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EFFECTS OF OZONE TREATMENT ON RECIRCULATING WATER IN A CLOSED FISH CULTURE SYSTEM

H. Rosenthal, G. Krüner, and G. Otte

Biologische Anstalt Helgoland, Zentrale Hamburg
Palmaille 9, 2 Hamburg 50, Fed.Rep.Germany

ABSTRACT

The effects of ozone on recirculated water were studied by measuring several water characteristics at the inlet and outlet of the treatment unit. Three ozone doses were used (2.4 mg/l, 5.2 mg/l, 6.8 mg/l) at a flow rate of 1200 l/h through the reaction chamber (S ~ 8‰; t = 23-26° C; volume of the culture system 5.4 m^3; total fish load = 200-230 kg). Nitrite was almost quantitatively oxydized to nitrate. Ammonium oxidation had been partly achieved in 72% of the treatments. Nitrate levels did not change significantly. Oxygen levels were raised substantially, but oversaturation was reached in approcimately 41% of the treatments only, when the initial dissolved oxygen concentration was already above 5.5 mg/l. pH values were generally higher at the outlet of the treatment unit. Yellow substances were removed at a rate of 24-28%, depending on ozone concentration and total organic load. BOD increased substantially at the outlet of the ozonation unit at high ozone concentrations, indicating that low biodegradable organics were degraded into compounds which are more easily digested by bacteria. Thus, ozonation - properly applied - supports biological filtration.

INTRODUCTION

During the past three years intensive studies were carried out to evaluate the usefulness of ozone application in fish culture recycling systems (Rosenthal and Sander, 1975; Rosenthal and Westernhagen, 1976). Destruction of yellow substances by ozone have been demonstrated by Otte et al. (1977). This study summarizes some observations on changes in water quality during ozone treatment.

MATERIALS AND METHODS

Details of the layout of the reciculating fish culture system are described by Otte and Rosenthal (1978) (total volume of the system = 5.4 m^3; fish tanks = 1.52 m^3; settling tank = 3.0 m^3; denitrification column 1.06 m^3). The total fish load increased during the investigation period from 200 kg to 230 kg, which is equivalent to a weight gain of 0.3 % /d. Employing data reported in the literature, this fish load will produce a daily waste load Of approximately 920 g BOD_5/d (Scherb and Braun, 1971).

The ozonation unit consists of the ozonizer and a reaction tower, in which intensive mixing of ozone containing air with water takes place. The water enters the reaction tower tangentially near the top and leaves at the bottom. In the lower third of the reaction tower, ozone containing air is dispersed by a high speed rotating disc (2400 Rpm). The continuously produced foam moves upward countercurrently into the separation tube where turbulence is reduced by a sieve plate. The relatively dry foam produced is continously removed.

The amount of ozone applied to the reaction tower was adjusted by the air flow through the ozonizer. The efficiency of the ozonizer depends on the volume of dry air passing the discharge per time unit. Figure 1 indicates the amount of ozone produced under different operational conditions. The data have been reproduced fairly well with an error of 5-8 %. Ozone concentrations mentioned in this paper refer to calculated values.

Water samples for chemical analyses (NH_4^+-N; NO_2^--N; NO_3^-+N; pH; BOD) were taken simultanously at the inlet and Outlet of the reaction tower at intervals of 30 min during the daily ozonation period of 2 h.

RESULTS

Nitrite oxidation was dependent on ozone concentration (Fig. 1). Ozone concentrations of 2.4 mg O_3/l resulted in an average

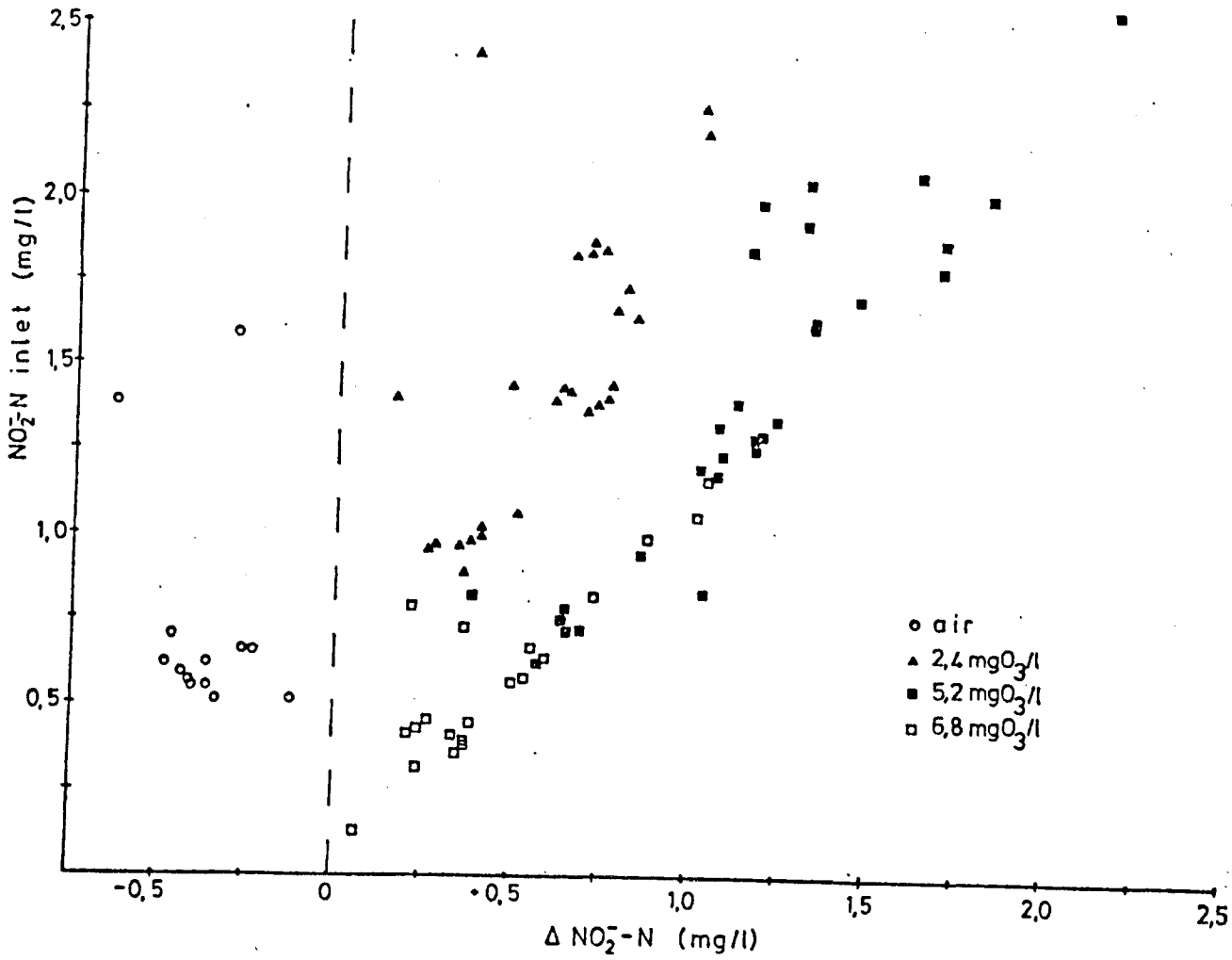

Fig. 1: Nitrite oxidation by ozone in relation to initial nitrite level at the inlet of the reaction chamber and ozone concentration. Average retention time = 10 min.; water flow rate 1200 l/h.

reduction of about 50 % of the initial nitrite concentration ($n = 30$; $r = 0.49$). Higher ozone concentrations led to an almost quantitative oxidation of nitrite to nitrate (5.2 mg O_3/l : 90 % nitrite oxidation ($n = 20$, $r = 0.90$; 6.8 mg O_3/l : 95 % nitrite oxidation ($n = 25$, $r = 0.97$)). In contrast, foam stripping without ozone resulted in a slight increase of the nitrite levels at the outlet of the ozonation unit. This observation indicates that intensive aeration supports the first step of nitrification (Ammonia oxidation) rather than the second step (nitrite oxidation) leading to a slight increase of the nitrite concentration in the reaction tower.

Ammonium oxidation

According to Jürs (1966) substantial ammonium oxidation in waste water cannot be achieved by ozonation. Figure 2 depicts our finding on changes of ammonium concentrations due to ozone treatment. Although the data obtained are fairly scattered, the overall results of the trials indicate that about 72 % of all treatments showed lower ammonium levels at the outlet of the ozonation unit than at the inlet, especially at higher ozone concentrations. Around 23 % of the ozonation trials gave indifferent results or showed a slight increase in ammonium concentrations.

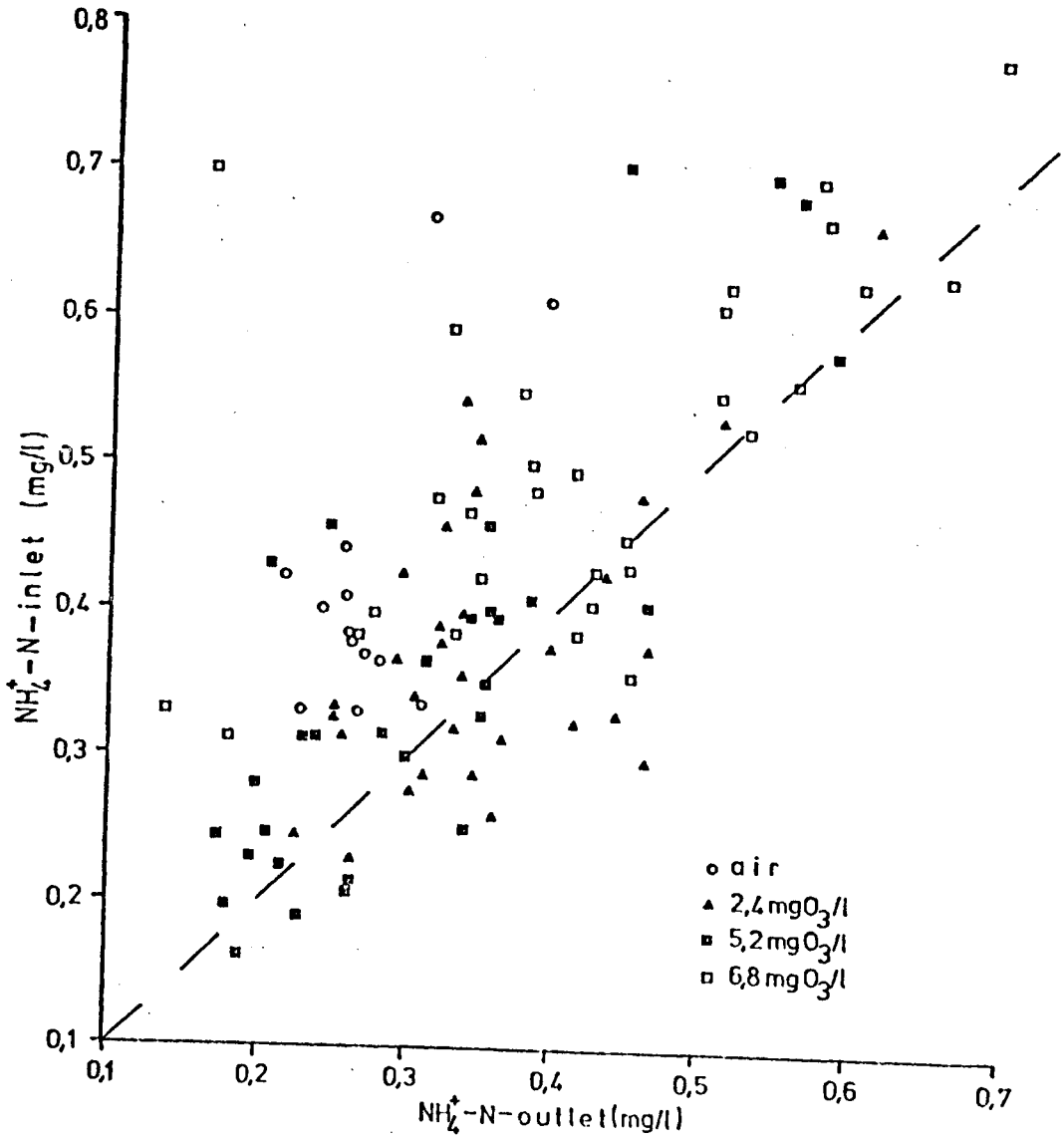

Fig. 2: Ammonium concentrations at the inlet and outlet of the ozonation unit in relation to ozone treatment.

Nitrate

If nitrite is oxidized quantitatively by ozone to nitrate, one would expect an increase of the nitrate concentration in the treated waste water. It is further well known that an ozonizer also produces some nitrate and other oxides of nitrogen when dried air is passed through the electrical discharge. As can be seen from Figure 3, there is no significant deviation between nitrate concentrations in the inlet and outlet of the treatment unit under the existing experimental conditions. Compared to to the relatively high nitrate levels in the system (between 100 mg/l and 450 mg/l the amount of nitrate produced due to nitrite oxidation (0.L - 2.5 mg/l NO_2^--N differs by two orders of magnitude and is therefore negligible. The high variation of the data obtained is mostly due to necessary dilution of the sample taken for analysis.

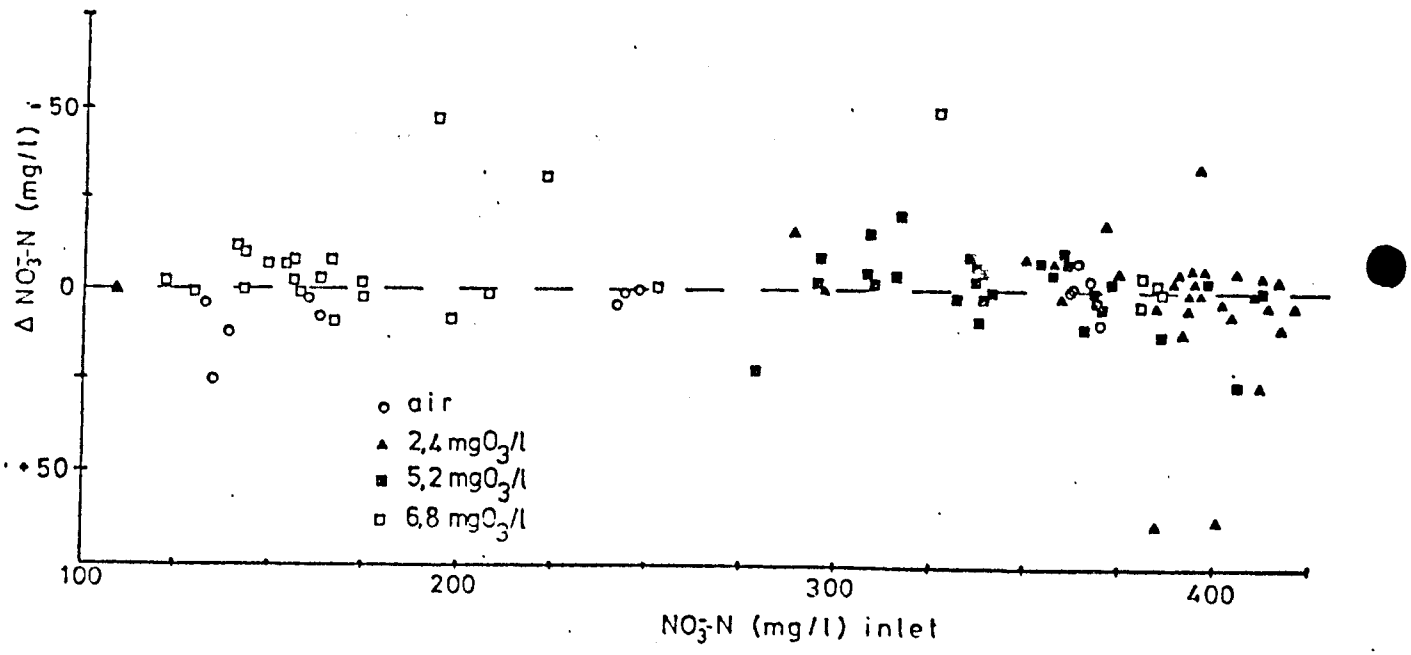

Fig. 3: Effects of different levels of ozone treatment on nitrate concentration in a fish culture recycling system.

Changes in oxygen content

When dispersing ozone containing air in the reaction tower one would expect a substantial increase of the oxygen level in the treated water. Earlier investigations evaluated the efficiency of the reaction tower in terms of rates of oxygen transfer into the water treated under different operational procedures, such as flow rates, initial oxygen levels and air-bubble size (Rosenthal and Sander, 1975). Figure 4 indicates

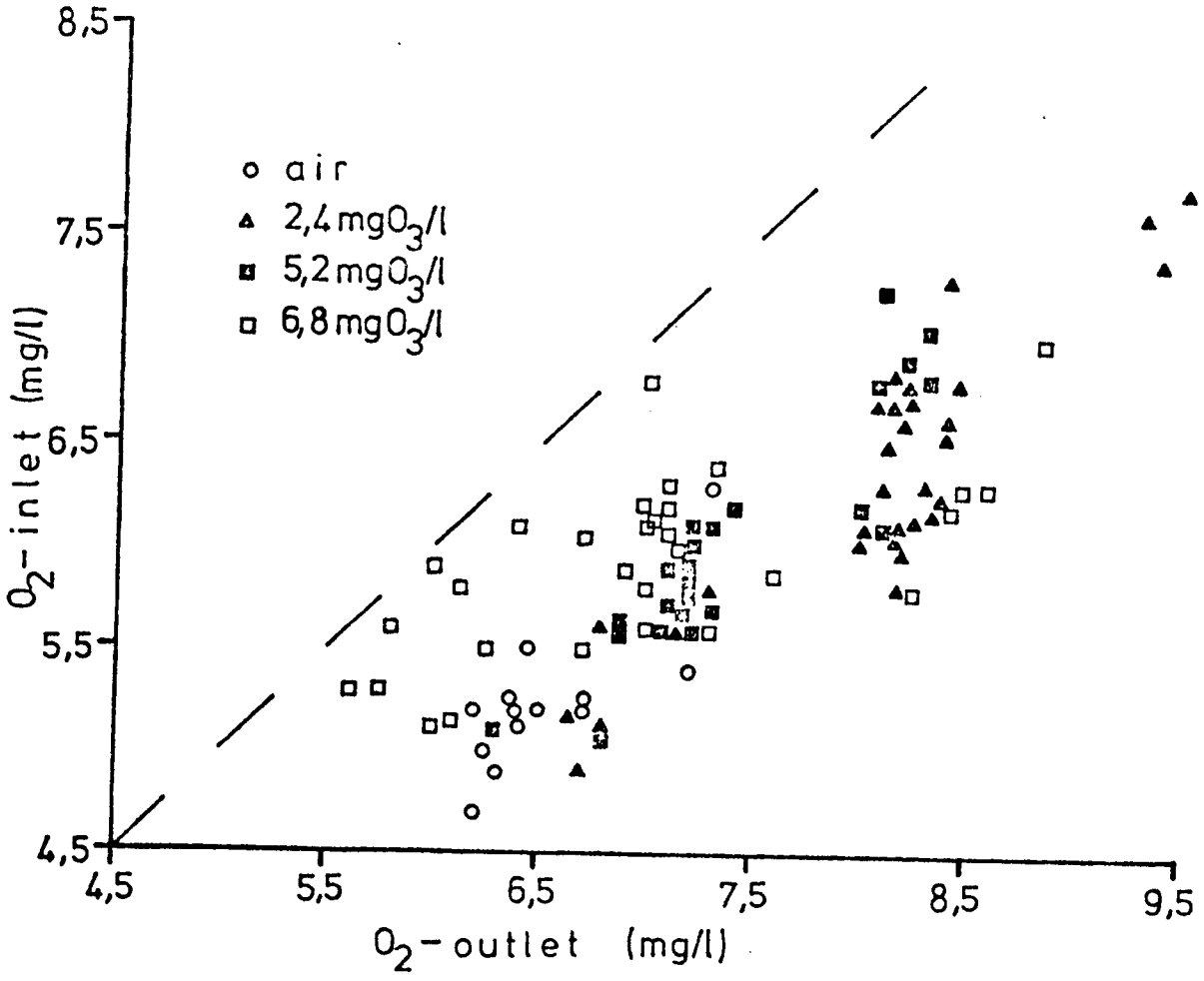

Fig. 4: Oxygen enrichment of ozone treated fish culture waste water in relation to initial oxygen level and ozone concentration.

the oxygen levels measured at the inlet and outlet of the treatment unit when applying different ozone concentrations. A substantial increase of the oxygen concentrations had been reached in all cases, but the correlation between inlet and outlet oxygen levels is lowest at the highest ozone concentration (6.8 mg O_3/l : 3 = 0.66, n = 30), whereas the lower ozone concentrations seem to attain stronger correlations (5.2 mg O_3/l : r = 0.90, n = 23; 2.4 mg O_3/l : r = 0.89, n = 31). Oxygen saturation level at 8‰ salinity, 25°C and 760 Torr is calculated at about 8.0 mg O_2/l. Only some treatments with initial oxygen concentrations higher than 5.5 mg O_2/l at the inlet of the reaction tower reached oxygen oversaturation.

pH changes

In a fish culture recycling system, stabilization of pH values is of vital importance. In general, pH values tend to decrease in closed systems. When treating fishtank run-off water with ozone in combination with counter-current foam stripping, pH values tend to increase between 0.15 and 0.40 units. Figure 5 shows the results obtained when treating fish waste water at three different ozone levels. There seems to be no correlation between initial pH value, pH increase and ozone concentration. Even without ozone, counter-current foam stripping raised the pH level substantially.

This observation is somewhat surprising. From the literature it is known that ozone treatment without foam stripping tends to shift $\overset{pH}{\wedge}$ to the neutral point (Kirk, 1972). Since pH values in our system were always above 7.0, one would expect a slight decrease rather than an increase of the pH. Presumably those ozonation products causing pH reduction are removed in part via foam separation.

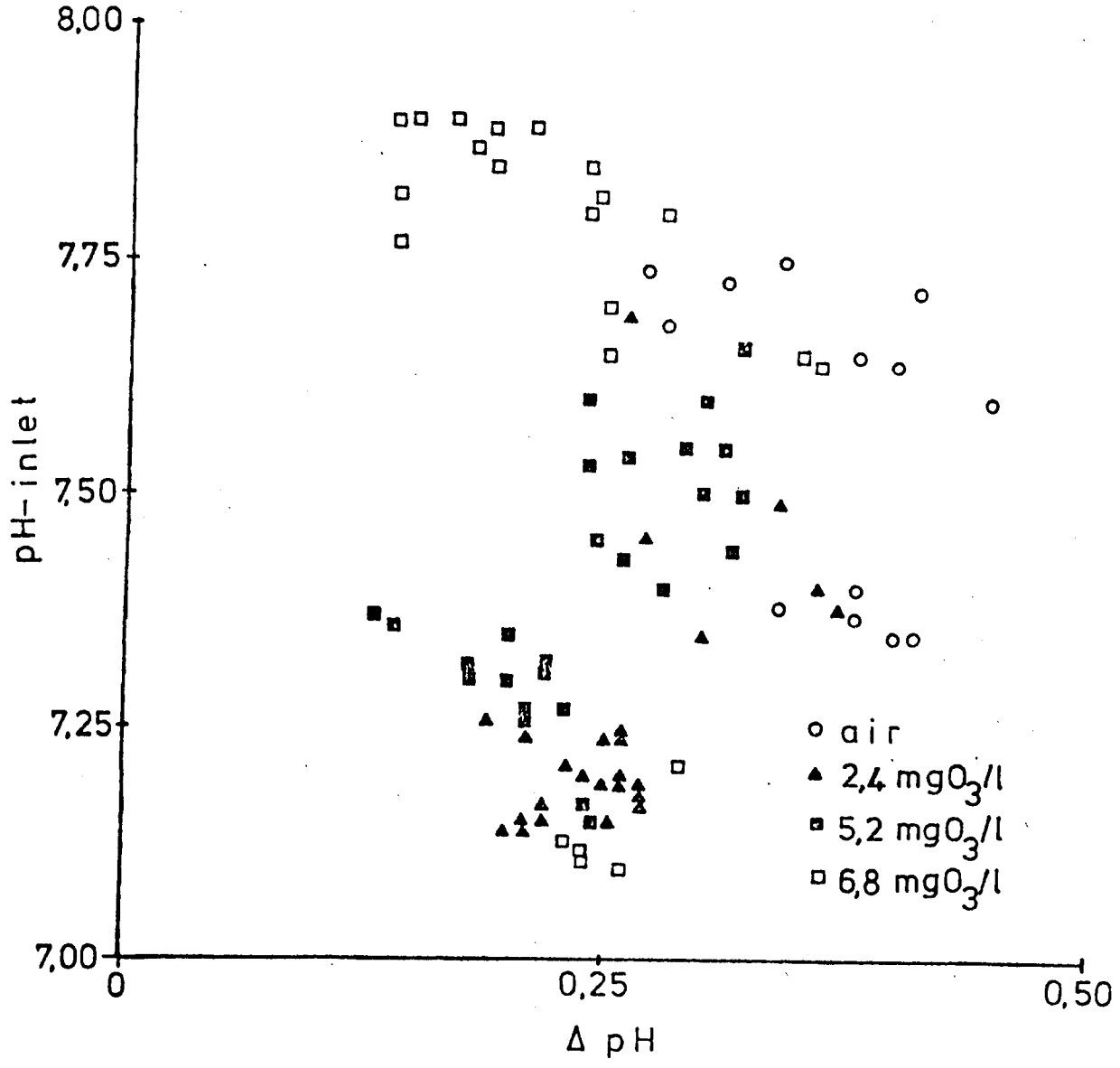

Fig. 5: pH alterations during ozone treatment of brackish water in a fish culture recycling system.

Effect of ozone on low degradable organics

All ozone levels employed affected the BOD load considerably. Differences of BOD_2 values between inlet and outlet varied between -30 % and +48 %. At low ozone concentrations (2.4 mg^3/l and 5.2 mg O_3/l) ΔBOD_2 values are negative, indicating that easily degradable organics have been oxidized (Fig. 6). At higher ozone levels (6.8 - 10.4 mg O_3/l) the BOD_2 load increases substantially during ozone treatment. The same holds for BOD_5 measurements (Fig. 7). It is obvious that high ozone levels degrade those organics which are highly resistant to biological decomposition. Therefore, ozonation supports biological decomposition.

Removal and discoloration of detritus and solids

Earlier studies (Otte et al. 1977) used yellow substances as an indicator for the accumulation of undegradable compounds. Yellow substances can be easily analyzed by Spectro photometry at a wave length of 315 nm. The duration of ozonation of the recycled water was determined by the extinction rate. The reduction efficiency of yellow substances during a 10 min contact period in the reaction tower varied between 24 % and 26 % of the initial extinction values. It was directly correlated to the ozone concentration employed.

Besides the destruction of yellow substances by ozone, solid particles are also discolored and removed from the reaction tower by counter-current foam stripping. Figure 8 demonstrates this effect in two experimental series on two successive days. Water samples taken at the inlet and outlet of the ozonation unit were filtered through Membrane filters (λ 0.22 μ, Millipore). The amount of solids retained on the filter is substantially reduced in samples from the outlet of the ozonation chamber.

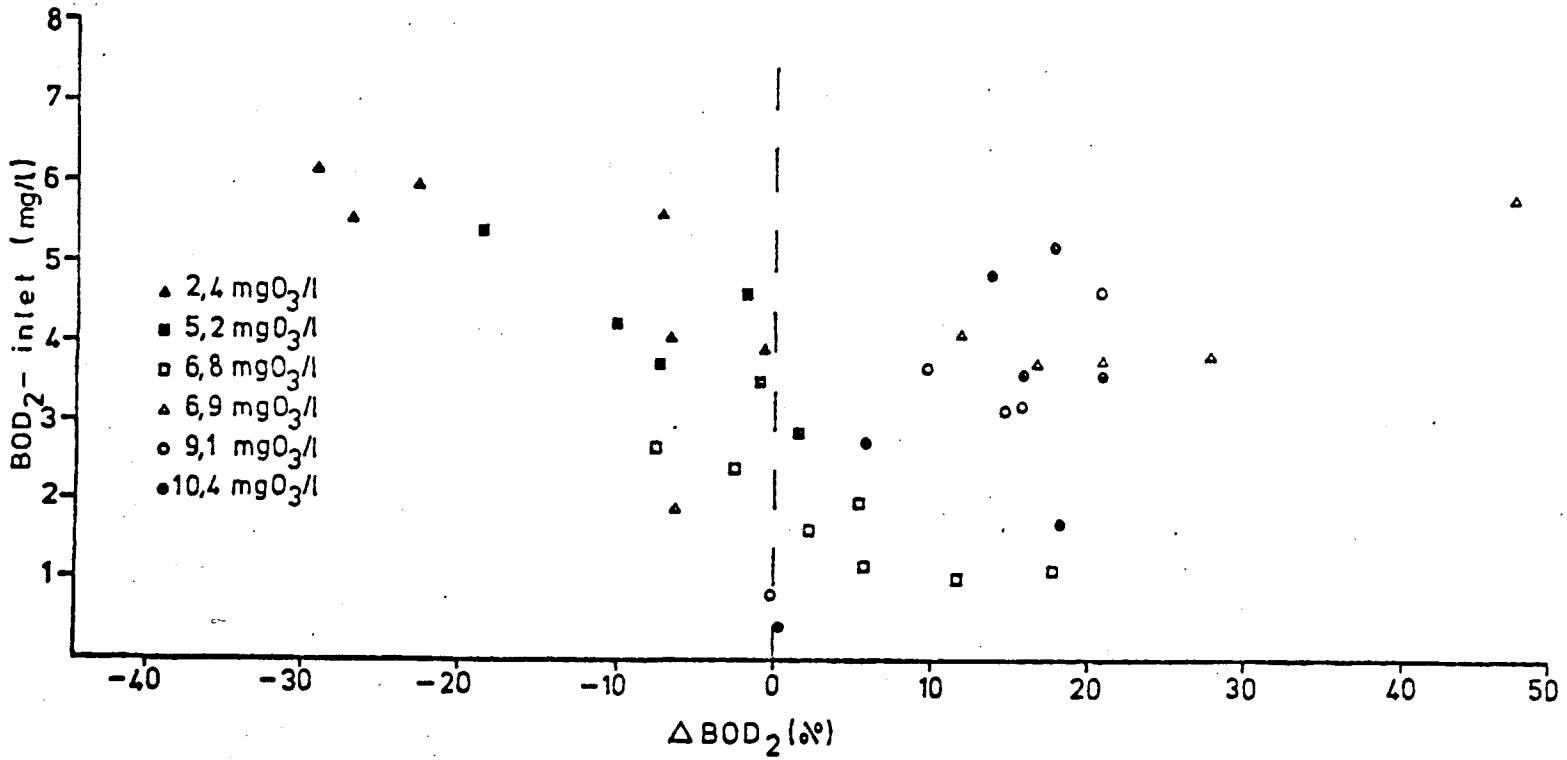

Fig. 6: Effects of ozone on the BOD_2 load in a fish culture recycling system.

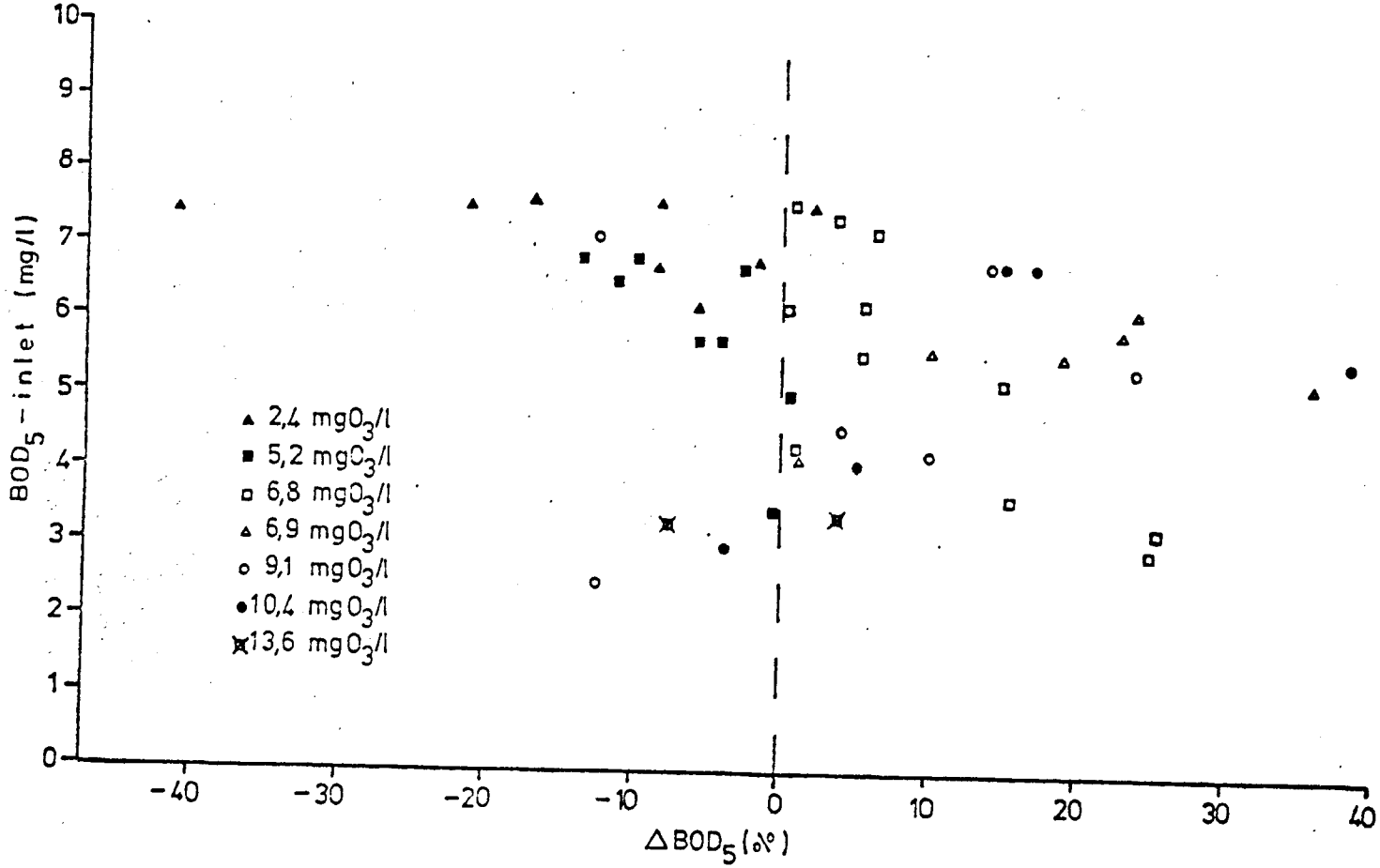

Fig. 7: Effects of different ozone levels on the BOD_5 load in a fish culture recycling system.

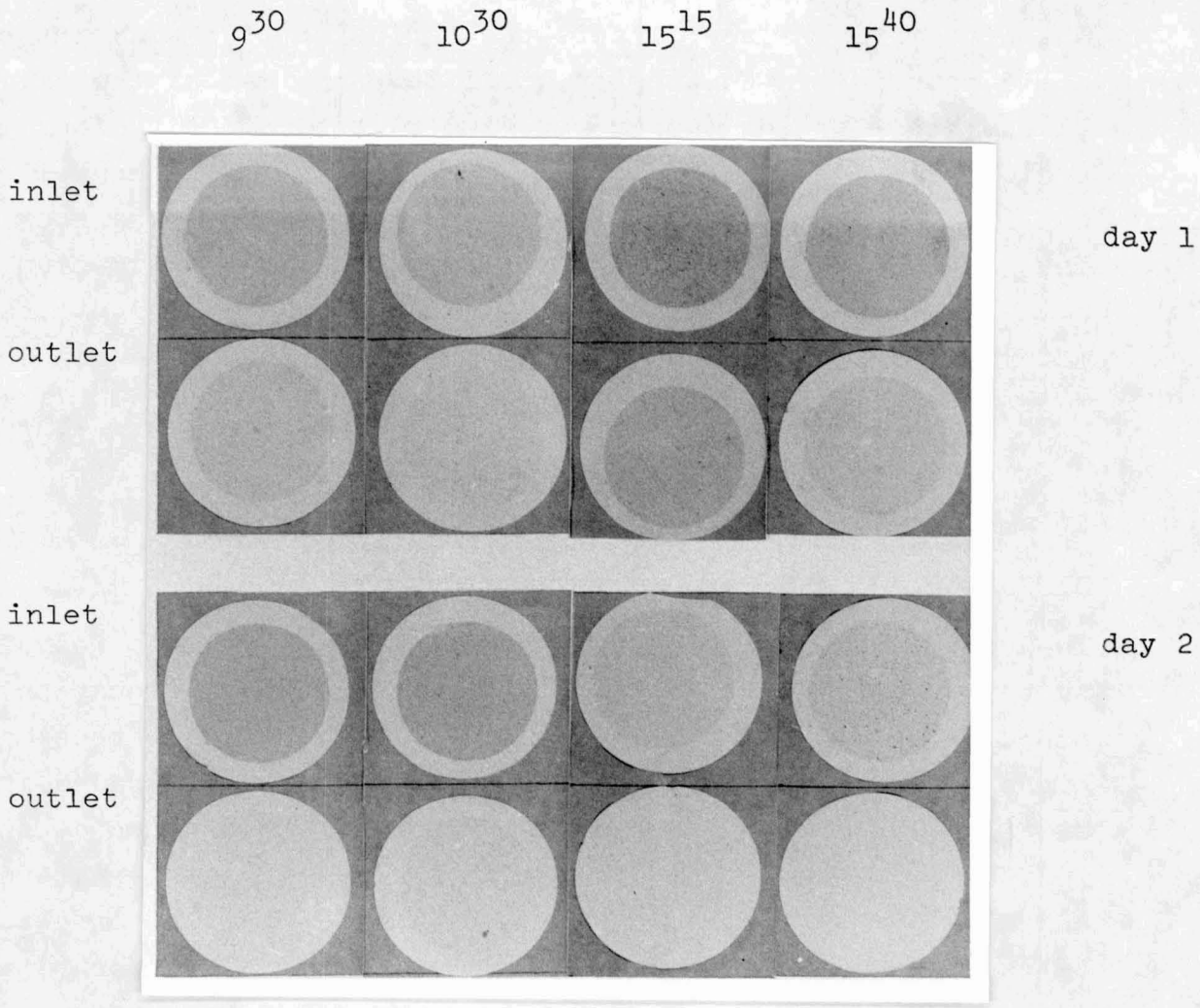

Fig. 8: Content of suspended solids prior and after ozonation and foam separation of recycled fish culture medium (8‰ S, in relation to day time and ozone concentration; day 1 = 5.2 mg O_3/l, fish feeding early afternoon; day 2 = 6.8 mg O_3/l, fish feeding during morning hours.

The time series also reflects the variation of the amount of solid material in suspension at different times of the day. In the first series (upper row Fig. 8) the main fish feeding period occurred in the early afternoon whereas on the following day (lower row, Fig. 8) fish were fed during morning hours. The removal of suspended particles from the culture medium seems also to be influenced by the ozone concentration. Less material was found on the filters, when higher ozone concentrations were used (Figure 8, 5.2 mg O_3/l : upper row; 6.8 mg O_3/l : lower row).

DISCUSSION

The present study proved that the water quality in a recycling system can be influenced substantially by Bypass-ozonation. Since yellow substances are considered to belong to those higher molecular compounds which are not easily degraded in biofilters, their decomposition by ozone can be taken as an indication that ozonation of recirculated fish waste waters under certain operational conditions is useful. The effects of ozone on the BOD load supports also this conclusion.

At present, no satisfactory explanation can be given on the effect of ozone on pH changes. One may assume that ozone reaction with organic compounds sets free many amino-groups which cause the observed pH-shift to alkaline conditions. On the other hand, nitrite oxidation will change the situation rather to acidic conditions.

Regarding nitrite oxidation, one should consider the efficiency of the oxidation process in relation to the ozone concentration. At 5.2 mg O_3/l about 90 % of the nitrite were oxidized, whereas a 30 % increase of the ozone load to 6.8 mg O_3/l gained only 5 % of the efficiency. Since ozone production is very costly,

it seems reasonable to operate on ozonation unit at the lowest satisfactory level.

The results of the present study indicate that ozone application in a closed fish culture system can improve the water quality considerably. We are convinced that biological filtration alone is insufficient for longterm operation of closed systems. Combined water treatment using biofilters and ozonation provides a means for reliable and continuous operation.

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