinois State Water Survey,

TABLE 4

Trace metal	Concentration mg/l	Gas	Percent Composition of Gas	Free Gas/ 1000 gal, cu ft	
Sr	0.35	co ₂	25.9	1.8	
Cu	0.0	H ₂	0.0	0.0	
Cr	0.01	CH	24.6	1.7	
Zn	1.19	N	43.5	3.0	
Pb	0.05	Air	6.0	0.4	
Cd	0.0				
Ni	0.05				

TRACE METAL AND GAS ANALYSIS OF RAW WATER AT URBANA, ILLINOIS

Urbana, Illinois. This analysis was done to evaluate the concentrations of trace metals that may have either catalytic or inhibitory effects on the oxidation of ferrous iron in raw water. The gas analysis similarly was made to determine the composition of the dissolved gases. Table 4 indicates that while the gas analysis showed nothing unusual, the trace metal analysis showed an unusually high concentration of zinc. This may have been partly due to galvanized pipe and tank used in pumping system. Other analysis carried out on raw water at Urbana showed that there was about 0.04 mg/l of total phosphate of which 0.03 mg/l was orthophosphate as PO_{μ} , and there was about 0.1 mg/l of organic nitrogen. The chemical oxygen demand of the raw water as determined in the laboratory averaged 11.8 mg/l, within a range of 6.1 to 17.2 mg/l. The concentration of H₂S in the raw water was found to be about 0.75 mg/l, though no measurable amount was found in the settled water.

Silica in raw water was about 19 mg/l. Several raw water samples examined by Illinois State Public Health Laboratory over the period of ten months of study showed no colliform organisms.

Equilibrium Considerations

It is possible to evaluate theoretically the degree of saturation with respect to calcium and ferrous carbonates for the raw water. Equilibrium constants reported in the literature can be used in such calculations. However, it is necessary to calculate the activities of the constituent ions in order to use the equilibrium constants. The common assumption that the activity coefficients are unity at the low concentrations encountered in waters is not always correct. The procedure for the calculation of the ionic strength and activity coefficients is first described below. The following assumptions were made to facilitate the calculations for ionic strength and activity coefficients:

Iron, manganese, calcium and magnesium are in the form of respective divalent ions, namely, Fe^{+2} , Mn^{+2} , Ca^{+2} , and Mg^{+2} . Sulfate is present as $SO_{4}^{=}$. Sodium, fluoride, nitrate and chloride are respectively in the form of monovalent ions, namely, Na^{+} , F^{-} , NO_{3}^{-} and Cl^{-} .

Ammonia may be in the form of ionic ammonium ion or nonionic form of ammonia molecule. The dissociation reaction,

$$NH_{l_4}^+ \implies NH_3 + H^+ \qquad pK = 9.5$$

indicates that at neutral pH, the fraction NH_3/NH_4^+ equals $10^{-2.5}$. Since the ground waters studied were close to neutral pH, the ammonia present is essentially all present as ammonium ion. Similarly, the ionic species of the reported concentration of silica is determined. Silica is reported as SiO₂, but is actually present as silicic acid, Si(OH)_h. The dissociation reaction,

 $Si(OH)_4 \implies SiO(OH)_3 + H^+ pK = 9.5$

indicates that the ratio $SiO(OH)_{3}^{-}/Si(OH)_{4}$ at neutral pH is $10^{-2.5}$. In other words, the ionic form (silicate) of 'silica' is negligible at the nearneutral pH's encountered in the waters in this study. It is therefore assumed that all of the silica present is in the nonionic form of silicic acid. Hence, it does not enter into calculations of ionic strength.

While boron is reported in the analysis as B, in natural waters, it is generally present as borates, and not as elemental boron. Borates may be present in any of the following forms: BO_3^{-3} , BO_2^{-} , $B_4O_7^{-}$ or $B_6O_{11}^{-4}$. It may also be present as undissociated boric acid, H_3BO_3 . Boron is determined primarily because of its significance in the agricultural use of water. Its importance in potable water supplies and the form of borate which naturally occurs is not well known at the present (55). It is assumed that boron in the water is in the form of BO_2^{-} . It should be noted that, for a given weight concentration of boron, the molar concentration of borate ions would depend on the type of borate ion. However, the contribution of borate to the ionic strength of water would be the same whether the borate is monovalent metaborate or divalent tetraborate. Because the mineral containing boric acid and hexaborate are less common, the assumption made appears to be reasonable.

The distribution of the bicarbonate and carbonate ions are determined by the alkalinity and pH. From the definition of alkalinity normally applicable to ground waters,

Alkalinity = $HCO_3 + 2CO_3^{=} + OH^{-} H^{+}$

it is possible to calculate the individual species present knowing the equilibrium constant for the dissociation of water as well as the first and second dissociation constants for carbonic acid, K₁ and K₂. However, it is first necessary to correct the equilibrium constants for the ionic strength and

temperature. The temperature correction may be applied by using the Vant Hoff's equation,

$$\log K_{T2} - \log K_{T1} = \frac{-\Delta H_{f}}{4.576} \times (1/T2 - 1/T1)$$

where K_{T1} and K_{T2} are the equilibrium constants at temperatures T1 and T2 respectively, and ΔH_{f} is the heat of reaction (ΣH_{f} (Products) - ΣH_{f} (reactants)). An approximate correction for ionic strength is first applied to the equilibrium constant K_{1} , using the equation (56),

$$K_{1} = K_{1} - \sqrt{\mu} / (1 + 1.4\sqrt{\mu})$$

where μ is the ionic strength calculated from the following equation,

$$\mu$$
 = 0.000025x(Total Dissolved Solids)

The equilibrium constants K_2 and K_w are corrected as,

$$K_{2}^{\dagger} = K_{2} - 2\sqrt{\mu} \cdot (1 + 1 \cdot 4\sqrt{\mu} \cdot)$$
$$K_{W}^{\dagger} = K_{W} - \sqrt{\mu} \cdot (1 + 1 \cdot 4\sqrt{\mu} \cdot)$$

The corrected equilibrium constants K_1 , K_2 and K_w are used to calculate the bicarbonate and carbonate ion concentrations from alkalinity and pH measurements. The concentrations so determined will be included in the calculation of ionic strength of the water. The ionic strength is calculated as,

$$\mu = \frac{1}{2} \Sigma \mathbf{c_i z_i^2}$$

where c_i is the molar concentration of ion of charge z_i. From the calculated value of ionic strength, the activity coefficients of individual ionic species is computed from the Extended Debye Huckel Limiting Law (EDHLL), as given by equation,

$$-\log \gamma = \frac{Az_{i}^{2}/\mu}{1 + B a/\mu}$$

where, y is the activity coefficient of ion of charge z;,

A =
$$1.825 \times 10^6 (CT)^{-1.5}$$
 and B = $50.3 (CT)^{-0.5}$

where ε is the dielectric constant of water at temperature, T, in degree K, and "a" is a parameter corresponding roughly to the effective size of the hydrated ion. The values of "a" have been estimated and reported by Keilland (57).

The calculated values of ionic strength and activity coefficients are used in the recalculation of species of alkalinity (bicarbonate and carbonate ions) and the procedure is repeated again to arrive at the final values for the ionic strength and activity coefficients. These calculations were done conveniently using a computer program. Table 5 summarizes the results of these calculations. It may be seen from the table that while the activity coefficients for most of the ionic constituents are close to unity, those for iron, manganese, calcium, magnesium, sulfate and carbonate are significantly lower. Because these are the ions of greatest importance in succeeding calculations with respect to calcium carbonate and ferrous carbonate solubility, it is evident that large errors would be involved in failing to calculate the activity coefficients.

It is now possible to determine the degree of saturation with respect to ferrous and calcium carbonate for the waters used in this study. From the calculated values of K_w , K_1 and K_2 , corrected for temperature as per Vant Hoff's equation, a pC-pH diagram is constructed as shown in Figure 2. The total carbon, C_T , is first calculated by computing the concentration of H_2CO_3 (total CO_2 , free and dissolved combined) from the first dissociation constant K_1 , and adding to it the concentrations of bicarbonate and carbonate ions. Figure 2 represents the water at Urbana, Illinois. From the figure,

TABLE 5

IONIC STRENGTH AND ACTIVITY COEFFICIENTS FOR RAW WATER CONSTITUENTS AT URBANA AND RANTOUL, ILLINOIS

Ion	Z,	Keilland's	Urbana, I	Raw Wat	ter at Rantoul.	Illinois
	1	2	c _i , moles/1	activity coefficient	c _i , moles/1	activity coefficient
Fe	+2	6	1.97x10 ⁻⁵	0.6902	5.01x10 ⁻⁵	0.6819
Mn	+2	6	3.6x10 ⁻⁷	0.6902	1.82x10 ⁻⁶	0.6819
NH4	+1	3	7.86x10 ⁻⁵	0.9043	2.00x10 ⁻⁴	0.9010
Na	+1	4	1.61x10 ⁻³	0.9068	6.09x10 ⁻⁴	0.9037
Ca	+2	6	1.47×10^{-3}	0.6902	1.49×10 ⁻³	0.6819
Mg	+2	8	9.75x10-4	0.7031	1.51x10 ⁻³	0.6955
В	-1	3	9.24×10-5	0.9043	-	65
F	-1	3	1.58x10 ⁻⁵	0.9043	1.58x10 ⁻⁵	0.9010
so ₄	-2	4	1.25x10 ⁻⁵	0.6762	3.12x10 ⁻⁵	0.6670
NO ₃	-1	3	-	-	1.61x10-6	0.9010
Cl	-1	3	-	-	5.64x10 ⁻⁵	0.9010
HCO3	-1	4	6.47x10 ⁻³	0.9068	6.63x10 ⁻³	0.9037
^{CO} 3	-2	5	4.71x10 ⁻⁶	0.6834	7.41210-6	0.6746
H	+1	9	7.94×10 ⁻⁸	0.9177	5.01x10 ⁻⁸	0.9153
OH	-1	3	5.01x10 ⁻⁸	0.9043	6.16x10 ⁻⁸	0.9010
		Ionic strength	0.009101 mc	oles/l	0.009929 Mol	les/l


the $CO_3^{=}$ ion concentration at the average raw water pH of 7.16 is $10^{-5.4}$ molar. The concentration of calcium is 1.47×10^{-3} molar.

The ion product for CaCO3, including activity coefficients is,

$$Q_{CaCO_3} = 0.6902 \times 1.47 \times 10^{-3} \times 0.683 \times 10^{-5.4}$$

= $10^{-8.57}$

The equilibrium solubility product for $CaCO_3$, Ksp = $10^{-8.3}$ at 25° (58), corrected for temperature by Vant Hoff's equation is found to be $K_{sp}^{!} = 10^{-8.22}$. The quotient Q/K is calculated to be

$$(Q/K_{sp}')_{CaCO_3} = 10^{-8.57}/10^{-8.22}$$

= 0.446

It may be noted here that the value of the quotient Q/K indicates the solubility condition.When Q/K = 1, the solution is saturated. When Q/K is less than 1, the solution is undersaturated and Q/K greater than 1 represents supersaturation. The raw water at Urbana is thus calculated to be undersaturated with respect to $CaCO_3$. Similarly, for ferrous carbonate,

Q
FeCO₃ = 0.6902x1.97x10⁻⁵ x 0.6834 x 10^{-5.4}
= 10^{-10.44}

The equilibrium solubility product for FeCO₃, $K_{sp} = 10^{-10.6}$ at 25°C (58), corrected for temperature is found to be $K'_{sp} = 10^{-10.48}$. The quotient Q/K is calculated as,

$$(Q/K'_{sp})_{FeCO_3} = 10^{-10.44}/10^{-10.48}$$

= 1.1096

The raw water at Urbana is thus found to be supersaturated with respect to FeCO3.

Similar calculations for raw water at Rantoul showed that,

$$Q_{CaCO_3} = 10^{-8.40}$$
, $K_{sp}'(CaCO_3) = 10^{-8.20}$ and
 $(Q/K)_{CaCO_3} = 0.631$
 $Q_{FeCO_3} = 10^{-9.87}$, $K_{sp}'(FeCO_3) = 10^{-10.44}$ and
 $(Q/K)_{FeCO_3} = 3.725$

The raw water at Rantoul, Illinois, is found to be undersaturated with respect to CaCO₃ solubility and supersaturated with respect to FeCO₃ solubility.

It should be pointed out that the above represents theoretical calculations, subject to the accuracy of the equilibrium constants employed. Since in many cases the equilibrium constants are not known with great precision, the condition of saturation calculated are only indicative of the solubility. It should also be mentioned that these conclusions refer to raw water at ground level where the measurements were made. The situation may be different when the water was underground in contact with the minerals. The aeration of raw water also alters the saturation condition by increasing the carbonate ion concentration (with increasing pH) and decreasing ferrous ion concentration (with oxidation of ferrous iron).

III. ANALYTICAL METHODS

Sanitary Engineers tend to accept 'Standard Methods' (59) as the bible of analytical determinations. While reporting results of an investigation, it is not enough to simply mention that Standard Methods procedures were used. because of the existence of more than one method for certain determinations. For example, of the 59 tests for "Physical & Chemical Examination of Natural & Treated Water in the Absence of Gross Pollution" described in the Standard Methods, 30 have one method each, 12 have two methods each, 14 have three methods, two have four methods, and one test has eight methods. Different methods for the same determination rarely give the same result. In addition, many investigators adapt or modify the Standard Methods procedures to suit their particular needs. It is therefore imperative that the procedure used be described so that the numbers reported would be more meaningful to others engaged in similar work. It is particularly important to describe the procedure if it is not found in the Standard Methods. With this in mind, the following tests are described as to the procedures used and reasons for departures from Standard Methods wherever made: temperature, pH, dissolved oxygen (DO), alkalinity, hardness, ammonia nitrogen, nitrite nitrogen, nitrate nitrogen, total iron, total and filtrable ferrous iron, silica, chemical oxygen demand (COD), and total plate count.

Each sample was collected in a temperature-equalized one-liter beaker, except the sample for dissolved oxygen which was directly collected into the D0 bottle. Aliquots of sample were taken from the beaker for pH measurement, ferrous iron (filtrable and total), total iron, silica, and chemical oxygen demand (total and filtrable) tests immediately after collection. The remainder of water sample was transferred to completely fill a quart-size

polyethylene bottle and capped. The total iron aliquot was transferred into a 125-ml erlenmeyer flask as storage of sample in polyethylene could affect the total iron determination by absorption on bottle surface. Samples for bacteriologic examination were collected directly in sterilized D0 bottles.

All colorimetric determinations were made using a Beckman Spectrophotometer, Model DU, using 1-cm cells. The same set of cuvettes was used in a given test, with marked cells for sample and reference solutions, in order to minimize the errors due to unmatched pairs. Extra care was taken to check the O and 100 percent transmittance settings of the instrument before and after each sample was read.

Demineralized water was used in the preparation of all reagents. Analyses were performed generally in accordance with the procedures described in the eleventh edition of Standard Methods, and are described briefly here.

Temperature was measured using a mercury thermometer graduated to a tenth of a degree centigrade. All temperature measurements were made within a minute of collection of sample in the beaker.

A battery operated Beckman Model N pH meter was used during the work at Rantoul. For the work at Urbana, pH was measured using a Beckman Expanded Scale pH Meter and a combination electrode. The pH meter was standardized at the beginning of a set of measurements. Occasionally, the drift of the Beckman Expanded Scale pH meter was checked at the end of the measurements in a set of samples, approximately an hour later. The drift of the instrument was never greater than 0.04 pH unit and hence no correction for drift was made. The pH meter was standardized at room temperature, 25°C using a prepared Beckman buffer solution. However, water sample temperatures ranged from 15 to 18°C most of the time, except in the case of samples from one filter unit in which the temperature was about 22°C. Instrument corrections were applied

to the observed values of pH in stoichiometric calculations (0.003 unit per degree centigrade as determined by the pH meter) in order to take into account the difference between the temperatures of standardization buffer and water samples. The pH of samples was read to a hundredth of a unit. All pH measurements were made within one minute of collection of sample.

Dissolved oxygen was measured according to the azide modification of the Winkler Method described in the Standard Methods. The samples were collected into DO bottles with a delivery tube inserted down to the bottom of the bottle. At least twice the volume of bottle was displaced. The DO samples were fixed immediately after collection by the addition of MnSO₄ and alkaliiodide-azide reagents and acidification after the precipitate had settled down. The titration of the sample was carried out at a convenient time within a day.

Alkalinity was determined according to the Standard Methods procedure using the methyl orange indicator for Rantoul water, and for first few weeks of work with Urbana water. A buffer solution of pH 4.60 was prepared as described by Clark (60) so that the color at the end point of the alkalinity titration may be compared to the color of the indicator at the end point pH, 4.6. For most of the work at Urbana, a Corning pH Meter, Research Model 12, with Corning glass and calomel electrodes, and an autothermocompensator electrode, was used. The end-point pH was experimentally determined for a few water samples initially by noting the pH at which the rate of change of pH was greatest for small additions of titrant. This end-point pH was found to be between 4.60 and 4.65. The alkalinity titrations were made within two days of collection of samples, the samples having been refrigerated after collection. Refrigeration was necessary to minimize the bacterial alteration of alkalinity, which was found to be significant at room temperature over a

period of a day. Also, the use of pH meter with autothermocompensator was desirable because of temperature effects of refrigerated samples on the pH of solution.

Hardness was determined according to the Standard Method procedure employing EDTA as titrant with Eriochrome Black-T as indicator. The determinations were made within two days after collection of samples, the samples having been refrigerated.

Ammonia nitrogen was determined according to the Standard Methods procedure using the distillation and nesslerization method during the work at Rantoul. The samples were acidified with concentrated HCl at one ml/ liter prior to transportation of samples from Rantoul to Urbana and also samples were analyzed within one day. For the work at Urbana, the direct nesslerization method described in the Standard Methods was adapted with some modifications. The Standard Methods procedure calls for precipitation of hardness with caustic soda at a pH of 10.5 before filtration and nesslerization of samples. However, it was found that for the water samples at Urbana, a pH of 10.5 was insufficient to precipitate the hardness completely and the residual hardness interfered with nesslerization by forming a precipitate. It was therefore necessary to increase the pH to 11, and this was found to be satisfactory. The procedure as modified compared very well with the method of distillation and nesslerization and found to agree within 5 percent. The direct nesslerization method as modified was used in all of the work at Urbana. The ammonia nitrogen determination in the work at Urbana were made generally within 6 hours, and always within 12 hours, the samples having been refrigerated after collection. Overnight storage of samples in the refrigerator without acidification was found to have no noticeable effect on the results.

Nitrite nitrogen was determined according to the Standard Methods procedure. Addition of reagents for color development, and reading of the color were all synchronized with a stop watch so that each sample had the same time for color development. This minimized the errors due to variation in time for color development. Standards solutions were often used with the samples for the purpose of calibration. Determinations were made within one hour of collection of samples.

Nitrate nitrogen determinations were made according to Standard Methods procedure using the brucine sulfate method. This method is sensitive to many variables in the procedure, particularly the time of color development. The time of addition of reagents and measurement of color was synchronized with a stop watch in a given set of samples to ensure precision in the determinations. A set of standard solutions was always used to obtain a calibration curve for each set of samples. Determinations were made within two hours following the collection of the samples.

Total iron was determined according to the Standard Methods procedure using the orthophenanthroline reagent but with changes in the amount of reagents added. Two milliliters of hydroxylamine hydrochloride and five milliliters of orthophenanthroline reagents were used in the place of one and two milliliters respectively described in the Standard Methods. At least 30 minutes were allowed for color development, but not more than two hours. The samples were analyzed within two days.

The ferrous iron determination was perhaps the most critical in this study. When the bathophenanthroline (4-7 diphenyl, 1-10 orthophenanthroline) method was first described for the determination of ferrous iron, it showed great promise (61). The proponents of the method claimed that the factors

contributing to the superiority of the bathophenanthroline-ferroin reaction

"Specificity- The familiar acid anions of hydrochloric, sulfuric, nitric, acetic and perchloric acids do not interfere. If copper is present, certain anions such as iodide, thiocyanate, cyanide, thiosulfate, sulfide and phosphate may cause precipitation, but such precipitates do not interfere with the quantitative extraction of the ferrous complex.

The following metal cations: Li, Na, K, Be, Mg, Ca, Sr, Ba, Ce^{**}, Pr^{**}, Ce^{**} and the rare earth metals in general, including Th^{**}, Ti^{**}, Zr^{**}, V as vanadate and vanadyl ion, Cr^{**}, W^{**}, U^{**}, Mn^{**}, Fe^{**}, Ru^{**}, Os^{***}, Ni^{**}, Pd^{***}, Pt^{***}, Ag^{**}, Zn, Cd, Hg^{***}, Hg^{**}, B^{***}, Al^{***}, Ga^{***}, Tl, Sn^{***}, Sn^{***}, Pb^{***}, P^{****}, As^{***}, and Be^{****} do not interfere. Tellurates and selenates are reduced to the metal by hydroxylamine. Cobalt forms a light yellow color but is not extracted from acid solution.^{*****} "The reagent reacts with no known metal ion other than Fe^{***}, to give a colored complex that can be extracted by isoamyl alcohol at pH 4.0.^{***}

In spite of the impressive claims quoted above, the applicability of the bathophenanthroline method to natural waters appears to be in doubt. The method has been modified by Lee and Stumm (62), Shapiro (63) and Ghosh (64).

The essential features of most of the adaptations of the bathophenanthroline method are:

- (a) acidification
- (b) pH adjustment
- (c) color development
- (d) extraction of color complex
- (e) measurement of color

Lee and Stumm proposed boiling the water sample with acid (one milliliter of concentrated HCl per 25 ml sample) to free the ferrous iron chelated by organic matter. Shapiro showed that such a procedure could reduce ferric iron to ferrous iron. Ghosh <u>et al.</u> (65) recommended adding enough acid to lower the pH to about 1.0 to 1.5. However, Ghosh (64) used 0.5 ml concentrated HCl per 5 to 10 ml sample, resulting in a pH considerably less than 1.0. Since the addition of acid may not result in the instantaneous dis-

are:

solution of precipitated ferrous iron, a certain amount of time is necessary. Because boiling may involve reduction, acidification and letting it stand at room temperature appears to be desirable. Since reduction could take place even at room temperature over a period of several hours according to Shapiro, a reasonably short reaction time, sufficient to dissolve all precipitate, would be desirable. There is no indication of any time allowed for this in Ghosh's procedure.

After the acidification, pH adjustment was made by either sodium acetate solution or a sodium acetate-acetic acid buffer to raise the pH to 4.0. There is general agreement about this step among all workers.

The color development step appears to be variable according to different workers. Lee & Stumm said that bathophenanthroline reagent was added and mixed after pH adjustment. Shapiro suggested that if pH adjustment was made after addition of bathophenanthroline, higher absorbance was observed for the resulting complex. In the procedures of Ghosh, a 15 minute color development was allowed after the addition of bathophenanthroline and before color extraction (41), whereas, other workers did not specify how much time was allowed for such a color development. From the current study, it appears that the formation of a colored complex in a standard solution of ferrous iron appears to be complete in a matter of few seconds.

Extraction of the colored complex by either iso-amyl alcohol or hexanol again appears to be important. Ghosh noted that as the aqueous and alcohol phases were allowed to separate, if more than 5 to 10 minutes were allowed, an increase in the color of the alcohol phase was observed. An increase in color was also noted by Ghosh in the alcohol phase even after the aqueous phase had been separated. But this increase was reported to be smaller than that occurring in contact with the aqueous phase. Lee & Stumm said that 5 to 10 minutes should be allowed for adequate phase separation.

Measurement of color in all cases was made at 533 m μ on the spectrophotometer. Whereas Lee & Stumm have recommended reading of the color within 10 minutes after extraction, this may not be possible when samples have to be transported long distances as in the case of Ghosh's work.

On the basis of the discrepancies noted above in the procedures reported in the literature, it was found necessary to investigate, as part of the current studies, the influence of various parameters on the determination of ferrous iron by bathophenanthroline. It was first recognized that the initial acidification was desirable to dissolve any precipitated ferrous iron. For the water used in the study in Urbana, five drops of 1+1 H2SO, was found to be sufficient to lower the pH to about 1.5. In order to determine how much time would be needed for dissolution of precipitated ferrous iron, as well as to determine the effects of allowing a 15 minute color development after the addition of bathophenanthroline, a series of tests were made. Eight identical aliquots (25 ml) of aerated and settled ground water at Urbana (total iron, 1.04 mg/1) were taken for analysis. Aerated and settled water sample was taken to include the effects of precipitated ferric iron in the determination. All aliquots were acidified as described above immediately after collection. The addition of buffer and bathophenanthroline were made one minute, and one, two and six hours after acidification in sets of two aliquots each. Fifteen seconds of mixing after adding the acid, buffer or bathophenanthroline was provided. One of the aliquots in the set was extracted immediately after mixing with the bathophenanthroline, while the other was extracted after 15 minutes of color development as in Ghosh's procedure. The aqueous and alcohol phases were allowed to separate for about 10 minutes and the extracted color was measured within 15 minutes. The same color was also measured one, two, six and 24 hours after extraction to see the effects of storage at room temper-Table 6 shows the results of these tests. ature.

	on	15 minute color development	before extraction	24 hr	•	0.59	0.73	С Г	7•01	1.20	
	after extracti			6 hr		0.46	0.65	C C F	C0.1	1.13	
				2 hr		0.42	0.63		0.97	1.09	
	ed time			efore e	l hr		0.41	0.62	L C	ck•0	1.07
	at state			15 min		0.39	0.62	()	0.93	1.06	
	mg/l,										
	tration,	itration,		24 hr		0.32	0.38	000	0.30	0.38	a aler aler aler aler aler aler aler ale
	ed ferrous iron concer	No color development	before extraction	6 hr		0.19	0.30		0.29	0.28	
				2 hr		442.0	0.26		0.20	0.24	
				l hr		0.12	0.25	0	0.24	0.23	
	Indicate			15 min		0.10	0.24		0.23	0.23	
	Time of acidifi- cation				l min	1 hr		2 hr	6 hr		

TABLE 6

EFFECTS OF TIME OF ACIDIFICATION AND COLOR DEVELOPMENT, AND STORAGE ON THE INTENSITY OF COLORED COMPLEX



From Table 6 it can be seen that, when no time was allowed for color development, the one minute acidification time gave a low value of 0.10 mg/l. The value remained almost constant between one and six hours at 0.23 mg/l. It is quite likely that the increase in indicated ferrous iron occurred soon after acidification. However, a time up to six hours appears to be permissible. On the other hand, when 15 minute color development was allowed, a higher value was obtained even when one minute acidification time was allowed. The indicated ferrous iron concentrations were excessively high for acidification times of one to six hours, indicating some reduction of ferric iron to ferrous. In view of the fact that color development in standard ferrous iron solutions, as in the determination of calibration curves, when ferrous iron is in the form, Fe⁺², is almost instantaneous, and also considering that acidification has dissolved all precipitated ferrous iron so that all ferrous iron is in Fe⁺² at the low pH, the suggestion of Ghosh that a 15 minute color development time is required appears to be questionable. Besides, such a step may interfere by permitting some reduction of ferric iron as found in the tests above. The extracted color complex, whether or not time was allowed for color development in the aqueous phase, appears to be increasing in intensity by approximately same magnitude. For one minute of acidification, the net increase in the extracted color over a period of 24 hours was 0.22 mg/l in case of no color development, and 0.20 mg/l in case of color development. With one to six hours of acidification, the increase was 0.14 to 0.15 mg/l in case of no color development, and 0.11 to 0.14 mg/l in case of color development.

In another series of tests as above, the effect of suspended matter including the precipitated ferric iron was evaluated. Four aliquots of aerated settled water samples were taken, two of them after filtration through

a 0.45 micron membrane filter, and acidified. After three hours of acidification, the total ferrous iron in the unfiltered samples were, 0.15 mg/l with no color development, and 1.13 mg/l with 15 minute color development. The filtered samples however indicated the ferrous concentration to be 0.06 mg/l with no color development, and 0.08 mg/l with color development. Thus, it may be seen that the high value of ferrous iron concentration in unfiltered sample with color development was probably due to reduction of suspended ferric iron precipitate. The reducing agent in such cases may be substances naturally present in the water such as sulfides or the bathophenanthroline reagent itself. The alcohol-water mixture existing during the color development step apparently changes the behavior of reducing agents, and accelerates the reduction process. longer detention following acidification appears to especially favor such reductions. In view of the above tests, it is concluded that the color development step was undesirable, and hence was not used in the procedure used in this investigation. The procedure used in the determination of total ferrous iron is:

1. Acidify a 25 ml aliquot of sample in a separatory funnel immediately after collection with 5 drops of 1+1 $H_2SO_{|_1}$ acid, and mix gently for about 15 seconds, to lower the pH to about 1.5.

2. After one hour of acidification (usually it was two to three hours in this work) add six ml of Sodium acetate-acetic acid buffer (pH 4.0) and mix gently for about 15 seconds.

3. Add 15 ml of 0.001 M bathophenanthroline solution in 50 percent ethanol and mix gently for about 15 seconds.

4. Add 10 ml of iso-amyl alcohol and shake vigorously for about one minute and let stand for separation of phases.

5. After 10 minutes, but within 15 minutes, draw off and discard the aqueous phase carefully.

6. Draw off the alcohol phase in a volumetric flask, rinsing the separatory funnel with ethanol and making up the volume in the volumetric flask with ethanol.

7. Within 15 minutes of extraction, measure the color intensity of ferrous complex in the Spectrophotometer at 533 m μ .

The concentration of ferrous iron was determined using a calibration curve obtained after standard solution has been carried through the above procedure. A double check of the standard solution was made by preparing standard solutions from iron wire and ferrous ammonium sulfate (reagent grade). The agreement between the two standards was very good.

A further test of the applicability of the procedure to the natural system was made by the "internal standard" method. Eight identical aerated and settled ground water samples were taken in separatory funnels and acidified. Standard solution of ferrous iron (0.002 mg/ml) in the amounts of 5, 10, and 20 ml were added to duplicate flasks for checking the reproducibility. After two hours of acidification, the colored complex was extracted from each flask and the absorbance was measured. The calculated and observed absorbance of samples to which standard ferrous iron solutions have been added are compared in Table 7. It may be seen from Table 7 that the calculated total absorbance agreed very well with the observed absorbance. This internal standard method also indicated that there was no chelation of ferrous iron in the water being studied, as otherwise some of the added ferrous iron would have been 'lost' by chelation in the determination. These studies lent further credence to the procedure used in the work reported here.

The increase of color intensity of the ferrous complex with time after extraction was investigated to some extent by obtaining the absorption spectra immediately and 24 hours after extraction. The spectra are shown in Figure 3, which indicates that a large amount of the increase of color was observed which may be due to reduction of ferric iron. It was observed that even a standard ferrous iron solution increased in color intensity very slightly over

TABLE 7

INTERNAL	STANDARD	METHOD	FOR	TESTING	THE	PROCEDURE

Composition	Observ	ed Absorban	се	Calculated Absorbance			
of sample	Aliquot l	Aliquot 2	Average	Sample only	Added Fe*	Total	
Sample only	0.038	0.038	0.038				
Sample+0.01mg Fe ⁺²	0.100	0.102	0.101	0.038	0.068	0.106	
Sample+0.02mg Fe ⁺²	0.177	0.172	0.174	0 .03 8	0.136	0.174	
Sample+0.04mg Fe ⁺²	0.316	0.318	0.317	0.038	0.272	0.310	

*The absorbance due to the added ferrous iron was read off the calibration curve.

a 24 hour period, which may be due to nature of the complex itself. But because all measurements of color were made within 15 minutes after extraction for the work at Urbana, there was no reason for concern in this regard. However, during the work at Rantoul, transportation of samples may have involved up to five to six hours of delay in reading the color. The error in this case was neglected because the total ferrous iron concentration in settled and filtered water was very low. Filtrable ferrous iron was determined by first filtering the sample through a 0.45 micron membrane filter using the above procedure.

Silica was determined according to the Standard Methods procedure using the colorimetric molybdosilicate method. The pretreatment of digestion of sample with sodium bicarbonate was omitted, and only the molybdate-reactive silica was determined. Also, the standard solution used in the preparation of calibration curve was not standardized by gravimetric analysis; instead,





the standard solution was prepared from reagent grade sodium metasilicate nona-hydrate. The silica determinations were made within one hour of collection of samples.

Chemical oxygen demand (COD) test was determined according to the 12th edition of the Standard Methods using the alternate procedure of dichromate reflux method for dilute samples. Because water samples of low COD were involved, the concentrations of standard dichromate and the titrant ferrous ammonium sulfate were reduced as given in Standard Methods. Two hours of refluxing was allowed. In determining the COD of deposits of sand taken from filter beds, a known wet weight of sand sample was taken in the reflux flask with 20 ml of demineralized water in the place of 20 ml of sample. The results of the tests were extrapolated to the wet weight of the sand sample taken. Additions of dichromate and silver sulfate were made immediately after collection of sample, but addition of acid and refluxing was generally done within eight hours. The titration was carried out within a day.

Total plate count of bacteria were made according to Standard Methods procedure, using nutrient agar as the medium. An incubation temperature of 20[°]C and time of 48 hours was used. The bacteriologic water samples were collected in sterilized D0 bottles and placed in an ice-chest immediately. Plating of samples was done within eight hours.

When counts of bacteria on sand samples from the filter bed were to be made, a known wet weight of sand was added to 50 ml of sterile water in a flask and shaken vigorously for two minutes. The resulting suspension was used in plating. The counts from plates were related to the wet weight of sample. Because moisture content of wet sand varied between a narrow range of 15 to 20 percent, the results were expressed on a wet weight basis.
IV. PILOT PLANT STUDIES AT RANTOUL, ILLINOIS

General

A natural water supply was used in this investigation rather than a synthetic water. In order to obtain a continuous raw water supply it was necessary to locate the pilot plant at a municipal water treatment plant. Since the water treatment plant at Urbana derives its raw water from many wells situated far apart from each other with varying raw water characteristics, it was thought desirable to locate the pilot plant at Rantoul, Illinois. The Water Softening Plant at Rantoul, Illinois, has four wells within a distance of about 250 yards. The raw water characteristics from each well are similar, with minor variation in some constituents. Also, at Rantoul, Illinois, the raw water contains iron and ammonia in sufficient amounts thought to be necessary for studies reported here.

Raw water tapped from the raw water intake pipe of the Rantoul plant was first passed through a constant head device as shown in Figure 4. The constant head device was an overflow type, with the overflow going to waste. The constant flow obtained from this device was passed through a multiplepass aerator. Aeration was accomplished by passing compressed air through a porous stone diffuser. The aerator provided a detention time of about two minutes. This was sufficient to raise the dissolved oxygen concentration from near-zero in the raw water to near-saturation in the aerated water. The aerated water was allowed to settle in a plexiglass tank, 44 inch x 12 inch x 20 inch in size. A baffle wall with perforations was provided at the midpoint of this tank to prevent short-circuiting of flow. The theoretical detention time in this tank was about one hour. A V-notch type effluent weir collected the settled water.

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FIGURE 4. SCHEMATIC REPRESENTATION OF PILOT PLANT AT RANTOUL

The settled water flowed by gravity into a distributor which was open to the atmosphere. Each filter unit was connected to an outlet from this distributor. An overflow was provided for this distributor so that the flow through the aerator and settling tank could be held constant even while an individual filter was being backwashed.

The filter units consisted of six-foot lengths of $\frac{1}{4}$ inch thick plexiglass tubing, (3 inch ID). A 30 inch sand bed was supported on four inch gravel by a perforated plate at the bottom of the filter unit. The sand used in these filter beds had an effective size of 0.5 mm and a uniformity coefficient of 1.6. Holes on the side of the plexiglass tubing were provided for the purposes of obtaining sand or water samples at different depths whenever desired. These holes were normally stoppered tightly during operation. Four filter units were supported on a wooden frame. U-tube mercury manometers were used to indicate the headloss across the sand beds. Each manometer was connected to a filter unit.

The filtered water from the filter unit passed through a rate-of-flow control box. The rate-of-flow control box consisted of a tank float regulating the flow from the filter into this box, and an outlet at the bottom of the box. The outflow from the box was adjusted to give a rate of flow through the filter of 2 gpm/sq ft. The purpose of this device was to maintain throughout a filtration cycle, a nearly constant total headloss equal to the difference between the water levels in the distributor and the box. At the beginning of a filter run, the tank float in the rate-of-flow control box caused a maximum headloss when the headloss through the filter bed was a minimum. As clogging of the filter bed proceeded during filtration, the float valve opened more, thus reducing the headloss through it. The water level in the rate-of-flow control box decreased as the float descended to open the float

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valve. Because the rate-of-flow control box was only 12 inches deep, the lowering of the water level in the box diminished the outflow. Therefore, the outflow from the box had to be adjusted manually to take into account the variation in the water level. This proved to be time-consuming, but necessary, in order to maintain a reasonably constant flow through the system.

Gardenhose, 5/8 inch ID, and plastic tubing of varying sizes were used in the hydraulic connections between different units of the pilot plant. Difficulties were encountered occasionally when partial clogging of hose and tubing due to deposits of iron precipitates or to air-binding caused a reduction in the flow through the system. As a result, only about one-third of the 128 filter runs had a rate of filtration of 2 gpm/sq ft within \pm 10 percent. Only these runs were taken into account in the average values reported in this section. Since the variations in the flow were greater in the other filter runs, the results were disregarded.

Pilot Plant Operation and Procedures

The four filters of the pilot plant were designated filters A through D for identification. All filter runs were consecutively numbered; a new run beginning with the beginning of filtration after a backwash operation. Five minutes of backwash time was arbitrarily chosen and found to be sufficient to give a clear backwash water at the end. The following is the chronology of experimental work.

On June 12, 1967, the pilot plant was placed into operation, beginning Run 1, with clean sand in the filter beds. Initial operation of the pilot plant indicated that the filter runs could last as much as about 48 hours with terminal headloss of eight feet of water. However, with successive runs, the length of filter run decreased over a three week period to about 24 hours. A serious problem in the cleaning of the sand bed during backwash was en-

countered after one week's operation. At the end of filter run, a filter cake of about one to one and a half inches thick accumulated at the top of the filter bed. During a normal backwash procedure, this cake would break into lumps and settle down to the gravel layer when the backwash water was shut off. As a result, a simple backwash failed to clean the sand that had formed into a filter cake and allowed the caked sand, commonly called mudballs, to accumulate. The formation of filter cake and mudballs was primarily due to the nature of the suspended material being removed by the filter. In this case, the suspended matter was, primarily, ferric hydroxide floc in colloidal suspension.

At the end of Run 7, on the 15th day, the filters were disconnected, and the settled water was bypassed to waste. The sand from each filter unit was taken out and the mudballs were removed. The sand was replaced in the filter units after cleaning. Operation of the pilot plant was then resumed, with the length of the filter runs set at about 24 hours with the hope of avoiding the formation of filter cake and mudballs. However, the problem persisted. Ultimately, surface wash devices had to be installed in order to break up the filter cake prior to backwashing.

At the end of Run 17, on the 27th day, the accumulated mudballs were removed as before and surface wash jets were installed. Glass tubing, $\frac{1}{4}$ inch ID, bent at right angles, was placed in such a way as to direct the jet of water down on the filter cake; the tip of tubing was about $1\frac{1}{2}$ inch above the sand bed surface. In subsequent filter runs, it was found that about two minutes of surface wash at about 40 gpm/sq ft of wash water flow was sufficient to completely break up the filter cake prior to backwashing. This rate of application of wash water is not representative of any design parameter, but, rather, was found to be required under the operating conditions. Similarly,

the rate of backwash water was about 30 gpm/sq ft, providing about 50 percent expansion of the sand bed. It may be mentioned here that the theoretical rate of wash water required is calculated to be about 10 gpm/sq ft. The high rate was required mostly due to the wall effects of filter tubes during backwash, though the wall effects during normal filtration was negligible (66). With the installation of the surface wash devices, the problem of mudball formation was eliminated.

Water samples (raw, aerated, settled and filter effluents) were often taken for the determination and analysis of temperature, pH, DO, iron, alkalinity, hardness and ammonia, and total plate count. The results of such analysis formed the basis for the study of the progress of bacterial growth on the filter sand.

During Run 48, on the 59th day, samples were taken of the raw, aerated, settled water and the filter effluents of Filters B, C and D, at four hour intervals from the beginning of filter run to the end, for analysis in order to ascertain the variation in the water quality during the run. This analysis showed that the ammonia and DO present in the filter influent were depleted during filtration.

At the end of Run 59, on the 71st day, Filter A was backwashed as usual, and was disconnected from the pilot plant. The sand was removed from this unit and used in studies of the kinetics of the uptake of potassium permanganate by the filter sand, as described below.

Uptake of Potassium Permanganate by Filter Sand

Aliquots of 200 grams (wet weight) of sand taken from Filter A were placed in one-liter beakers. A solution of KMnO_{\downarrow} in 0.1 N Na_2CO_3 was used to obtain a pH of about 10.5. At this pH, the KMnO_{\downarrow} is reported to be most effective in oxidizing organic matter (67). The following concentrations of

 $\rm KMnO_4$ solutions were prepared: 250 mg/l, 500 mg/l, 1000 mg/l, 2000 mg/l and 5000 mg/l. Measured amounts of these $\rm KMnO_4$ solutions were added to the beakers containing the wet sand and liquid samples were withdrawn from the beakers to determine the concentration of $\rm KMnO_4$ remaining, at regular intervals of time. Applying corrections for the amount of permanganate withdrawn for the analysis, the cumulative uptake of $\rm KMnO_4$ in mg for the 200 grams of sand in each beaker was calculated.

On the 73rd day, at the end of Run ól, the filters were backwashed as usual. Filters B and C were then treated with potassium permanganate solution at the concentration and contact time determined in the kinetic studies. Filter D was left as a control. The procedure used in the permanganate treatment was as follows:

Filters B and C to be treated were drained. Potassium permanganate solution, 5000 mg/l in 0.1 N Na₂CO₃, was allowed to flow by gravity from a 5-gallon carboy into the filters through the backwash lines, until the filter sand was completely submerged. Thereafter Filter C was kept agitated using compressed air applied through the backwash lines while Filter B remained quiescent. The filters were left in contact with KMnO, solution for three hours. The permanganate solution was then drained from both of the filters, and the filters were backwashed again until the backwash water was free of any permanganate color. The filters, including the control, were then returned to operation. Sand samples from filter beds of Filters C and D at depths of 4.5 and 14.5 inches from the top of bed were taken both before and after the permanaganate treatment so that bacterial counts could be made. Mater samples were also obtained at the end of Run 61 and at six-hour intervals during Run 62 to evaluate the effectiveness of treatment. Occasional sampling of the water continued through successive filter runs so that the regrowth of bacteria on the filter sand might be observed.

On November 7, 1967, after Run 128, on the 149th day, the pilot plant operation at Rantoul, Illinois was terminated.

Results & Discussion

The progress of bacterial growth in the filters was followed by measuring the dissolved oxygen concentration in the filtered water and the depletion of ammonia during filtration. Oxidation of the ferrous iron in the raw water was almost complete at the end of the sedimentation period. The filters satisfactorily removed iron continually giving an effluent that met the U.S.P.H.S. Drinking Water Standards (43). Table 8 shows the results of analysis of samples taken during Run 35, (July 26-27, 1967), six weeks after the pilot plant was placed in operation.

TABLE 8

-												
				Concentration in mg/l								
Sampl	.e	Temp.	D.0.	Ferrous	Total	NH ₃ -N	Alk	Hdns				
	والمحاجب والمحاجب ومراسعاتهم ومرود والمحاط			10	16							
Raw		13.5	0.0	1.52	-	1.3	367	304				
Aerat	ed	13.6	7.3	0.45	1.4	1.33	365	301				
Settl	ed	13.8	7.3	0.18	0.70	1.22	367	298				
Eff.	Filter A	14.7	2.8	0.02	0.15	0.85	348	3 01				
Eff.	Filter B	14.6	1.7	0.02	0.0	0.8	348	298				
Eff.	Filter C	14.8	1.7	0.06	0.03	0.6	348	3 06				
Eff.	Filter D	14.8	1.7	0.09	0.20	0.55	350	298				

WATER QUALITY DURING RUN 35 OF PILOT PLANT STUDIES AT RANTOUL

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Table 8 indicates that during the six weeks of the operation of the pilot plant, conditions developed within the filters which resulted in a partial depletion of ammonia and dissolved oxygen. The observed depletion of dissolved oxygen and ammonia was presumably due to bacterial activity.

Table 9 shows the results of Run 48, on the 59th day, showing the variation in various parameters during the filter run. Some variations in the concentration of ammonia were found in the raw, aerated and settled water during the Run 48. The characteristics otherwise remained essentially the same. The bacterial count was reduced by aeration considerably and was essentially the same after settling. This reduction from raw water is considered unusual.

The filter effluents showed that nearly complete DO depletion took place during filtration, though there was some variation in the ammonia-N concentration. The average values of ammonia-N for all filters was low compared to settled water concentration. The bacterial plate count increased during filtration. Hardness remained essentially the same throughout. There was depletion of ammonia accompanied by decreases in alkalinity and pH during filtration. These changes indicated the occurrence of nitrification in filters.

The results of the kinetic studies of potassium permanganate uptake by the filter sand from Filter A is shown in Figure 5. It may be seen from the figure that the initial rate of permanganate uptake (slope of the curves) is greatest for the highest KMnO_{μ} concentration used, and all the curves approach asymptotic values after about three hours. It should be recognized that the moisture content of sand reduced the effective concentration of the permanganate solution applied by an estimated 20 percent. From the kinetic studies, it was concluded that a concentration of 5000 mg/l of KMnO_{μ} in 0.1 Na_2CO_3 may be used over a contact period of three hours for the purpose of oxidizing the organic matter on the sand.

TABLE 9

ANALYSIS OF WATER SAMPLES DURING FILTER RUN 48 OF PILOT PLANT STUDIES AT RANTOUL

Sampling				Conc	entratio	ons, in	mg/l		Plate
time after backwash, Hrs.	Temp oC	pH units	DO	Ferrous Fe	Total Fe	^{NH} 3 ^{-N}	Alk	Hdns	count nos/ml
Raw Water									
1 5 9 13 17 21 25	13.2 13.2 13.1 13.0 13.2 13.0 13.2 13.0	7.5 7.5 7.6 7.6 7.6 7.7	0.0 0.1 0.3 0.0 0.0 0.0	1.5 1.35 1.25 1.15 1.6 <u>-</u> 1.6		1.46 1.34 2.20 1.4 1.8 1.7	376 359 380 382	329 322 328 331 328	2190 12130 700 7100
nicrago	<u> </u>	1.0						<u> </u>	
Aerated Wate 1 5 9 13 17 21 25	13.4 13.4 13.3 13.2 13.1 13.2 13.2 13.2	7.8 7.8 7.9 7.9 7.9 7.9	7.1 7.1 7.2 7.0 7.1 7.1 7.4	0.82 0.82 0.68 0.64 0.96 -	1.04 1.04 0.68 0.68 1.16 1.56 1.34	1.76 1.44 1.40 1.46 1.50 0.72 1.76	374 359 376 <u>354</u>	329 314 328 319	32 95 112 234
Average	13.2	7.9	(.2	0.83	1.07	1.43	366	323	118
Settled Wate	r								
1 5 9 13 17 21 25 Average	13.7 13.6 13.6 13.7 13.4 13.2	7.9 7.8 7.9 7.9 7.9 7.9 7.9 7.9	7.3 7.0 7.3 7.0 7.0 7.1 6.9 7.1	0.17 0.17 0.14 0.08 0.38 - 0.2 0.16	1.0 1.08 0.64 0.68 0.38 1.6 0.32 0.81	0.66 1.10 1.34 1.56 1.26 2.84 1.7 1.49	370 361 376 359 367	334 325 325 317 325	122 138 126 <u>346</u> 183
Filter B	5 (2 ⁻¹)	*** *****							nger van op naam van die allematiens
1 5 9 13 17 21 25	14.4 14.5 14.3 13.8 14.0 14.3	7.5 7.5 7.6 7.6 7.6 7.6	0.2 0.1 0.1 0.1 0.1 0.1	0.03 0.03 0.07 0.04 0.07	0.01 0.01 0.0 0.38 0.05 0.07	0.0 0.5 0.02 0.02 0.0 0.0 0.0 0.02	357 354 363 - 340	325 328 325 319	1760 24 3 0 2 <i>9</i> 40 1750
werage	14.2	1.0	U.T	0.07	0.01	0.00	224	24	2220

Sampling				Conce	ntratio	ns, in	mg/l		Plate
time after backwash, Hrs.	Temp °C	pH units	DO	Ferrous Fe	Total Fe	^{NH} 3 ^{-N}	Alk	Hdns	count nos/ml
Filter C									
1 5 9 13 17 21 25 Average	14.4 14.3 14.3 14.0 14.0 14.3 14.3	7.6 7.5 7.6 7.6 7.6 7.6 7.6	0.2 0.1 0.1 0.1 0.1 0.0 0.1 0.1	0.04 0.03 0.05 0.04 0.04 - 0.04 0.04	0.02 0.04 0.0 0.01 0.08 0.04 0.0 0.03	0.54 0.26 0.0 0.0 0.0 0.22 0.17	363 346 359 348 354	328 322 325 319 324	6800 1700 2170 6 <u>300</u> 42140
Filter D									
1 5 9 1 3 17 21 25	14.5 14.4 14.0 14.0 14.0	7.5 7.6 7.5 7.6 - 7.6	0.1 0.1 0.1 0.1 0.1 0.1 0.1	0.12 0.04 0.08 0.01 0.03 - 0.07	0.02 0.0 0.04 0.11 0.2 0.0	0.08 0.144 0.34 0.6 0.3 0.0 0.3	357 350 352 346	328 319 331 <u>317</u>	1790 3430 4900 3700
Average	14.3	7.6	0.1	0.06	0.05	0.29	351	324	3450

TABLE 9 (continued)

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The permanganate treatment of Filters B and C was carried out at the end of Run 61, on the 73rd day. The results of analysis of water samples taken just before and during Run 62 are shown in Table 10. The variation in pH and DO for raw, aerated and settled water samples was not significant. However, some variations were observed in the iron and ammonia concentrations as also in alkalinity values. Averages are shown in the table so as to afford a comparison of the values before and after treatment. Filter D, which was a control, was not treated, and the characteristics recorded for this filter did not change. Results for Filters B and C indicated that bacterial activity was diminished as shown by the persistance of dissolved oxygen. Ammonia concentration values, while somewhat erratic, indicated that the utilization of ammonia had virtually ceased.



FIGURE 5. CUMULATIVE UPTAKE OF KMnO_4 BY FILTER SAND vs TIME



TABLE 10

ANALYSIS OF WATER DURING RUN 62 OF PILOT PLANT STUDIES AT RANTOUL

Sampling			Concentr	ation, in	mg/l		Plate
time after backwash, Hrs.	Hợ	DO	F err ous Fe	Total Fe	^{NH} 3-N	Alk	count nos/ml
Raw Water							
-1* 1 7 13 19 25	7.6 7.5 7.6 7.5 7.5 7.5	0.0 1.1 0.9 0.5 0.5 1.0	1.35 1.65 1.55 1.55 0.98 1.1	1.6 1.9 1.9 1.5 2.3	2.7 1.7 2.1 1.55 2.2 2.4	344 344 358 376 350	1260 700 1110 272 13500 2070
werage	1.2	0.0	1.07	1.7	1.77		0000
Aerated Water							
-1 [*] 1 7 13 19 25 **	7.75 7.8 7.8 7.85 7.6 7.7	6.0 7.2 6.6 7.2 8.3 7.1	1.06 0.4 0.54 0.36 0.44 0.35	1.1 1.34 1.44 1.50 - 1.46	1.8 2.1 1.85 2.1 2.86 1.1	- 342 352 348 378 348	247 520 146 1210 214
Average	(.0	(.3	0.42	1.44	2.00	354	407
Settled Water -1 [*] 1 7 13 19 25 Average ^{**}	7 • 7 7 • 8 7 • 8 7 • 8 7 • 7 <u>7 • 7</u> 7 • 8	6.0 6.5 6.3 7.2 8.3 6.9 7.0	0.30 0.12 0.15 0.12 0.2 0.1 0.14	1.04 1.24 1.48 1.58 0.94 1.14 1.28	2.50 2.45 1.4 1.1 1.20 1.45 1.52	352 350 356 393 372 365	33 0 640 250 530 520 <u>302</u> 448
-1 [*] 1 7 13 19 25 Average ^{***}	7.5 7.9 7.85 7.9 7.7 <u>7.75</u> 7.8	0.1 7.1 6.8 7.6 8.3 6.9	0.02 0.01 0.0 0.0 0.0 0.0	0.06 0.1 0.05 0.08 0.08 0.1	1.04 1.14 2.15 3.1 2.45 3.05	359 354 346 395 365	2020 930 450 195 470 267

*-1 hr refers to one hour before the end of Run 61

The average is for values of Run 62 only. (-1 hr values are omitted)

Sampling			Concent	ration, in	n mg/l		Plate
time after backwash,	pH	DO	Ferrous Fe	Total Fe	NH3-N	Alk	count nos/ml
nrs.							
Filter C							
-1 [*] 1 7 13 19 25 Average ^{**}	7.6 7.95 7.85 7.9 7.7 <u>7.75</u> 7.8	0.05 7.2 7.0 7.6 8.4 6.8 7.4	0.01 0.01 0.0 0.0 0.0 0.0 0.0	0.04 0.29 0.04 0.07 0.09 0.1 0.08	0.65 0.65 2.1 2.8 1.55 1.9 1.8	357 354 350 391 370 364	1400 415 178 137 420 <u>390</u> 308
Filter D							
-1 [*] 1 7 13 19 25 **	7.6 7.5 7.55 7.55 7.5 7.5 7.55	0.1 0.05 0.05 0.1 0.1 0.1	0.01 0.01 0.0 0.0 0.0 0.0 0.0	0.04 0.15 0.1 0.07 0.07 0.13	0.7 0.7 0.7 0.7 0.7 0.3	342 342 340 374 359	1720 3910 1490 1420 1920 910
Average	1.5	0.07	0.0	0.1	0.6	351	1930

TABLE 10 (continued)

*-1 hr refers to one hour before the end of Run 61

*** The average is for values of Run 62 only. (-1 hour values are omitted)

Table 11 summarizes the filtration parameters and their average values for the filter runs in which the flow rate did not vary more than 10 percent. It may be seen that the flow conditions, both initially and at the end of a filter run, were essentially same both for the permanganate-treated and the control filters. The length of filter runs also remained essentially the same, i.e., about 24 hours, at an average rate of flow of 2 gpm/sq ft. Following permanganate treatment, there was a significant change in the initial and final headloss readings in all the filters including the control. The reduction in headloss values were not necessarily the effect of permanganate treatment alone, even though the reduction was slightly more marked in permanganate treated filters than in the control. It is felt that the loss of fines from the filter sand through successive filter backwashings together with the effect

TABLE 11

· OPERATIONAL PARAMETERS OF PILOT PLANT STUDIES AT RAWFOUL

Parameter	Perma Filt	nganate ti er B	reated fil	ters er C	Control.	Filter D
	Before Treat	After ment	Before Treat	After ment	Before	After
Initial flow, avg., grm/sq ft	2.10	2.10	2.09	2.13	2.10	2.12
Final flow, avg., gpm/sq ft	1.91	1.95	1.98	l.99	1.99	l.92
Average flow, avg., gpm/sq ft	2.00	2.02	2.03	2.06	2.05	2.02
Initial headloss, avg., ft water	0.75	0.69	0.76	0.70	0.77	0.69
Final headloss, avg., ft water	7.6	5.3	6.4	4.5	6.4	5.2
Length of filter run, avg. hrs.	23.2	23.8	23.5	23.7	23.8	23.7



of coating of sand particles by iron floc removed during filtration may have brought about the reduction in the final headloss readings.

The progress of bacterial growth as evidenced by the depletion of dissolved oxygen as water passed through the filter is illustrated in Figure 6. The dissolved oxygen concentration in the raw, aerated and settled water, averaged over the period of observation both before and after permanganate treatment, are shown in the figure for comparison. For both of the permanganate-treated filters, Filters B and C, the dissolved oxygen concentration in the filter effluent at the beginning and the end of filter runs are shown in the figure. The dissolved oxygen concentration in the filter effluent of both filters at the beginning of a filter run (about an hour after a backwash) and at the end of the run (immediately before the next backwash) gradually decreased and, after the 55th day, the oxygen was almost totally depleted. Between the 40th and 55th days, the dissolved oxygen decreased most rapidly from the beginning of the filter run to the end. The filters were treated with parmanganate solution on the 73rd day. The treatment was effective in inhibiting nitrification as concluded from the presence of dissolved oxygen in the filter effluent. The dissolved oxygen was maintained at a high level for about three weeks, from 73rd day to 95th day, after which depletion began again (Figure 6). The dissolved oxygen was once again almost totally depleted after the 115th day, suggesting the reestablishment of the bacterial growth.





V. PILOT PLANT STUDIES AT URBANA, ILLINOIS

General

The operation of the pilot plant used at Rantoul, Illinois, resulted in the design of a new pilot plant for studies conducted at Urbana, Illinois. The new pilot plant was located in the basement of the Civil Engineering Building of University of Illinois. It was thus possible to avoid the difficulties involved in the transportation of samples. This was particularly desirable from the point of view of sampling and analysis. In addition, new features were built into the design and construction of the pilot plant to obviate difficulties encountered at Rantoul, Illinois. Important among the changes were better devices for rate-of-flow control, and minimum use of plastic tubing. Galvanized iron piping was used in most of the plumbing, and a Unistrut steel frame work was used to support the units of the pilot plant.

The pilot plant was specially designed and built for the work at Urbana, Illinois. It consisted of a constant head device, counter-current flow aerator, settling tank, eight filter units with rate-of-flow controllers and U-tube mercury manometers for loss of head measurement. The general layout of the pilot plant is shown in Figure 7. Orifice meters were provided for indicating the flows on the raw water line and backwash water line. Gate valves or quarter-turn plug valves were used wherever required.

A well drilled outside the Civil Engineering Building supplied the raw water. The ground water was pumped through a pressure tank system, operating under the control of a pressure switch, in the range of 20 to 40 psi. Accordingly, there was considerable variation in the rate of delivery of raw water. A constant head device of the overflow type shown in the figure was used to obtain a uniform flow. The overflow was wasted, and the constant flow was passed to the aerator.

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The aerator was designed on the principle of counter-current flow. Compressed air was bubbled through a diffuser at the bottom of the center well of the aerator. The raw water flowing down came in contact with the rising air bubbles in the center well. Further contact between air bubbles and water was provided in the outer well as the mixture of air bubbles and water moved upwards. The compressed air was filtered through an air-line filter to remove oil and dust. Using sodium chloride as a tracer, the detention time in the aerator was found to be about three minutes at the modal point, and about nine minutes at the mean point from a plot of tracer concentration vs time. The aerator readily raised the D0 concentration in the aerated water to near-saturation.

The serated water was allowed to settle in a 100-gallon oval tank, 4 ft x 2 ft x 2 ft in size. The tank was provided with a perforated baffle wall at the midlength of flow. The effluent was taken over a V-notch weir box as shown in the figure. Tracer studies indicated the detention time in the tank to be 37 minutes at the modal point and 63 minutes at the mean point as determined from a plot of tracer concentration vs time.

The settled water was distributed to filter units from a header pipe through filter boxes at the top of the filters. Each filter unit consisted of plexiglass tubing, $4\frac{1}{2}$ inch x $\frac{1}{4}$ inch (4 inch ID), and 9 ft long. The top of the filter unit was open to atmosphere, and the bottom was provided with a small effluent chamber with outlet for filtered water. The filter bed consisted of 30 inches of sand, effective size 0.55 mm and uniformity coefficient 1.5, supported over a bed of 12 inches of gravel, 1/8 to 1/4 inch, over a perforated plate at the bottom. Surface washing was provided by a jet through $\frac{1}{4}$ inch copper tubing bent and placed so that the tip of tubing was about $1\frac{1}{2}$

from the filter box at the top of the filter unit which also served as the wash water gutter. The wash water was distributed from a header to each filter unit for surface wash as well as backwash. The city water supply available in the building was used for the backwash water supply. The city water was found to contain between 0 to 0.5 mg/l of combined chlorine residual in the building. This was considered not significant in this study.

The effluent from the filter passed through a rate-of-flow control device. The rate-of-flow control device used in the pilot plant at Rantoul, Illinois, involved considerable and constant manual adjustment of the outflow from the box to compensate for the varying water levels in the box. A floating siphon was installed in the rate-of-flow box at Urbana, as shown in Figure 7 so that a constant out-flow was obtained regardless of the water level in the box. The float carrying the siphon was provided with a counter-weight and guide-tube to keep the motion of the float free. This device was found to be very satisfactory in maintaining a constant flow through the filter. An occasional check on the actual rate of flow was made after it was set initially. The variation observed was never greater than five percent, and often as little as three percent.

The filter units provided a static head of about five feet of water above the top of sand bed during operation. From a tracer study, it was found that at a rate of filtration of 2 gpm/sq ft, the time of travel for water from the filter box at the top of the unit to the top of the sand bed was, on the average, about 12 minutes. The average travel time of water from the top of the sand bed to the sampling point on the effluent line was found from tracer studies to be eight minutes. Since this travel time included the time required for passing through the gravel bed and the effluent lines, it is estimated that the residence time of water in the 30 inches of sand bed was about five minutes.

The room temperature where the pilot plant was located averaged 25°C.

Experimental Procedure

The filter units of the pilot plant were designated Filter 1 through 8 for the purpose of identification. The well was pumped for about two months at about an average rate of two gallons per minute, in order to avoid any variability in the water characteristics associated with a new well. The orifice meters on the raw water and wash water lines were calibrated. The flow from the constant head device was adjusted to correspond to the eight filter units at the rate of 2 gpm/sq ft. This flow was calculated as 1.h gpm through the pilot plant. The siphons on the rate-of-flow control boxes were also adjusted to correspond to the flow through each unit, namely, 0.175 gpm or 661 ml/minute. Filter 8 was not used in this study. Instead, Filter 8 was used as an overflow for excess settled water. An overflow standpipe in the sedimentation tank was also provided. The elevation of the sedimentation tank was adjusted so that gravity flow would ensure a sufficient depth of water in the filter box at the top.

At the beginning of a filter run, the rate-of-flow control box was filled with water to the top, with water flowing through the siphon. The influent and effluent valves were opened, keeping the surface wash, backwash and waste water valves closed. At the end of the run, the influent and effluent valves were closed and the waste valve opened. The surface wash valve was opened gradually over a period of 10 to 15 seconds to establish the desired flow which was maintained for $1\frac{1}{2}$ minutes. It was gradually closed over a period of 10 to 15 seconds at the end of surface wash. The total time of surface wash was thus two minutes. Then the backwash water valve was gradually opened over a period of about 30 seconds to the desired level to obtain a desired expansion of sand bed and maintained at that level for $4\frac{1}{2}$ minutes. The valve was gradually closed

over a period of 30 seconds, thus involving a five minute backwash. The total time of surface wash and backwash was seven minutes. At the end of each washing operation, the waste valve was first closed, then the influent and effluent valves were opened in that order. The effluent valve was gradually opened so as to avoid any surge in flow through the filter, after the rate-of-flow control box was filled with water.

The water samples at the beginning of a filter run were obtained at least $l\frac{1}{2}$ to 2 hours after the filter was placed into service so that the wash water left in the filter unit at the end of washing was displaced. The sampling procedure consisted of first noting the headloss on the manometer and then breaking the siphon from the rate-of-flow control box. The float valve was then immediately closed and the sampling outlet on effluent line was gradually opened to obtain the same headloss as noted earlier, resulting in the same rate of flow. The sampling line was allowed to flow under these conditions for at least five minutes before collecting any sample. At the end of sampling, the sampling line was closed, the float valve was opened and the siphon started again.

Operation and Results

On June 21, 1968, the pilot plant was placed in service, beginning Run 1, with four filter units, Filters 1 through 4, including the surface wash system. A surface wash rate of about 40 gpm/sq ft was found to be required for completely breaking up the filter cake in two minutes time. Surface wash preceded the backwash. A backwash rate of about 30 gpm/sq ft was found to be required for a 50 percent expansion of the sand bed. The rates of surface and backwash were experimentally determined and are not representative of the design rates in bractice. These rates were very high compared to the design rates, but were required taking into account the size and geometry of filter

The theoretical rate of backwash was calculated to be about 11 gpm/ units. sq ft. The higher rate used was mostly due to wall effects during backwash conditions. The wall effects during normal filtration were negligible (66). Filters 1 and 2 were backwashed at 50 percent expansion; Filter 3 was backwashed first at 25 percent expansion for 2 1/2 minutes and at 50 percent expansion for the rest of the time, and Filter 4 was backwashed at 25 percent expansion for five minutes. Different degree of expansion of sand bed for different filters was used to observe any effect of backwash rates on the filtered water quality. Raw water, settled water and filter effluent samples were routinely obtained at the beginning and end of each run. Routine analysis of samples included temperature, pH, DO, total ferrous and total iron, alkalinity, hardness and ammonia-N. Filtrable ferrous iron determinations were made on raw water and settled water samples only, as the total ferrous iron concentration in the filtered water was generally low. Occasional analysis for silica, COD, and bacterial plate count were made.

During Run 1, samples were taken at eight hour intervals to ascertain the variation in the quality of filter effluent with respect to filter influent. Figure 8 shows the plot of characteristics of filter influent (settled water) and filter effluent for this first run. It can be seen from the figure that the results were similar for all four filters. There was a slight increase in temperature since the room temperature was higher than the water temperature. The slight rise in pH was probably due to loss of carbon dioxide from the water. No significant changes in the concentrations of alkalinity, hardness, ammonia and DO were observed. Iron removal was satisfactory (43).

Sampling and analysis continued through Run 40 on the 81st day of operation. During Run 41, samples at eight hour intervals were once again taken for analysis to observe the variation in quality of filtered water after 11



weeks of operation. Figure 9 shows the plot of filter effluent and settled water during this run for the four filters. It may be seen from the figure that there was again a slight increase in temperature. D0 concentration in the filtered water decreased, and ammonia-N was depleted. This was accompanied by decreases in pN and alkalinity. Hardness remained essentially constant. Quantitatively, about 0.8 mg/l of ammonia-nitrogen was consumed while the D0 decrease was about 3.5 mg/l. The decrease in pH was about 0.15 unit while the decrease in alkalinity was about 10 mg/l. These concurrent changes strongly suggested that biological nitrification was taking place in the filters. Iron removal still was satisfactory (43). Following Run 41, sampling and analysis was not done for every run, but, on an average, on alternate runs.

Ammonia-nitrogen concentration in the raw water was about 1 mg/l. At the end of the settling period, this was reduced to about 0.9 mg/l, due to some nitrification in the sedimentation tank itself. Complete nitrification of the 0.9 mg/l of ammonia-nitrogen would theoretically require 4.1 mg/l of This demand, if exerted, would still leave considerable DO in the filter DO. effluent. Since earlier investigators have suggested that anaerobic conditions in filters may be associated with breakthrough of iron during the filtration of waters containing ammonium ions (64), attempts were made to bring about anaerobic conditions in the filters in this work. Reduced aeration was attempted during Run 50-51, to give a low DO concentration. Anaerobic conditions occurred in the filters as a result, but anaerobic conditions also occurred in the dead spots in the sedimentation tank causing unsightly gas bubbles to rise and interfere with sedimentation. Because of these undesirable conditions, the aeration was increased to the normal level at the end of Run 51.



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FIGURE 9. PERFORMANCE OF FILTERS 1 THROUGH 4 DURING RUN 41



In another attempt to obtain anaerobic conditions, a solution of ammonium chloride was added to raw water just before aeration to increase the concentration of ammonia-N. The addition of ammonium chloride was started at the beginning of Run 55, on the 109th day of operation. A positive displacement pump* was used for maintaining a constant feed of ammonium chloride solution to the raw water, so as to increase the ammonia-N concentration to about 2.5 mg/l. Samples were obtained at eight hour intervals during Run 55 to observe the effect of increased armonia-II in the filter influent. Figure 10 shows the results for this run for all four filters. It may be seen from the figure that the temperature rise was as usual, and hardness remained essentially the same. However, a larger depletion of ammonia-N was observed with concurrent larger decreases in DO, pH and alkalinity. The DO concentration was close to zero during the latter half of the run with about 2 mg/l of ammonia-N depletion. The pH decrease was about 0.35 unit and the alkalinity decrease was about 20 mg/l. Once again, the iron removal was satisfactory (43).

Although the chemical changes observed were justifiably assumed to be due to nitrification, confirming evidence of nitrification, the formation of nitrite and nitrate was not available. Therefore, beginning with Run 86 on the 170th day of operation, determinations of nitrite and nitrate were also made on water samples. Because varying the expansion of a sand bed during backwash had not shown any significant effect on the effluent quality, (possibly because of the effectiveness of the surface wash), all filters were backwashed at 50 percent expansion beginning with Run 86. The surface wash was discontinued for Filter h effective Run 86 in order to observe the effects of the



FIGURE 10. PERFORMANCE OF FILTERS 1 THROUGH 4 DURING RUN 55

absence of surface wash on the filtered water quality. In earlier work in which nitrification was associated with breakthrough of iron in filters (64), surface wash was not employed.

Three more filters, Filters 5 through 7 were placed in service beginning with Run 86, on the 170th day of operation, without surface wash facilities. Filter 5 was identical to Filters 1 through 4 and was backwashed for seven minutes at 50 percent expansion of sand bed. Filter 6 was provided with a Camp's nozzle (Jalker Process) in the place of gravel bed support to permit the use of compressed air for two minutes of air-scour at the beginning of the backwash. This was followed by five minutes backwash at 50 percent expansion. The purpose of employing air-scour was to observe the effect of such a procedure on the effluent water quality. Filter 7 was identical to Filter 5 except that an immersion heater was placed at the top of filter unit at the entrance of the filter influent so as to raise the water temperature to about 23°C to observe the effects of temperature on the filtered water quality. Earlier studies (41) have indicated that temperature may influence the biologic activity resulting in deterioration of filtered water quality. Filter 7 was backwashed at 50 percent expansion for seven minutes. Routine sampling and analysis were carried out on samples from all seven filter units beginning with Run 86 on the 170th day of operation.

In order to evaluate the effects of a longer residence time of water in the filter bed, the flow was reduced to 1 gpm/sq ft in Filters 4 and 5 beginning with Run 99 on the 196th day of operation.

The raw water at Urbana has been calculated to be supersaturated with respect to ferrous carbonate. Similar calculations showed that the aerated water was undersaturated with respect to ferrous carbonate. These theoretical

calculations are based on equilibrium constants which may be accurate only within an order of magnitude. In order to evaluate the effects of higher degree of saturation of ferrous carbonate in the filter influent on the filtered water characteristics, a solution of ferrous ammonium sulfate (acidified to pH 3 to keep the iron from being oxidized) was added to the raw water before aeration. The total ferrous iron concentration was about 5 mg/l, compared to the l.l mg/l in the natural water. The addition of ammonium chloride solution was discontinued during the time ferrous ammonium sulfate solution was added because the ammonium ion from the latter was sufficient to raise the ammonia-N concentration to about 2.5 mg/l. The addition of ferrous ammonium sulfate solution was started with Nun 112, on the 222nd day of operation, and was terminated with Hun 128, on the 245th day of operation. Addition of ammonium chloride solution was resumed to augment the ammonia-N in the raw water beginning with Run 129.

The sampling of all units of the pilot plant continued until the end of Run 157 on April 17, 1969, the 300th day of operation. However, the pilot plant was operated until April 28, 1969, the 311th day of operation for additional studies. Individual filters have also been used in studies in which (a) glucose was added to the filter influent to observe the effect of increased COD; (b) ferrous carbonate was added to the filter influent to observe the effect of precipitated ferrous iron and (c) different dosages of chlorine solution were used to evaluate the effectiveness of chlorine as a chemical agent for the control of becterial growth on sand beds.

General Observations

Operation of Pilot Plant

Table A-1 of the Appendix summarizes the operational data for the pilot plant for those runs in which sampling and analysis were carried out. During

the 300 days of operation, only twice was the flow interrputed and then only for a few hours. On the early morning hours of August 4, 1968, at the end of Run 22 (44th day of operation), there was a power loss for about four hours in the building due to a heavy thunderstorm. During this time, the well pump had stopped and the filters were drained. On January 17, 1969, at the end of Run 105 (208th day of operation), the pilot plant was shut down, with filters standing full, for about seven hours for the purpose of replacement of the pressure tank which had sprung a leak.

Table A-l of Appendix shows operational data for the 90 of the 157 runs that have been sampled. The average length of run is found to be 1.97 days, within a range of 1.20 to 2.15 days. The lower values for the length of run were due to the early clogging of filter beds during the runs when ferrous ammonium sulfate was added to the raw water.

General Characteristics of Settled Water

Table A-3 of the Appendix summarizes the averages of characteristics of settled water for the 90 runs listed in Table A-1. Table 12 shows the mean, minimum, maximum and the standard deviation for each of the parameters listed in Table A-3. Figure 11 shows a plot of the data of Table A-3. Referring to Table 12 and Figure 11, it may be seen that the variations in temperature and hardness were small throughout the period. The DO concentration averaged about 8 mg/l except during Run 50-51 (99th to 101st day) when reduced aeration resulted in a DO concentration of about 6 mg/l. The trough in the DO curve in Figure 11, on the 100th day, coincides with a trough in the curve on the time scale. This is as expected because of the reduced release of carbon dioxide due to reduced aeration. The ammonia-N concentration was about 0.9 mg/l up to the 108th day. Due to the addition of the emmonium chloride solution, the emmonia-N concentration was higher from the

TABLE 12

Parameter	Mean	Minimum	Maximum	Standard Deviation
Temperature, ^o C	16.9	15.1	19.1	1.11
pH, units	7.80	7.52	7.92	0.09
D0, mg/l	8.6	6.4	9.8	0.46
Total Iron, mg/l	1.31	0.89	5.23	0.89
Total ferrous, mg/l	0.18	0.0	0.41	0.08
Filtrable ferrous, mg/l	0.06	0.0	0.22	0.06
Ammonia-N, mg/l	1.67	0.78	5.20	0.90
Nitrite-N, mg/l	0.02	0.0	0.05	0.01
Nitrate-N, mg/l	0.35	0.17	0.52	0.09
Alkalinity, mg/l	331.6	321.5	336.5	2.9
Mardness, mg/1	245.5	238.0	249.0	2.0

MEAN, MINIMUM, MAXIMUM AND STANDARD DEVIATION OF OBSERVED CHARACTERISTICS OF SETTLED MATER AT URBANA, ILLINOIS

109th day as seen in Figure 11. Mechanical troubles with the operation of the sigma pump caused erratic variation in the rate of addition of ammonium chloride solution. Therefore, a large variation in the ammonia-N concentration was observed in the settled water after the 109th day. The small amounts of nitrite and nitrate in the settled water was presumably the product of some nitrification taking place in the sedimentation tank itself. The raw water did not contain any significant amount of nitrite and nitrate.

Ferrous ammonium sulfate solution was added to the raw water between the 222nd to 245th day of operation, as seen from Figure 11. During this time,

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the average total iron concentration was about 5 mg/l. Coinciding with this peak in the total iron curve were troughs in the pH and alkalinity curves. Such decreases in pH and alkalinity were partially the result of the oxidation of ferrous iron and partially the result of the addition of the acidic ferrous ammonium sulfate solution. Oxidation of ferrous iron, according to reaction,

$$4Fe^{+2} + 0_2 + 10H_20 \longrightarrow 4Fe(0H)_3 + 8H^2$$

produces hydrogen ions which in turn neutralizes some alkalinity and decreases the pH. Figure 11 shows that the oxidation of ferrous iron was nearly complete with only about 0.25 mg/l of the 5 mg/l or about five percent remaining as ferrous iron in the settled water during the period ferrous ammonium sulfate solution was added. The ferrous iron in the settled water during other periods was also low as can be seen from Figure 11. Table 12 gives the average total ferrous iron for the whole period to be 0.18 mg/l of which only 0.06 mg/l was filtrable.

General Characteristics of Filter Effluents

Tables A-4 through A-10 in the Appendix summarize the average characteristics of filter effluents for Filters 1 through 7 during the runs in which the samples were obtained and analyzed. Figures 12 through 18 show the plots of variation in effluent characteristics respectively for Filters 1 through 7, except for the concentrations of ammonia-N, nitrite-N and nitrate-N. Figure 11 shows that the ammonia-N concentration in the settled water varied significantly due to malfunction of the pump used for the addition of the ammonium chloride solution. The filter effluents also, therefore, contained ammonia-N in varying concentrations as can be seen from Tables A-4 through A-10. Figures 12 through 18 show the following curves for forms of nitrogen:

Ammonia uptake (AM. UPTK) = Ammonia-N in filter influent-Ammonia-N in filter effluent






















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Nitrite formed (NO2-N) = Nitrite-N in filter effluent-
Nitrite-N in filter influent
Nitrate formed (NO3-N) = Nitrate-N in filter effluent-
Nitrate-N in filter influent
```

The plots of data for all filters as seen in Figures 12 through 18 show some similarities. Considering Filters 1 through 4, shown in Figures 12 through 15, it may be seen that the variation in temperature and hardness was small. During the first 10 days, the ammonia uptake in the filters was very small, with alkalinity, pH and DO remaining essentially the same. During the next 10 days, the ammonia uptake increased and alkalinity, pH and DO decreased. Ammonia uptake approached the influent concentration of ammonia-N by about the 20th day. Nearly steady-state conditions existed between the 20th and 99th days. The troughs in the curves for DO and pH between the 99th day and lolst day correspond to similar troughs in the curves for settled water shown in Figure 11, when aeration was reduced. When additional ammonia-N was added to the raw water beginning with the 109th day, increased armonia uptake was noticed in all four filters. The increased armonia uptake was reflected in the decreased alkalinity and pH, with DO being near-zero. The ammonia uptake, after the 109th day, was always limited by the availability of DO and not by the ammonia-N concentration in the settled water which was always 2 mg/l or more (except on the 195th day, when it was about 1.5 mg/l). The changes noted above in the concentrations of ammonia-N, alkalinity, pH and DO are attributed to nitrification in filters. For reasons not yet known, a few days later the ammonia uptake decreased briefly as shown by the trough in the AM. UPTK curve and by peaks in the alkalinity, pH and DO curves. This "recovery" from nitrification occurred in Filters 1 and 2 between the 120th and 140th day, in Filter 3 between the 130th and 160th day, and in Filter 4 between the 140th and 160th day as seen in Figures 12 through 15. It is

interesting to note that the phenomena took place in all four filters reasonably close together on the time scale and lasted three to four weeks. The phenomena were repeated in all filters between the 190th and 200th days. This may be related to some factors in the life cycles of the bacteria on the filter sand, particularly the slow-growing nitrifiers. The nitrite and nitrate formed during filtration are shown for the period between the 170th and 300th days. The figures also show that nitrate-N was predominant in the effluent of Filter 1, while nitrite-N was predominant in effluents of Filters 2 through 4. Since two species of bacteria are involved in complete nitrification, it was thought that the sand bed of Filter 1 contained a predominance of Nitrobacter bacteria which resulted in higher nitrate concentrations, and the sand beds of Filters 2 through 4 contained a predominance of Nitrosomonas bacteria which resulted in higher nitrite concentrations in the filter effluents. The kinetics of nitrite and nitrate formation may also be responsible for predominance of either nitrite or nitrate in filter effluents. Why this should be so is not understood in view of the fact that all four filter units were identical and received the same filter influent. Troughs in ammonia uptake curves and peaks in alkalinity, pH and DO curves were observed again in Filters 1 through 3 between the 222nd and 245th days, as seen in Figures 12 through 14. This time the phenomena coincided with the period when the ferrous ammonium sulfate solution was added to the raw water. It is hypothesized in this instance that the high concentration of iron in the settled water may have coated the filter sand containing the bacteria and decreased the availability of ammonia to the bacteria. It may be seen from Figure 15, that Filter 4 did not experience the phenomenon between the 222nd and 245th days. This was attributed to the lower rate of filtration at 1 gpm/sq ft during this period in Filter 4. The longer residence time due to lower

filtration rate was probably sufficient for nitrification to proceed in spite of the deposition of iron in the filter sand. The troughs in alkalinity and pH curves during this period for Filter 4 were due to similar variations in the settled water.

Figures 16 and 17 are the plots of the characteristics of effluents from Filters 5 and 6 respectively. Filter 5, though started on the 170th day at 2 gpm/sq ft was operated at a lower rate of 1 gpm/sq ft between the 196th day and 231st day, and then changed back to 2 gpm/sq ft for the rest of the period up to the 300th day. Figure 16 shows that for Filter 5, there was little ammonia uptake until the rate of filtration was reduced on the 196th day after which there was a sharp rise in the ammonia uptake curve, with sharp decreases in alkalinity and pH, with D0 near zero. No significant changes were observed in the temperature or the hardness. The filter effluent contained higher concentrations of nitrite-N than nitrate-N. When the rate of filtration was changed back to 2 gpm/sq ft on the 231st day, there was no significant change in the effluent characteristics.

Figure 17 shows the plot of effluent quality for Filter 6. It may be seen from the figure that ammonia uptake was minimal for about thirty days at the beginning of operation (from the 170th to 200th day), with alkalinity, pH and DO remaining essentially the same. This long period before higher ammonia uptake was observed was attributed to the air-scour employed as part of the backwash operation for Filter 6. When the ammonia uptake increased after the 200th day, there were decreases in alkalinity and pH, with DO near zero. Figure 17 also shows higher concentration of nitrite-N in the filter effluent.

Special Studies

Individual filter units were used to evaluate the influence of some environmental factors on the filtered water quality. The effects of decreased

rate of filtration have already been described with reference to Filters 4 and 5.

Filter 3 was used in the study of effect of increased COD of filter influent. Glucose solution was used to augment the COD of the filter influent to about 50 mg/l, beginning with Run 102 on the 202nd day. The surface wash was discontinued during the time the COD was added to the influent. Referring to Figure 1h, it may be seen that there was a sharp decrease in ammonia uptake indicating interference with nitrification. This was attributed to the growth of heterotrophic bacteria that proliferated on the filter sand due to the glucose feed. As a matter of fact, the bacterial growth was so great that the filter cake was about six inches thick and caused high headloss. The headloss at the beginning of filter run was as great as four feet of water, and the length of filter run was shortened drastically to about eight hours. Finally, the glucose addition was discontinued at the end of Run 107 on the 214th day and the surface wash was reinstalled. Nitrification was observed after the glucose addition was discontinued.

Filter 7 was used in the evaluation of effects of temperature, hardness and ferrous carbonate precipitate in the influent, on the characteristics of filter effluent. When Filter 7 was started on the 170th day, the filter influent was heated to about 23°C by an immersion heater. Figure 18 shows the characteristics of filter effluent for Filter 7. Ammonia uptake rapidly increased after about 10 days of operation, due to the increased bacterial activity at the higher temperature. Otherwise, there was no other significant effects noticed. Calcium chloride solution was added to the filter influent beginning with Run 135 on the 256th day to observe the effects of high hardness on nitrification and effluent quality. The amount of calcium chloride solution added was increased in successive runs as seen in Figure 18. The

rate of flow in the filter was reduced to $1\frac{1}{2}$ gpm/sq ft after the 270th day in order to increase the residence time of the water in the filter. The total hardness reached a maximum of 748 mg/l on the 276th day with no significant change in the filtered water quality. No precipitation of hardness was observed though the quotient (Q/K)_{CaCO3} was calculated to be 1.95 indicating a high degree of supersaturation. The addition of calcium chloride solution was discontinued from the 284th day, and the flow rate changed back to 2 gpm/ sq ft from the 292nd day.

A suspension of saccharated ferrous carbonate * was used to increase precipitated ferrous iron in the filter influent, beginning with Run 154 on the 292nd day. When about one mg/l of ferrous iron in the form of the precipitate was added to the filter influent at the top of the filter unit, it was found that all of it was oxidized by the time it reached the top of the filter Increasing the ferrous carbonate added to about 2 mg/l gave about 0.6 bed. mg/l of total ferrous at the top of the filter bed. Addition of saccharated ferrous carbonate to the filter influent was observed to inhibit the nitrification in the filters as seen in Figure 18. This may have been due to the increased COD derived from the sugar and lactose present in the solution along with ferrous carbonate. It may be recalled that additional COD had interfered with nitrification in Filter 3 (Figure 14). It was estimated that about 25 mg/l of sugar and lactose was added to the filter influent. Along with some inhibition of nitrification in the filters, evidence of denitrification was observed during the period when ferrous carbonate was added to the filter influent. This appears in Figure 18 as negative values of nitrate formed after the 292nd day. The DO was near zero, and ammonia uptake decreased

A prescription compound made by Mallinckrodt Chemical Company, New York, containing, according to the Merck Index, 70% sugar, 10% lactose and 20% ferrous carbonate (7.23%) iron).

during this period. The alkalinity increased slightly both due to inhibition of nitrification and the addition of carbonates.

Depth Studies

In order to determine the changes in the water quality as the water passed through the sand bed, water samples were obtained at different depths from the sampling ports on the side of the filter unit. During Run 96, on the 190th day, Filter 4 was sampled at the beginning and end of the run when the rate of filtration was 2 gpm/sq ft. Figure 19 shows the plot of values determined in this study. It may be seen from the figure that the temperature increased slightly with depth as a result of higher ambient temperature. Hardness remained essentially the same throughout the depth. Most of the changes in iron, DO, pH, alkalinity, armonia-N, nitrite and nitrate-N took place within the top nine inches of the sand bed indicating that the bacterial activity was greatest at the top of the filter bed. The effluent contained some DO, because the ammonia-N concentration in the filter influent was only about 1.75 mg/l. Comparing the removals at the beginning and end of run, it may be seen that most of the changes took place within the top six inches of the sand bed of the filter at the end of the run. This is probably due to filtration through the cake formed at the top of filter bed at the end of filter run.

Figure 20 shows the changes in water characteristics with depth for Filter 7 during Run 158 on the 301st day, when saccharated ferrous carbonate was being added to the filter influent. Only one set of samples was obtained at the middle of the run. Figure 20 shows that hardness remained essentially constant. In this instance, the temperature decreased with depth due to cooling because filter influent was at a higher temperature than the ambient temperature. Most of the changes in characteristics of water took place in the top nine inches of the filter bed. Because of increased COD in the filter influent



of run)

end

I

1

Beginning of run and

FIGURE 19. VARIATION IN WATER CHARACTERISTICS WITH DEPTH DURING RUN 96 IN FILTER 4

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associated with added ferrous carbonate, nitrification was again inhibited. The DO was near-zero at depths below 15 inches from the top of the bed. Nitrate-N increased initially at the one inch level, but decreased rapidly with depth, and was zero below the 15 inch depth from the top of the bed. This denitrification was possibly due to the presence of ferrous carbonate in the filter influent which may have acted as a reducing agent. It is interesting to note that denitrification took place even when DO was present in water. This may be due to existence of pockets of anaerobic areas in the filter bed, such as filter cake or mudballs. Aerobic denitrification (68) though possible, occurs at rates which are too slow to account for the changes observed in the filter bed.

Iron Removal

In all filters and under all conditions of operation of the pilot plant described above, the iron removal was satisfactory (43). In Filter 6, the concentration of iron sometimes was as high as about 0.4 mg/l particularly at the beginning of the filter operation. Overall, the average concentration of iron in the filter effluents of Filters 1 through 7, was found to be from 0.06 to 0.13 mg/l, as seen in Table 13 which shows the mean and ranges of concentration of iron in effluents of Filters 1 through 7.

In contrast with the work of Ghosh (41), nitrification did not have any effect on the iron removal in the filters studied in this investigation. Filters 1 and 2 were operated for 10 months with surface wash prior to backwash. The surface wash was effective in keeping the sand beds free of mudballs. The average iron concentration in effluents from Filters 1 and 2 was 0.09 and 0.11 mg/l respectively (Table 13). Surface wash was discontinued in the operation of Filter 4 between the 170th and the 300th day, permitting mudball formation to take place. The average iron concentration in the effluent from Filter 4

TABLE 13

2007 1 0	Concentration of iron, mg/l			
Filter	Nean	Minimum	Maximum	Standard Deviation
l	0.09	0.0	0.32	0.08
2	0.11	0.0	0.53	0.09
3	0.09	0.0	0.31	0.08
14	0.10	0.0	0.28	0.08
5	0.07	0.0	0.22	0.07
6	0.13	0.0	0.43	0.14
7	0.06	0.0	0.22	0.07

IRON CONCENTRATION IN EFFLUENT FROM FILTERS 1 THROUGH 7 OF PILOT PLANT STUDIES AT URBANA

was 0.10 mg/l as seen from Table 13. Filter 5, which was operated for 130 days (between 170th and 300th day, Figure 16) without surface wash also removed iron satisfactorily (Table 13). From these observations, it may be concluded that the presence of mudballs in sand bed of filters did not have any effect on the iron concentration in the filter effluents. Considerable mudballs were present in the anaerobic zone of filter brought about by depletion of D0 due to nitrification. The fact that iron concentration was low in filter effluent indicates that there was no chemical reduction of ferric iron (deposited in the mudballs or on sand particles) due to anaerobic conditions in filter bed as was hypothesized by Chosh (41). Redissolution of ferrous carbonate precipitate also does not appear to be a possible mechanism of breakthrough as seen from the studies carried out on Filter 7 in this investigation.

General

Bacterial growth on the filter sand has been suggested to be responsible for the chemical changes observed in the water during filtration (41). It is desirable to destroy the bacterial growth because of its possible significance in the iron breakthrough in filters (64). High concentration of bacteria as determined by the total plate count in the filtered water may be undesirable from aesthetic point of view. In the selection of an agent for control of bacterial growth in filter beds and required dosage and time of contact, economic factors are important. In this study, only chlorine was used as the control agent while potassium permanganate was used in the study at Rantoul, Illinois. The pH of the chlorine solution was adjusted to 4 to ensure optimum effectiveness.

Procedure for Control of Bacterial Growth

The filter to be treated with chlorine solution was allowed to drain for about 30 minutes after a backwash operation, so that the moisture content of the sand was reduced. An aspirator bottle containing four liters of chlorine solution of desired strength was connected to the sampling outlet on the effluent line. The float valve of the rate-of-flow control box was closed. By raising the aspirator bottle to a level above the sand bed surface, the solution was allowed to flow by gravity from the aspirator bottle into the filter unit. The filter unit was filled so as to submerge the sand bed by about four inches. Four liters of solution was sufficient to do this. After the desired contact time, the aspirator bottle was lowered below the level of sampling outlet so that the solution flowed back into the aspirator bottle. After mixing the contents of the aspirator bottle, an aliquot was taken for analysis to determine the concentration of chlorine remaining. The solution

was reapplied to the filter bed for further contact time. This procedure was repeated either until very little change was observed between two consecutive analyses or until all of the chlorine had been consumed.

The chlorine solution was prepared from household bleach (Clorox brand) and adjusted to pH 4 with sulfuric acid in order to convert OCl⁻ to Cl₂ and HOCl. The Drop Dilution Method using the orthotolidine reagent and a comparator was employed in determining the concentration of chlorine in the solution (69).

Results

Filters 2 through 5 were treated with chlorine solutions to observe the effects of treatment on the filtered water quality. Filter 2 was treated with a chlorine solution of 75 mg/l of chlorine for a contact time of $1\frac{1}{2}$ hours at the beginning of Run 148 on the 280th day. Filters 3 and 4 were treated with chlorine solutions of 200 and 400 mg/l of chlorine respectively, at the beginning of Run 150 on the 284th day, with contact times of three and five hours respectively. Filter 5 was treated with a chlorine solution of 200 mg/l of chlorine solution of Run 150 on the 284th day, with contact times of three and five hours respectively. Filter 5 was treated with a chlorine solution of Run 151 on the 286th day. Figure 21 shows the kinetics of chlorine consumption determined from these experiments.

The moisture content of wet sand in the filters caused an immediate dilution of the solution applied. A broken vertical line is drawn in Figure 21 in all cases to represent the immediate dilution. The degree of dilution was estimated to be 20 percent from the percent moisture of wet sand.

Figure 13 for Filter 2 shows that the treatment with 75 mg/l of chlorine solution was ineffective, as no changes were observed as a result of the treatment on the 280th day, and nitrification continued as if nothing had happened. Figure 14 for Filter 3 also showed that 200 mg/l of chlorine for a


FIGURE 21. KINETICS OF CHLORINE CONSUMPTION BY FILTER SAND



contact time of three hours was ineffective even though more than 99 percent of the chlorine applied had been consumed according to Figure 21, and nitrification continued in spite of the treatment. Figure 15 for Filter 4 shows that a dosage of 400 mg/l of chlorine and a contact time of five hours was able to partially reduce the bacterial concentration on the filter sand as seen from reduced ammonia uptake and increased D0 in the filter effluent. However, nitrification was again observed after two days.

Figure 21 indicates that a solution of 1000 mg/l of chlorine applied to Filter 5 was depleted to 40 mg/l in seven hours. As a result of this treatment, as shown in Figure 16 for Filter 5, nitrification was nearly arrested as indicated by the very low ammonia uptake and the high D0 in the filter effluent. The effect of treatment lasted only for a short period. Nitrification was observed within ten days indicating reestablishment of bacterial growth in the filter beds.

VI. CHEMICAL AND MICROBIOLOGICAL ASPECTS OF FILTRATION

General

The pilot plant operation at Urbana included monitoring the quality of raw, settled and filtered water over a period of 10 months. Except for a short period at the beginning, there was always considerable depletion of ammonia and DO, with decreases in alkalinity and pH during filtration. Thus, the filter bed was a "chemical reactor" where chemical changes were observed to take place. As such, considering the filter bed to be a closed reactor system, the chemical changes taking place within the system would be expected to conform to stoichiometric relationships and mass balances from equilibrium considerations. Because the changes observed appear to have reached steady state conditions most of the time, assumption of equilibrium conditions is reasonably valid. The data represented in Tables A-3 through A-10 in Appendix have been analyzed to compare the calculated values with the observed values as a result of nitrification which took place in the filter.

Stoichiometric Relationships

General

The process of nitrification is represented by the following reactions:

$$NH_{L}^{+} + 1_{2}^{1} O_{2} \longrightarrow NO_{2}^{-} + H_{2}O + 2H^{+}$$
(VI-1)
$$NH_{L}^{+} + 2O_{2} \longrightarrow NO_{3}^{-} + H_{2}O + 2H^{+}$$
(VI-2)

The hydrogen ions produced during oxidation of ammonia as shown in reactions VI-1 and VI-2, can neutralize part of the alkalinity present in the water. At near-neutral pH, the alkalinity is predominantly present as bicarbonates. The neutralization reaction is represented by:

$$H^+ + HCO_3^- \longrightarrow H_2CO_3$$
 (VI-3)

The amount of alkalinity neutralized is converted to equivalent amount of carbonic acid. (It is convenient to refer to free carbon dioxide and the carbonic acid in the water as "carbonic acid" as a whole.) The carbonic acid thus produced alters the carbonate equilibrium,

$$H_2CO_3 \iff H^+ + HCO_3^- K_1 = 10^{-6.3} \text{ at } 25^{\circ}C (58) (VI-4)$$

In the detailed calculations shown below, the + or - signs on the ions are omitted for convenience (e.g., H for H⁺). Subscripts are used to distinguish the quantities: c for "consumed," d for "demand," f for "formed," in for "influent," eff for "effluent," obs for "observed," and cor for "corrected." The calculations described below were made using a computer program. The variable names are capitalized as used in the computer program. A detailed explanation of all variables is given in the Appendix.

Mass balance on nitrogen is made by considering the ammonia-N, nitrite-N and nitrate-N in the influent and effluent of each filter. The organic nitrogen was found to be very small, and hence disregarded in the mass balance considerations. The mass balance of nitrogen is represented by:

$$(\mathrm{NH}_{4}+\mathrm{NO}_{2}+\mathrm{NO}_{3})_{\mathrm{in}} = (\mathrm{NH}_{4}+\mathrm{NO}_{2}+\mathrm{NO}_{3})_{\mathrm{eff}} + \mathrm{AMUP} \mathrm{in mg/l as N}$$

where AMUP represents nitrogen incorporated into cell mass of bacteria, calculated as the difference between the total nitrogen in the influent and effluent. This is expressed as a percent, PCNV, as

$$PCNV = \frac{(NH_{1}+NO_{2}+NO_{3})_{in} - (NH_{1}+NO_{2}+NO_{3})_{eff}}{(NH_{1}+NO_{2}+NO_{3})_{in}} \times 100 \%$$

A mass balance on oxygen is made by considering the DO concentrations in the influent and effluent and the oxygen required for nitrification. Equations VI-1 and VI-2 indicated that,

From the above relationships, the oxygen required for nitrification is calculated to be:

 $O_{2(d)} = NO_{2(f)} \times 3.42 + NO_{3(f)} \times 4.55$ in mg/l

where,

$$NO_{2}(f) = NO_{2}(eff) - NO_{2}(in)$$
 in mg/l

and

$$NO_{3(f)} = NO_{3(eff)} - NO_{3(in)}$$
 in mg/l

The mass balance on oxygen is thus found to be:

$$DO_{in} = DO_{eff} + O_{2(d)} + DOUP$$
 in mg/l

where DOUP represents oxygen requirement of heterotrophic bacteria and endogenous respiration of all bacteria in the aerobic part of the filter. The oxygen required for oxidation of ferrous iron is about 0.14 mg/l of O_2 per mg/l of ferrous iron. Since the average ferrous iron in the filter influent was only 0.18 mg/l, the oxygen demand was, at most, 0.03 mg/l of O_2 , which is negligible.

The degree of nitrification may be defined as the extent to which nitrification has proceeded to completion as seen by the formation of nitrates. An indicator of the degree of nitrification is obtained by calculating the

theoretical DO demand per mg/l of ammonia-N undergoing nitrification (TRDOD) as:

$$IRDOD = O_{2(d)} / (NO_{2(f)} + NO_{3(f)})$$

It may be seen that a value of 3.42 for TRDOD would indicate formation of nitrite only, and a value of 4.55 would indicate formation of nitrate only. A value of TRDOD between 3.42 and 4.55 would indicate the extent to which the nitrification has proceeded to completion.

The amount of hydrogen ion formed during nitrification is calculated from Equations VI-1 and VI-2 as:

$$H_{f} = 2(NO_{2(f)} + NO_{3(f)})$$
 in moles/l

From Equation VI-3 it is seen that the alkalinity consumed in the neutralization by the hydrogen ions is:

$$HCO_{3(c)} = H_{f}$$
 in moles/l
= 2(NO_{2(f)} + NO_{3(f)}) in moles/l

Since the alkalinity as $CaCO_3 = HCO_3/2$ in moles/l,

Alk_c =
$$HCO_{3(c)}/2$$
 in moles/l as $CaCO_{3}$
= $HCO_{3(c)}$ x 50000 in mg/l as $CaCO_{3}$

The computed alkalinity (ALKCOM) of the filter effluent due to nitrification is therefore given by:

where, DHDNS represents the change in hardness of water (as CaCO₃) between the filter influent and effluent. Changes due to precipitation of hardness were always very small. The variation between the computed and observed alkalinity (AIKVAR) is calculated as:

In the calculations for pH, it is necessary to correct the observed pH and equilibrium constant, K_1 . It may be recalled that pH was measured at room temperature, and the value of K_1 is reported for 25° C. The observed pH is corrected for instrument errors for temperature according to the equation,

$$pH = pH_{obs} + 0.003(25 - Temp(in)obs)$$

The correction of 0.003 unit per degree centigrade was experimentally verified for the water. The temperature correction for K_1 is applied according to the vant Hoff's equation. The correction for ionic strength is made according to Dye (56), as:

$$pK_{1} = pK_{1} - \sqrt{\mu} / (1 + 1.4\sqrt{\mu})$$

where pK_1 is - $\log K_1$, and μ is the ionic strength of the water, calculated as 0.009101 moles/l. For the filter influent:

$$HCO_{3(in)} = Alk_{in} / 50000$$
 in moles/l

The "carbonic acid" content of the filter influent is calculated from the equilibrium represented by the Equation VI-4 to be:

$$H_2^{CO}_3(in) = H_{in} \times H^{CO}_3(in) / K_1(in) \text{ cor in moles/l}$$

or,

$$p(H_2CO_3(in)) = pH_{in}' - log(Alk_{in}/50000) - pK_1(in)cor$$

 $H_2CO_3(in) = 10^{-p(H_2CO_3(in))}$ in moles/1

The additional carbonic acid formed from the neutralization of part of the alkalinity as a result of nitrification is calculated from Equation VI-3 to be:

$$H_2^{CO}_3(f) = H^{CO}_3(c)$$
 in moles/1

The total carbonic acid content of the filter effluent is therefore:

$$H_2^{CO}_3(eff) = H_2^{CO}_3(in) + H_2^{CO}_3(f)$$
 in moles/1

From Equation VI-4 again, the pH of the effluent is calculated to be:

$$pH_{eff} = p(H_2CO_3(eff)) + log (AIKCOM/50000) + pK_1(eff)cor$$

Applying the instrument correction, the computed pH of effluent (PHCOM) is:

PHCOM =
$$pH'_{eff} - 0.003 (25-Temp_{eff})$$

The variation in the computed and observed pH of effluent (PHVAR) is then:

$$PHVAR = pH_{off} - PHCOM$$

In order to compare the variations between the observed and computed values of alkalinity and pH, the following differences are calculated:

$$DALKOBS = Alk_{in} - Alk_{eff} \qquad in mg/l$$

$$DALKCOM = Alk_{in} - AIKCOM \qquad in mg/l$$

$$DPHOBS = pH_{in} - pH_{eff} \qquad units$$

$$DPHCOM = pH_{in} - PHCOM \qquad units$$

The above calculations were performed using a computer program for data in which the nitrite and nitrate determinations were made, namely, Runs 86 through 157 for all seven filters. The results of these calculations for each run observed are given in the Appendix in Tables A-11 through A-17 for Filters 1 through 7 respectively. Also included at the bottom of the tables are the results of the statistical evaluations of the observed and computed values. Table 14 summarizes the mean values obtained in the statistical evaluations. It may be seen from the table that the mean total nitrogen in the effluent closely agreed with the mean total nitrogen in the influent. The percent variation was found to range from -1 to -4 percent. The minus sign indicates

MEAN VALUES OF OBSERVED AND COMPUTED AIKALINITY AND PH OF FILTERED WATER - RUN 86 THROUGH 157 OF PILOT PLANT STUDIES AT URBANA

T mg/l	Computed	8	318.17	315.87	316.24	315.77	318.32	318.61	316.44
ALKALINIT	Observed	330.88	317.70	316.02	316.28	315.98	318.22	318.94	314.98
D OXYGEN	DOUP mg/l	8	0.88	0.78	0.93	0.80	0.68	0.614	1.24
DISSOLVE	TRDOD	Į	4.36	3.74	3.78	3.80	3.72	3.66	3.59
ROGEN	PCNV Percent	I	-1.76	-3.73	-4.48	-3.42	-3.30	-1.76	-0.88
TOTAL NIT	0bserved mg/1	3.05	3.09	3.16	3.18	3.15	3.15	3.10	3.08
	Sample	Influent	Effluent Filter 1	~	m	14	гл	9	7

TABLE 14 (continued)

	Computed Decrease	ł	0.34	0.38	0.37	0.39	0.32	0.31	0.36	
	Observed Decrease	1	0.32	0.37	0.36	0.36	0.30	0.27	0.33	
STINU H	Variation	ł	0.02	0.02	0.02	0.03	0.02	0*0	-0.02	
	Computed	ĩ	7.36	7.31	7.32	7.31	7.38	7.39	7.34	
	Observed	7.70	7.38	7.33	7.34	7.34	7.40	7.43	7.32	
	Computed Depletion	Ĩ	12.71	15.01	14.64	15.11	12.56	12.27	14.444	
L/gm TTINLIAMIA	Observed Depletion	Ε	13.18	36.4L	14.60	06.4L	12.66	11.9h	15.90	
	Variation	Ĩ	-0.47	0.15	0.04	0.21	-0.10	0.33	-1.46	

that the effluent total nitrogen was slightly higher, which may be due to experimental errors. This also indicates that no measurable amount of nitrogen was fixed into bacterial cell mass. This is in contrast with the observation of Ghosh, who found that up to 1.6 mg/l of ammonia-nitrogen was unaccounted for during filtration (39), which was assumed to be due to biological fixation. The ratio of TRDOD in Table 14 is seen to vary from 3.59 to 3.80 except in the case of Filter 1, when it is 4.36. In other words, nitrification was more complete in Filter 1 than in other filters, an observation noted in the previous chapter. The value of DOUP, averaged about 0.9 mg/l within a range of 0.6 to 1.2 mg/l. The higher value of oxygen uptake occurred in Filter 7 in which the filter influent was heated resulting in higher biologic activity.

The agreement between the mean observed and computed values of alkalinity in the filter effluent is excellent. The mean depletion of alkalinity varied between 12 to 15 mg/l in the filters.

The mean computed values of pH also agreed well with the mean observed values. The mean observed decrease in the pH was found to vary from 0.27 unit to 0.38 units for different filters. The variation of mean computed values from the mean observed values is seen from the table to range between -0.02 to 0.04 unit.

The agreement between the mean observed and computed values discussed above enables one to predict such changes due to nitrification in the quality of water during filtration.

The calculations described previously were repeated for the data from all runs, observed and sampled, assuming that all of the AM UPTK underwent nitrification in the filter. The results of the calculations are tabulated in the Appendix in Tables A-18 through A-24, including the statistical

evaluations of the observed and calculated values. The mean values are shown in Table 15 for alkalinity and pH. It may be seen that the agreement between the mean observed and calculated values is very good even though the difference was smaller when nitrate and nitrite data were used.

Results shown in Table 15 indicate that, generally, the calculated alkalinity was slightly higher than observed values whereas the calculated rH was slightly lower than the observed pH values. This apparent anomaly is probably due to the assumption made in the calculations that the filter bed is a closed chemical system. However, the filters were open to atmosphere at the top suggesting some possible loss of carbon dioxide to atmosphere. In addition, carbonate and carbon dioxide may serve as a carbon source for the autotrophic bacteria in the filter bed. Thus it may be seen that when carbonate served as a carbon source for cell growth, the observed alkalinity values would be lower than the calculated values. Similarly, when carbon dioxide served as a carbon source for cell growth or lost from the system, the observed pH values would be higher than calculated values. The differences between the observed and calculated values of alkalinity and pH shown in Table 15 are considered to be due to the assumptions made in the calculations.

Chemical Treatment

From the studies of uptake of potassium permanganate by filter sand (Figure 5), a solution of 5000 mg/l of KMnO₄ was selected for the control of bacterial growth in the filter beds during the study at Rantoul, Illinois. Table 16 compares the quality of filtered water with respect to the influent quality before and immediately after the treatment. Filters B and C were treated with permanganate solution at pH 10.5, while Filter D was a control filter. Filter C was kept agitated with compressed air during the contact

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NEAN VALUES OF OBSERVED AND CALCULATED AIKALINITY AND PH OF FILTERED WATER FOR ALL RUNS OF PILOT PLANT STUDIES AT URBANA

		AIK	A LINITY .	ng/l				PH. UNIT		
		Calcu-	Devi-	Obs.	Cal.		Calcu-	Devi-	Obs.	Cal.
Sample	Observed	lated	ation	Depl.	Depl.	Obs.	lated	ation	Decrease	Decrease
Influent	331.64	ł	1	ł	I	7.80	ł	3	1	I
Effluent										
Filter 1	322.58	322.77	-0.19	9.07	8.87	7.58	7.51	0.07	0.21	0.28
0	321.72	321.57	0.15	9.92	10.07	7.56	7.50	0.06	0.23	0.30
m	321.76	321.87	-0.12	9.89	9.77	7.57	7.51	0.07	0.22	0.29
14	321.74	321.91	-0.18	9.91	9.73	7.57	7.50	0.07	0.22	0.29
л	318.22	319.09	-0.87	12.66	11.79	7.40	7.39	0.01	0.30	0.31
9	318.9h	318.99	-0.05	11.94	21.89	7.43	7.40	0.03	0.27	0.30
2	314.98	316.70	-1.72	15.90	14.18	7.32	7.34	-0.02	0.38	0.36



FILTERED WATER QUALITY BEFORE AND AFTER PERMANGANATE TREATMENT DURING PILOT PLANT STUDIES AT RANTOUL

	NH3-N	mg/l	DOm	g/1	AIKALIN	IITY, mg/l	pH,	<u>units</u>
Sample	Inf.	Eff.	Inf.	Eff.	Inf.	Eff.	Inf.	Eff.
Before Treatment	1.49	0.08	7.1	0.1	367	354	7.9	7.6
FILTER B After Treatment	1.52	2.38	7.0	7.3	365	364	7.8	7.8
Before Treatment	1.49	0.17	7.1	0.1	367	354	7.9	7.6
After Treatment	1.52	1.80	7.0	7.4	3 65	364	7.8	7.8
Before Treatment	1.49	0.29	7.1	0.1	367	351	7.9	7.6
FILTER D After Treatment	1.52	0.60	7.0	0.1	3 65	351	7.8	7.5

time of three hours. It may be seen that all filters showed signs of nitrification, namely, ammonia uptake and DO depletion, and decreases in alkalinity and pH before treatment. These changes continued in the control Filter D, but were not observed in Filters B and C after the treatment. The effectiveness of the permanganate treatment is also reflected in the changes in the bacterial concentrations on the filter sand. Table 17 compares the plate count of bacteria on sand and in water samples obtained before and after the treatment from Filter C and corresponding samples from control Filter D. The reductions of bacterial concentration due to permanganate treatment does not appear to be great, though the reduction in Filter C at the 4.5 inch level

BACTERIAL CONCENTRATION BEFORE AND AFTER PERMANGANATE TREATMENT DURING PILOT PLANT STUDIES AT RANTOUL

		PLATE COUN	IT - BACTERIA	
	Water samp	les, no/ml	Sand samp	oles, no/gm
Sample	Influent	Effluent	4.5 inch from top	14.5 inch from top
Before Treatment	183	4240	6.5 x 10 ⁴	3.9 x 10 ⁴
FILTER C After Treatment	1118	308	7.5 x 10 ³	2 x 10 ³
Before Treatment	183	3450	4.1 x 10 ⁴	11.1 x 10 ⁴
FILTER D After Treatment	1118	1930	4.5 x 10 ⁴	4.2 x 10 ⁴

was about 88 percent. It should be noted here that the nitrifying bacteria are not counted in the bacterial plate count using nutrient agar media. The nitrifiers are slow growers and would need specific media and long incubation times for enumeration. The fact that nitrification was inhibited as a result of permanganate treatment would support the conclusion that nitrifying bacteria have been minimized on the filter sand. The Table 17 shows the reduction in other bacteria present on the filter sand. Concentration of bacteria in the filtered water can also be seen to be reduced from Table 17 as a result of permanganate treatment.

Chlorine solution was used in the control of bacterial growth in sand filters used in the work at Urbana, Illinois. Filters 2 through 5 were treated with chlorine solutions at pH 4 of concentrations 75, 200, 400 and 1000 mg/l respectively. Table 18 shows the averages of results of analysis of influent and effluent water samples during runs before and immediately

FILTERED VATER QUALITY BEFORE AND AFTER CHLORINE TREATMENT DURING PILOT PLANT STUDIES AT URBANA

Con-	Time, Hours	ע ר	1	c	ſ	Ъ	<u>^</u>	٢	-
Chlo-	Dosage, mg/l	75	2	000	000	¢,	100		
units	Eff.	7.32	7.36	7.31	7.48	7.34	7.61	7.29	7.69
pH, 1	Inf.	7.75	7.71	7.72	7.73	7.72	7.73	7.67	7.74
mg/l	Eff	316	316	313	321.5	315	320.5	316	328.5
Alk.,	Inf.	332	330	330	331.5	330	331.5	332	331
mg/l	Eff.	0.33	0.39	0.0	0.93	0.25	1.57	0.29	2.09
·N-EHN	Inf.	2.43	2.38	2.19	2.26	2.19	2.26	2.40	2.43
mg/1	Eff.	0.05	1.20	0.1	2.8	0.05	5.2	0.0	7.5
DO,	Inf.	9.3	9.2	9•0	8	9.0	м. С	8°5	8.4
an i [rmaD	Time	End of Run	After BW* & Treatment	End of Run	After BM $\&$ Treatment	End of Run	After BM & Treatment	End of Run	After BM $\&$ Treatment
	Run	9tL	8µLL	94L	150	941	150	150	151
	Filter	FILTER 2		FILTER 3		FILTER 4		FILTER 5	

 $*^{*}BW = Backwash$

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after chlorine treatment of filters. In all cases, the analysis of samples before treatment showed nitrification, as seen from the ammonia uptake and D0 depletion and decreases in alkalinity and pH. Treatment of Filter 2 with chlorine solution of 75 mg/l was ineffective in bringing any significant change in the filtered water quality. Filter 3 treated with 200 mg/l solution of chlorine showed only a very small effect, as seen by the low concentrations of ammonia and D0 in the effluent. Filter 4, treated with 400 mg/l of chlorine, showed a greater inhibition of nitrification, but some nitrification was taking place in the filter. A solution of concentration of 1000 mg/l of chlorine was applied to Filter 5, and very little nitrification was observed in the filter as a result of the treatment. As had been observed before, the treatment was effective in inhibiting the nitrification for a short period of about a week, after which nitrification was taking place as before the treatment, due to reestablishment of nitrifiers.

Table 19 shows the comparison of COD and bacterial plate count on water and sand samples for Filters 2 through 5. The bacterial concentrations in water and on sand, before and after the backwash operation, and after the chlorine treatment for all filters were small. The variations observed in the numbers are not significant although the numbers were higher for the top of the bed. The COD of water is low and shows no significant change between influent and effluent, regardless of the chlorine treatment. The COD of sand samples leads to some interesting observations. There was generally some reduction in COD after a backwash operation possibly due to cleaning of the bed by backwashing. However, the chlorine treatment apparently failed to reduce the COD on sand significantly. This is perhaps due to the fact that the organic matter including the bacteria on the sand was not oxidized by chlorine. The bacteria were inactivated by chlorine. Once again, the

ATER		
FILTERED	ATMENT	URBANA
TID .	TRE	AT 5
SAND 4	ORINE	TUDIES
NO	CHI	E
NTRATIONS	AND AFTER	PIIOT PLAN
BACTERIAL CONCE.	BEFORE	DURING

			00	A			щ	Sacteria, Plant Co	unt
		later	Samples	Sand	Samples	Water S	amples	Sand S	amples
		Bm	/1	'Sur	ma/	n/ou	L L	no/g	m
lilter	Sampling Time	Inf.	Eff.	Top of Bed	Bottom of Bed	Inf.	Rff.	l Inch From Top of Bed	21 Inches From Top of Bed
	Before BW*	18.3	14.2	111.0	61.5	1290	810	10100	172
TLTER 2	After BW	1	1	74.5	67.2	ı	ı	483	75
(with	After								
(米花台	Treatment	10.7	13.2	85.5	113.0	920	140	198	2
	Before BW	О	5.6	163.0	50.5	54	12	1240	321
FILTER 3	After BU	I	I	0.4161	51.0		ł	162	212
(with SU)	Af ter								
	Treatment	2.6	2.6	84.5	46.0	42	12	6	-
	Before BW	0.5	4.6	358.0	27.0	54	20	3300	984
TLTER 4	After BU	1	I	353.0	45.6	1	I	1850	298
(vi thout	After								
SW)	Treatment	2.6	4.6	334.0	31.0	42	5	8100	19
	Before BW	10.3	12.3	280.0	42.6	21	49	254	88
FILTER 5	After BW	1	1	299.0	40.4	I	I	14120	34
(without	After								
(MS	Treatment	18.1	13.1	314.0	39.0	21	m	1130	2

^{}BW = Backwash ***SW = Surface wash 116
bacteria plate count did not include the nitrifiers. Hence the plate counts are not indicative of either the presence or absence of nitrifying bacteria.

No correlation between the COD and bacterial plate counts, either for water samples or for sand samples, was apparent from Table 19. However, Filters 2 and 3 operated with surface wash showed lower accumulation of organic matter in sand (as seen from COD values) than Filters 4 and 5 without the surface wash.

Chlorine was used at Urbana and potassium permanganate was used at Rantoul for the control of bacterial growth in filter beds. Though the work was carried out at two places with different waters, the similarities of nature of growth in filters allows a fair comparison. Comparing the treatment of filters with potassium permanganate and chlorine, it may be seen that the former was effective in inhibiting nitrification for about three weeks while the latter was effective at high concentration only for a short period of one week. The molar concentration of the solutions used, 5000 mg/l of permanganate (at pH 10.5) and 1000 mg/l of chlorine (at pH 4) are comparable, namely, 0.031 moles/1 of permanganate and 0.028 moles/1 of chlorine. It would therefore appear that permanganate at pH 10.5 is a better chemical agent for the control of nitrifying bacteria. Potassium permanganate has the advantage of being reusable with only makeup requirement of chemicals. Chlorine has the advantage of being readily available in a water treatment facility. Longer contact times are required with chlorine, with more frequent applications for the control, while shorter contact time and less frequent applications are sufficient for permanganate. These observations may be used in economic considerations for the chemical agent to be used in any given situation.

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Cost Estimates of Chemical Treatment

Making certain assumptions, it is possible to compare the costs of treatment of filters with potassium permanganate and chlorine. Considering a filter consisting of a 30 inch sand bed supported by 12 inches of gravel, and assuming that the porosities of sand and gravel are respectively 35 and 50 percent, the solution required to submerge the filter bed by six inches is calculated to be 14 gallons per square foot of filter bed exclusive of storage in pipes, underdrains, etc. For a filter of size 10 ft x 10 ft, the amount of solution required is 1400 gallons.

Since it was found that a solution of potassium permanganate of 5000 mg/l, in 0.1 N $\operatorname{Na_2CO_3}$ (to give a pH of 10.5) was effective in inhibiting nitrification for three weeks, and estimating that the make-up requirement of chemicals is 1/3 for each reuse of the solution, it is calculated that the weekly requirement of chemicals are: 6.5 lbs of $\operatorname{KMnO_4}$ and 6.9 lbs of $\operatorname{Na_2CO_3}$. A contact time of three hours was found to be necessary. The chemical cost per week for permanganate treatment is therefore:

5.5	lbs of	$KhinO_{\mu}$ at $\mu O \phi/1b$	Ξ	\$ 2.60
5.9	lbs of	Na2CO3 at 40/1b	Ξ	 0.27
	Cos	t per week		\$ 2.87

On the other hand, it has been found that a solution of chlorine, 1000 mg/l of pH μ , with a contact time of seven hours, was effective in inhibiting nitrification for one week. When chlorine solution is prepared from gaseous chlorine in distilled water, the pH of resulting solution is calculated to be considerably less than μ . However if bleaching powder is used, considerable acid will be required to lower the pH to μ . It is assumed here gaseous chlorine is used so that no pH adjustment is necessary. The chemical

requirement is calculated to be 11.7 lbs of chlorine/week. The chemical cost at $10\phi/1b$ of chlorine is \$1.17/week. It is concluded from these estimates that chemical cost for chlorine treatment is less than that for permanganate.

Microbiological Aspects

General

The microbiological quality of water is usually judged from the concentration of coliform organisms (43). Recently, interest in fecal coliform and fecal streptococci has increased so that these organisms are used as indicators of pollution in addition to, or in the place of, coliforms as a group. It should be realized that there may be present in water many other kinds of bacteria of unknown public health significance. Most of the bacteria that can be grown on agar media as in a total plate count are probably harmless. However, their occurrence in large numbers in water supplies should be cause for suspicion.

A sand filter is normally able to remove a high percentage of coliform bacteria during filtration. At the same time, high concentrations of bacteria determined by the total plate count method in the filtered water have been reported (41). Because of the large surface area of the sand particles and laminar flow of water through the filter, a sand bed often becomes a breeding site for bacteria. The bacteria of interest that are known to be responsible for chemical changes in water quality will be briefly considered here.

Nitrifiers

Nitrifiers are chemoautotrophic aerobic bacteria, and utilize carbon dioxide and bicarbonate as a carbon source and ammonia-nitrogen as a nitrogen as well as an energy source. They are present in soil and are of great importance in the nitrogen cycle in nature. The most common genera of

of nitrifiers are <u>Mitrosomonas</u> and <u>Nitrobacter</u>. The former is known to oxidize ammonia to nitrite, and the latter, nitrite to nitrate. This oxidation rate has been reported to be greatest at pH between 8.5 and 8.8, with an optimum temperature of about 30° C (46). These bacteria are inhibited by the presence of excessive amounts of organic matter. Thiourea was used as an inhibitor of nitrification by Ghosh (41), and a 0.2 percent sugar solution is reported to be strongly inhibitory (70).

In the present investigation, the presence of nitrifiers in the filter was inferred from the chemical changes observed during filtration.

Iron Bacteria

It is generally believed that iron bacteria are autotrophic and can derive the energy required for metabolism from the oxidation of ferrous iron to ferric iron. The formation of a sheath or stalk is a typical morphological feature or iron bacteria (46).

<u>Gallionella</u> is recognized by its twisted ribbon-like stalks, made up of ferric hydroxide and organic matter. Figure 22 shows the photomicrograph of slime taken from the wall of the sedimentation tank at the inlet end of pilot plant at Urbana. The twisted stalks seen in the Figure 22 were identified based on morphological features to be those of Gallionella.

<u>Sphaerotilus</u> is the other most common genus among the iron bacteria (46). The bacteria comprise sheathed filaments. Figure 23 shows some filaments presumed to be <u>Sphaerotilus</u> based on morphological features. The bacteria that are lost from the sheaths start new sheaths. The figure shows some half-empty sheaths.

Sulfate-Reducing Bacteria

Sulfate-reducing bacteria are strict anaerobes. They are curved rods of the vibrio type (46). The optimum temperature of their growth has been



FIGURE 22. CLUSTER OF GALLIONELLA STALKS FOUND IN THE SLIME OBTAINED FROM SEDIMENTATION TANK (x830)

FIGURE 23. "IRON BACTERIA", SHEATHS OF SPHAEROTILUS (×830) FOUND IN THE SLIME FROM SEDIMENTATION TANK reported to be about 30°C (71). The muisance from these bacteria is greater in the warmer months of the summer in distribution systems and other water treatment units (71). Because they are strict anaerobes, all of the oxygen must disappear before sulfate-reducing bacteria can grow, and reduce sulfate to hydrogen sulfide. The production of hydrogen sulfide has many secondary effects in addition to imparting a rotten-egg odor to the water. Important among these changes are the precipitation of metal sulfides and the possible reduction of iron from the ferric to ferrous state. In the latter case, the significance of sulfate-reducing bacteria in filter beds may be very great indeed, though not widely recognized so far. The bacteria are curved rods, belonging to the genus, <u>Desulfovibrio</u>. The slime taken from the raw water line of the pilot plant at Urbana showed typical vibrio type bacteria as shown in Figure 24, which may be sulfate-reducing bacteria. The presence of some hydrogen sulfide found in the raw water was perhaps due to these bacteria.



FIGURE 24. VIBRIC TYPE BACTERIA POSSIBLY SULFATE REDUCING BACTERIA FOUND IN THE SLIME FROM RAW WATER PIPE ×2100



VII. SUMMARY AND CONCLUSIONS

General

The rapid sand filter as presently designed and used in practice has the highest cost-benefit ratio of any unit water treatment process (72). However, instead of being beneficial, some filters have been known to be harmful in that the filtered water has deteriorated in quality in some respects (41). Many iron removal plants fail to remove iron satisfactorily. Often, considerable iron is found in the filtered water (41, 42, 45, 73-75). Such conditions have been reported to be due to bacterial growths in the filters (41).

Most recent studies dealing with filtration consider primarily the removal of suspended matter by the filter media (26-29, 76). Chemical aspects, when considered, have been limited to the effects of the chemical environment on the removal of suspended matter (77, 78). The effects of filtration rate on the quality of filtered water has also been reported (31, 32, 33). Backwash operations have been studied in relation to the quality of filtered water (79-81), and a new method proposed (82).

Most often, studies on filtration have been made employing clean filter beds. It is well known that the character of the filter medium changes with continuous operation, a process generally called "filter-ripening." The problems associated with distribution systems resulting from long usage have been described by Jarson as "disorders of age" (71). The fact that filter repairing and rebuilding is practiced (83-85) in the case of old filters, emphasizes the need for taking preventive measures towards avoiding the "disorders of age" in the filters.

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The investigation described here draws attention to the implications and significance of bacterial growths in filter beds in relation to the chemical changes taking place during filtration.

Summary

Pilot plant studies were carried out for nearly five months at Rantoul and for ten months at Urbana, Illinois, in the treatment of aerated ground waters for the removal of iron by filtration.

In the work at Rantoul, nearly complete depletion of DO and considerable depletion of ammonia were observed during filtration after about eight weeks of operation. Accompanying the depletion of DO and ammonia were decreases in alkalinity and pH. These changes were attributed to the biological process of nitrification.

The work at Urbana indicated that nitrification occurred in the filters in four weeks of operation as seen from the depletion of ammonia and decrease in DO, accompanied by decreases in alkalinity and pH. These were confirmed to be due to nitrification from the observation of the formation of nitrite and nitrate. The observed chemical changes were in very good agreement with the stoichiometric relationships.

Surface wash devices employed in the experimental filters were effective in cleaning the sand that formed into a filter cake at the top of the bed during filtration. The absence of surface wash as part of backwash created extensive mudball formation in the filter bed. Use of compressed air to scour the filter bed during backwash was also found to be effective in cleaning the filter bed, though the extra plumbing and source of compressed air required may not be economical compared with the surface wash devices. The air scour only delayed the growth of bacteria on the filter sand, but did not prevent

it.

Treatment of filters containing the bacterial growth with a potassium permanganate solution of concentration of 5000 mg/l at a pH of about 10.5 and a contact time of three hours was found to be effective in inhibiting the nitrification for a period of about three weeks in the pilot plant studies at Rantoul. A chlorine solution was used in an effort to control the bacterial growth in filters at Urbana. A solution of chlorine, 1000 mg/l at pH 4, and a contact time of seven hours was found to be effective in inhibiting the nitrification for only about a week.

Iron removal in all filters, both at Rantoul and Urbana, was very satisfactory. The concentration of iron in the filtered water averaged well below the 0.3 mg/l as given in the Drinking Water Standards of U.S.P.H.S. (43). Iron breakthrough in filters was not observed in the operation of filters for periods of up to ten months, although Ghosh has suggested that nitrification is responsible for breakthrough of iron in filters (41)

Conclusions

Based on the experimental results of this investigation, it is concluded that:

1. Surface washing devices are required to adequately clean the filter bed and prevent the formation of mudballs in the operation of filters for iron removal. However, surface wash will not prevent the growth of bacteria on the filter sand.

Alternately, the use of compressed air to scour the filter bed during backwash is not any more effective in controlling the growth of bacteria on the filter sand than surface wash, although air scour was also effective in preventing mudball formation.

2. The mudball formation which took place in the experimental filters without surface wash had no effect on the filtered water quality.

3. Nitrification takes place in the filter when the filter influent contains ammonia and DO, resulting in the formation of nitrite and nitrate in the filter effluent. Nitrification could result in dissolved oxygen depletion in the water being filtered and may cause anaerobic conditions in the filter bed. Decreases in alkalinity and pH accompany the process of nitrification in the water being filtered. Denitrification may take place in the filter under conditions of favorable temperature and presence of reducing agents like ferrous carbonate.

4. The chemical changes in the alkalinity and pH observed during filtration of aerated ground waters were found to closely conform to stoichiometrically predicted values based on the process of nitrification.

5. Iron removal was very satisfactory in the filters in spite of nitrification, though the work of Ghosh had suggested that breakthrough of iron may take place in filters under such conditions (41). It now appears that nitrification may be a necessary, but not a sufficient, condition for the breakthrough of iron in filters.

6. Potassium permanganate was found to be more effective than chlorine in inhibiting the process of nitrification in filters, though the chemical cost for chlorine treatment was estimated to be less than that for permanganate treatment.

Engineering Significance

Water Quality Criteria set by the AWWA Task Group 2225 M describe quality water as (86):

"Ideally, water delivered to the consumer should be clear, colorless, tasteless, and odorless. It should contain no pathogenic organisms and be free from biological forms which may be harmful to human health or aesthetically objectionable. It should not contain concentrations of chemicals which may be physiologically harmful, aesthetically objectionable, or economically damaging. The water should not be corrosive or incrusting to, or leave deposits

on, water-conveying structures through which it passes, or in which it may be retained, including pipes, tanks, water heaters, and plumbing fixtures. The water should be adequately protected by natural processes, or by treatment processes, which insure consistency in quality."

The quality water desired, though technologically attainable, is economically impractical in most cases at the present time. The work reported here is aimed at understanding the chemical forces at work in the filtration of aerated ground waters, which in turn will hopefully contribute towards achieving the above goal of quality water.

Whether nitrification in filter beds is objectionable or not may depend on many circumstances. If the nitrification increases the nitrate concentration in the filtered water to undesirable levels (h_3) , it would be desirable to inhibit nitrification not only in the filters, but also in the distribution system. If the nitrification contributes to other secondary effects such as breakthrough of iron, then also it should be inhibited. If the nitrate and ammonia concentration of the filter influent is small (less than 1 mg/1), the oxygen demand is not large enough to cause anaerobic conditions in the filter when the raw water is aerated sufficiently. It may, in such cases, be desirable to allow the nitrification to proceed in the filter as otherwise the slime growths may occur in water mains (71). Removal of ammonia may be considered for the raw water so as to prevent nitrification in filters as well as distribution systems. When the filter bed contains other bacteria, in addition to nitrifiers, chemical control may be desirable. Economical considerations usually would dictate the course of action in any given problem.

Because physical methods, e.g., air scour or surface wash prior to backwash, for the control of bacterial growth in sand filters were not effective, chemical methods become necessary. Potassium permanganate and chlorine have been found to be effective. When chemical treatment of filters need be

practiced regularly as indicated in the studies reported here, some changes in the design and operation of water treatment plants become imperative. Important among the changes is the provision for storage and application of solution of desired chemical agent to the filters. In case of potassium permanganate, a pump may be needed to enable the solution to be reused. In case of chlorine, more frequent treatment would be required with longer contact time so that filter area requirement may be increased. Storage and handling of the chemicals also should be considered.

Suggestion for Future Work

Breakthrough of iron in many iron removal plants is a real problem. Nitrification has been reported to be responsible for the phenomenon. However, the present work has shown that nitrification alone does not result in breakthrough of iron in filters. More work needs to be carried out to determine all of the factors involved in breakthrough of iron. In this connection, the role of sulfate reducing bacteria deserves serious consideration because of the possibility that the hydrogen sulfide produced by sulfate reduction may be responsible for breakthrough of iron. After all the factors involved are recognized, the mechanism of iron breakthrough also need be delineated. After a complete understanding of the phenomena and mechanism involved, modification of design and operation of iron removal plants would be necessary to ensure a finished water of high quality with respect to iron.

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APPENDIX

This Appendix contains the data obtained from the pilot plant studies at Urbana, Illinois. Tables A-1 through A-10 represents the data obtained during experimental work. The abbreviations used for the column titles in the tables are:

RUN NO		The run during which the sampling was made. The values
		given for a particular run are averages for that run.
TEMP	*	Temperature of water samples, C
PH	:	pH of water samples, units
DO	:	Dissolved oxygen concentration in water, mg/l
FE2T	•	Total ferrous iron concentration, mg/l
FE2F	:	Filtrable ferrous iron concentration, mg/l
FET	*	Total iron concentration, mg/1
ALK	:	Alkalinity, mg/l as CaCO3
HDNS	:	Hardness, mg/l, as CaCO3
NH3N	:	Ammonia nitrogen concentration, in mg/l
NOSN	:	Nitrite nitrogen concentration, in mg/l
NO3N	:	Nitrate nitrogen concentration, in mg/l

In Tables A-11 through A-17, the abbreviations used for the column titles are:

NRUN	: RUN NO as above
THIN	: Total nitrogen concentration in the filter influent, (NH3N+ NO2N+ NO3N), in mg/l
TNEF	: Total nitrogen in the effluent. in mg/l
PCNV	: Percent variation of TNEF with reference to TNIN
TDOD	: Theoretical dissolved oxygen demand, mg/l, calculated as 4.55 x (NO3N formed) + 3.42 x (NO2N formed)
TRDOD	: A ratio. TDOD/(NO3N formed+NO2N formed). to indicate
	the degree of nitrification
DOUP	: The difference in the mass balance of dissolved oxygen between filter influent and effluent, assumed to be due
	to biological uptake. mg/l
AIKCOM	: Computed alkalinity of filter effluent from the data of
	nitrite and nitrate formed
ALKVAR	: Observed alkalinity of filter effluent - ALKCOM
DAIKCOM	: Observed alkalinity of filter influent - AIKCOM
DAIKOBS	: Observed difference between the alkalinities of
	filter influent and effluent
PHCOM	: pH of filter effluent calculated from the data of
	nitrite and nitrate formed
PHVAR	: Observed pH of filter effluent - PHCOM
DPHOBS	: Observed difference between the pH's of filter
	influent and effluent
DPHCOM	: Observed pH of filter influent - PHCOM

DOD : Difference between the dissolved oxygen concentrations of filter influent and effluent RDOD : A ratio, DOD/(NH3N in influent - NH3N in effluent) AIKIN : Alkalinity in the filter influent, mg/l as CaCO3. (Observed) AIKEF : Alkalinity in the filter effluent, mg/l as CaCO3. (Observed) AIKCAL : Calculated alkalinity in the filter effluent from the data of ammonia depletion in the filter AIKDEV : Observed alkalinity of filter effluent - AIKCAL DAIKOBS : Observed difference between the alkalinities of filter influent and filter effluent DAIKCAL : Observed alkalinity of filter influent - AIKCAL PHIN : Observed pH of filter influent PHEF : Observed pH of filter effluent PHCAL : Calculated value of pH of filter effluent from the data of ammonia depletion on the filter : Observed pH of filter effluent - PHCAL. PHDEV DPHOBS : As before DPHCAL : Observed pH of filter influent - PHCAL

For all values found in a given column, the statistical evaluations were made and the results given at the bottom of all tables.

Tables A-18 through A-24 contain the following abbreviations:

TABLE A-1

	RUN	NC DAY BEGIN	DAY END	RUN LENGTH
	1	0.25	2.35	2.00
	3	4.35	6.35	2.00
	4	6.35	8.40	2.05
	6	10.35	12.35	2.00
	7	12.35	14.35	2.00
	q	16.35	18.35	2.00
	10	18.35	20.35	2.00
	11	20.35	22.35	2.00
	13	24.35	26.35	2.00
	14	26.35	28.35	2.00
	16	30.35	32.35	2.00
	17	32.35	34.35	2.00
	19	36.35	38.35	2.00
	20	38.35	40.40	2.05
	22	42.35	44.35	2.00
Í	23	44.35	46.35	2.00
	2.5	49.45	50.45	2.00
	20	50.35	52.35	2.00
	28	54.35	56.30	2.00
	29	56.30	58.35	2,05
	31	58+35 60+35	60.15	2.00
	32	62.40	64.40	2.00
	34	64+4(66+4C	66.4C 68.40	2.00
	25	68.40	70.40	2.00
	36	70.40	72.40	2.00
	38	74.40	76.40	2.00
	40	76.40 78.4C	78.40 80.40	2.00 2.00
	41	80.40	92.40	2.00
	43	86.40	86.40	2.05
	4.6	90.35	92.30	1.95
ł.	4.8 50	94.25	56.30 100.35	2.05
	51	100.35	102.35	2.00
	53 55	104.35	106.40	2.05
	57	112.50	114.5C	2.00
	61 61	116.50	118.50	2.05
	63	124.55	126.55	2.00
	£4 £6	126.55	128.55	2.00
	6.9	134.50	136.55	2.05
	70	138.50	140.45	1.95
	74	146.50	148.50	2.00
1	76 78	150.50	152.50	2.00
	εc	158.50	160.50	2.00
U.	F 2	162.45	164.40	1,95
	85	168.45	170.45	2.00
	96	170.45	172.50	2.05
	SC	179.65	190.65	2.00
	<5 6 0	188.45	190.45	2.00
	c.y	104.45	196.45	2.00
	102	202.50	204.55	2.05
	110	212.50	220.55	2.10
	113	223.65	224.95	1.30
	110	231.20	232.45	1.20
	123	236.20	237.45	1.25
	131	241.20	248.80	1.30
	134	252.40	254.50	2.10
	137	258.50	266.50	2.00
	143	270.35	272.25	1.90
	146	276.35	278.40	2.05
	161	286.55	288.55	2.00
	153	290.50	292.55	2.05
	157	29 P. 45	300.55	2.10

TABLE A-2

RUN NO	TEMP	РН	FE 2 T	FE2F	FET	NH3N	ALK	HDNS
1	15.90	7.25	1.15	1.07	1,17	1.14	331.50	240.00
2	17.00	7.16	1.C2	C.92	1.14	1.15	334.50	249.00
3	15.10	7.19	1.04	0.88	1.08	1.11	332.50	246.50
4	16.90	7.17	1.20	0.98	1.10	1.15	334,50	246.00
6	16.20	7.14	1.37	1.23	1.22	1.33	332.00	248.00
7	16.10	7.14	1.36	1.23	1.17	1.13	331.50	248.00
9	15.80	7.13	1.25	1.17	1.20	1.05	331.50	246.00
10	16.50	7.10	1.38	1.10	1.29	1.11	330.50	243.00
11	15.80	7.12	1.27	1.24	1.12	1.09	331.00	240.00
12	15.70	7.09	1.33	1.21	1.01	1.04	331.00	239.50
14	16.60	7.13	1.23	1.13	1.20	0.94	330.00	240.50
15	15.50	7.10	1 • 2 C	1.08	1.02	0.98	331.00	241.50
16	16.00	7.12	1.21	1.08	1.19	0.98	334.50	246.0C
18	17.40	7.08	1.20	1.05	1.16	1.05	333.50	246.00
19	15.70	7.11	1.23	1.13	1.19	1.01	334.00	246.00
20	15.80	7.19	1.24	1.10	1.23	1.02	332.00	244.00
22	15.90	7.18	1.20	1+15	1.11	0.56	330.50	245.00
23	17.50	7.16	1.43	1.11	1.26	1.00	333.50	248.00
24	16.90	7.14	1.27	1.07	1.28	1.01	377.00	247.00
25	16.30	7.10	1.24	1.10	1.31	1.01	332.50	246.00
27	15.60	7.1C	1.25	1.14	1.21	0.98	331.00	245.00
28	16.90	7.17	1.28	1.08	1.20	1.05	334.00	247.00
30	17.00	7.08	1.12	1.19	1.38	1.14	334.00	247.50
31	17.60	7.14	1.15	1.03	1.47	1.07	373.00	245.50
32	16.90	7.18	1.16	1.04	1.28	1.10	335.50	246.00
3.3	16.60	7.13	1.19	1.05	1+14	1.06	332.00	246.50
35	16.40	7.13	1.23	1.11	1.11	1.04	332.50	246.00
36	16.60	7.17	1.26	1.13	1.11	1.01	331.50	248.00
38	16.40	7.10	1.28	1.21	1.24	1.05	331.50	248.00
39	16.40	7.07	1.28	1.10	1.21	1.12	333.50	246.50
40	16.40	7.14	1.30	1.06	1.28	0.94	333.50	245.00
43	16.20	7.15	1.37	1.15	1.13	1.00	337.00	246.00
44	16.10	7.18	1.37	1.11	1.12	1.00	374.50	245.50
46	15.60	7.15	1.28	1.09	1.05	1.13	333.00	245.50
50	15.50	7.17	1.27	1.11	1.14	1.08	333.50	246.00
51	15.50	7.21	1.27	1.09	1.09	1.15	326.50	246.50
53	15.30	7.20	1.17	1.06	1.08	1.13	337.50	247.00
57	15.40	7.17	1.21	1.12	1.15	1.05	336.00	246.00
59	15.70	7.16	1.22	1.15	1.19	1.07	331.50	246.00
61	15.20	7.18	1.20	1.12	1.04	1.12	334.50	246.00
64	14.90	7.20	1.25	1.12	1.20	1.08	338.50	248.50
66	15.10	7.21	1.20	1.10	1.15	1.06	335.00	248.00
68	15.00	7.19	1.22	1.11	1.16	0.99	336.00	247.00
72	15.20	7.22	1.30	1.13	1.13	1.00	334.50	249.50
74	14.80	7.21	1.27	1.19	1.23	1.05	336.50	244.00
76	14.90	7.23	1.34	1.17	1.13	0.99	336.00	245.00
80	15.00	7.21	1.24	1.12	1.14	0.99	336.00	243.00
82	14.90	7.21	1.23	1.11	1.13	0.95	327.00	247.00
85	14.70	7.21	1.29	1.18	1.33	1.00	335.50	245.00
86	14.50	7.21	1.25	1.06	1.29	0.96	336.50	245.50
88	14.60	7.1t	1.34	1.14	1.17	0.95	336.00	249.00
95	14.40	7.17	1.31	1.20	1.34	1.02	339.50	246.00
98	14.40	7.24	1.33	1.20	1.38	1.02	335.00	246.00
102	14.30	7.18	1.30	1.21	1.39	1.02	374.00	245.50
107	15.40	7.17	1.42	1.13	1.18	1.04	335.50	245.50
110	14.30	7.19	1.22	1.07	1.13	0.98	336.00	246.50
113	14.40	7.15	1.29	1.27	1.19	0.99	334.00	246.00
119	14.60	7.18	1.60	1.24	1.46	1.01	337.00	247.00
123	14.80	7.10	1.22	1.22	1.09	0.99	336.50	247.00
127	14.70 14.70	7.16	1.28	1.18	1.06	0.97	333.50	242.00
134	14.80	7.14	1.28	1.18	1.11	0.98	332.50	243.00
137	15.00	7.14	1.45	1.37	1.26	0.97	33.00	243.50
143	14.90	7.10	1.49	1.25	1.20	0.99	334.00	244.00
146	14.80	7.16	1.35	1.26	1.62	0.96	372.50	244.50
149	14.70	7.16	1.32	1.21	1.28	0.95	332.00	243,00
1=3	14.90	7.14	1.45	1.31	1.27	0.99	334.00	245.00
155	14.60	7.12	1.45	1.75	1.15	0.98	334.00	244.00
157	15.20	7.15	1.55	1 + 4 1	1.12	0.97	156.00	245.00
STATISTI	CAL EVALUA	AT LONS						
Mean	15.63	7.17	1.28	1.15	1.20	1.04	333.82	245.68
Minimum	14.20	7.07	1.02	0.88	1.01	. 0.94	326.50	239.50
Standard Deviation	0.88	7.39	0.10	0.09	0.11	0.08	2 24	249.50



TABLE A-3

DATA	0F-	FILTER	INFLUENT

RUN NU	TEMP	₽н	D.C.	FE 2 T	FET	ALK	HDNS	NH 3N	N02N	N0.3**	F F > F
1	17.70	7.01	8.40	0.30	1.07	332.00	246.00	1.11			0.07
2	18.30	7.83	9,70 8,50	0.15	1.08	332.00	248.00	1.20	_		0.01
4	16.80	7.81	8.4(0.23	1.11	329.00	247.00	1.06		_	1.11
5. E	17.40	7.84 7.82	8.40 8.50	0.31 0.34	1.13	331.00 329.00	246.00	1.11	_	_	0.11
7	16.70	7.84	8.50	0.41	1.09	327.00	246.00	1.07	-	-	0,22
c	17.10	7.82	8.00	0.37	1.18	330.00	246.00	0.97		_	0.14
10	17.50	7.86	8.80	0.33	1.20	331.00	242.00	0.98	-	_	0.21
12	18.40	7.79	P.40	0.20	0.91	330.00	238.00	0.85	-	_	2.21
13	18.30	7.88	8.40	0.24	0.08	331.00 331.00	240.00	0.90	_	_	0.17
15	17.90	7.97	P.70	0.21	0.98	331.00	241.00	0.93	-	-	2.11
17	18.60	7.85	8.20	0.14	1.16	335.00	246.00	0.91	_	_	0, r x
19	18.50	7.86 7.84	8.20 8.70	C.16 0.21	1.09	332.00 335.00	246.00 246.00	0.97	_	_	7.05
20	17.20	7.85	8.70	0.21	1.09	329.00	245.00	0.89	-	-	2.11
22	17.00	7.84	8.80	0.17	0.92	330.00	244.00	0.87	_		2.13
23	19.10	7.83	8.1C 8.30	C.22	1.26	332.00	247.00	0.82	_	_	0.11
25	18.50	7.90	A.40	0.12	1.26	330.00	246.00	0.86	-	_	0.54
26	17.60	7.85	8.80 8.80	0.15	1.23	331.00 333.00	245.00 245.00	0.85	_	-	2.05
28	18.40	7.87	8.5C	0.35	1.17	335.00	246.00	0.96		-	7.11
30	18.60	7.84	8.40	0.17	1.36	332.00	245.00	0.91	_	_	0.05
31 32	10.10	7.92	8,5C 8,40	0.11	1.31	332.00	245.00 247.00	0.89	_		0.0
33	18.30	7.85	9.60	0.12	1.05	332.00	246.00	0.85	-		2.01
35	17.40	7.89	8.60	0.16	0.99	330.50	245.50	0.88	_	_	7.04
36 37	17.70	7.89	8.EC 8.7C	0.14	1.04	337.00 331.00	248.00	6.93 6.93	_	_	7.04
38	17.50	7.89	8.60	0.21	1.19	331.50	248.50	0.97	_		1.00
40	17.50	7.82	8.40	0.13	1.12	332.50	246.50	C.78	_	_	0.02
41	17.60	7.89 7.85	8.5C 8.7C	0.24 0.21	1.10	334.00	245.50 245.50	0.79	_	_	0.00
44	17.50	7.89	9.60	0.23	1.01	335.50	244.00	0.90	_	-	. 10
40	17.50	7.92	6.60	0.19	0.89	334.00	247.50	0.67	_	_	1.96
50 51	17.00	7.63	6.5C	0.24	1.11	331.50 332.00	246.00	0.98	_	_	5.00 0.00
53	16.70	7. 55	8.70	0.10	0.99	335.50	247.50	7.52	-	-10	1.11
57	16.20	7.PC	8.6C	0.16	1.05	337.50	246.00	2.2?	_	_	n.n
59	17.20	7.81 7.80	8.6C 8.5C	0.17	1.08	328.00	246.00	2.33	_	_	0.04
63	16.70	7.82	P.60	0.1-	1.13	333.00	248.00	2.58	_	-	1.12
64	16.40	7.79	8+5C 8+6C	0.13	1.10	332.00	249.00	2.44	_	_	0.01
£8 70	16.40	7.77	8.40	0.11	1.09	332.50 334.00	248.00	2.17	_	-	0.0
72	16.40	7.82	8.80	0.19	1.05	333.50	249.00	1.97		_	0.07
74	16.30	7.8C 7.7S	8.70	0.18 0.23	1.05	334.00 334.00	243.00	2.02	-	_	0.00
78	16.30	7.79	9.10	0.15	1.03	332.50	245.00	2.05	-	-	2.03
82	16.70	7.74	8.20	c.0	6.94	333.00	247.00	2.04	_	_	0.0
83 85	16.70	7.73 7.69	8.40 8.40	0.11 0.07	0.95	333.00	245.00 245.00	2.19	_	-	0.03
86	15.50	7.71	9.20	0.14	1.20	333.50	244.00	2.05	C. C2	0.74	1.02
90	15.70	7.86	8.20	0.16	1.25	336.50	247.00	2.19	0.01	0.24 0.74	0.07
95	15.30	7.65	8.70 8.60	0.15	1.21	334.00	247.00 245.00	2.03	0.02	0.45	0.06
99	15.10	7.74	R. 70	0.21	1.20	333.50	245.50	5.20	0.02	0.41	0.11
102	15.60	7.74	9.50	0.11	1.04	336.00	245.00	3,55	0.0?	0.38	0.01
110	15.10	7.77 7.58	9.60	0.04	1.43	334.50	246.50	3.50 2.51	0.05	0.27	2.02
115	15.60	7.52	8.50	0.25	4.88	325.00	246.00	2.73	0.04	0.28	0.0
119	15.70	7.65	9.1C 8.70	0.25	5.23	326.50	247.00	2.62	0.04	C.43	0.02
127	15.40	7.59	9.00	0.22	4.85	321.50	242.50	2.82	0.02	0.39	1.03
134	15.80	7.70	5.5C	0.10	0.94	332.50	247.50	2.67	0.01	0.17	0.01
137	15.90	7.69	5.30 9.6(C.18 0.23	1.16	332.50	242.50	2.60	C.01	0.28	C.06
143	15.50	7.75	09.0	0.11	0.98	331.00	244.00	2.42	0.02	0.48	2.0
140	15.30	7.72	9.00	0.06	1.04	330.00	244.00	2.19	0.02	0.43	0.0
151	16.30	7.76	8.50 8.20	0.11 0.10	1.19	331.00 332.00	243.CO 244.CO	2.46	0.02	0.24	1.03
155	15.70	7.74	9.40	0.19	1.06	330.00	244.00	2.81	0.02	0.50	0.03
	10.10	1.19	0.41	0.19	0.74	0.00					
STATISTI	CAL EVALUA	TIONS									
Mran	16.89	7.80	8.62	0.18	1.31	331.64	245.47	1.67	0.02	0.35	0.06
Minimum	15.10	7.52	6.40	0.0	0.0	321.50	238.00	0.78	0.0	0.17	0.00
Maximum	19.10	7.92	9.80	0.41	5.23	336.50	249.00	5.20	0.05	0.52	0.22
Oeviation	1.11	0.09	0.46	0.08	0.89	2.87	2.03	0.90	0.01	0.09	0.06

TABLE A-4 CATA OF FILTER #1 EFFLUENT

1 1 0 0 1 0 1	RUN NO	TEMP	PH	0.0.	FE21	FET	ALK	HONS	NH3N	NO 2N	ND 3N
1 1 0	1	18.30	7.86	8.10	C.C1	0.23	323.00	240.00	1.05	_	_
1 1 0 0 1 3 0 0 0 1 1 1 1 0	2	19.00	7.87	8.20	0.0	0.15	331.00	248.00	1.13	_	
S 18.20 7.60 7	3	18.00	7.92	8.30	0.03	0.11	330.00	246.00	1.07	_	_
6 184.10 7.41 6.00 0.23 325.00 247.00 0.45	5	18.20	7.85	7.80	0.09	0.26	329.00	246.00	0.98	_	-
1 1	6	18.10	7.01	8.00	0.23	0.23	325.00	247.00	0.96	-	-
B B	7	17.90	7.82	7.70	0.21	0.21	326.00	246.00	0.80	_	_
10 14.50 7.73 6.10 0.21 0.20 337.60 242.60 0.33	9	18.30	7.73	6.10	0.17	0.22	323.00	244.00	0.37	_	-
1 1	10	18.50	7.73	6.10	0.21	0.20	327.00	242.00	0.32	-	-
13 19.10 17.70 4.40 0.07 0.03 224.00 240.00 0.00	12	18.40	7.63	5.40	0.17	0.08	322.00	239.00	0.17	_	_
1 9-40 7.12 4-26 0.00 0.01 332.00 240.00 0.01 15 13.4 7.13 4-16 0.02 0.01 337.00 244.00 0.02 15 13.4 7.13 4-16 0.02 0.01 337.00 244.00 0.02 16 14.10 7.13 4-16 0.01 0.02 334.00 244.00 0.01 21 18.20 7.13 4-16 0.01 334.00 244.00 0.01 23 18.20 7.16 4-16 0.01 334.00 244.00 0.01 24 19.20 7.16 4-16 0.01 334.00 244.00 0.01	13	19.30	7.74	4.90	0.07	0.03	324.00	240.00	0.0	_	_
16 16 17 15 16 17 15 16 17 15 16 17 15 16 17 15 16 17 15 16 17 15 17 17 15 17 17 18 17 17 <th18< th=""> 17 18 17<!--</td--><td>14</td><td>19.40</td><td>7.72</td><td>4.20</td><td>0.08</td><td>0.01</td><td>322.00</td><td>240.00</td><td>0.01</td><td>_</td><td>-</td></th18<>	14	19.40	7.72	4.20	0.08	0.01	322.00	240.00	0.01	_	-
17 19.40 7.71 4.10 0.63 0.19 324.00 2.46.00 0.65 - - 18 19.40 7.71 4.40 0.60 0.64 - - - 20 18.10 7.71 4.40 0.60 0.40 0.44.00 0.64 - - 21 18.20 7.71 4.40 0.60 0.44.00 0.60 - - - 22 19.20 7.75 4.10 0.60 0.12 325.00 2.44.00 0.60 - - - 25 19.20 7.75 4.10 0.63 0.13 325.00 2.44.00 0.60 - - - 26 19.20 7.75 5.10 0.63 0.13 325.00 2.44.00 0.60 -	16	19.10	7.65	4.30	C.04	0.08	327.00	247.00	0.05	_	-
B B B C <thc< th=""> C <thc< th=""> <thc< th=""></thc<></thc<></thc<>	17	19.40	7.71	4.10	0.03	0.19	328.00	246.00	0.05	-	-
20 18:10 7:11 4:70 0:10 0:00 324:00 244:00 0:00	18	19.40	7.73	4.10	C.04	0.09	327.00	248.00	0.08	_	_
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	20	18.10	7.71	4. PO	0.10	0.06	326.00	245.00	0.04	_	-
25 25.00 7.66 7.67 4.62 0.607 0.12 25.00 244.00 0.603 25 13.20 7.76 5.10 0.607 0.12 235.00 244.00 0.603 26 13.20 7.76 5.10 0.607 0.12 235.00 244.00 0.603	21	18.20	7.73	5.10	0.09	0.0	324.00	244.00	0.0	-	-
25 19.60 7.77 4.62 0.03 0.12 235.00 244.00 6.06	23	20.00	7.69	4 . CC	0.07	0.11	327.00	247.00	0.0	_	_
25 13.20 7.76 5.10 0.303 0.13 335.00 244.00 0.606	24	19.80	7.77	4.60	0.07	0.12	325.00	246.00	0.03	_	-
25 14.20 7.72 5.27 0.022 0.07 356.00 244.00 0.022 29 13.30 7.71 5.32 0.040 0.11 39 13.30 7.71 5.32 0.040 0.12	25	19.20	7.76	5.10	0.03	0.19	325.00	244.00	0.06	-	-
28 19.30 7.72 5.22 0.00 0.15 325.00 245.00 0.12	27	18.50	7.70	5.20	0.02	0.07	326.00	245.00	0.02		_
31 13:30 7.71 3.30 0.23 325.00 243.00 0.243.00	28	19.30	7.72	5.20	0.06	0.15	325.00	245.00	0.12	-	-
1 19,70 7,79 5,22 0,27 39x,00 245,00 0,11 31 18,20 1,75 5,22 0,0 0,01 32,00 245,00 0,01 33 18,20 1,75 5,22 0,0 0,01 325,00 245,00 0,01 34 18,50 7,74 5,22 0,00 0,04 333,50 246,00 0,07 35 18,50 7,74 5,10 0,04 0,11 325,50 246,00 0,07 36 18,40 7,77 5,10 0,04 0,07 333,50 246,00 0,01 41 18,40 7,77 5,10 0,046 0,07 332,50 246,00 0,01 43 18,40 7,75 5,10 0,046 0,03 327,07 245,00 0,01 <td>29</td> <td>19.30</td> <td>7.71</td> <td>5.30</td> <td>C • 1 3 0 • 04</td> <td>0.23</td> <td>325.00</td> <td>243.00</td> <td>0.24</td> <td>_</td> <td> </td>	29	19.30	7.71	5.30	C • 1 3 0 • 04	0.23	325.00	243.00	0.24	_	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	31	19.70	7.79	5.30	C.02	0.27	326.00	245.00	0.11	_	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	32	19.80	7.78	5.10	0.01	0.16	325.00	245.00	0.11	-	-
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	34	18.20	7.75	5.40	0.01	0.01	325.50	245.00	0.08		_
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	35	18.70	7.75	5.40	C.01	0.03	325.00	246.00	0.11		-
38 18.40 7.75 5.10 1.60 1.77 325.80 224.80 0.13 40 18.30 7.65 5.10 0.64 0.15 326.00 224.50 0.02 41 18.40 7.75 5.10 0.64 0.01 327.00 235.50 0.00 42 18.40 7.75 5.10 0.64 0.01 327.00 245.50 0.01 44 18.40 7.75 5.10 0.64 0.05 327.50 244.00 0.14 50 17.70 7.56 2.40 0.66 307.50 244.00 0.14 51 18.70 7.46 1.70 0.66 0.15 329.50 246.50 0.28 53 17.70 7.40 1.70 0.66 0.15 329.50 246.50 1.30	36	18.50	7.76	5.20	0.06	0.04	323.50	246.00	0.02	-	-
39 18.30 7.67 5.10 0.024 0.15 322.00 244.30 0.09	38	18.40	7.76	5.10	0.09	0.17	325.50	246.50	0.13	_	_
40 18.40 1.65 9.40 0.00 0.00 24.40 0.00 0.00 24.40 0.00 0.00 24.40 0.00 0.00 24.40 0.00 0.00 24.40 0.00 0.00 24.40 0.00 0.00 24.40 0.00 0.00 24.40 0.00 0.00 24.40 0.00 0.01	29	18.30	7.67	5.10	0.04	0.15	326.00	245.50	0.09	_	-
43 18.30 7.75 5.50 0.64 0.64 322.60 222.50 0.23	40	18.30	7.65	5.00	0.04	0.07	326.00	244.00	0.02	_	_
44 16.40 7.75 5.10 0.04 0.10 327.50 245.00 0.014	43	18.30	7.75	5.90	0.04	0.04	329.00	242.50	0.23		_
**** ***** ****** ************************************	44	18.40	7.75	5.10	0.04	0.10	327.00	245.00	0.01		-
50 17.00 7.55 2.46.0 0.05 329.50 246.50 0.25	40	18.30	7.80	4.80	0.03	0.00	325.50	243.00	0.02	_	_
51 18.00 7.46 2.40 0.02 0.15 329.50 246.50 0.25	50	17.90	7.55	2. PC	0.06	0.05	329.50	246.00	0.18	_	- 1
35 17.40 1.40 C.03 0.06 15.50 244.00 0.64 1 1 57 17.70 7.40 C.40 0.07 120.00 245.50 0.02	51	18.00	7.46	2.40	0.02	0.15	329.50	246.50	0.25	_	-
57 17.73 7.40 C.4C 0.07 320.00 246.00 0.36	55	17.60	7.40	1.20	C.03	0.06	315.50	246.00	0.46	_	
59 18.40 7.46 6.22 0.62 0.69 11.60 0.46 0.36	57	17.70	7.40	C . 4 C	0.0	0.07	320.00	245.50	0.02	_	
18.00 7.59 7.62 4.62 0.05 0.06 333.00 244.00 1.70	59	18.40	7.40	0.20	0.02	0.09	315.00	246.00	0.36	_	_
66 17.50 7.62 4.40 0.00 0.09 330.00 246.50 1.03	63	18.00	7.59	2.80	0.05	0.08	323.00	246.00	1.36	_	_
68 17.60 7.25 1.60 0.02 0.11 318.20 247.60 0.24 77 16.00 7.51 C.50 0.06 0.04 321.00 247.60 0.24 77 17.80 7.52 1.40 0.06 0.03 321.00 247.50 C.53 76 17.90 7.42 C.10 0.01 0.23 322.50 247.50 C.53 81 17.90 7.42 C.10 0.01 0.23 326.50 245.50 0.46	64	17.50	7.62	4.40	0.0	0.09	330.00	249.00	1.70	-	-
70 18.00 7.51 C.50 0.04 0.04 121.00 246.00 0.24 74 17.80 7.52 1.20 0.065 0.12 322.50 245.00 0.49 76 18.00 7.42 C.10 0.01 0.03 30.00 245.00 0.49 78 17.90 7.42 C.110 0.01 0.03 30.00 245.00 0.49 80 17.90 7.42 C.110 0.00 0.05 319.00 245.00 0.43 83 18.40 7.41 C.16 0.01 0.13 319.50 245.00 0.43 86 17.20 7.37 0.10 0.01 0.13 320.02 245.00 0.43 0.21 1.76 96 17.40 7.53 3.70 0.66 0.22 324.00 245.00 1.90 <td>68</td> <td>18.10</td> <td>7.49</td> <td>1.80</td> <td>0.02</td> <td>0.09</td> <td>320.50</td> <td>240.50</td> <td>0.71</td> <td>_</td> <td>_</td>	68	18.10	7.49	1.80	0.02	0.09	320.50	240.50	0.71	_	_
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	70	18.00	7.51	C. 50	0.04	0.04	321.00	246.00	0.24		-
Te 18.00 T445 12.00 0.01 0.02 320.00 245.00 0.449 I I T8 17.40 7.42 C.1C 0.01 0.02 320.00 245.00 0.449 I I I 80 17.40 7.42 C.1C 0.01 0.12 320.50 245.00 0.466 I I I 80 17.40 7.42 C.1C 0.00 0.04 318.00 245.00 0.433 I <t< td=""><td>72</td><td>17.80</td><td>7.52</td><td>1.40</td><td>0.04</td><td>0.03</td><td>321.00</td><td>247.50</td><td>0.35</td><td>-</td><td>- </td></t<>	72	17.80	7.52	1.40	0.04	0.03	321.00	247.50	0.35	-	-
7817.907.42C.1C0.C10.12322.50245.000.298017.907.41C.EC0.00.05319.00247.000.7338318.407.41C.EC0.00.01318.50245.000.438417.207.370.100.C10.13320.50245.500.630.671.408617.207.33C.1C0.020.05320.50245.500.630.6871.409017.407.510.160.020.05320.50245.500.170.5481.499316.707.553.200.660.22322.50246.000.390.371.789416.707.553.200.660.22322.50246.000.490.211.7616216.807.340.5C0.630.17321.00245.001.960.621.4316717.607.35C.100.010.03320.00245.001.960.621.43116116.907.38C.2C0.00.13319.50245.001.960.621.43116717.607.350.100.011.03320.00245.001.960.621.43116116.907.38C.2C0.00.01311.00246.001.600.141.68117 <td< td=""><td>76</td><td>18.00</td><td>7.45</td><td>0.30</td><td>0.01</td><td>0.0</td><td>3?0.00</td><td>245.00</td><td>0.49</td><td>_</td><td>_</td></td<>	76	18.00	7.45	0.30	0.01	0.0	3?0.00	245.00	0.49	_	_
80 17.90 7.41 C.EC 0.0 0.05 319.00 243.00 0.46 83 18.40 7.41 C.EC 0.0 0.04 318.50 245.00 0.43 85 18.40 7.37 0.10 0.C1 0.13 320.00 245.00 0.48 0.87 1.40 86 17.20 7.37 0.10 0.C1 0.13 320.00 245.50 0.17 0.58 1.40 90 17.40 7.51 0.1C 0.04 0.19 319.50 245.50 0.17 0.58 1.49 97 16.70 7.55 3.70 0.C6 0.22 322.00 245.00 0.99 0.32 1.78 98 16.80 7.45 1.10 0.13 0.20 0.25 1.76 1.76 10 18.90 1.44 0.17 0.03 318.50 245.00 1.96 0.21 1.76 110 19.90 1.42 0.00 0.01 319.00 24	78	17.90	7.42	C.1C	0.01	0.12	320.50	245.00	0.29	-	-
B3 IB CO CO CO CO State State CO CO State CO State CO CO State CO State CO CO CO CO State CO CO CO CO State CO CO CO CO CO CO State CO State CO CO CO State CO State CO State State State CO State State </td <td>80</td> <td>17.90</td> <td>7.4C 7.41</td> <td>0+10</td> <td>0.0</td> <td>0.05</td> <td>319.00</td> <td>243.00</td> <td>0.46</td> <td></td> <td>_</td>	80	17.90	7.4C 7.41	0+10	0.0	0.05	319.00	243.00	0.46		_
85 14, C0 7, 37 0, 16 0, C1 0, 13 310, 50 245, 50 0, 55 86 17, 20 7, 33 C, 10 0, 02 0, 05 320, 00 245, 50 0, 63 0, 65 1, 40 90 17, 40 7, 51 0, 10 0, 04 0, 19 319, 50 245, 50 0, 63 0, 65 1, 49 95 17, 00 7, 61 0, 10 0, 04 0, 19 319, 50 245, 50 0, 19 0, 72 1, 78 94 16, 70 7, 65 3, 20 0, 66 0, 22 322, 50 246, 00 3, 49 0, 21 1, 76 107 17, 40 7, 25 C, 10 0, 01 0, 00 320, 00 245, 50 1, 97 0, 80 1, 60 110 16, 90 7, 38 C, 2C 0, C 0, 01 311, 00 245, 50 1, 77 0, 16 1, 81 113 17, 30 7, 34 2, CC 0, 00 0, 01 312, 50 24, 60 1, 64 0, 01 1, 51 113	83	18.40	7.41	C.10	0 • C	0.01	318.50	245.00	0.43	_	_
Re 17.20 7.37 0.10 0.11 0.13 0.00 246.50 0.16 0.03 1.40 G0 17.40 7.51 0.10 0.04 0.19 319.50 246.50 0.17 0.55 1.20 G0 17.40 7.51 0.10 0.04 0.19 319.50 246.50 0.17 0.58 1.49 G5 17.00 7.45 3.70 0.66 0.22 322.50 246.50 1.49 0.76 1.47 G6 16.70 7.55 3.70 0.66 0.22 322.50 245.00 1.96 0.62 1.47 G7 17.40 7.35 C.10 0.01 0.0 319.00 245.00 1.96 0.62 1.43 G7 0.735 0.74 0.10 0.0 320.00 245.00 1.96 0.62 1.43 G7 0.735 0.10 0.0 0.03 319.00 245.00 1.60 1.60	85	18.00	7.37	0.10	0.01	0.13	319.50	245.50	0.55		
90 17.40 7.51 0.1C 0.04 0.19 314.50 245.50 0.17 0.58 1.49 95 17.00 7.55 3.20 0.06 0.22 324.00 245.00 0.39 0.32 1.78 94 16.70 7.55 3.20 0.06 0.22 324.00 245.00 0.19 0.26 1.47 97 16.80 7.45 1.10 0.13 0.20 322.50 246.00 3.49 0.21 1.76 102 16.80 7.35 C.10 0.01 0.0 319.00 245.50 1.77 0.58 1.49 110 16.90 7.28 0.10 0.0 0.01 311.00 246.00 1.60 1.62 1.61 113 17.50 7.28 0.10 0.0 0.01 311.00 246.00 1.44 0.01 1.52 123 17.50 7.34 2.0C 0.04 0.01 312.07 242.00	88	17.20	7.33	C.1C	0.02	0.05	320.50	246.50	0.63	0.85	1.20
55 17.00 7.43 0.5C 0.623 0.17 321.00 245.00 0.39 0.37 1.78 99 16.80 7.45 1.10 0.13 0.20 322.50 246.00 3.49 0.21 1.76 102 16.80 7.45 1.10 0.01 0.00 318.50 245.00 1.96 0.623 1.43 110 16.90 7.35 C.10 0.01 0.0 320.00 245.00 1.59 0.80 1.63 113 17.30 7.26 0.10 0.0 0.12 311.00 245.00 1.59 0.80 1.63 113 17.40 7.38 C.2C 0.0 0.0 311.00 245.00 1.60 1.60 0.16 311.00 245.00 1.60 1.60 0.61 1.63 1.75 1.63 1.75 1.63 1.63 1.61 1.63 1.61 1.63 1.61 1.63 1.61 1.63 1.61 1.63 1.61 1.63 1.61 1.61 1.61 1.61 1.61 1.61	90	17.40	7.51	0.10	0.04	0.19	319.50	245.50	0.17	0.58	1.49
39 16.80 7.45 1.10 0.13 0.20 322.50 246.00 3.47 0.71 1.76 102 16.80 7.45 0.10 0.07 0.03 318.50 245.00 1.96 0.42 1.43 101 16.90 7.35 C.10 0.01 0.0 320.00 245.50 1.77 0.35 1.43 110 16.90 7.38 C.20 0.0 0.01 311.00 245.50 1.77 0.35 1.89 113 17.30 7.26 0.10 0.0 0.01 311.00 245.00 1.20 0.05 1.82 113 17.50 7.34 7.00 0.01 315.00 247.00 1.44 0.01 1.52 123 17.50 7.34 2.00 0.01 312.00 242.00 1.84 0.11 1.27 131 17.20 7.33 C.30 0.01 0.03 318.50 243.00 0.33 0.85	55	17.00	7.43	0.50	0.03	0.17	321.00	245.00	0.39	0.32	1.78
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	99	16.80	7.45	1.10	0.13	0.20	322.50	246.00	3.49	0.21	1.76
110 16.90 7.35 C.10 0.01 0.0 320.00 245.50 1.77 0.35 1.88 113 17.30 7.28 0.10 0.0 0.02 0.10 311.00 245.50 1.77 0.35 1.88 113 17.30 7.28 0.30 0.02 0.10 311.00 245.50 1.77 0.35 1.88 119 17.40 7.25 0.30 0.02 0.10 311.00 245.00 1.60 0.01 1.52 123 17.50 7.34 2.00 0.04 0.414.55 246.00 1.44 0.01 1.52 127 17.40 7.38 2.80 0.01 0.03 312.07 242.00 1.84 0.10 1.28 131 17.20 7.33 C.30 0.01 0.03 317.50 243.00 0.73 0.85 1.75 134 17.50 7.33 0.26 0.01 0.03 318.50 243.00 0.67 0.15 2.16 140 17.40 7.36 0.10	102	16.80	7.74	0.10	0.07	0.03	318.50	245.00	1.96	0.63	1.93
113 17.30 7.28 0.10 0.0 0.12 311.00 246.00 0.81 0.02 2.01 115 17.40 7.25 0.30 0.02 0.10 311.00 246.00 1.20 0.05 1.82 119 17.20 7.44 2.00 0.04 314.50 246.00 1.20 0.05 1.82 123 17.50 7.34 2.00 0.01 315.00 247.00 1.44 0.01 1.52 123 17.50 7.33 C.30 0.01 0.0 312.00 243.00 0.33 0.85 1.51 131 17.20 7.33 0.30 0.60 0.01 318.50 243.00 0.74 0.60 1.79 134 17.50 7.33 0.10 0.04 0.11 319.50 242.50 0.84 0.11 1.95 144 17.40 7.35 0.10 0.04 0.318.00 244.00 0.67 0.15 2.06 144 17.40 7.36 0.6 0.0 0.32 316.00	110	16.90	7.38	C.2C	0.01	0.0	320.00	245.00	1.77	0.35	1.88
115 17.40 7.25 0.30 0.02 0.10 311.00 245.00 1.20 0.66 1.82 119 17.20 7.44 2.00 0.04 314.57 240.00 1.60 0.01 1.52 123 17.50 7.34 2.00 0.01 0.03 315.00 247.00 1.44 0.03 1.51 127 17.40 7.38 2.80 0.01 0.0 312.07 243.00 0.33 0.86 1.75 131 17.20 7.33 0.30 0.00 0.01 318.50 243.00 0.74 0.50 1.73 134 17.50 7.33 0.10 0.04 0.11 319.50 243.00 0.74 0.50 1.73 137 17.60 7.35 0.10 0.04 0.0 318.00 244.00 0.67 0.15 2.06 144 17.30 7.40 0.0 0.0 0.32 316.00 244.00 0.50 0.33 2.78 144 17.30 7.38 0.0 0.0 <	113	17.30	7.28	0.10	0.0	0.12	311.00	246.00	0.81	0.02	2.00
123 17.50 7.34 2.60 0.00 0.01 314.00 247.00 1.44 0.63 1.51 127 17.40 7.38 2.80 0.01 0.0 312.60 247.00 1.44 0.63 1.51 131 17.20 7.33 C.36 0.c1 0.0 317.50 243.00 0.74 0.50 1.74 134 17.50 7.33 0.6 0.0 0.0 317.50 243.00 0.74 0.50 1.74 137 17.60 7.35 0.10 0.04 0.11 319.50 242.00 0.84 0.51 1.74 140 17.40 7.35 0.10 0.04 0.11 319.50 242.00 0.84 0.51 1.74 140 17.40 7.35 0.10 0.04 0.11 319.50 244.00 0.74 0.50 1.74 144 17.30 7.36 0.0 0.0 318.50 244.00 0.75 0.16 2.18 144 17.30 7.36 0.0 0.0	115	17.40	7.25	0.30	0.02	0.10	311.00	245.00	1.20	0.05	1.82
127 17.40 7.38 2.60 0.01 0.0 312.00 242.00 1.84 0.10 1.28 131 17.20 7.33 0.6 0.01 0.0 317.50 243.00 0.33 0.85 1.25 134 17.50 7.33 0.6 0.00 0.0 317.50 243.00 0.74 0.50 1.74 137 17.60 7.35 0.10 0.04 0.11 319.50 242.00 0.74 0.50 1.74 140 17.40 7.35 0.10 0.04 0.11 319.50 242.00 0.84 7.11 1.95 143 17.30 7.40 0.00 0.00 318.00 244.00 0.50 0.33 2.04 143 17.30 7.35 0.0 0.00 0.318.00 244.00 0.50 0.33 2.04 149 17.30 7.35 0.0 0.00 0.23 316.00 244.00 0.25 0.16 2.18 151 17.40 7.37 0.6 0.00 0.02 <	123	17.50	7.34	2.00	0.0	0.01	315.00	247.00	1.44	0.03	1.51
131 17.20 7.33 C. 3C 0.01 0.0 317.50 243.00 0.33 0.45 1.75 134 17.50 7.33 0.0 0.0 0.0 314.50 243.00 0.74 0.60 1.79 137 17.60 7.35 0.1C 0.04 0.11 319.50 243.00 0.74 0.60 1.79 140 17.40 7.35 C.C 0.04 0.0 318.00 244.00 0.67 0.15 2.04 143 17.30 7.40 0.0 0.0 318.00 244.00 0.67 0.15 2.04 144 17.30 7.38 0.0 0.0 0.12 316.00 244.00 0.74 0.5 0.16 2.16 151 17.80 7.38 0.0 0.00 0.23 317.00 243.00 0.64 0.24 2.27 153 17.90 7.37 0.10 0.02 317.00 244.00 1.22 0.10 1.94 157 17.60 7.38 0.0 0.02 318	127	17.40	7.38	2.80	0.01	0.0	312.00	242.00	1.84	0.10	1.28
137 17.60 7.35 0.10 0.04 0.11 319.50 242.50 0.84 0.11 1.95 140 17.40 7.36 C.C 0.04 0.0 318.00 244.00 0.67 0.15 2.04 143 17.30 7.40 0.0 0.0 0.0 318.00 244.00 0.67 0.15 2.04 144 17.30 7.38 0.0 0.0 0.32 316.00 244.00 0.74 0.15 2.16 144 17.30 7.38 0.0 0.0 0.32 316.00 244.00 0.74 0.15 2.16 151 17.60 7.38 C.C 0.0 0.12 316.00 244.00 0.75 0.16 2.18 151 17.60 7.38 C.C 0.0 0.12 316.00 244.00 0.75 0.21 2.10 155 17.60 7.38 C.C 0.0 0.02 319.00 244.00 1.22 0.11 1.99 157 17.60 7.37 0.10 0.02 </td <td>131</td> <td>17.20</td> <td>7.33</td> <td>C•3C</td> <td>0.01</td> <td>0.0</td> <td>317.50</td> <td>243.00</td> <td>0.33</td> <td>0.85</td> <td>1.79</td>	131	17.20	7.33	C•3C	0.01	0.0	317.50	243.00	0.33	0.85	1.79
140 17.40 7.36 C.C 0.04 0.0 318.00 244.00 0.67 0.15 2.04 143 17.30 7.40 0.0 0.0 0.0 318.00 244.00 0.67 0.15 2.04 144 17.30 7.38 0.0 0.0 0.03 318.00 244.00 0.67 0.15 2.16 149 17.30 7.38 0.0 0.0 0.12 316.00 244.00 0.74 0.15 2.16 151 17.80 7.38 C.C 0.0 0.23 316.00 244.00 0.64 0.24 2.27 153 17.90 7.37 0.0 0.0 0.02 319.00 244.00 0.64 0.24 2.27 153 17.60 7.38 C.C 0.00 0.02 319.00 244.00 1.22 0.11 1.94 155 17.60 7.37 0.1C 0.02 0.03 318.50 242.50 0.71 0.34 1.99 STATISTICAL EVALUATIONS Mean	137	17.60	7.35	0.10	0.04	0.11	319.50	242.50	0.84	2.11	1.95
146 17.30 7.38 0.0 0.0 318.00 244.00 0.70 0.53 2.16 149 17.30 7.38 0.0 0.0 0.32 316.00 244.00 0.74 0.15 2.16 149 17.30 7.35 0.0 0.0 0.12 316.00 244.00 0.75 0.16 2.18 151 17.80 7.38 0.0 0.00 0.02 317.00 243.00 0.64 0.24 2.29 153 17.90 7.37 0.0 0.00 0.02 316.00 244.00 0.75 0.21 2.10 155 17.60 7.38 0.0 0.02 316.00 244.00 1.22 0.10 1.94 157 17.60 7.37 0.10 0.02 0.03 318.50 242.50 0.71 0.34 1.99 STATISTICAL EVALUATIONS Mean 18.14 7.58 3.22 0.05 0.09 322.58 244.88 0.51 0.33 1.77 Minimum 16.70 7.25<	140	17.40	7.36	C.C	0.04	0.0	318.00	244.00	0.67	0.15	2.04
149 17.30 7.35 0.C 0.0 0.12 316.00 244.00 0.35 0.16 2.18 151 17.80 7.38 C.C 0.0 0.02 317.00 243.00 0.64 0.24 2.20 153 17.90 7.37 0.C 0.00 0.02 316.00 244.00 0.75 0.71 2.10 155 17.60 7.38 C.C C.C3 0.04 316.00 244.00 1.22 0.12 1.1 1.1 1.4 1.2 0.10 1.22 0.10 1.24.00 1.22 0.10 1.4	146	17.30	7.38	0.0	0.0	0.32	316.00	244.00	0.74	0.15	2.16
121 17.80 7.38 C. C 0.0 0.02 317.00 243.00 0.64 0.24 2.20 153 17.90 7.37 0.0 0.02 319.00 244.00 0.75 0.71 2.10 155 17.40 7.38 C.C C.C3 0.04 316.00 244.00 1.22 0.10 1.94 157 17.40 7.37 0.1C 0.02 0.03 318.50 242.50 0.71 0.34 1.99 STATISTICAL EVALUATIONS Mean 18.14 7.58 3.22 0.05 0.09 322.58 244.88 0.51 0.33 1.77 Minimum 16.70 7.25 0.0 0.0 311.0 238.0 0.0 0.01 1.20 Standard 0.00 7.92 8.30 0.23 0.32 331.0 249.0 3.49 0.87 2.20 Standard 0.75 0.18 2.62 0.05 0.08 4.7 2.12 0.60 0.28 0.31	149	17.30	7.35	0.0	0.0	0.12	316.00	244.00	0.35	0.19	2.18
155 17.60 7.38 C.C C.C3 0.04 316.00 244.00 1.22 0.10 1.94 157 17.P0 7.37 0.10 0.02 0.03 318.50 242.50 0.71 0.34 1.99 STATISTICAL EVALUATIONS Mean 18.14 7.58 3.22 0.05 0.09 322.58 244.88 0.51 0.33 1.77 Minimum 16.70 7.25 0.0 0.0 311.0 238.0 0.0 0.01 1.20 Standard 51andard 0.75 0.18 2.62 0.05 0.08 4.7 2.12 0.60 0.28 0.31	151	17.90	7.38	0.0	0.0	0.02	317.00	243.00	0.75	0.24	2.10
157 17.60 7.37 0.10 0.02 0.03 318.50 242.50 0.71 0.34 1.99 STATISTICAL EVALUATIONS Mean 18.14 7.58 3.22 0.05 0.09 322.58 244.88 0.51 0.33 1.77 Minimum 16.70 7.25 0.0 0.0 0.01 311.0 238.0 0.0 0.01 1.20 Maximum 20.00 7.92 8.30 0.23 0.32 331.0 249.0 3.49 0.87 2.20 Standard 0eviation 0.75 0.18 2.62 0.05 0.08 4.7 2.12 0.60 0.28 0.31	155	17.60	7.38	C.C	C.C3	0.04	316.00	244.00	1.22	0.19	1.95
STATISTICAL EVALUATIONS Mean 18.14 7.58 3.22 0.05 0.09 322.58 244.88 0.51 0.33 1.77 Minimum 16.70 7.25 0.0 0.0 0.0 311.0 238.0 0.0 0.01 1.20 Maximum 20.00 7.92 8.30 0.23 0.32 331.0 249.0 3.49 0.87 2.20 Standard 0.75 0.18 2.62 0.05 0.08 4.7 2.12 0.60 0.28 0.31	157	17.00	7.37	0.10	0.02	0.03	318.50	242.50	0.71	9.34	1.99
STATISTICAL EVALUATIONS Mean 18.14 7.58 3.22 0.05 0.09 322.58 244.88 0.51 0.33 1.77 Minimum 16.70 7.25 0.0 0.0 0.0 311.0 238.0 0.0 0.01 1.20 Maximum 20.00 7.92 8.30 0.23 0.32 331.0 249.0 3.49 0.87 2.20 Standard Oeviation 0.75 0.18 2.62 0.05 0.08 4.7 2.12 0.60 0.28 0.31											
Mean 18.14 7.58 3.22 0.05 0.09 322.58 244.88 0.51 0.33 1.77 Minimum 16.70 7.25 0.0 0.0 0.0 311.0 238.0 0.0 0.01 1.20 Maximum 20.00 7.92 8.30 0.23 0.32 331.0 249.0 3.49 0.87 2.20 Standard 0.75 0.18 2.62 0.05 0.08 4.7 2.12 0.60 0.28 0.31	STATISTI	CAL EVALUA	TIONS								
Minimum 16.70 7.25 0.0 0.0 0.0 311.0 238.0 0.0 0.01 1.20 Maximum 20.00 7.92 8.30 0.23 0.32 331.0 249.0 3.49 0.87 2.20 Standard Oeviation 0.75 0.18 2.62 0.05 0.08 4.7 2.12 0.60 0.28 0.31	Mean	18.14	7 58	3.22	0.05	0.09	322.58	244.88	0.51	0.33	1.77
Hontmum 16./0 7.25 0.0 0.0 0.0 311.0 238.0 0.0 0.01 1.20 Maximum 20.00 7.92 8.30 0.23 0.32 331.0 249.0 3.49 0.87 2.20 Standard Oeviation 0.75 0.18 2.62 0.05 0.08 4.7 2.12 0.60 0.28 0.31		16					212.0	230.0	0.0	0.01	1.20
Standard Deviation 0.75 0.18 2.62 0.05 0.08 4.7 2.12 0.60 0.28 0.31	Minimum Maximum	20.00	7.25	0.0 8.30	0.0	0.0	311.0	238.0	3.49	0.87	2.20
	Standard Oeviation	0.75	0.18	2.62	0.05	0.08	4.7	2.12	0.60	0.28	0.31

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RUN NO	темр	РН	D.C.	FE2T	FET	ALK	HONS	NH3N	NO2N	ND3N
1	18.30	7.86	8.10	0.04	0.23	322.50	235.00	1.04	_	-
	17.90	7.94	8.20	0.0	0.53	328.00	247.00	1+12	_	_
4	17.90	7.84	8.30	0.02	0.19	332.CO	248.00	1.04		_
5	18.40	7.86	B.CC	0.11	0.27	337.00	246.00	0.97	_	-
6	18.10	7.81	7.90	C.17	C.22	324.00	247.50	0.88	-	-
7	17.60	7.84	7.80	0.20	0.21	324.00	246.00	0.82	_	-
9	18.20	7.73	6.40	0+12	0.24	324.00	245.00	0.33	_	_
10	18.40	7.72	5.60	0.22	0.17	322.50	240.50	0.27	_	_
11	18.30	7.71	5.20	0.17	0.11	322.00	238.50	0.15	_	_
12	19.10	7.63	4.50	0.17	0.0	32?.00	239.50	0.02	-	-
13	19.20	7.74	4.70	0.09	0.02	323.00	239.00	0.0	-	-
15	19.30	7.73	4.30	0.10	0.04	319,50	238.50	0.01	_	_
16	19.10	7.67	4.60	0.04	0.09	329.00	246.00	0.03	_	-
17	10.40	7.73	4.60	0.05	0.15	326.50	246.50	0.06	_	
18	19.30	7.74	4.40	C.C5	0.16	327.50	246.00	0.06	_	
19	18.50	7.68	4.EC	0.09	0.06	327.50	244.00	0.05	-	-
20	1/.90	7 73	4.70	0.08	0.15	328.00	244.00	0.07	_	_
22	17.90	7.71	4.EC	0.08	0.0	323.00	242.00	0.0	_	_
23	19.90	7.68	4.50	0.02	0.13	326.50	246.50	0.0	_	_
24	19.70	7.76	4.70	0.04	0.16	326.50	246.00	0 • C 1		-
25	19.20	7.76	5.20	0.03	C.03	325.50	244.50	0.05	-	-
26	18.50	7.72	5.50	0.02	0.15	327.00	244.50	0.07	-	-
28	19.30	7.71	5.10	0.05	C.12	327.00	246.00	0.11	_	_
29	19.20	7.70	5.20	0.12	0.24	325.50	244.50	0.17	_	_
30	19.30	7.70	5.1C	0.05	0.31	324.50	244.50	0.15	-	_
21	19.60	7.78	5.10	0.01	0.22	325.00	243.00	0.06	-	-
32	19.10	7 77	5.80	0.0	0.19	325.00	24 5.50	0.23	-	-
34	18.50	7.76	6.00	0.02	0.06	325.50	244.00	C.18	_	_
35	18.60	7.75	5.50	0.03	C.04	324.50	245.50	0.08		_
36	18.40	7.76	5.20	0.04	0.06	322.00	244.00	0.02		-
37	18.30	7.74	5.70	0.04	0.19	324.00	245.00	0.08	-	-
38	18.30	7.67	5.4(0.07	0.21	324.00	246.00	0.14	-	-
40	18.30	7.68	5.30	0.01	0.05	325.00	243.50	C.02	_	_
41	18.50	7.73	5.60	0.09	0.03	327.00	243.50	0.0	-	_
43	18.30	7.75	6.20	0.06	0.09	328.00	243.00	0.29	-	-
44	18.30	7.74	5.30	0.05	0.09	375.00	242.50	0.11	_	-
48	18.20	7.80	5.10	0.03	0.04	325.00	245.50	0.12	_	_
50	17.90	7.53	2.00	0.05	0.06	329.00	247.00	0.18	_	
51	18.00	7.48	3.00	0.02	0.12	329.50	246.00	0.72	_	- 1
53	17.90	7.65	5.40	0.01	0.04	328.00	246.00	0.05	-	-
55	17.50	7.37	0.50	0.01	0.06	318.50	246.00	0.15	_	-
57	18.20	7.41	0.10	0.02	C.11	318.00	245.00	0.01	_	_
61	17.70	7.36	0.10	0.0	0.0	315.50	246.50	0.52	_	_
63	18.10	7.47	1.°C	C.C7	0.12	318.00	246.00	0.68	_	-
64	17.80	7.47	1.40	0.10	0.13	323.00	247.00	1.37	-	-
66	17.50	7.56	2.80	0.02	0.09	318.00	246.00	1.19	-	-
70	17.90	7.50	2.EC	0.01	C.11	322.00	247.00	0.25		_
72	17.70	7.47	1.20	0.05	0.12	320.00	247.50	0.07		_
74	17.70	7.44	0.70	0.07	0.14	320.50	243.00	0.18	_	-
76	17.70	7.40	0.10	0.05	0.01	318.50	246.00	0.25	_	-
10	17.00	7 37	0.40	0.0	0.02	318.50	244.00	0.19		-
82	18.10	7.35	0.20	0.0	0.03	319.00	246.00	0.08		<u> </u>
63	18.10	7.38	C.10	0.01	0.01	317.00	245.00	0.25		
85	17.60	7.33	0.10	0.0	0.08	318.00	245.00	0.41		-
88	17.10	7.34	C.20	0.01	0.14	320.50	245.00	0.05	1.67	0.61
90	17.40	7.45	0.10	0.04	0.17	320.00	246.50	0.15	1.48	0.83
95	16.80	7.40	C.50	0.04	0.20	322.00	245.00	C.15	1.39	1.04
98	16.50	7.52	3.20	0.06	0.20	325.00	244.00	0.37	0.83	0.70
99	16.70	7.41	1.5C	0.11	0.18	320.00	245.50	3.46	1.49	0.80
102	17.30	7.30	0.10	0.01	0.02	318.00	245.50	1.09	2.32	0.71
110	16.80	7.33	0.10	0.0	0.02	317.00	247.00	1.30	2.13	0.63
113	17.20	7.23	0.10	0.01	0.19	307.00	245.00	0.46	1.96	0.67
115	17.30	7.18	0.10	0.0	0.05	308.00	245.00	0.69	1.70	0.92
119	17.20	7.38	1.50	0.03	0.09	312.00	246.00	1.35	0.65	1.25
127	17.20	7.37	2.50	0.10	0.0	312.50	242.00	1.80	0.43	1.05
131	17.20	7.31	C.10	0.0	0.0	319.00	243.00	0.28	1.32	0.93
134	17.60	7.29	0.0	0.01	0.08	317.00	243.50	0.50	1.53	1.00
137	17.50	7.31	C.C	0.01	0.10	316.00	243.00	0.51	1.57	0.83
140	17.20	7.32	C.1C	0.02	0.06	315.00	243.00	0.43	1.49	1.13
146	17.20	7.34	6.6	0.0	0.19	316.00	244.00	0.44	1.47	1.16
149	17.20	7.30	C.1C	0.0	0.05	313.00	244.00	0.0	1.75	0.96
151	18.00	7.31	0.0	0 . C	0.13	314.00	243.00	0.22	2.03	0.77
153	17.80	7.31	0.0	0.0	0.05	314.00	244.00	0.33	2.02	0.82
155	17.80	7.2P	0.70	0.0	0.04	314.00	243.00	0.88	1.95	0.41
	1100	1.22	0.0	0.00	0.0	310.30	2-2-50	0.50	1	0.05
STATISTIC	AL EVALUAT	IONS								
Mean	18.08	7.56	3.28	0.05	0.11	321.72	244.39	0.41	1.54	0.88
Minimum	16.50	7 18	0.0	0.0	0.0	307 0	235 0	0.0	0.35	0.40
Maximum	19.90	7.94	8.30	0.22	0.53	337.0	248.0	3.46	2.32	1 42
Standard										
Deviation	0.76	0.20	2.69	0.05	0.09	5.30	2.30	0.55	0.51	0.22



TABLE A-6

RUN NO	TEMP	РН	D.C.	FE2T	FET	ALK	HDNS	NH3N	N0 2 N	NE 3 N
1	18.40-	7.P5	8.00	0.02	0.23	332.07	248.00	1.06	_	_
2	18.90	7.87	P.10	0.0	0.18	329.00	245.50	1.07	-	-
4	17.80	7.93	8.10	0.0	0.09	321.50	241.50	1.11	_	_
5	18.40	7.88	7.90	0.06	0.28	327.00	246.00	1.02	-	_
۴ ٦	17.90	7.82	P.10	0.14	0.31	325.00	245.50	C.94	_	
A	17.80	7.77	6.80	C.15	0.24	321.00	245.00	C.53	_	_
с	18.20	7.74	6.10	0.16	0.21	322.50	245.00	C.35	-	—
10	16.40	7.72	5.30	C.18	C.19	322.50	244.00	0.19	-	-
12	19.00	7.6?	4.50	0.16	C.0	327.00	238.50	0.01	_	_
13	19.20	7.74	4.60	0.09	C.02	323.00	238.00	C.O		-
14	19.30	7.71	4.20	0.09	0.01	322.50	238.00	0.01	-	-
10	10.10	7.65	4.70	0.04	C.07	327.50	247.00	0.09	_	_
17	19.40	7.7?	4.4C	0.04	0.17	327.50	246.00	C.10	_	
19	19.30	7.75	4.50	0.03	0.11	327.50	245.50	C.07	-	-
20	18.10	7.72	5.00	0.08	0.08	325.50	243.00	0.04	_	
21	18.20	7.74	5.10	0.10	0.0	322.00	241.00	0.03	_	
22	17.90	7.71	4.70	C.11	0.0	320.00	242.00	0.03		-
24	19.60	7.77	4.80	0.04	0.09	326.00	245.50	0.02	_	_
25	19.10	7.77	4.°C	0.02	0.19	326.50	245.00	C.07	_	-
24	19.50	7.73	5.30	0.05	0.16	326.50	243.50	0.07	-	-
28	16.30	7.71	5.20	0.06	0.12	326.00	245.50	0.10	_	_
29	19.10	7.70	5.10	0.10	C.22	323.50	242.50	C.17	-	-
30	19.30	7.70	5.10	0.06	0.26	324.50	244.00	0.13	-	-
32	19.80	7.77	5.30	0.01	C.18	325.50	244.00	0.07	_	_
33	19.10	7.74	5.4C	0.01	C.O	326.00 -	245.00	0.09	_	-
34	18.73	7.74	5.50	0.01	0.03	323.50	243.50	0.10	_	_
36	18.40	7.75	5.10	C.C3	C.C1	319.50	243.50	C.02	_	
37	18.30	7.75	5.40	0.03	0.20	323.50	246.50	C.07	_	-
39 29	18.20	7.77	5.30	C.06	0.21	323.50	245.50	0.18		_
40	18.30	7.67	5.30	0.01	0.03	324.50	241.50	0.03	_	_
41	18.60	7.73	5.30	C.08	0.05	326.00	243.50	0.01	_	-
43	18.30	7.75	ۥ10 5.20	0.06	0.08	328.00	241.50	0.27		_
46	18.30	7.74	5.40	0.03	0.04	328.00	243.50	0.11		-
4 P	18.20	7.80	4.60	0.03	0.0	324.00	241.50	C.06		-
50	17.90	7.53	2.FC 2.PC	0.04	0.04	329.00	246.00	0.18	_	_
53	17.90	7.69	5.40	0.0	0.04	328.50	246.50	C.03	_	_
55	17.60	7.30	0.30	C.C3	C.C7	317.50	246.00	0.14	-	-
57	17.70	7.35	0.40	0.0	0.07	318.00	246.00	0.0	_	-
61	17.70	7.33	C.1C	0.01	0.08	315.00	246.00	C . 4 2	-	-
63	18.10	7.45	0.30	C.C4	C.07	316.00	246.00	C.42	-	-
64	17.80	7.40	0.30	0.01	0.09	321+50	249.00	0.42	_	-
E P.	10.00	7.50	2.40	0.0	0.04	323.00	247.50	0.83	-	-
70	17.90	7.71	5.70	0.05	0.07	329.00	247.00	1.36		-
74	17.7)	7.68	4.50	0.04	0.05	326.50	248.00	1 • 1 *	_	_
76	17.50	7.57	2.50	0.03	0.02	325.50	245.00	1.10	-	-
78	17.80	7.4C	C.4C	0.01	C.01	319.00	245.00	0.27		-
62	18.00	7.36	C.10	0.0	0.0	319.00	245.00	C.07	_	_
P 3	18.40	7.38	C.10	0.0	0.0	318.50	246.00	0.28		-
25 26	17.60	7.33	C.1C	0.0	0.11	319.00	245.00	C.43	1 6 9	
89	17.10	7.31	0.10	0.03	0.04	320.00	245.00	0.00	1.50	2.71
¢Ç.	17.30	7.47	0.30	0.06	0.15	321.00	245.00	0.09	1.51	0.99
55 58	17.00	7.40	0.30	0.04	C.18	370.00	245.00	0.11	1.42	1.08
Q.C.	16.80	7.39	0.60	0.10	C.22	319.50	247.00	3.23	1.49	1.05
102	18.00	7.70	C.20	C.1C	0.0	316.00	245.00	2.05	1.60	0.74
167	17.30	7.45	2.4(0.02	0.07	329.00	245.00	2.90	0.03	0.79
113	17.20	7.22	C.1C	0.01	0.18	308.00	245.00	0.45	1.75	0.90
115	17.00	7.19	0.1C	0.0	0.04	309.00	245.00	0.80	1.65	0.96
123	17.10	7.33	C.3C 1.EC	0.02	0.0	310.00	246.00	1.61	1.22	1.19
127	17.10	7.4C	3.4C	0.0	0.0	312.50	242.00	1.93	0.77	1.05
131	17.00	7.34	C. 9C	0.0	C.O	316.50	242.50	C.41	1.09	0.97
134	17.50	7.32	0.10	0.01	0.0	317.50	243.50	0.61	1. 20	1.11
140	17.30	7.32	0.0	0.03	C.06	316.00	244.00	0.40	1.45	1.16
143	17.20	7.34	0.0	0.0	0.02	315.00	244.00	0.26	1.79	1.04
149	17.20	7.24	0.0	0.0	0.13	315.00	245.00	C.49	1.74	0.96
151	17.90	7.36	0.10	0.0	0.09	316.00	243.00	0.45	1.96	0.81
152	17.80	7.31	C.C	0.0	0.06	314.00	244.00	0.32	2.01	0.75
157	17.70	7.33	C.1C	0.0	0.03	316.50	243.00	C.34	2.07	0.81
STATISTIC	CAL EVALUAT	IONS								
Mean	18.08	7.57	3.32	0.04	0.09	321.76	244.39	0.45	1.46	0.90
Minimum	16.70	7.19	0.0	0.0	0.0	308.0	236.5	0.0	0.03	0.41
Maximum Standard	19.80	7.93	8.20	0.20	0.31	332.0	249.0	3.23	2.29	1.18
Deviation	0.74	0.20	2.66	0.05	0.08	5.27	2.22	0.61	0.54	0.18

TABLE A-7

RUN NO	TEMP	₽н	D.F.	FE2T	FET	ΔLK	HONS	NH 3N	N02N	MC 2N
1	15.30	7.96	8.10	C.C1	0.23	334.50	247.50	1.03	_	_
2	18.80	7.98	8.10	0 • C	0.18	329.00	244.50	1.08		-
3	17.70	7.64	P.20	0.0	0.10	321.50	244.00	1.08	-	-
5	11.30	7.90	8.20	C.C8	0.25	328.00	248.00	1.16	_	_
t	17.80	7.84	8.4C	0.17	0.28	327.00	249.00	3.01	_	-
7	17.60	7.07	8.1C	0.19	0.25	327.00	245.50	0.89	-	-
c c	17.70	7.80	7.50	0.12	0.23	325.50	246.00	0.67	-	_
10	11.40	7.75	5.00	0.20	0.22	323.00	242.50	0.35	_	_
11	18.20	7.74	5.70	0.15	0.12	322.00	239.50	C.24	-	- 1
12	19.00	7.64	4. AC	0.15	0.0	322.00	239.50	0.01	-	-
15	19.20	7.71	4.60	0.07	0.01	322.00	238.50	0.01	_	_
1 "	18.60	7.73	4 . 4 C	0.04	0.04	320.00	237.00	0.23	_	-
16	18.90	7.66	4.60	0.02	0.05	328.00	247.00	0.04	-	-
18	19,30	7.75	4.50	C. C3	0.10	327.50	245.50	0.09		_
19	18.40	7.70	4.80	^.C3	0.07	326.50	246.00	0.05	_	_
20	18.00	7.71	4.90	0.08	0.12	324.50	244.00	0.06	_	-
21	17.90	7 71	4.81 5.1i	0.07	0.01	323.00	24 4 50	0.02	-	
23	19.73	7.70	4.50	0.04	0.13	327.50	247.00	C.C1		_
24	1¢.60	7.77	4.5(C.C.4	0.15	323.50	243.00	0.02	_	_
25	16.10	7.76	5.00	0.03	0.19	325.50	244.50	0.07	_	-
27	18.50	7.70	5.90	C.C1	0.13	325.50	245.00	6.01	_	_
2 "	14.20	7.71	5.26	0.02	0.11	327.00	247.00	C.11		_
29	10.10	7.70	5.10	0.13	0.25	324.00	243.50	0.19		-
30	19.30	7.78	5.10	0.01	0.29	325.00	245.50	0.15	_	-
32	19.60	7.78	5.30	C. C1	0.17	325.50	245.00	0.15	-	_
33	1°.10	7.76	5.60	C.C	0.03	325.50	244.50	C.13		-
34	18.60	7.76	5.60	0.03	0.03	326.50	245.50	0.18	_	-
34	18.40	7.78	5.10	0.04	0.01	321.00	243.00	0.09	_	_
37	16.20	7.75	5.50	0.04	0.17	374.00	246.50	0.06	_	_
36	18.20	7.77	5.40	C.13	0.13	324.50	245.50	0.12	-	-
4C	18.20	7.67	5.20	0.0?	0.03	323.00	241.50	0.02	_	_
41	18.60	7.74	5.20	C.07	0.03	325.00	242.50	0.01	_	
47	18.30	7.76	6.10	0.03	0.04	328.00	242.50	0.27	_	-
44	18.30	1.14	5.20	0.08	0.10	325.00	242.00	0.01	_	
4.8	18.20	7.8C	4.80	C. C5	0.01	324.50	241.50	0.12	_	
50	17.90	7.54	2.80	C.C8	0.08	328.57	246.00	0.21	_	-
51	18.00	7.50	3.30	0.02	0.15	330.00	246.00	0.37	-	
55	17.50	7.41	0.80	0.01	0.06	318.CO	246.50	0.75		_
57	17.70	7.4C	0.30	C.O	0.07	319.00	245.50	0.01	_	-
e c	18.20	7.40	0.10	0.02	0.09	319.00	246.50	C.14	_	-
61	18.00	7.48	0.10	0.07	0.01	314.57	246.00	0.55	_	_
64	17.70	7.42	0.10	0.01	0.10	372.00	24 00	0.55	_	
66	17.60	7.43	C.1C	C.C2	0.08	317.50	245.00	0.61		
70	17.80	7.49	0.10	0.05	0.06	320.00	247.50	0.15	-	-
72	17.60	7.59	3.20	0.04	0.05	325.50	249.00	C.70	_	_
74	17.7)	7.68	4.EC	0.05	0.07	329.00	244.50	1.28	-	-
76	17.80	7.61	Z.40	0.01	C.10 0.01	373,50	245.00	1.35	_	-
PO PO	17.90	7.27	0.10	0.C	0.05	316.50	244.00	C.23	_	
82	18.10	7. 77	1.00	0.0	0.01	317.00	244.00	0.07	_	
83	18.30	7.38	C.1C	0.02	C.C1	317.00	245.50	0.21	_	_
86	17.10	7.35	0.20	C.C	0.12	319.50	246.00	0.07	1.58	0.75
88	17.20	7.32	C.3C	0 • C 2	0.06	320.50	246.50	C.26	1.55	0.41
90	17.40	7.47	0.30	0.05	0.20	322.00	246.50	0.15	1.42	0.89
5H	16.70	7.51	2.60	C.04	0.19	323.00	244.00	0.08	1.10	0.72
05	17.70	7.30	C.10	0.10	0.1 %	317.50	247.00	2.80	1.95	2.92
102	18.00	7.31	0.10	0.06	0.02	317.00	245.50	1.77	1.91	0.46
110	18.10	7.34	0.10	0.0	0.01	315.50	245.00	1.44	1.90	0.49
113	18.30	7.23	C.1C	C.C?	0.18	300.00	245.00	0.55	1.73	0.81
115	18.50	7.15	C.10	0.11	0.20	109.00	245.50	0.78	1.51	0.86
123	18.20	7.23	C.10	0.01	0.00	309.00	247.00	0.70	1.54	0.02
127	18.20	7.22	C.C	0.02	0.0	306.50	242.00	0.85	1.57	0.09
131	18.00	7.32	0.C	0.0	0.01	317.00	242.50	0.34	1.16	1.01
137	18.50	7.32	C.1(0.0	0.09	316.50	242.00	0.59	1.21	1.12
140	18.20	7.76	C.C	0.04	L.06	316.00	242.00	0.48	1.15	1.22
143	16.00	7.36	C.C	C.O	0.0	317.00	244.00	0.72	1.35	1.78
149	18.10	7.34	C.C	0.0	0.0	15.00	244.00	0.25	0.70	1.43
151	17.90	7.50	2.80	0.0	0.06	322.00	244.00	1.21	() . 44	1.33
153	17.90	7.37	0.56	0.0	0.15	370.00	244.00	0.60	1.15	1.36
157	17.40	7.30	0.0	0.04	0.03	317.00	242.50	0.46	1.59	1.14
STATISTIC	AL EVALUAT	IONS								
Mean	18.22	7.57	3.23	0.04	0.10	321.74	244.64	0.42	1.40	1.03
Minimum	16.70	7.19	0.0	0.0	0.0	306.50	237.00	0.0	0.44	0.61
Maximum Standard	19.70	7.94	8.40	0.20	0.28	334.50	249.00	2 80	1.99	1.52
Oeviation	0.61	0.20	2.78	0.05	0.08	5.50	2.26	0.48	0.39	0.26

TABLE A-8

RUN NO	TEMP	рн	0.0.	FE2T	FEI	ALK	HONS	NH 3N	NO2N	ND3N
εe	17.00	7.74	8.70	0.01	0.09	333.00	245.00	2.00	0.04	1.32
88	17.30	7.67	7.60	0.03	0.04	334.00	246.00	2.03	0.02	0.23
90	17.30	7.88	7.70	0.03	0.22	335.00	245.00	1.97	0.05	0.32
C.S.	16.90	7.70	7.76	C.C4	0.17	333.00	246.00	1.01	0.10	0.74
5 A	16.80	7.68	6.5C	C.C4	0.16	329.00	245.00	1.01	0.47	0.43
09	18.00	7.42	1.40	0.11	C.14	320.00	248.00	3.16	1.95	0.55
102	18.00	7.30	C.1C	0.08	0.01	316.00	245.50	1.66	2.36	0.44
107	18.40	7.30	C.1C	0.0	0.0	318.00	246.00	1.22	2.54	0.40
110	18.00	7.32	C.10	0.C	0.03	314.00	245.00	1.21	2.55	7.34
113	18.40	7.20	C.16	0.0	6.09	309.00	246.00	0.52	2.45	0.31
115	18.40	7.16	C.1C	0.02	0.18	307.00	246.00	0.59	2.35	0.32
119	17.20	7.28	0.20	0.03	0.01	307.50	246.00	0.60	2.41	0.34
123	17.40	7.20	0.0	0.01	0.0	309.00	246.00	0.40	2.28	0.42
127	17.30	7.17	0.0	0.01	0.0	301.00	245.00	0.73	2.35	0.26
131	17.20	7.25	C.1C	0.C	0.0	314.50	244.00	0.14	1.98	0.46
134	17.60	7.24	C . C	0.0	0.C	313.00	243.00	0.42	2.03	0.5?
137	17.50	7.28	C . C	0.02	0.09	315.50	242.50	0.36	1.98	0.60
140	17.40	7.30	0.0	0.03	0.03	315.00	243.00	0.28	1.92	0.72
143	17.30	7.33	0.0	0.C	C.O	316.00	244.00	0.27	2.10	0.80
146	17.10	7.33	0.10	0.C	0.19	317.00	244.00	0.27	2.00	0.00
149	17.10	7.32	0.40	C.O	0.04	315.00	244.00	C.0	2.00	0.50
151	18.00	7.71	6.86	0.0	0.07	329.00	243.00	2.11	0.18	0.52
153	17.90	7.60	5.00	0.0	0.10	325.00	243.00	1.76	0.67	0.61
155	17.50	7.33	C.8C	0.0	0.04	316.00	244.00	0.00	1.95	0.59
157	17.80	7.33	0 • C	0.02	0.02	316.00	243.00	0.33	2.17	0.52
STATISTI	CAL EVALUA	TIONS				- -				
Mean	17.55	7.40	2.14	0.02	0.07	318.22	244.72	1.04	1.63	0.48
Minimum	16.80	7.16	0.0	0.0	0.0	301.0	242.50	0.0	0.02	0.29
Maximum	18.40	7.88	8.70	0.11	0.22	335.0	248.0	3.16	2.55	0.80
Standard Deviation	0.47	0.21	3.25	0.03	0.07	9.27	1.38	0.82	0.93	0.15

TABLE A-9

RUN NO	TEMP	РН	0.0.	FE2T	FET	ALK	HPNS	NH3N	N 92 N	V031
86	17.10	7.74	8.ec	0.0	C•21	332.50	244.50	1.93	n.0ª	0.20
88	17.20	7.67	7.EO	0.05	0.33	333.00	246.00	1.61	0.02	0.55
90	17.20	7.91	7.80	0.05	C.41	335.50	245.50	1.08	0.03	0.44
95	17.20	7.75	8.00	0.08	0.43	334.00	245.00	1.95	0.05	0.74
9.8	16.70	7.78	8.10	0.03	0.19	332.00	244.00	1.30	0.10	.0.75
99	16.80	7.76	7.60	0.09	0.18	332.00	246.50	5.07	0.15	0.33
102	17.00	7.41	6.00	0.08	C.01	330.50	246.50	3.31	0.58	0.40
107	17.40	7.32	C.20	C.C1	0.01	318.00	245.00	1.29	2.52	0.38
110	17.00	7.36	C.30	C.C	C.02	316.50	246.50	0.92	2.21	0.30
113	17.10	7.23	C.7C	C.02	0.41	311.00	245.00	0.56	2.03	0.35
115	17.40	7.20	0.30	C.C1	0.0	300.00	246.00	0.68	2.35	0,23
119	17.20	7.32	0.90	0.02	C.01	309.50	245.00	0.08	2.22	0.30
123	17.30	7.25	C.EC	0.01	C.01	310.00	246.50	0.74	2.04	0,10
127	17.30	7.20	C.(C	0.02	C.C3	307.50	242.50	1.29	1.00	0,32
131	17.20	7.31	C.4C	0.0	C . O ·	315.00	247.50	0.12	2.01	0.44
134	17.70	7.31	C . C	C . C	0.7	314.50	244.00	0.27	2.06	7.59
137	17.60	7.28	0.10	0.02	C.11	315.50	243.00	0.42	2.01	C.55
140	17.40	7.32	C.7C	0.0	C.C	315.00	244.00	0.45	2.00	0.60
143	17.20	7.33	C.1C	0.0	0.04	314.00	244.00	0.18	2.24	0.56
146	17.CO	7.23	C.2C	0.C	0.27	316.00	244.00	0.33	2.16	0.65
149	17.20	7.32	0.PC	0.0	0.14	315.00	244.00	r.n	2.14	0.65
151	17.00	7.34	0.10	0.C	0.13	312.00	242.00	C.10	2.10	0.56
152	17.80	7.33	0.10	0.0	C.12	316.00	244.00	C.33	2.20	0.61
155	17.60	7.29	C . F C	0.01	0.04	314.00	243.00	0.79	2.10	0.44
157	17.70	7.34	0.10	0.01	0.06	316.50	242.00	C • 35	5.00	0.65
STATISTIC	CAL EVALUAT	IONS								
Mean	17.29	7.43	2.44	0.02	0.13	318.94	244.53	1.05	1.58	0.47
Minimum	16.70	7.20	0.0	0.0	0.0	307.50	242.00	0.0	0.02	0 2 3
Maximum Standard	17.90	7.91	8.80	0.09	0.43	335.50	246.50	5.07	2.52	0.68
Oeviation	0.30	0.21	3.39	0.03	0.14	9.23	1.33	1.16	0.93	0.14

145

RUN NO	TEMP	РН	0.C.	FE2T	FET	ΛLK	HONS	NH3N	NO2N	NOPN
86	21.90	7.72	8.50	0.06	0.16	333.00	.246.00	1.88	0.04	0.20
88	21.90	7.62	6.50	0.04	0.02	331.50	246.00	1.79	0.14	0.46
90	21.40	7.81	6.60	0.06	0.18	332.50	746.50	1.82	0.14	0.46
95	22.60	7.41	0.40	0.01	0.13	320+00	247.00	0.07	1.96	0.58
98	22.00	7.51	3.1C	0.04	0.22	322.00	245.00	0.12	1.33	0.45
99	21.90	7.36	0.40	C.12	0.17	319.00	246.00	3.25	2.11	0.58
102	22.30	7.30	0.10	0.07	0.0	314.00	246.00	1.68	2.35	0.44
167	23.30	7.30	0.10	0.02	0.02	318.00	246.00	1.39	2.30	0.44
110	22.10	1.32	G.10	0.0	0.0	315.50	247.00	1.40	2.11	0.43
113	22.80	7.18	0.10	0.01	0.14	307.00	245.00	0.52	2.32	0.31
115	23.00	1.18	6.36	0.02	0.10	289.00	228.00	C • 18	2.07	n.25
119	23.10	7.28	C.10	0.04	C.02	298.00	239.50	0.63	2.18	0.12
123	22.90	7.19	0.0	0.0	0.0	336.50	246.00	0.41	2.25	0.49
127	23.60	7.15	0.50	0.01	C • O	303.00	241.50	C.65	2.78	C.47
131	22.90	7.28	0.20	C.C	0.0	315.00	247.00	0.12	1.91	0.52
134	22.90	7.27	C.1C	0.C	C.C	315.00	243.50	0.36	2.09	0.58
137	23.00	7.70	0.C	0.0	0.03	315.50	443.00	0.45	1.96	0.55
140	23.00	7.18	C.10	0.04	n.o	313.00	55P.00	0.33	2.00	n. 76
143	24.60	7.21	C • C	C.O	0.0	313+00	619.00	0.29	2.09	0.66
146	25.80	7.16	0.10	C.O	0.10	312.00	748.00	C.48	1.97	0.90
140	23.60	7.21	0.20	0.C	C°Ú8	311.00	604.00	C. C6	1.92	0.80
151	25.00	7.32	0 • C	C.C	0.02	316.00	244.00	0.30	1.55	0.69
153	25.20	7.31	0.0	0.C	0.02	316.00	243.00	C.40	2.00	0.75
155	23.20	7.24	C.C	0.C	0.09	316.00	244.00	0.80	5.03	0.05
157	24.00	7.30	C • C	0.01	C.C5	323.00	242.50	0.43	0.40	0.16
STATISTIC	CAL EVALUATIO	NS								
Mean	23.12	7.32	1.13	0.02	0.06	314.98	313.90	0.84	1.75	0.49
Minimum	21.40	7.16	0.0	0.0	0.0	289.0	228.0	0.06	0.04	0.06
Maximum Standard	25.80	7.81	8.50	0.12	0.22	333.0	748.0	3.35	2.35	0.80
Deviation	1.11	0.17	2.44	0.03	0.07	9.89	150.18	0.78	0.70	0.20

TABLE A-10

TABLE A-11 Verification of stoichicketrickships of chserved chemical changes in water FCR Filter NO. 1 Using NO2 and NC3 FORMED DATA

OPHC OM	0.38 0.38 0.43 0.28 0.28 0.24 0.24 0.24 0.24 0.24 0.24 0.39 0.19 0.35 0.35 0.35 0.36 0.36 0.38 0.38 0.38 0.38 0.38 0.38 0.38 0.38	
0PH08S	0.314 0.22 0.32 0.32 0.35 0.33 0.33 0.33 0.33 0.33 0.33 0.33	
PHVAR	0.00 0.00 0.00 0.10 0.10 0.10 0.01 0.02	
PHC OM		N ちょうちょうてゅうちょうよ 800 ちゅみゅてて
OALKCO	13, 36 13, 36 13, 64 14, 21 16, 57 16, 57 16, 57 11, 65 11, 65 13, 57 13, 57 14, 57 14	06VIATI0 0.1 11 11 35 25 25 00 00 00
0L AK 0.8		510
AL KV AR		ME ME ME ME ME ME ME ME ME ME
ALKCOM	321.14 321.14 322.34 322.36 322.46 322.40 312.479 3170 3170 31000000000000000000000000000	
COUP		7 044 VIC 370 0000 000 000 000 000 000 000 000 00
TROCO	4 4 9 9 9 9 9 9 9 9 9 9 9 9 9 9 9 9 9 9	CN N N N N N N N N N N N N N N N N N N
TDCC	6.118 7.24 7.24 7.25 5.55 5.55 5.55 5.55 5.55 5.55 5.55	14 142 V
PCNV		
TNEF		AL EVALU ILLES: ILLES: ILLES: ILLES: ILLES: ALLES: VALLES:
ININ		5511 5511 5511 5511 5511 5551 5551 5551 5551 5551 5551 5551 5551 5551 5551 5551 5551 5551 5551 5551 5551 5551 5551 5551 5551 5551 5551 5551 5551 5551 5551 5551 5551 5551 5551 5551 5551 5551 5511 5551 5551 5511 5551 5511 5511 5551 5511 5511 5551 5511 5511 5551 5511 5511 5551 5511 5511 5551 5511 5511 5551 5511 5511 5551 5511 5511 5551 5511 5511 5551 5511 5511 5551 5511 5511 5551 5511 5511 5551 5511 5511 5551 5511 5511 5551 5511 5511 5551 5511
ARUN	880 990 990 990 990 990 990 111 111 111 11	3363553555555555555555555555
NO	666 666 666 666 666 666 666 666 666 66	

TABLE A-12 VERIFICATION OF STCICHTCRFFTIC "ELITIONSHIPS OF CHSFFVED CHEMICAL CHANGES IN WATER USING NUZ AND NC2 FURMUD DATA

0 PHC OM	0.38 0.38 0.34 0.34 0.423 0.423 0.423 0.423 0.423 0.423 0.424 0.424 0.4410000000000	
0PH/JBS	0.31 0.37 0.37 0.37 0.33 0.33 0.33 0.34 0.33 0.34 0.34 0.34	
PHVAR	-0.01 -0.01 0.05 0.06 0.00 0.01 0.01 -0.01 -0.01 0.01 0.01 0.	
PHCOM	7, 29 7, 21 7, 21 7, 24 7, 24 7, 25 7, 29 7, 20 7, 20,	2 ちてのものここものまちょうててちますの
OALKCD	14, 50 14, 50 14, 50 15, 50 15, 50 17, 50 17, 50 17, 50 17, 50 17, 50 17, 50 17, 50 17, 50 17, 50 11, 50 11	0 - 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
OLAKOB	1126-000 1126-000 1126-000 1127-0000 1127-0000 1127-00000000000000000000000000000000000	510
ALKVAR	0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	MEAN 3.05 -3.16 -3
ALKCUM	320.00 320.00 325.00 325.00 325.00 325.00 325.00 325.00 312.25 31	
CCUP		10000000000000000000000000000000000000
TROCO	3.64 3.64 3.64 3.66 3.66 3.66 3.66 3.65 3.65 3.67 3.67 3.67 3.67 3.67 3.67 3.67 3.67	AXI AXI 3325 3325 3325 17 17 17 17 17 17 17 17 17 17
TOGE	7, 25 7, 15 7, 15 7, 15 7, 26 8, 57 8, 57 8, 57 7, 55 7, 55 7, 55 8, 37 7, 55 7, 55	ХАНТАТ
PCNV	5.68 5.68 5.68 5.68 5.68 5.68 5.68 5.68 5.68 5.55 5.55	AIICAS CO PINIMUN 1.55 1.55 1.55 4.64 1.55 1.55 2.57 5.55 2.57 5.55 2.57 5.55 1.55 1.55 1.55 1.55 1.55 1.55 1
INEF		AL CLUES: AL CLUES: ALLES:
TNIN		1 1 1 1
NRUN	<pre>4 7 7 886 9 95 9 95 9 95 9 95 9 110 9 110 1 10 1 10 1 10 1 10 1 10 1</pre>	
N		



TABLE A-13 VERIFICATION OF STOICHICPETRIC RELATIONSHIPS OF CHSERVED CHEMICAL CHANGES IN WATER FOR FILTER NO. 3 USING NC2 AND NO. 3

OPHCOM	0. 39 0. 39 0. 39 0. 48 0. 48	
0 PH08 S	0.35 0.39 0.39 0.39 0.25 0.25 0.25 0.25 0.25 0.25 0.25 0.25	
PHVAR	0.03 0.09 0.09 0.09 0.00 0.00 0.00 0.00	
P HC OM	2 6 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	2 うちゅううちょうてょうてんちょう
OALKCO	14.70 15.71 16.64 10.56 10.56 13.56 13.56 15.57 16.47 16.47 16.47 16.47 16.47 16.47 16.57 16.57 11.56 11.57 11.56	06 VIATIO
OL AK 0.8	144.50 144.50 144.00	S T O
ALKVAR	0.01 0.01	MEAN MEAN MEAN MEAN MEAN MEAN MEAN MEAN
ALKCOM	314.55 314.55 314.75 314.75 327.00 327.00 327.00 314.55 314.65 314.65 314.65 314.65 314.65 314.65 314.67 313.35 314.67 312.63 317.21 317.21	
CCUP	1 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	7 7 7 7 7 7 7 7 7 7 7 7 7 7
TRUCO	3 日本1000000000000000000000000000000000000	C N S 0001111 300 0001111 00001111 00001111 00001111 00001111 00001111 00001111 00001111 00001111 00001111 00001111 000011111 000011111 000011111 0000111111 0000111111 000011111111
1000	7, 52 7, 52 7, 55 7, 55 7, 55 7, 55 7, 55 7, 55 7, 65 7, 84 7, 84 84 84 84 84 84 84 84 84 84 84 84 84 8	. VARIATI
PCNV	СС1-7 0 0 0 0 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0	ATICAS CF PINIFUF PINI
TNEF	0.0001494034035600000000000000000000000000000000	AL AL AL AL AL AL AL AL AL AL
ININ	4 年 2 4 5 4 5 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	1 4 1
IC ARUN	66 86 86 86 86 86 86 86 86 86 86 86 86 8	44464666644466666666666666666666666666
	1	

TABLE A-14 VERIFICATION OF STOTCHICPETRIC RELATIONSHIPS OF CUSERVED CHEMICAL CHANGES IN MATER FOR FILLER NO. 4 ΙA

CΔ
P ME 0
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E CIN
AAC
N02
1 NG
US

OPHC CM	000 000 000 000 000 000 000 000	
OPHOB S	9.33 (0.33) (0.3	
PHVAR	0.07 0.01 0.01 0.01 0.01 0.01 0.05 0.05 0.02 0.02 0.02 0.02 0.02 0.02	
PHCOM	7, 31 8, 52 9, 52 1, 52,	Z らてつよるic N 5 のよすの 4 て 5 に 1 ら 5
DALKCO	15.00 15	8 8 9 9 9 9 9 9 9 9 9 9 9 9 9
OL AKUB	14.00 14.50 12.00 12.00 15.00 16.00 15.50	S 10
ALKVAR	0.50 0.14 0.14 0.14 0.15 0.28 0.28 0.28 0.28 0.28 0.28 0.28 0.28 0.28 0.28 0.28 0.28 0.28 0.28 0.29 0.28	H E A N A A A A A A A A A A A A A A A A A
ALKCOM	320.07 318.07 318.07 318.07 318.07 318.07 318.18 318.18 316.08 316.08 316.08 316.08 316.00 316.00 316.00 317.43 31	
COUP	000 00 00 00 00 00 00 00 00 00	2 80810010010000000000000000000000000000
TRCCC		CNS 3333624499555 182 182 182 9999 192 192 192 192 192 192 192 192 1
TOLE	4 3 2 7 5 5 6 6 8 6 7 7 7 7 7 7 8 8 8 7 7 4 5 8 8 8 7 7 7 8 8 8 7 7 7 8 8 8 7 7 9 8 8 8 7 9 9 8 9 7 9 9 8 9 9 9 9	V A R I A T I
PCAV		TICAS TICAS TASE
TNEF	2,455 2,455 2,455 2,455 2,455 2,455 1,556 2,455 2,4566 2,456 2,456 2,456 2,456 2,456 2,456 2,456 2,456	IL EVALUA LLES: LLES: LLES: LLES: LLES: LLES: LLES: ALLES:
VINT	ククク ショウ み ご う ころう う う ク ク ク ク ろ ろ ろ ろ ろ う う ろ う う う う う	FATISTIC
ARUN	9 9 9 9 9 9 9 9 9 9 9 9 9 9 9 9 9 9 9	C C C C C C C C C C C C C C C C C C C
S Z	0 0 0 1 1 1 1 1 0 0 0 0 0 0 0 0 0 0 0 0	

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TABLE A-15 VEFIFICATION UF STCICHICPETRIC RELATIONSHIPS OF OBSERVED CHEMICAL CHANGES IN WATER FOR FILTER NG. 5 USING NOZ AND NG FORMED DATA

	.03 0.03	0.02 0.02	02 0.02	0.0 -0.00	05 0.12	.32 0.41	40 0.45	44 0.46	45 0.50	.38 C.36	36 0.33	37 0.40	37 0.34	42 0.36	45 0.41	46 0.42	41 0.42	43 0.43	47 0.48	40 0.43	40 0.41	0.09	15 0.23	41 0.39	42 0 • 44			
HAD YE	06 - 0.	04 -0.	04 -0.	05 -0.	77 0.	0 0.	05 0.	92 0.	05 A.	02 0.	03 0.	03 0.	03 Ú.	06 0.	04 0.	04 Ú.	01 0.	00 00	06 0.	03 7.	01 0.	04 0.	08 0.	02 0.	02 0.			
AH4 MI	8 0.	.3 0.	14 0.	5 0.	.1 0.	3 0.	5 0.	.0	7 0.	-0-	-0- 6	5	-0-	·3 -0°	-0-	•0- 8	7 0.	-0-	-0 L	0 0	1 0.	7 0.	2 0.	-0- 5	1 0.			
0 PHC	9 7.6	3 7.6	1 7.8	9 7.6	1 7.6	9 7.3	9 7.7	7 7.2	1 7.2	3 7.2	9 7.1	7 7.2	3 7.2	3 7.2	0 7.2	3 7.2	9 7.2	7 7.3	4 7.2	3 7.3	6 7.3	4 7.6	7 7.5	4 7.3	7 7.3			
B CALKC	0 -0.2	0 1.4	0 2.2	0 0.7	0 3.2	0 12.2	0 18.2	0 17.0	0 20.2	0 16.9	0 16.7	0 18.0	0 16.9	0 13.9	0 14.5	0 17.4	7.11 0	0 17.0	0 18.1	0 17.4	0 15.3	0 2.1	0 7.5	0 13.6	0 16.0			
R OLAKI	9 0.5	3 .0.5	1 1.5	1.0	9 5.0	1 13.5	9 17.5	3 18.0	9 2C.5	3 16.0	1 1A.0	7 17.5	7 18.5	7 20.5	7.0(7 19.5(1 17.0	7 16.0	4 15-0	3 17-0	5 15.0	5 3°0(7 7.00	5 14.00	3 17.5			
ALKVA	-C.7	7 C.S	c.7	L -C.2	-1.7	1 -1.2	1 C.7	6-0-6	9 -0.2	7 0.9	1 -1.2	0.5	-1.5	1 -6.5	7.5(1 -2.0	1 -0.2	3 1.0	3.14	7 0.4	. 0.3	-0-8(3 0°2.	-0-36	9 -1.4			
ALKCO	7.23. T	332.0	34.2	333.2	1.00°E	321.2	315.2	318.9	-14°2	308.0	338.2	306.9	309.5	307.5	307.00	315.0	315.7	313.9	312.80	316.5	314.6	328.8(324.4	316.3(317.4			
CUP	C.07	C+04	0.52	1.23	0.56	0.76	-C.29	0.72	0**0	0.85	0.32	0.71	1.08	1.07	1.25	1.00	0.94	1.41	0.59	1.27	1.05	0.02	-C.25	0.98	0.59			
TROCD	4.32	4.36	2.67	7.56	3.42	3.50	3.51	3.43	3.47	3.40	3 - 44	3.42	3.41	3.41	3.52	3.59	3.60	3.64	3.62	3 • 5 8	3.51	3° 95	3.75	3.47	3.47		1 C K C	I C M S
TCLC	C • 4 2	C • 2 6	C. C P	-C.23	1.54	7.24	8°53	8.68	9.10	8.C5	0°.CE	e.15	7.62	7.82	7.65	P.5C	8.46	8°15	5.21	e.23	7.55	1.10	3.45	6.62	7.81		F VARIAT	L VULLE
PCNV	-2.16	-2.18	7.11	6.0C	-0-53	-0.53	-6.64	-5.05	-8-64	-13.10	-6.85	-6.31	- C - 32	- é . 5 C	-2.36	-4.21	-3.85	1.05	-12.23	-5.32	1.52	1.75	-5.1c	-2.7C	-5°C5		ATTEAS (
TAEF	2.36	2.34	2.25	2.35	1.91	5.66	4.5C	4.16	4.15	3.28	3.26	15.5	3.10	3.44	2.58	2.57	2°04	ž • 82	3.12	2.17	2.60	2.81	3 - 04	3.42	3.12		AI FVAL	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
TNIN	2.31	2.29	2.53	2.50	1.90	5.63	4.22	3.56	3.82	2.9C	3.05	3.17	3°C3	3.23	2.52	2.65	K . 8 3	2.65	2.78	3.01	2.64	2.86	2.85	3 • 33	2.97		STATISTIC	
APUA	θ¢	9.9	06	55	86	66	102	107	110	113	115	119	123	127	131	134	137	14C	143	146	149	151	153	155	157			ĺ

		FINIMUN	MUMINAM	MEAN	STO DEVIATIO
F C R	25TNIN VALUES:	1.50	5.63	3.05	0.7
F OR	25TNEF VALLES:	1.51	5.66	3.15	0.8
FCR	25PCNV VALLES:	-13.10	7.11	-3.30	1
FCR	25TDD0 VALUES:	-0.23	9.21	6.11	
FCR	25TRCGC VALLES:	2.67	7.56	3.72	8.0
FCR	2500UP VALUES:	-0.25	1.41	0.68	04.0
FCR	254LKIN VALLES:	321.5C	336.50	330 . 88	
FCR	25ALKEF VALLES:	361.60	335.00	318.22	6.6
FCR	25ALKCCM VALLES:	206.5 ²	334.29	318.32	1.0
F OR	25ALKVAR VALLES:	-6.57	7.50	-0.10	2.3
FCR	250HONS VALLES:	-2.50	2.0C	0.12	0-1
FCR	25CALKC8 VALUES:	C. 5C	20.50	12.66	7.0
F C.R	25FALKCC VALLES:	- C • 2 S	20.21	12.56	6. 7
F C R	25PHIN VALLES:	7.52	7.86	7-70	
FCR	25PHEF VALLES:	7.16	7.68	7.40	0.2
F OR	25PHCCM VALLES:	7.15	7.84	7.38	1.0
FCR	25PHVAR VALLES:	-C.ć	0.09	0.02	
F CR	250PHDAS VALLES:	-0°C5	0.46	0.30	0.1
F C R	250PFCCM VALLES:	-0.00	0.50	r.32	0.1

TABLE A-16 verification of sicichicmetric relationships of coserved chemical changes in mater using not and not fertier data

02	N RUN	NINI	TNEF	FCNV	TDCC	TRCCC	COUP	ALKCOM	ALKVAR	OL AKOB	OALKC 0	PHCOM	PHVAR	0PH08S	OPHCOM
66	βé	2.31	15.5	C.C	C.31	6:.4	0.09	332.50	-1-00	1.00	0.0	7.69	G • 05	-0.03	0.02
5	88	2.25	2.38	-3.93	1.44	4.51	-1-14	331.21	1.79	1.50	3.29	7.57	0.10	-0-05	0.08
2 0	06		<pre></pre>	3.10	× • • •	0 0 0	20.0-	194°14	1 4.00	0.0	5.20	10 01			
		1.00	1.76	2.270		i 4 i 4	2 2 2 C	50°258		00.0	1.07	7.72	0.06	-0-02	0-01
2 =	00	5.6.2		C . 5 3	0.31	3.08	0.79	333.79	-1-79	1.50	-0-29	7.71	0.05	-0.02	0.03
2	102	4.22	4.29	-1.66	2.54	3.63	0.26	329.50	1.00	3 • 0 0	4.00	7.53	0.08	0.09	0.17
2	107	3.96	4.19	-5.81	E.52	3.42	0.78	318.21	-C.21	18.00	17.79	7.28	0 . 04	0.42	0.46
5	110	3.82	3.52	7.65	1.93	3.48	1.37	318.21	-1.71	18.00	16.29	7.32	0* 04	0.41	0.45
5	113	2° 5C	2.54	-1.38	6.75	3.41	1.51	305.79	1.21	14.00	15.21	7.26	-0.03	0.35	0.32
÷	115	3.05	3.26	-6.85	7.67	3.39	0.53	308°86	0.14	16.00	16.14	7.20	-0.00	C. 32	0.32
-	119	3.17	2.60	17.58	7.26	3.39	0°94	307.71	0.79	16.50	17.29	7.27	0.05	0.33	0.38
80	123	3.05	3.17	-2.55	6.66	3.40	1.44	312-00	-2.00	16.50	14.50	7.26	-0.01	0.32	0.31
0	127	3.23	2.50	-E.36	é.CE	3.38	2.22	308.64	-1.14	14.00	12.86	7.29	0.01	0.29	0.30
0	131	2.52	2.57	-1.98	7.66	3.51	0.94	206.43	8.57	6.50	15.07	7.29	0.02	0.39	0.41
-	124	2.85	2.92	-7.46	C 0 - H	3.61	0.58	315-36	-0-86	18.00	17-14	7.26	0.05	0.39	0.44
4 6															
N	151	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	20.0	0.0	8• 3E	200	78.0	67.010	2.0	00.1	12.01	07.5		1	
*5	141	12 . 7	3.00	20.01 -	0 + 20	0 - 20	* 0 * 0	00.010	C • 20	10.00		1.02	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	1	
4	143	2.78	2.98	-7.15	e.59	3.52	1.11	313.57	0.43	17-00	17.43	1.29	0.04	0.42	0.40
2	146	3.01	3.14	-4.32	e.cs	3.50	1.31	316.50	-0.50	18.00	17.50	7.30	0.03	0**0	0.4
-0	145	2.64	2.81	- 6.44	8.32	3.53	-0.12	313.14	1.86	15.00	16.86	7.28	40.04	0++0	0.44
5	151	2.86	2.94	- 2 . 80	P.24	3.51	C.56	313.21	-1.21	19.00	17.79	7.30	0.04	0.42	0.46
• •			2.14		R.AF	15.5	- U - S B	314.50	1.50	16-00	17.50	7.29	0-04	0.42	0-46
0 0		2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2			2.00	1.4		310 015	1 14	14.00	17.14	7.30	-0-01	0.45	14.0
7 .				1201-	· · ·	10.00	n e 1 -			00.00					
0	15/	15.51	3.06	-3.03	10.1	5 • 4 4	56.03	61 - 1 15	67.1-	11.000	17.61	1.32	0.02	1+*0	0.4
		STATI STICA	L EVALUA	ATICNS CF	VARIETI	CMS									
				PINIPLE		MAXI	MUM		MEAN	S T 0	OEVIATIC	NG			
	ŝ	Actives were				u			200		c				
	ž č	JAN NINICZ) / · · ·					0.0		° °				
	¥ S	STOCHE VAL					000		0.1						
	ž	JAV VAUVES	LES:	10.0		-	L		0		0	67			
-	L R	251000 VAL	LES:	-0.40			26*		5.85		÷.	0			
-	F C R	25TRCOC VA	LLES:	55.4-		4	16.		3.65		1.1	6.8			
-	F CR	25COUP VAL	LES:	-1.14			.22		0.64		•	73			
-	FCR	25ALKIN VA.	LLES:	321.50		336	50		330.88		4.	32			
-	FCR	25ALKEF VA	LLES:	2C7.5C		335	.50		218.94			53			
-	R C R	25ALKCCM V	ALLES:	506.43		324	-14		218-61		0	19			
	00 4	25ALKUAR V	ALEST	- 2.00		ď	5.7		55.0			-			
		SPLICNC VA	10000	-1-00			00		0.50			10			
		25CALKON V	ALUES			101			11.94		1.6				
		SECALACION	ALLES -			• •	000		10 01		4	10			
		CLHENES V				4					5 0				
	F C R	Z5PHIN VAL	LES:	1.56		- 1	.86		1.70		0	1.1			
	FC K	Z5PHEF VAL	LE 5 :	7.20			16*		1.43		°.	21			
_	FCR	25PHCCM VA	LUES:	7.20		~	.81		7.39		••	19			
_	FCK	25PHVAR VA	LLES:	-0°C3		0	.10		0.04		0*0				
-	FCR	25CPHORS V	ALUE S:	-C.10		c	.45		0.27		•0	61			
-	FCR	25CPFCCM V	ALLFS:	-C.C1		0	1.46		0.31		•0	17			
TABLE A-17 VERIFICATION OF STOTCHICPETRIC RELATIONSHIPS OF CUSERVED CHEMICAL CHANGES IN WATER FOR FILTER NG. 7 USING NO2 AND NO3 FORPED DATA

		_		_																					_	 		 	
DPHC OM	0.00	0.09	0.10	0.37	0.30	0.44	0.45	0.45	0.45	0.36	0.33	0.39	0.35	0.38	0.42	0.45	0.42	0.46	0.47	0.43	0.44	0* 40	0.47	0.35	0.13				
прнов S	-0.01	0.03	0.05	0.24	0.22	0°38	0.40	0.44	0.45	0 - 40	0.34	0.37	0.38	0.40	0.42	0.43	0.49	n. 55	0.54	0.57	0.51	0.44	0.44	0.50	0.45				
PHVAR	0.01	0.06	0.05	0.13	0.08	0.06	0.05	0.01	0.00	-0-04	-0.01	0.02	-0.03	-0.02	-0*00	0.02	-0.07	-0.09	-0.07	-0.14	-0.07	-0.04	0.03	+0.15	-0.32				
PHCOM	7.71	7.56	7.76	7.28	7.43	7.30	7.25	7.29	7.32	7.22	7.19	7.26	7.22	7.21	7.28	7.25	7.27	7.27	7.28	7.30	7.28	7.36	7.28	7.39	7.62				
OALKCO	-2.14	3.50	2.29	14.79	9.50	15.64	17.43	15.64	15.36	17°C0	32.29	23.64	17.14	17.71	15.43	17.79	16.29	17.64	17.07	15.86	16.21	12.14	18.07	11.21	3.50			0EVIATION	0.75
OL AKOB	0*50	3.00	4.00	14.00	12.00	14.50	19.50	18.00	19.00	18.00	36.00	27.00	20.00	18.50	6.50	17.50	17.00	18.00	18.00	22.00	19.00	15+00	16.00	14.00	10.50			STD	
ALKVAR	-2.64	0.50	-1.71	0.79	-2.50	1.14	-2.07	-2.36	-3.64	-1.00	-3.71	-3.36	-2.86	-C.79	P.93	0.29	-0.71	-0.36	-0.93	-6.14	-2.79	-2.86	2.07	-2.79	-7.00			MEAN	3.05
ALKCOM	335.64	331.00	334.21	319.21	324.50	317.86	316.07	32C.36	319.14	306.00	292.71	301.36	309.36	303.79	306.07	314.71	316.21	313.36	312.92	318.14	312.79	318.86	313,93	318.79	330.00				
CUP	0.81	-0.45	0.71	1.07	20°03	0.38	-0.08	1.36	1.73	1.30	1.39	1.79	0.91	-0*00	1.12	0.42	1.14	0.51	1.26	1.55	0.62	2.27	-0.44	3°53	7.37			MUM	•63 •
TRDUD	5.68	4.13	3.96	3.49	3.44	3°50	3.50	3.45	3.50	3.39	3.40	3.40	3.44	3.46	3.56	3.61	3 . 58	3.64	3.57	3.58	3.60	3.60	3.61	3.10	2.45		S N S	MAXI	5,
TDOC	-C.11	1.45	C.99	7.23	4.57	7.52	e.7E	P.04	7.77	7.6C	£.81	7.22	7.75	8°C5	7.6F	E. 5 E	E.16	6°3	8.54	7.95	e.1e	6.63	8.64	4.E7	1.03		VERIATI		
PC NV	8.23	-4.37	4.35	-4-4C	-0.00	-7.28	-5.92	-4.25	-3.14	-8.62	-1.64	1.2¢	-1.62	-5.26	-1.19	-6.32	-4.59	-8-42	-8°30	-6.31	-5,3C	11.19	-5°00	13.21	36,36		TICAS CF	MINIM	1.50
TNEF	2.12	2.39	2.42	2.61	1.90	£ • 04	4.47	4.13	3.54	2.15	3.1C	3.13	3.14	3.40	2°55	3.03	ž • 96	3.09	3°C3	3.20	2.7B	2.54	3.15	2.89	1.85		FVALUA		ES:
ININ	2.31	2.25	2.53	2.50	1.90	5.63	4.22	3.5¢	3.82	2°2C	2°C5	3.17	3.09	3 • 23	2 + 5 2	2.85	2.83	2.65	2.7E	3.01	2.64	2。8ć	2.89	5.33	2.57		211511C41		ININ VALL
NRUN	Еć	88	90	55	98	66	102	107	110	113	115	119	123	127	131	134	137	140	143	146	145	151	153	155	157		514		CR 251
NC	é é	67	68	90	70	11	72	22	14	15	16	17	18	52	80	61	82	63	B 4	85	86	87	8	68	90				

STD DEVIATION	0.75	0.87	9. E2	2.77	0.52	1.54	4.32	9.89	10.01	3.62	3.98	7.44	7.05	0.07	0.17	0.15	0°0	0.16	0.13
MEAN	3.05	3.08	-0.88	6 . 5 5	3.59	1.24	330.88	314.98	316.44	-1.46	1.08	15.90	14 . 44	7.70	7.32	7.34	-0.02	0.38	0.36
MUMIXAM	5.63	6 • C 4	36.36	3°49	5.68	7.37	336.50	333.00	325.64	8°53	19.00	36.00	32.29	7.86	7.81	7.76	0.13	C.47	0.47
MININ	1.50	1.69	-9.CC	-C.11	2.45	-C.45	321.50	209.CC	292.71	-7.60	-2.00	C.5C	-2.14	7.52	7.16	7 °] c	-C.32	+C.Cl	C. CC
	251NIN VALLES:	25TNEF VALUES:	25PCNV VALLES:	251000 VALLES:	25TPCOC VALUES:	2500UP VALLES:	25ALKIN VALLES:	25ALKEF VALLES:	25ALKCCM VALLES:	25ALKVAR VALLES:	25CHENS VALUES:	25CALKOR VALLES:	25CALKCC VALLES:	25PHIN VALLES:	25PHEF VALLES:	25PHCOM VALLES:	25PHVAR VALUES:	250PHOHS VALLES:	25UPHCCP VALUES:
	FCR	FCR	F OR	F OR	F C R	F C R	F C R	FCK	F C R	F C R	F C P	FCK	F C R	FCK	F OK	F C K	F C P	FCF	F.C.R

TABLE A-18 VEPTFICATION OF STOICHICPETATIONSLIPS OF CASEPVED CHEMICAL CHANGES IN WATER USING APPONIA DEPLETION DATA

OPHC AL	0.03 0.03 0.05 0.010 0.05 0.010 0.010 0.010 0.010 0.025 0000000000
0PH08S	-0.05 -0.05 -0.05 0.01 0.01 0.01 0.01 0.01 0.114
PHŪEV	0.07 0.07 0.07 0.06 0.07 0.07 0.07 0.07
PHCAL	7. 58 7. 79 7. 79 7. 79 7. 79 7. 79 7. 79 7. 59 7. 50 7. 50
PHEF	<pre></pre>
NIHd	18.1 18.1 18.1 18.1 18.1 18.1 18.1 18.1
OALKCA	6.43 0.53 0.54 0.55
0ALKOB	
ALKOEV	00.00 0.
ALKCAL	325-57 321-50 322-55 22-55 22-55 22-55 22-55 22-55 22-55 22-55 22-55 22-55 22-5
ALKEF	3224.00 3224.00 3224.00 3224.00 3225.00 325.000 325.000 325.000 325.000 325.000 325.00
ALKIN	3324.0CC 3224.0CCC 3224.0CCC 3224.0CCC 3224.0CCC 3224.0CCC 3224.0CCC 3224.0CCC 3224.0CCC 3224.0CCC 3224.0CCC 3224.0CCC 3224.0CCC 3224.0CCCC 3224.0CCCC 3224.0CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
R000	П П П П 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4
CCL	00000000000000000000000000000000000000
PUN	12~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
VU VU	- NF 4 5 9 - N F 4 5 - N F 4 5 9 - N F 4 5 - N F 4 5 - N F 4 5 - N F 4 5 - N F 4 5 - N F 4 5 - N F 4 -

TABLE A-18 (Continued) VILIFICATION OF STUTCHORDELING OF GUSEPVED CHIMICES IN MATCH FUNCTION OF CONTRACTOR OF THE NUCLE USING APPONIA SEPERTION DATA

CPHCAL 00.44 00000000	
0PH CES 0 28 0 28 0 28 0 29 0 2	
PHJFV 0.00 0.00 0.07 0.07 0.07 0.07 0.07 0.0	
PHCAL 7.443 7.445 7.445 7.445 7.445 7.445 7.445 7.445 7.441 7.	
AFFH 1, 5, 1 1, 5, 1 1, 5, 2 1, 5, 2 1, 5, 2 1, 5, 2 1, 4, 1 1, 4, 1 1, 5, 2 1, 4, 1 1, 5, 2 1, 5,	0 • 6 4 4 • • 8 4 • • 8 4 • • 8 4 • • 6 4 • • 6 6 • • 1 6 • • • 1 6 • • • 1 6 • • • 1 6 • • • • • • • • • • • • • • • • • • •
PHIN PHIN	
DALKCA DALKCA 11.43 13.973 13.973 13.64 11.657 12.557 12.557 12.557 12.557 12.557 11.71 12.57 11.71 11.71 11.71 11.71 11.71 11.77 11	1488 7 2 8 7 7 1 0 8 1 7 1 8 8 9 7 1 1 0 8 1 7 1 8
DALKUJ 12.50 12.50 14.50 14.50 15.50 1	4 - NN 000 & K K K 000 C
ALKEEV -0.57 -0.57 -0.57 -0.57 -0.57 -0.57 -0.57 -0.57 -0.57 -1.48 -0.57 -1.49 -0.57 -1.49 -0.57 -1.49 -0.57 -	
ALKCAL ALKCAL 3201-C7 3201-C7 3201-C7 320-679 320-679 320-679 320-679 320-679 320-679 320-679 3210-979 3210-114 3117-50 3117-50 3117-50 3118-670 3118-700 310000000000000000000000000000000000	6.22 3326.50 3316.50 9.71 18.00 18.00 16.21 16.21 16.21 16.21 16.21 7.95 7.95 7.95 0.47 0.47
ALKF ALKFF ALFFFF ALFFFF ALFFFF ALFFFF ALFFFF ALFFFF ALFFFF ALFFFF ALFFFF ALFFFFFF ALFFFF ALFFFFF ALFFFFFFF ALFFFFFFFF	
ALKIN ALKIN ALKIN 233,555 2555 2	1
х с с с с с с с с с с с с с с с с с с с	C C C C C C C C C C C C C C C C C C C
0CU 7.460 7.460 7.460 8.300 8.300 8.300 8.300 8.300 8.300 8.300 8.300 8.300 8.300 8.300 8.200 8.200 8.200 8.200 8.200 8.200 8.200 8.200 8.200 8.200 8.200 9.2000 9.2000 9.2000 9.2000 9.2000 9.2000 9.2000 9.2000 9.2000 9.2000 9.2000 9.2000 9.2000 9.2000 9.20000 9.20000 9.20000000000	Y DUC Y DUC Y DUC Y DUC Y DUC Y DUC Y DU Y DU
A B C C C C C C C C C C C C C C C C C C	7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7
2 0000000000000000000000000000000000000	

TABLE A-19 VEPIFICATION UF STCICHICPETRIC RELATIONSET OBSERVED CHEMICAL CHANGES IN WATER FCR FILTER NG. 2 USING AVPONIA DEPLETION DATA

- 1		-						_		_				_					_	_	-				_	-	_	_	-	-		_			_	_	_					-	-	_					
	OP HC AL	0.04	0.03	10.0-	0.05	0.09	0.09	0.20	0.23	0.26	0.23	0.30	0.28	0.26	0.25	0.26	0.27	0.27	0.26	0.26	0. 20	0.20	0.25	0.25	0.26	0.25	0.23	0.29	0.24	0.25	0.26	0.27	0.27	0.27	62.0	0.26	0.19	0.26	0.27	0.27	0.15	0.13	0.440	0.46	0.47	0.48	0.44		10 • 21
	0 РНОВ S	-0-05	-0.05	E0 0 -	-0.02	0.01	0.0	0.10	0.14	0.15	0.16	0.16	0.17	41 ° C	0-12	0.12	0.16	0.18	0-14	0.13	0.15		0-13	0.14	0.16	0.14	0.14	0°1*	0.13	0.13	0.14	0.13	0.13	0.13	110	0.16	9.10	0.15	0.18	0.12	0.10	0.16	44.0	0.42	0 4 0	0.44	0.35	0.02	C 7 411
	РНОЕ V	0.09	0.08	0.04	0.07	0.09	0.09	0.10	0.09	0.11	0.07	0.14	0.11		0.13	0.14	0.11	0°09	0.12	0.13	20°0		0.12	0.11	0.10	0.11	0.09	0.15	11.0	0.12	0.12	0.14	0.14	0.14		0.10	0.09	0.11	0.09	0.15	0.05	0.02	0.05	0.04	0.07	C. 04	50°0-		с
	PHCAL	7.77	7.80	7.80	7.79	7.73	7.75	7.63	7.63	7.60	7.56	7.60	7.60	1 5 7 5 T	7.60	7.60	7.57	7.62	7.61	7.58	1.054 F	7.63	7.60	7.59	7.61	7.59	7.61	1.03	1 678	7-64	7.63	7.62	7.60	7.62	1.50	7.63	7.66	7.63	7.64	7.65	7.48	7.50	7.32	7.34	7.34	7.32	7.51	7.48	0 • •
	PHEF	7.86	7.88	7.84	7.86	7.81	7.84	c1 • 1	7.72	7.71	7.63	7.74	11.1	7 67	7.73	7.74	7.68	7.71	7.73	1. 11	1.00	7.76	7.72	7.70	7.71	7.70	1.70	1.18	1.1.1	7.76	7.75	7.76	7.74	7.76	7.68	7.73	7.75	7.74	7.73	7.80	7.53	7.40	7.37	7.38	7.41	7.36	1.41	7.56	2 •
	PHIN	7.81	7.83	7.81	7.84	7.82	7.84	7.83	7.86	7.86	7.79	7.90	7.88	1001	7.85	7.86	7.84	7.89	7.87	7.84	7 000	00.4	7-85	7.84	7.87	7.84	7 - 84	26.1.	7 80	7.89	7.89	7.89	7.87	7.89	C 8 - L	7.89	7.85	7.89	10°1	7.92	7.63	23.7	7.81	7.80	1.81	7.80	7.70	7.79	
	OALKCA	11.50	1.57	-0.86	1.00	0.43	1.79	4°14	6.57	7.29	4°43	7.50	9.36	7.01	5.57	4.07	8.57	6.86	6 ° 29	10.21	6.30 0000	00. 4		6.43	6.07	6.43	5.93	1.95	8°21 5 43	A.14	5.71	9.79	9.07	8.43 .43	00°°0 87°8	7.64	6.50	7.14	5.79	10.36	4 • 00	1/ . 4	16.57	15.79	16.50	16.79	10.26	00.0	F-0.4 L
	0AL KOB	9.50	00° 4	00.6-	-6.00	5 •00	3.00	00.8	8.50	6.00	е "ОО	R .00	8.50	11-20	8.50	4 .50	7.50	3 •00	5.50	7 .00	00000		00.4	6.00	8 •00	5°20	7.50	00-1	000 4	00.7	é . 00	e •00	7.00	7.50	1.50	7.00	0 ° 9	10.50	5 °0 C	00. 0	2.50	26.4	13.50	12.00	10.00	15 .00	13.50	14.00	
	ALKOEV	2.03	-2.43	-0.14	7.00	-4.57	-1.21	-0.43	-1.93	1.29	-3.57	-0.50	0.86		- 2 - 0 3	1.57	1.07	3.96	0.79	3.21	0.80	06.2	2.43	0.43	-1.93	0.93	-1.57	0.43	-1.57	1 - 1 4	-0.29	1.79	2.07	0.93	10.92	0.64	0.51	-3.36	0.79	1.36	1.50	3.21	3.07	97.0	6.50	1.79	14.0-	- 5-00	
	ALKCAL	320.50	330.43	324.24	330.00	328.57	325.21	324.43	324.43	320.71	325.57	323° 50	321.64	221.073	329.43	325.93	326.43	322.14	322.71	319.79	325.64	12 222	324.57	326.57	328.93	324.57	326.07	324°01	326 57	374-36	324.79	320.21	321°93	323.07	324.67	326.36	327.50	328.36	326.21	223.54	327.50	320.24	315.43	316.71	311.50	313.71	316.64	123.00	
	ALKEF	322.50	328.00	00.655	337.00	324.00	324.00	322.00	322.50	322.00	322.00	323.00	322.50	014.510	326.50	327.50	327.50	326.00	323°50	323.00	326.5U	220.00	327.00	327.00	327.00	3 25 . 50	324.50	325.00	325 50	375.50	324.50	322°CO	324.00	324.00	3.25.00	327.00	328.00	325°CC	327.00	325.00	329.00	00.825	318.50	320.50	318.00	315.50	214°C2	318.00	0.0 + o T C
	ALKIN	332.CC	332°CC	329-60	331.00	329.00	327°C0	330,00	331.00	328.00	330.CO	331°CC	331.00	221.00	335.00	332.00	335 CC	329°CC	329°C0	330 ° C C	332.00		331.00	333.CO	335°CC	331°C0	332°C0	332 • CC	00.000	332.50	330.50	33C . CC	331.CC	331.50	232.656	334.00	334 • CC	325°5C	332 • 00	534°CC	331.50	336 • CC	372.00	332 . 5C	328.CC	330.5C	331010	332.60	
	ROCE	4.25	1.25		2.000	3.70	4.4	16.4	4.51	4.C7	4.70	4°C7	4°90	10.04	1 - V - V - V - V - V - V - V - V - V -	4.59	4.24	4°86	5.06	4 • 60	5.0.0	2 C L J	86.5	3.37	4.00	2.73	4 - 34	4•1C	50 44 F	1000	3.37	4.2C	3.53	9 8 0 0 0 0 0	2 C 0 1	3.67	4.45	4.13	4 ° C 7	4.0	5. FC	5 T 5	 	2.67	3. 62	3.68 2.68	10 C 4	4.60	2
	000	C - 2C	c.10		0.40	1.00	1.10	2.50	3.20	3 = 30	3 ° 5 C	3 • 7C	3.90	, t , t , t	3.70	2.90	3.50	4.00	4.10	4°CC	30,00		3.20	2.80	3.4C	3 • 1C	3 . 30		2 ° ° C	2.5	2.70	3.4C	3°00	3°2C	2,10	2.90	2.50	3 ° 3 C	0.00	0 c	4.10) C C C C C C C C C C C C C C C C C C C	7.80	8.10	8.50	0**8	7.10	5.80	3 5 7
	NRUN	-	21	n 4	5	9	- 0	r o	10	11	12	13	14	1 4	17		19	2 C	21	22	53	5 5	26	27	28	25	30	1 0	25	14	35	36	37	6) (C	1 4	41	43	44	4.	4 U	2.	- F		57	56	61 43	n 49	÷ •	2
	0 N	-	~	n 4	5	J.		ro	10	11	12	13	4 4	1	114	18	19	20	21	22	52	5 U	20	27	28	29	200	10	2 1	1 4	32	÷с.	37	8	0 7	41	42	4	44	4	4 Q.	3 3	6.5	25	15	25	5		1

TABLE A-19 (Continued) VERIFICATION OF STOTCHICMETRIC RELATIONSPIPS OF DASEPVED CHEMICAL CHANGES IN WATER

ÿ

	AL	30	14	43	41	44	41	42	40	39	37	38	33	48	34	25	36	41	64	44	33	30	28	22	19	38	40	38	41	44	40	42	45	43	39	42
	ОРНС	•0	•	•	•	•	•	•	•	•	•	•	•	0	•	•	ů	•	•	•	•	0	°	•	•	•	•	0	0	•	°	•	°	•	•	•
	0PH08S	0.25	0.33	0.35	0.36	0.39	0.41	0**0	0.39	0.35	0.36	0.37	0.35	0.41	0.25	0.21	0.33	0.39	0.44	0.44	0.35	0.34	0.27	0.24	0.22	0.39	0.41	0.38	0.41	0**0	0.39	0.42	0°45	0.44	0.46	0.42
	PHOE V	0° Û 5	0.08	0.08	0.05	0.05	00 00	0.02	0.01	0.04	0.01	0.01	-0.02	0.07	0°09	0.04	0. 03	0.02	-0.01	0.00	-0.02	-0.C4	0.01	-0.02	-0.03	-0.01	-0.01	00 00	00 00	0.04	0.01	-0.00	- 0° 00	-0.01	-0.07	-0.00
	PHCAL	7.47	7.42	7.39	7.39	7.35	7.38	7.35	7.34	7.34	7.32	7.33	7.32	7.38	7.31	7.4 8	7.38	7.29	7.31	7.33	7.25	7.22	7.37	7.35	7.40	7.32	7.30	7.31	7.32	7.31	7.33	7.30	7.31	7.32	7.35	7.33
	PHEF	7.52	7.50	7 . 4 7	7 . 44	0 + ° L	7.38	7.27	7.35	7.38	7.33	7.34	7.30	7.45	7.40	7.52	7.41	15.71	7.30	7.33	7.23	7.18	7.38	7.33	7.37	7.31	7.29	7.31	7.32	7.35	7.34	7.30	7.31	1.31	7.28	FE.7
	NIHd	7.77	7.83	7.82	7.80	7.79	7.79	7.77	7.74	7.73	7.69	7.71	7.65	7.86	7.65	7.73	7.74	7.70	7.74	7.77	7.58	7.52	7.65	7.57	7.59	7.70	7.70	7.69	7.73	7.75	7.73	7.72	7.76	7.75	. 7.74	7.75
ATA	DALKCA	10.96	12.86	15.07	13.14	14.29	14.36	15.07	15.00	13.86	14.14	13.29	13.57	15.00	15.43	P.71	12.43	16.07	16.21	15.21	15.64	15.57	11.29	9.07	7.79	14.07	15.50	14.43	16.21	16.00	15.79	15.64	16 + 00	15.71	14.79	15.29
LETION 0	DAL KO8	8 •50	12.00	13.50	13.50	15.50	15.00	14.50	14.00	16.00	15.00	13.00	14.50	1 é • 0 0	12.00	00°6	13.50	16.50	1P .00	17.50	18.00	17.00	13.00	14 .00	10.00	3 • 50	15.50	16.50	16.00	15.00	1 P . O O	17.00	17.00	18.00	16.00	17.00
ULTER NO. Vonia def	ALKOEV	2.36	0.96	1.57	-0-36	-1.21	-0-64	0.57	1.00	-2.14	-0.86	0.29	-0.93	-1+00	3.43	-0.29	-1.07	-0.43	-1.70	-2 + 29	-2.36	-1.43	-1.71	-4.93	-2.21	10.57	00.00	-2.07	0.21	1.90	-2.21	-1.36	-1.00	-2.23	-1.21	-1.71
LSING AM	ALKCAL	321.64	321.14	318.43	320 - 86	319.71	319.14	318.93	318.00	319.14	318.86	320.21	320.93	321.50	318.57	325°29	321.07	317.43	319.79	319.29	309.36	309.43	317.71	317.43	313.71	307.43	317.00	318.07	314.79	315.00	318.21	314.35	315.00	316.29	315.21	318.21
	ALKEF	324.00	322.00	320.03	320.50	318.50	318.50	319.50	319.CO	317.0C	31P.CO	320.50	320.00	320.50	322.00	325°CO	320.00	317.07	318.00	317.CC	367.00	3 (8.00	312.00	312.50	211.50	218.00	317.00	316.00	315.00	316.00	316.00	313.00	314.00	314.00	314°CO	316.50
	ALKIN	332.50	334 • CC	333.5C	334 ° C C	334 . CC	333.5C	334 . CC	333.60	333°CC	333 ° CC	333.5C	334°5C	336.50	334 • CC	334 °CC	333°2C	333.5C	336.0C	334.50	325-00	325°CO	32 5. CC	326.5C	321.5C	321.50	332°5C	332 • 5C	331.CC	331.CC	334°CC	33C.CC	331.CC	332.CC	330°CC	333°5C
	RCOO	4.68	3°95	4°CC	4.25	4.06	4.65	3.92	4.C8	4.28	4.19	4.50	4.26	3.54	4.36	5.cc	4.14	3.87	4.14	4.32	4°34	4.12	5.2P	5.59	€°899	4.52	4.38	4.45	4.46	4°36	4 - E 4	4 . 0 6	3.57	3.73	3° 66	4 . C 6
	000	5. PC	6.9C	7.60	8.00	8.40	6.7C	8.00	8.00	6.3C	8.20	00.0	7. PC	8.00	8.2C	5.4C	7.20	e.7C	0**6	9°50	e. 5C	8.40	7.60	7.1C	é.cc	P. 5C	5.5C	5°3C	9.5C	5. PO	9°6C	8.5C	8.5C	P.2C	7.70	8.40
	ARUN	68	10	72	14	76	78	EC	P 2	83	52	69	F 8	5 C	95	5 B	66	102	107	110	112	115	119	123	127	131	134	137	140	143	146	149	151	153	155	157

STATISTICAL EVALUATICNS CF VARIATICNS

STD OFVIATION	2.83	1.39	2.87	5.30	5.01	2.51	1.63	5.10	4 ° 5 4	0°Vð	ن * 2 ن	0.16	0-05	0.14	C.11
MEAN	5.35	4.11	231。64	321.72	321.57	0.15	1.07	9.92	10.07	7.80	7.56	7.50	0.06	0.23	0.30
MUMINAM	9°80	6.4 E	236.5C	337.00	230.43	10.57	11.00	18.00	16.79	7.52	7.94	7.AR	0.15	3.46	0.40
FINIPLE	C.10	-7.50	321.5C	367.60	307.43	-5.00	-1.50	- 6 . CC	-C .E é	7.52	7.1P	7.22	- C . C 7	-C.C7	-0.01
	9000C VALUES:	90400C VALUES:	90ALKIN VALLES:	9UALKEF VALUES:	90ALKCAL VALLES:	9CALKOEV VALLES:	90CHCNS VALUES:	90UALKCE VALLES:	90CALKCA VALLES:	90PHIN VALUES:	GCPHEF VALLES:	90PHCAL VALUES:	9JPHCEV VALLES:	900PHUES NALUES:	SOUPHCAL VALLES:
	FCR	FCP	FCR	F OK	F C k	FCK	F CR	F C H	FCP	FCR	FCR	FCK	FCR	FUR	F C F

TABLE A-20 vepification of stoichicmetric relations of caserved chemical changes in water for fitter NG. 3 Using Amponia depletion data

		_		_		_	_			_		_		_	-		-	_		-	_		_	_		_	_		_		-			_	_	_	_	_	_	_		_	_	_		_	_		-
CPHCAL	0 • 02	0.05	0.01	0.04	0.08	0.10	0.15	02.00	0.26	0.23	0.30	0.28	0.28	0.24	67°0	0.26	0 2 2 C	0.26	0.26	0.24	0.28	0.27	0 - 24	0.25	0.27	67°0	0.28	0.27	0.25	0.27	02.00	0.27	0 - 26	0.23	0.23	0.26	0.19	0.28	0.28	0.15	0.13	0.26	0.49	0.47	0.48	0.49	14.0	0.44	
0 PH()B S	+0*0-	-0-04	-7.03	-0.04	0.0	-0.01	0.05		0.12	0-16	0.16	2.17	0.15	0.18	21-0	0.15	1.0	- 1 - 0	0.13	0.14	0.13	0.13	0.12	0.14	0.16	0.14	0.14	0.15	0.15	2.15	*1°C	0.12	0.12	0.13	0.15	0.16	0.10	0.17	0.12	0.10	0.12	0.16	0.42	0.40	0.42	1.4.0	0.39	75.0	•
РНОЕ V	0.06	0.09	0.04	0.08	0.09	0.11	0.10		0.1.0	0.07	0.14	0.11	0.13	0.06	0.13	0.15	11.0	0113	0.13	0.10	0.15	0.14	0.12	0.11	0.11	0.10	0.14	0.12	0.10	0.12	21.0	0.15	0.14	0.10	0.08	0.10		0.11	0.16	0.05	0.01	0.10	0.07	0.07	90°0	0° 65	0.04	0.07	•
PHCAL	7.79	7.78	7.80	7.80	7.74	7.74	7.67		7.60	7.56	7.60	7.60	7.59	7.59	1.60	7.60	000°1	7.61	7.58	7.59	7.62	7.63	7.61	7.59	7.60	1.60	7.64	7.65	7.64	7.62	1.03	7.60	7.63	7.57	7.59	7.03	7.65	10.01	7.64	7.48	7.46	7.59	2:-1	7.33	7.33	7.35	7.36	7.35	•
PHEF	7.85	7.87	7.84	7.88	7.82	7.85	7.7.7	1 1 - P - P	21 01	7.63	7.74	7.71	7.72	7.65	1.13	7.75		7.76	7.71	7.69	7.77	7.77	7.73	7.70	7.71	7 - 70	7.78	7.77	7.74	7.74	() - 1 7 75	7.75	7.77	7.67	7.67	7.73	() ° I	7.76	7.80	7.53	7.47	7.69	7.39	7.40	7.39	FE . T	7.40	7.47	
MIHQ	7.81	7.83	7.81	7.84	7.82	7.84	7.82		7 86	7.79	7.90	7.88	7.67	7.83	1.85	7.86		7.87	7.84	7.83	7.90	7.90	7.85	7.84	7.87	7.84	7.92	1.52	7.89	7.89	1 000	7.87	7.89	7.80	7.82	7.89	(D.)	10.1	7.92	7.43	7.59	7.85	7.81	7.80	7.81	1.80	24-1	7.79	•
BALKCA	-1-64	3.43	05.4	0.64	2.00	2.50	4 • 21 5 4 3		4 00 t	5.50	8.50	9.36	10.79	5.93	5.19	6.50	7 03	6.7.0 8.70	10.00	5.86	9.43	6 • 64	1.07	A.50	6.64	8.43	6.36	8.43	6.43	9.21	6.00 10 30	7.64	8 . 64	7.21	10.36	7.57	6 • 14 7 30	7.79	11.79	5.00	5.14	7.36	16.64	15.86	15.93	18.00	14.64	15,57	
0AL KOB	0*0	3 .00	05-0-	4 .00	00° +	3 *00	8.00	1.000	06.8		6 •00	8.50	11.00	5.50	1.50	4.50	0000		10-00	5 .50	7.00	3 • 50	4°20	7.50	00.0	7.50	1.00	9.50	6 °00	00° 0	6.00 10 50	7.50	6 •00	é •00	8 •0C	А •00	00.00	00.4	10.00	2.50	4 °G0	7.00	14.50	13.50	10.00	15.50	15.00	16.00	
ALKOEV	-1.64	0.43	-3.00	-3-36	-2.00	-0.50	-3.79	10.2-	-4.86	- 2 - 5 7	0.50	0. 84	-0.21	64.0	-1.1	2.00		· · · · · · · · · · · · · · · · · · ·	0.00	0.36	2.43	3.14	2.57	1.00	-2.36	-0.93 -0.93	-0.64	-1.07	0.43	0.21	0.00	0.14	0.64	1.21	2.36	-0.43	0.14	12.00	1.73	2.50	1.14	0.36	2.14	36.2	5.93	04°Z	0 * ° 0 +	-0.43	•
ALKCAL	333.64	328.57	924°50 928.29	330.36	327.00	324.50	324.79	10.426	327.36	324.50	322.50	321.64	320.21	327.07	329.21	325.50	120120	320.21	320.00	326-14	323.57	323.36	323.93	324.50	328.36	322.57	325.64	326.57	325.57	323.29	96.426	373-36	322.86	324.29	322.14	326.43	321. HO	12.025	322.21	326.53	326.86	328.14	315.36	316.64	312.07	312.50	321.86	316.43	
ALKEF	332.00	329.60	321.50	327-00	325.CD	324.00	321.00	06.225	322.50	00.002	323.00	322.50	320.00	327.50	321.50	327.50	321.UU	00.004	320.00	326.50	326.00	326.50	326.5C	325.50	326.00	323.50	325.00	325.60	326.00	323.50	324.53	323.50	323.50	325.53	324.50	326.CO	32H.00	00°025	324.00	329.00	328.00	328.50	217.50	319.00	318.00	315.00	310.0U	316.00	
ALKIN	332.00	332 • CC	329.00	331.00	329.00	327.00	329.CC	330.65	331.00		331.00	331.00	331.CC	333°C0	335.00	332 . 0C		324.60	330-66	332.00	333.00	330.00	331.CC	333.fC	335°CO	331.00	332.00	335 ° C C	332.CC	332.50	000 000 000 000 000 000 000 000 000 00	331.00	331.50	331.50	332.50	334 °CC	334 °CC	77.025	334.00	331.50	332 • CC	335.5C	332 • C C	332.55	329.00	340.55	335° CC 336° 50	337.00	*
g)C8	E.CC	1.54	4.55	5.56	3.81	4.29	4.67	20.44	4.43		4.18	4.72	4.85	4.46	4.81	4.52	1) v 2 • 7 •	1 . 2 U	2 L L L	4.51	4.22	6404	4.45	4.25	3.84	2.86 4.23	4.15	4. C P	4.21	4.12	* • • • •	1	4.18	4 - CC	4 • 1 3	4.1C	1 - 1 - 1 	- C 1	4.94	5.86	5.54	2 . 71	2.43	3.69	2.77	51 0 51 0 51 0	5 - 1 - 1 2 - 1 - 1 2 -	4 . 12	4
CCL	C.4C	0.20	0.20	0.4.0	C. EC	1.20	2.1C	2.40	- 2C		3. 80	4.20	4.3C	3.70	3.50	3.80	0.00	2.4.5	110	3.70	3.50	3.50	9.50	3 • 6 C	3.30	3.20	0.0	3.10	3+20	3.30	102 - 7	0.00	3.30	3 • 2 C	3.1C	3.20	2 ° ° C		00.4	4.1C	3.60	3+30	9.00	R . 2C	9.4 °C	74°	e.20	8.4C	
ARUN	1	2	r) d	r ur	\$	2	αcι		110	11	110	14	15	16	17	18		22	100	23	24	25	26	27	2.8	52	31	32	33	34	5 9	37	3.6	35	4 C	41	4	1 4	, w	50	15	53	4	57	50	61 63	6.4 6.4	5 2	
NC	-	2	m d	r ur	ų.	1	ແ		22	10	1	14	15	16	11	18		0, 0		23	54	25	26	27	28	50	31	32	33	50	0,0	37	3.8	60	40	41	25	1 7	1 47	\$	47	4.8	40	5		200	1 3	5	1

TABLE A-20 (continued) vepification of sicichicmetric relationships of cosfrved chemical chances in water for filter NU. 3 Using AMMONIA DEPLETION DATA

OP HC AL	00000000000000000000000000000000000000	
DPHUBS	N 1 1 N N 4 M N N N N N N N N N N N N N N N N	
PHOFV	0.07 0.07 0.07 0.07 0.07 0.07 0.07 0.07	
PHCAL	7,45 7,45 7,45 7,45 7,45 7,45 7,55 7,35 7,35 7,35 7,35 7,35 7,35 7,3	
PHEF	7.5 7.5 7.5 7.5 7.5 7.5 7.5 7.5	ATION 2.78 2.87 2.87 2.87 2.87 2.87 2.87 4.61 1.4.70 4.62 4.61 1.4.20 0.20 0.20 0.20 0.11 4.11 4.11 4.11 1.4.20 0.20 0.20 0.20 0.20 0.20 0.20 0.20
NIHd	1	5T0 0EV1
OALKCA	10.07 0.643 0.643 0.643 0.643 0.6443 112.00 112.00 112.00 112.00 0.862 112.43 113.43 113.43 113.43 113.43 113.43 113.43 114.93 114.	O-140 FNB0 FOFAFN0
01 KO8	0 0	2211-6 2211-6 2211-6 2211-6 221-6 221-6 221-6 221-6 22-0 22-0 22-0 22-0 22-0 22-0 22-0 22
ALKOEV	0.57 0.57 0.57 0.43 0.43 0.43 0.43 0.43 0.43 0.43 0.43	
ALKCAL	3225 43 3225 43 3229 67 3229 71 3229 729 71 3229 71 3219 720 720 3219 720 720 3210 720 720 3210 720 720 3210 720 720 3210 720 720 720 3210 720 720 720 3210 720 720 720 720 3210 720 720 720 720 720 720 720 720 720 72	AX IN 10 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
#LKEF	322.00 323.00 324.00 315.00 315.00 315.00 315.00 315.00 315.00 315.00 315.00 315.00 315.00 315.00 315.00 315.00 315.00 316.00 317.00 <td< td=""><td></td></td<>	
ALKIN	332.55 334.55 335.55 334.55 335.55 35.55	T T T T 1
ADOD	П П С С С С С С С С С С С С С С С С С С	F5: LF5: LF5: LLLE5: LLLE5: ALLE5: ALLE5: ALLE5: LLE5: LLE5: LLE5: ALLE5
CCC	AT 1 STICA	DDDDD VAL DJ-000 VAL DJ-000 VAL DJ-100 VAL DJ-100 VAL DJ-100 VAL DJ-100 VAL DJ-100 VAL DJ-100 VAL DJ-100 VAL DJ-100 VAL DJ-100 VAL
ARUN	5 5 5 5 5 5 5 5 5 5 5 5 5 5	7.7.7.7.7.7.7.7.7.7.7.7.7.7.7.7.7.7.7.
D z	2 3 4 5 5 5 5 5 5 5 5 5 5 5 5 5	

TABLE A-21 Vedification of stoichicmetric relations of observed chemical changes in water For filter wo. 4 Using Amegnia geneficion data

DP HC AL	9.00 9.00	
лениа \$		
PHOEV	0.000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.00000 0.000000	
рнс а г	88555777777777777777777777777777777777	
PHFF	2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	
MIHA	I & & & & & & & & & & & & & & & & & & &	
DALKCA		
DAL KOB	-2.50 -2.50	
ALKOEV		
ALKCAL	3225.00 325.00 300 300 300 300 300 300 300 300 3	
ALKEF	3324.50 3224.50 3224.00 3224.00 3224.00 3224.00 3224.00 3224.00 3224.50 324.50 3	
ALKIN		
RUCID	10.01 11.05 11	
CCE	00000001440044440444444444444444444444	
ARUN	まえき ゆき やす ほうし コンゴム ち そうじ こう うろう うろう うう うう うう う う かん みんみん かんか そうち う うう く そう く し し し し し し し し し こ こ こ こ こ こ こ こ こ こ	
NC	100.4 m. 9 L 2 L 2 L 2 L 2 L 2 L 2 L 2 L 2 L 2 L	

TABLE A-21 (Continued) verification of stothometeric relations vo. 4 confirmed and vo. 4 confirmed application pair

DP HC AL	0° 39	0.43	0.33	0.21	0.41	0.43	0.40	56.0	20.00	0.32	0.48	0.34	0.30	0.45	64.0	0.43	0.32	0.29	16.0	0.33	0.38	0.38	0.38	0.42	0.36	0.38	0.30	0.40	0.40						-							
DPH085	0.35	0.34	0.23	0.12	0.38	0**0	0.37	0.35	10.0	0 C • C	0.39	1.25	0.22	0.39	0.42	0.43	0.35	0.33	0.35	0.37	0.38	0.38	0.37	0.39	0.34	9.33	0.26	0.38	0.40													
PHDEV	0.04	0.09	0.10	0.09	0.03	0.03	EU * 0	0.04		-0.01	0.09	0.09	0.08	0.01	0.01	-0.00	-0°03	-0°C4	0.02	40°0-	-0.00	-0.00	0.01	0.03	0.04	00°U	0.04	20.04	0.00													
PHCAL	7.38	7.40	7.49	7.53	7.38	7.34	7.34	7.34	7 32	56.7	7.39	16.7	7.43	7.29	15.7	7.34	7.26	7.23	7 34	7.26	7.32	7.32	7.31	7.33	7.35	7.34	7.46	CE.1	7.35													
PHEF	7.42	7.49	7.59	7.68	7.41	7.37	75.7	7.38	7 36	7.32	7.47	7.40	7.51	7.36	7. 37	7.34	7.23	7.19	7.30	7.22	7.32	7.32	7.32	7.36	7.39	7.34	7.50	7 30	7.35		A 1 1 0 N	2.91	1.25	5.50	5.58	2.41	5.17	6 ° °	0.59	0.16	υ°ύε	
NIHd	7.77	7.83	7.82	7. PO	7.79	7.77	7.74	7.73	1.04	7.65	7. P6	7.65	7.73	7.70	7.74	7.77	7.58	7.52	7.65	65° L	7.70	7.70	7.73	7.75	7.73	7.72	7.76	61°1 72	7.75		STD DEVI											
DALKCA	13.57	14.07	9.07	3.79	13-64	15.07	17.07	13.64	12 12	12.21	15.00	14.64	10.79	15.64	15.36	16.21	14.93	14.43	16.21	14.57	14.14	14.79	14.96	15.00	16.30	13.86	60.1	15 21	14.57		z	6	-	1 1	1	a. r	1		0 •			
CALK08	12.50	14.00	e •00	5 .00	14.50	17.50	16.00	14.00	14.50	14,000	14.50	12.00	11.00	16.00	19-00	19.00	16.00	16.00	14 .50	15.00	4.50	15.50	15.00	14.00	22.00	15.00	00° 6	12.00	16.50		MEA	5 • 3	7°7	7.125	321.9	1.0-1	ς	9.7	7 . F	(•) (•)	0.0	
ALKDEV	1.07	0.07	1.07	-1.21	-0-86	-2.43	1.07	-2.36	1/*0-	r L - U -	0.57	2.64	-0.21	-0-36	- 3 - 64	-2.79	-1.07	-1.57	-0.29	64.0-	9.64	-0.71	-1.14	1.00	-5.64	-1.14	-1.07	1. 70	-1.93													
ALKCAL	318.93	319.93	324.43	330.21	319-86	318.53	315.93	319.36	17.416	92.125	321.50	319.36	123.21	317.86	320.64	318.29	310.07	310.57	308.79	306.53	307.36	317.71	317.64	216.00	317.64	316.14	323.07	315.21	318.93		MUMIXA	04°6	10.00	3-0-50 334.50	233.30	49°E	22.60	17.21	1.02		0.16	
ALKEF	32C.CO	320°CC	325.50	329.00	319-00	316.50	317.00	317.00	318.50	320.50	322.00	322.00	323.00	317.50	317.00	315.50	369.00	369.00	108°50	366.50	317.00	317.CC	316.50	317.00	312.00	315.CC	322.00	314 60	317.00	PIFTICNS												
ALKIN	332.5C	334 • C C	333.50	334°CC	33-555	334 . CC	333°CC	333.C(.	323.CU	334.50	326.50	334 ° Cr	334.CC	333.5C	336.00	334°5C	325.00	325.00	325 CC	321.50	321.50	332.50	332.50	331.00	334.60	320.60	331.CC	335.60	333.50	IICNS CF V∉	MUMLM	C. 1 C	-4.00	306.50	304.92	JJ-7-7-	~ 2 • 5 C	-2.26	25.6	7.52	- r • C 4	
RDCC	4.54	4.26	4.41	5.54	4.51	4.C8	3.65	4.19	CI • 4	4.27	40°E	4.35	4.38	3.58	1000	4.61	4.56	4.31	10.7 7	4.52	4.71	4.7C	4 ° 6 3	4.67	5.13	4 . 6 4	4 . F P	20.23	4.26	EVALUA	-	: S	ES:	UES:	stuffs:	JLLES:	STLES:	STLF S:	. L	.c LFS:	uís:	
DCD	8.20	7.PC	5.60	JI *	8.30	8.60	1.20	58	0 	7.60	8°.0	8 - 30	¢•00	P. 40	0 4 0	05.5	8°5C	9.4C	2000	ງ ບູບ ອີ	5.60	6.40	50	5 ° 6 C	9.40	5 ° C C	6.1C	0. rC	8.40	TATISTICA		DLOC VALL	CRULE VAL	DALKEF VAI	DALKCAL V	OFLKCEV V	OLALKER V	CEALKCD V	CPHIN VAL	CPHCAL VAL	UPHCEV VAL	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
NRUN	6F	10	12	74	78	βC	E 2	61 L	1		2C	96	39.6	102	102	110	112	115	115	127	131	134	141	14.3	146	145	141	155	151	s		F CR 9	FCR 9	+ CK	FUR 9	FCK 0	FCR 0	FCH 9	6 1 1 1 0 0	E L X I	FUR 9	

TABLE A-22 VERIFICATION UF STOTCHICMETRIC RELATIONSFIPS OF COSERVED CHEMICAL CHANGES IN WATER USING AMMCAIA DEPLETION DATA

CPHC AL	0.02 0.01 0.01 0.03	21.0 44.0 44.0 44.0 54.0	
0 P H U B S	-0.03 -0.02 -0.02	0, 75 0, 44 0, 46 0, 46 0, 48 0, 48	
РНОЕИ	0.05 0.03 0.10 0.08	0, 07 0, 07 0, 00 0, 00 0, 07 0, 00 0, 00 0,00000000	
PHCAL	7.69 7.64 7.78 7.62	7,51 7,30 7,30 7,30 7,24 7,25 7,23 7,23 7,23 7,23 7,23 7,23 7,23 7,23	
PHEF	7°74 7°67 7°87 7°89 7°70	7,68 7,98 7,98 7,930 7,930 7,933 7,935 7,9377 7,9377 7,93777 7,937777777777	A110N 33.52 33.52 4.32 4.32 2.55 7.00 7.00 7.00 7.00 0.21 6.01 7.00 0.21 0.21 0.21 0.21 0.15
NIHd	7.71 7.65 7.86 7.65		5 TO 0E VI
OALKCA	-0.64 1.07 3.50 1.86	3.14 12.07 15.65 15.65 15.65 15.65 16.57 16.57 16.57 16.57 16.57 15.00 15.00 15.00 15.00 15.00	< 5-8N5N N65000-00-
CALKUR	0.50 C.50 1.50	5.00 117.50 117.	7
ALKDEV	-1.14 0.57 2.00		
ALKCAL	334。14 333、43 333、00 332。14	310.86 321.43 321.44 311.44 312.66 316.65 309.36 309.36 309.36 315.93 315.93 315.93 315.93 315.93 315.93 315.93 315.93 315.93 315.93 315.93 315.93 315.93 315.93 315.93 315.93 315.95 316.93 317.71 315.95 316.93 317.71 315.95 316.93 317.71 315.95 316.93 317.71 315.95 316.93 317.71 315.95 316.93 317.71 315.95 317.71 31	 A A
ALKEF	323.CO 324.00 335.00 333.CO	33255 35555 35555 35555 35555 35555 35555 35555 35555 35555 35555 355555 355555 355555 355555 355555 355555 3555555	5 P I #1 I C N S
ALKIN	333,50 334,50 334,50 336,50 34,00	334,50 3334,50 3334,50 3334,50 3334,50 3334,50 3325,00 3255,00 3255,00 3325,00 3325,00 3325,00 3326,50 3327,50 3326,50 3326,50 3327,50 3326,50 3327,50 3326,50 3327,50 327,	IICAS CF V/ IAC CF V/ C C C C C C C C C C C C C C C C C C C
RDCC	10.0C 3C.CC 2.86 6.33	く 0	L EVALLES: LES: ALLE
CCC	0 · 50 C · 50 L · 60 L	И И И И И И И И И И И И И И И И И И И	TAT 1 S 1 I C A TAT 1 S 1 I C A SCUC VALU SALKEF VA VALO VAL VAL VAL VAL <
KRUN	8 8 9 9 9 9 0 0 0 0 0 0 0 0	000 100 100 100 100 100 100 100 100 100	5 555555555555555555555555555555555555
Dz	66 68 68 69	01011000000000000000000000000000000000	

TABLE A-23 VERIFICATION OF STUTCHFICATELER NC. C DESERVED CHEMICAL CHANGES IN WATER USING VMMCIAL DEPLETION DATA

						_										_	_						 									_							
CPHC AL	0.02	0.0P	0.03	0.05	50°0	0.43	0.49	0.32	0.30	0.44	0.30	0.27		0 * * O	14.0	0.44	0.42	0.42	0.45	0.43	0.41	0.42																	
DPHOB S	-0-03	-0.05	-0.13	-0.05	20.00	0.42	0.41	0.35	0.32	0.33	0.32	67°0		14 0	0.41	0.42	0.4	0-40	0.42	0.42	0.45	0.41																	
PHOFV	0.05 0.05	0.13	0.13	0.10	42°0	0.01	9.08	-0.03	-0.02	0.11	-0.02	-0.07	10.0			20.02	0.02	0.02	0.03	0.01	-0.04	0.01																	
PHCAL	7.69	7.78	7.67	7.58	7 55	16.7	7.28	7.26	7.22	7.21	7.27	7.32		12.1	7 20	16.7	15.7	7.30	7.31	7.32	7.33	7.32																	
PHEF	7.74	10.1	7.75	7.7R	7 61	7.32	7.36	7.23	7.20	7.32	7.25	7.30		16.7	1 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	7.33	EE . 2	7.32	76-2	7.33	7.29	7.34			NUIIS	3.62	1.54	4.32	9.23	- 1 - 5	1 4 • 2	1.09	6.40	C.C7	C.71	C.17	c.c5	0.10	0°16
NIHd	7.71	7.86	7.65	7.73	1 1 4	7.76	7.77	7.5P	7.52	7.45	7.57	7.59			7 73	7.75	C L L	7.72	7.76	7.75	7.74	7.75			STO DEVI														
CALKCA	0.0	5°53	2.57	2.07	-0.01	16.14	1A.43	14.93	14.64	21.36	13.93	10.93	14.1	10.04	15.07	16.00	16 57	15.54	17.21	15.71	15.43	15.07			2	6	6	В	14			4.0	61	C	(1)	c	~	7	2
CALKUB	1.00	1.00	0.0	2 ° U D			16.00	14 •OC	16.03	16.50	16.50	14.00	0.00	00.41		17.000		15.00		16.00	16.03	17.00			μ Π	¢ • 7	4.5	330.8	318.0	· 2 1 5		11.0	11.9	7.1	7.4	7.4	0	0.42	
ALKDEV	-1.00	1 . 0 2 1 . 0 2	2.57	10.01	14.1-	26-1-	0.44	0.93	-1.36	4 .85	-2.57	10.6-	1. · · ·					0.44	-1-79	-0-29	- 2.57	-1.03																	
ALKCAL	332.57	02°155	231.43	331.03	333.57	210,85	316.47	310.07	310.35	303.64	212.57	310.57	970014	010.010	6 4 ° 1 1 5	215.00	E7 212	214,36	62 ° e l e	316.29	314.57	210.43			MUMIX04	0°70	9.75	335.5C	325.50	16.165	3.65	19.00	21.36	7.86	16°1	7.7H	C. 13	0.45	0.44
ALKEF	352.50	5	334.00	332.00	352.000	210-015 00-015	316.50	C0-11-	369.00	3 C B . 5 C	00°016	367.50	515.00		00°010	214.00			312.60	316.00	314.00	116.50	RIFICNS																
ALKIN	33.50	1111-110 1111-110 1111-110	334.00	334 ° C C	333.50	2010-11C	334 . 50	325.00	325.CC	325.CC	326.5C	321.5C	ns 175	J2-255 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7	11.275 11.15	331.00	00.100 00.100		221.155		330.10	333.5C	ICNS CF VI		INIMUE	0° 30	1.30	321.50	367.50			ر د • ر ۱	- 6.67	7.52	7.20	7.71	- (• ر ۶	- (. 10	2] *)
RUCD	12.5	1.50	F. 75	5.53	P.45	1 • 1 0 1 - 1 0	2 4 6	4.26	4.00	3.03	4.21	5.42	\$. 5 . 7 .	5.50 	22 * 5	22.4		37.74	- 4		2.76	2.03	L EVALUAT	:	2	÷ S ÷	LE S:	LLES:	LLES:	AL LES:		ALLE 5:	ALLES:	LES:	LES:	:5371	LES:	ALLE S:	ALLES:
CCC	C . 4 Č		C • 7C	0.50	1.10	0 ×0	•	9 ° ° 8	F.2C	H.2C	P.1C	F. 3C		5 ° ° °	7 . r) (P ()		9 - 20	0	, , , , , , , , , , , , , , , , , , ,	7.60	ر ۱۳۰۰ ط	ATISTICA			DUC VALL	SHEDE VAL	SALKIN VA	SALKEF VA	DALKCAL V	SALKLEV V	SCALKEP V	FUALKCA V	JPHIN VAL	SPHEF VAL	SPHCAL VA	SPHCEV VA	V SHUHA IS	A JJJJJJJ
NEUN	E¢	D C L V	5.5	сβ	56.	201	110	113	115	115	123	127		521	131	141	771	140	151	153	155	157	ST			CH 20	UR 25	CK 21	CP 2	-11-25	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	1 1 2	LH 2'	LF 2:	CH 25	Ck 21	C+ 2	1. 2	X
NC	66	- u	69	10	27	22	14	75	76	17	78	52	0.8	1 2 0							6.6	06				LL.	ų.	ų.	a i	d.				4		4	Sd.	-	•

TABLE A-24 verification of stoichicmetric relations of observed chemical changes in water for filter no. 7 using ampended opta

OPHC AL	0.07 0.07 0.014 0.014 0.014 0.0240 0.0240 0.0240 0.0240 0.0240 0.0240 0.0240 0.0240000000000	
орнов S	-0.01 0.026 0.207 0.0070	
PHDEV	0.06 0.09 0.09 0.09 0.09 0.09 0.09 0.02 0.07 0.02 0.03 0.03 0.03 0.03 0.03 0.03 0.03	
PHCAL	7.68 7.58 7.58 7.59 7.59 7.31 7.29 7.29 7.29 7.29 7.29 7.29 7.29 7.29	
PHEF	7.57 18.77 18.77 1.6.71 1.6.71 1.6.71 1.6.71 1.7.330 1.7.330 1.7.3311 1.7.331	ATION 2.65 2.65 4.32 9.43 2.46 5.46 5.46 5.46 5.46 6.47 6.43 6.41 6.11 0.11
NIHd	17.65 17.65 17.65 17.65 17.65 17.65 17.65 17.65 17.65 17.65 17.65 17.65 17.65 17.65 17.65 17.65 17.65 17.65 17.75 17	STO CEVI
OALKCA	-0.79 2.79 2.79 9.50 9.50 9.50 15.50 15.50 15.50 15.50 15.50 15.50 15.50 15.50 15.50 15.50 15.50 15.23 15.50	N 0512 200 200 200 200 200 200 200 200 200 2
DAL KOR	<pre>6.50 7.50 19.50 19.50 19.50 19.50 19.50 19.50 17.55 17.</pre>	# 14 19 19 19 19 19 19 19 19 19 19 19 19 19
ALKDEV		
ALKCAL	334.29 331.71 331.71 320.60 324.50 327.65 327.65 327.65 327.65 327.65 309.79 309.70 306.20 316.00 316.70 315.71 315.77 315.77 315.75 31	AAXINUT 9.80 3335.660 334.20 334.20 15.60 334.20 21.93 7.86 7.72 7.86 7.72 7.86 7.72 7.86 7.72 7.86
ALKEF	333.00 332.59 332.59 332.50 334.60 334.60 334.60 335.60 35.6	RIATIONS
ALKIN	334,50 334,50 334,50 334,50 334,50 334,50 334,50 334,50 334,50 332,50 32,50 32,50 32,50 32,50 32,50 32,50 32,50 32,50 32,50 32,50 32,50 32,50 32,50 32,50 32,50 32,50 32,50 32,50 50,50,	ILLNS CF V/ ILLNIWLW 233156 233165 253165 255165 253165 255165 255165 255165 255165 255165 255165 255165 255165 255165 255165 255165 255165 255165 255165 25526 25556 25526 255676 255676 255676 255676 255676 255676 255676 2556
ROOC	0 C C C C C C C C C C C C C C C C C C C	E VALLES E VALLES E VALLES E LLES E LLES
000		AT IS 11 CA AT IS 11 CA COD VAL AALKIO VAL AALKEF VAL AALKEF VAL AALKEF VAL AALKEV VAL VAL VAL VAL VAL VAALKEV VAL VAALKEV VAL VAALKEV VAL VAALKEV VAL VAALKEV VA VAA
RUN	66 67 69 69 69 69 69 69 69 69 69 69 11 11 15 11 15 11 15 11 15 11 15 11 15 11 15 11 15 11 15 11 15 11 15 11 15 15	
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VITA

Kalyanpur Yeshavantha Baliga
October 24, 1934
 Board High School, Udipi, India - S.S.L.C. 1952 Mahatma Gandhi Memorial College, Udipi, India - I.Sc. 1954 Govt. College of Technology, Coimbatore, India - B.E. (Hons) 1958 University of Illinois, Urbana, Illinois, USA - M.S. 1964 University of Illinois, Urbana, Illinois, USA - Candidate for Ph.D 1969
 Junior Engineer, Highways Dept., Govt of Madras, India (6/58-7/58) Section Officer, Neyveli Lignite Corp., Neyveli, India (7/58-8/58) Lecturer, M.B.M. Engineering College, Jodhpur, India (9/58-9/60) Lecturer, University of Roorkee, Roorkee, India (9/60-1/61) Asst. Prof., Birla Institute of Technology, Ranchi, India (1/61-8/62) Research Asst., University of Illinois, Urbana, Illinois, USA (9/62-8/64) Asst. Prof., K. R. Engineering College, Surathkal, India (10/64-7/65) Research Asst., University of Illinois, Urbana, Illinois, USA (8/65-7/69)
Honour Societies:
American Society of Civil Engineers American Water Works Association Water Pollution Control Federation American Chemical Society Sigma XI
 'Benthic Sampling, Analysis and Ecological Studies of Nematodes', Sanitary Eng. Series No. 22, Civil Eng. Studies, University of Illinois, Urbana, Illinois 'A Technique for Benthic Sampling and Analysis of Nematodes', presented to the Midwest Benthological Society, Mt. Pleasant, Michigan, April, 1966 Co-authors: R. S. Engelbrecht and J. H. Austin 'Occurrence of Nematodes in Benthic Deposits', presented to American Public Health Association, San Francisco, Calif., November, 1966. Accepted for publication in WATER RESEARCH, the Journal of the International Association of Water Pollution Control Benerate Lander Evaluat

'Effectiveness of Potassium Permanganate in the Disinfection of Sand Filters', presented to Illinois Section, American Water Works Association, Chicago, Illinois, March, 1968 Co-author: J. T. O'Connor

'Chemical Control of Bacterial Growth in Rapid Sand Filters', presented to 2nd National Symposium on Sanitary Eng Research, Design & Development of American Society of Civil Engineers, Cornell University, Ithaca, N.Y., July, 1969 Co-author: J. T. O'Connor

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