Polish Journal of Environmental Studies Vol. 9, No. 2 (2000), 91-96

The Role of Physico-Chemical and Biological Processes in Manganese and Ammonia Nitrogen Removal from Groundwater

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Received 15 October, 1999
Accepted 10 December, 1999

Abstract

This paper presents investigation results which evaluate the role of biological processes in elimination of Mn (II) and NH_4^+ ions from groundwater. The raw water containing up to 1.4 mg/dm^3 manganese and up to 2.9 mg N/dm^3 ammonia nitrogen after aeration was treated using first and second stage sand filters at the "Letniki" water treatment plant near Elblag. Both ions were removed with high efficiency and the concentrations of these components after two stages of filtration were lower than the admissible values for drinking water in Poland (0.1 mg Mn/dm^3 and 0.5 mg N-NH4/dm^3). It was found that physico-chemical and biological processes were responsible for ammonia nitrogen elimination, while catalytic processes (physico-chemical and biological) contributed to manganese removal.

Keywords: groundwater, manganese, ammonia nitrogen, removal, processes

Introduction

One of the low cost and simple methods commonly applied to remove manganese from groundwater containing high concentrations of iron and ammonium ions is two-stage filtration on mature sand filter beds. Although the removal of manganese is usually related to physico-chemical processes, the significance of biological processes is also widely reported [1, 2, 3, 4, 5, 6, 7].

The evaluation of the role of physico-chemical and biological processes in the removal of Mn (II) and NH_4^+ ions from groundwater on the I-st and the II-nd stage mature sand filters was the aim of this work. The water and filter bed sand material were taken at the "Letniki" water treatment plant, where high contents of iron, manganese and ammonia nitrogen present in the raw water are effectively removed.

Materials and Methods

The investigations were carried out on two model filters (18 mm in diameter, 360 mm in height and 30 mm in diameter, 1000 mm in height) which were filled with sand with grains of diameter 0.8-1.2 mm, taken from the surface layer (0-150 mm) of the I-st and the II-nd stage filter beds. Both the sand filter bed and groundwater were collected from the "Letniki" treatment plant near Elblqg. The raw water (3.5-5.40 mg Fe/dm^3, 1.08-1.40 Mn/dm^3, 2.09-2.88 mg N-NH4dm^3) was aerated to 6.6-9.0 mg 02/dm^3 and subjected to filtration on the first stage model filters with linear water velocities of 3 m/h and 6 m/h (retention time was 4 or 20 minutes, depending on the dimensions of model filters). On the II-nd stage model filter the water collected in the "Letniki" plant after the I-st stage of treatment (aeration followed by filtration on the opened sand filters, on which the iron ion is removed) was directed. The rate of filtration on the II-nd stage model filters was 5-6 m/h and the retention time was approximately 4 minutes. The water after the II-nd stage filtration fully satisfied Polish requirements for drinking purposes (Tab. 1).

Two methods of inhibition of biological processes in the mature sand filters were applied: chemical (intoxication with sodium azide) and physical (treating with high temperature).

In the chemical method the NaN_3 (15 mM) [8, 9] was applied to the filter bed after test filtration. The NaN_3

solution was filtered for 2 hours with linear velocity of 3 m/h and then left at the model filter for the following 20 hours in static conditions. The first samples were collected after two hours of filtration (without sodium azide), which guaranteed six times exchange of the water in the bed. It was assumed that the water contained only trace concentrations of azide.

In the physical method of inhibiting microbial activity, the filter bed was heated to a pre-determined temperature, and after an assumed time of contact cooled to the initial temperature. The following times of contact were applied: 30 minutes for temperatures below 70°C and 15 minutes for temperatures above 70°C. (It should be pointed out that locally the temperature of the bed could be lower than it was assumed). The efficiency of water treatment on the filter beds previously warmed to temperatures ranging from 30°C to approximately 100°C was investigated.

The investigations were carried out on the two parallel model filters. The model filters were respectively filled with the sand taken from the I-st and the II-nd stage filtering beds. At one of the model filters the activity of bacterial microflora settled on the sand bed was inhibited, while at the second one the control filtration was performed. Four series of investigations were performed for the I-st stage filter bed and twelve series for the II-nd stage filter bed. The efficiency of manganese and ammonia nitrogen removal before and after suppressing microbial activity of bacteria settled on the sand bed was observed.

The concentrations of the following physico-chemical parameters in the water before and after filtration were determined: Fe_{tot}, Mn, $N\text{-}NH_4$, $N\text{-}NO_2$, $N\text{-}NO_3$. The biological investigations consisted of the following determinations: the most probable number of denitrifying, ammonium-oxidizing and nitrite-oxidizing bacteria on the liquid medium according to Polish Standards [10,11] and the total number of bacteria on the PTYG medium with manganese [12].

Results

The Efficiency of Applied Methods of Inhibition of the Microbial Activity of the Filter Beds

The microorganisms settled on the I-st and the II-nd stage filtering beds responded to applied methods of inhibition of their activity in a similar way. Fig. 1 presents

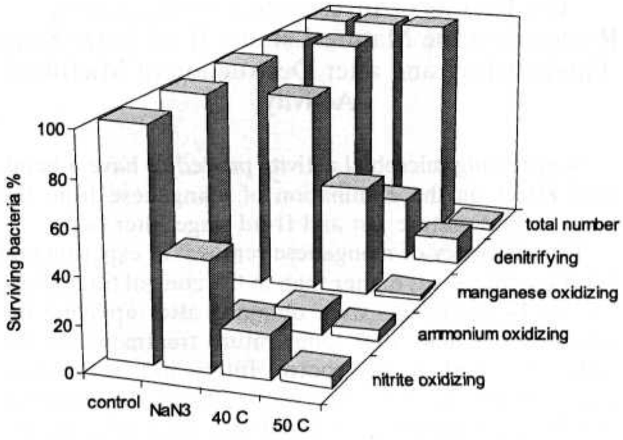

Fig. 1. The percentage share of bacteria surviving on the sand bed after intoxication with 15 mM NaN_3 and after treatment at 40°C and 50°C.

the efficiency of applied methods of inhibition microbial activity of the filter beds (from the first and second stage of filtration).

- *The influence of azide*

The growth of heterotrophic microflora of the beds (total number of bacteria, denitrifying bacteria, manganese-oxidizing bacteria) was inhibited by the solution of sodium azide (15 mM), but when it was removed, the bacteria regained the ability to grow. It was indicated by the results of biological investigations as well as the consumption of oxygen during filtration. The growth of autotrophic nitrifying bacteria (mostly ammonium-oxidizing) was almost completely inhibited, even when sodium azide was removed from the bed. It was indicated by the results of biological investigations and decreased production of nitrates.

- *The influence of temperature*

The filter bed bacteria showed various sensitivity to exposure to higher temperatures from 40°C to 97°C. The nitrifying bacteria were more sensitive than the heterotrophic bacteria. Beginning from 40°C significant inhibition of the growth of ammonium- and nitrite-oxidizing bacteria was observed, while at 50°C (and higher) the growth of both nitrifying and heterotrophic bacteria (the total number of bacteria, manganese-oxidizing bacteria and denitrifying bacteria) almost completely stopped.

Table 1. The concentrations (mg/dm^3) of selected chemical parameters of water quality at the "Letniki" groundwater treatment plant, before and after filtration on the mature sand filter beds.

Type of warter	Fe_{tot}	Mn	$N\text{-}NH_4^+$	$N\text{-}NO_2$	$N\text{-}NO_3^-$
Raw water	3.50 – 5.40	1.08 – 1.40	2.09 – 2.88	0.00 – 0.012	0.04 – 0.24
Water after I-st stage filtration	0.05 – 0.53	0.60 – 1.10	0.95 – 1.33	0.050 – 0.070	0.36 – 0.55
Water after II-nd stage filtration	0.05 – 0.40	0.02 – 0.10	0.08 – 0.40	< 0.010	0.50 – 2.00

The Results of Investigating of Manganese Removal on the Mature I-st and II-nd Stage Sand Filters before and after Destruction of Microbial Activity

Suppressing microbial activity proved to have a beneficial effect on the elimination of manganese from the water on the mature I-st and II-nd stage filter beds.

The efficiency of manganese removal in experimental I-st stage filters was higher than in the control filter (Figs. 2 a, b). Better results were obtained after applying the sodium azide than after temperature treatment. At the same time, both in the control filters and in the beds where the activity of bacteria was inhibited, the efficiency of manganese removal improved with time. The average concentration of manganese, which in the raw water was equal to 1.2 mg/dm^3, decreased to 0.65 mg/dm^3 after 35 hours of filtration on the control filters and ranged from 0.15 to 0.50 mg/dm^3 after filtration on the filter beds where microbial activity was inhibited.

The inhibition of microbial activity did not affect the process of elimination of manganese on the stage II filtering beds (from water containing over 1 mg N-NH_4/dm^3 and about 0.4 mg N-NO_3/dm^3). Both before and after inhibition of microbial activity (by both methods), high efficiency of manganese removal of over 95% was noted, and the concentration of this component in the water after filtration was below 0.05 mg/dm^3 (Fig. 3). The elimination of manganese from water containing from 0.6 to 1.1 mg Mn/dm^3 did not depend on the concentration of dissolved oxygen (in the range of concentrations from 2 to 9 mg O_2/dm^3). This agrees with the stoichiometry of the process, due to which oxidation of 1 mg Mn^{2+} to MnO_2 requires 0.3 mg O_2 [11].

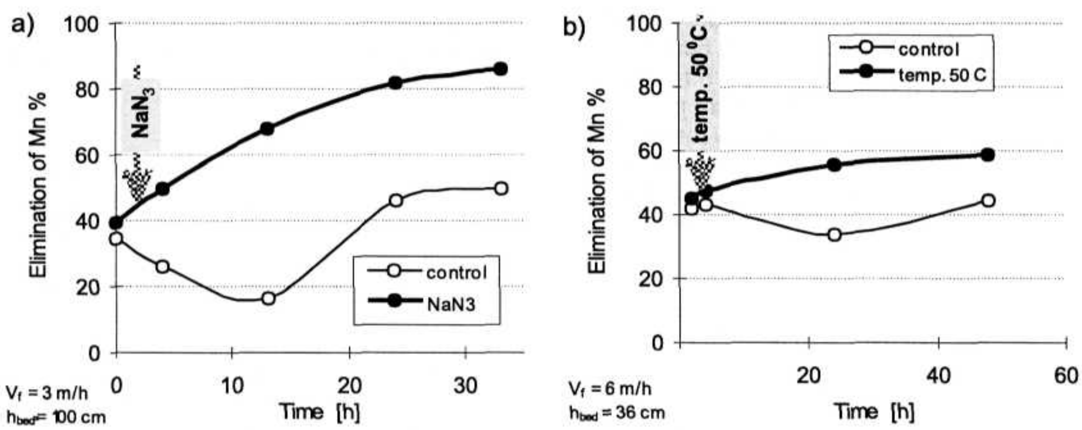

Fig. 2. Efficiency of manganese elimination during the I-st stage filtration on mature sand filter before and after inhibiting microbial activity by intoxicating the bed with NaN_3 (a) and by treating the bed with high temperature (b).

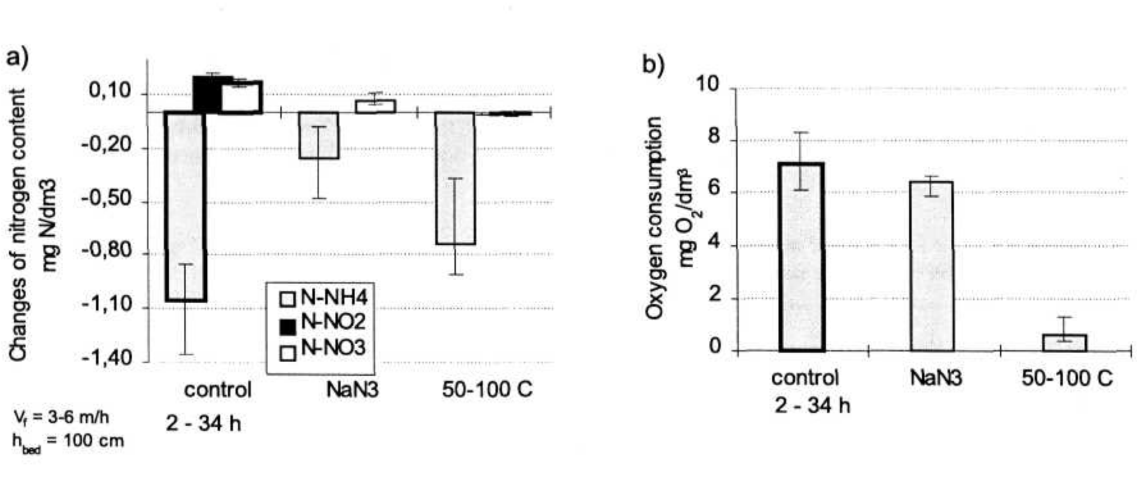

Fig. 3. Changes of contents of various forms of mineral nitrogen (a) and oxygen consumption (b) during the I-st stage filtration on the mature sand filter before and after inhibiting microbial activity.

The Results of Investigations of Ammonia Nitrogen Removal on the Mature I-st and II-nd Stage Sand Filters before and after Destruction of Microbial Activity

After control filtration using I-st stage filters, the average efficiency of elimination of ammonia nitrogen from the water was 40%. The concentration of this component declined from the mean value of 2.51 mg/dm^3 in the raw water to 1.50 mg/dm^3 after filtration (Fig. 4a). The increase of concentration of the oxidized forms of nitrogen (NO_2^- and NO_3^-) corresponded to only 19 to 45% of the removed ammonia nitrogen (28% on average). The remaining ammonia nitrogen was probably sorbed on the filtering bed.

Inhibition of the activity of bacterial microflora resulted in deterioration of the efficiency of elimination of ammonia nitrogen from the raw water (Fig. 4a). Sodium azide showed greater impact on the removal of the ammonium ion than temperature. In the first case the efficiency of elimination dropped to approximately 14%, while on the filters treated with the temperature of 50°C and higher, the efficiency of ammonia nitrogen elimination decreased to 31% (from 40% in control filters). The production of nitrate nitrogen on the filter exposed to NaN_3 was very small and completely stopped on filters treated with higher temperature.

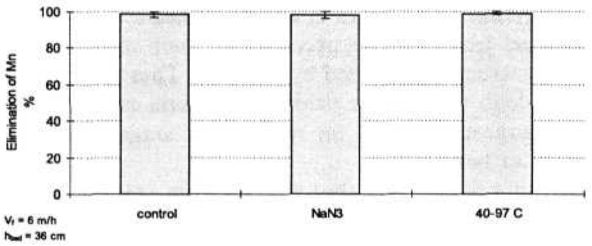

Fig. 4. Efficiency of manganese elimination during the II-nd stage filtration on mature sand filter before and after inhibiting microbial activity by intoxicating the bed with NaN_3 and by treating the bed with high temperature.

The consumption of oxygen dissolved in the water decreased insignificantly after the application of sodium azide, while after heating of the bed it was almost completely inhibited (Fig. 4b).

The II-nd stage filter bed was characterized by high (80-90%) efficiency of elimination of ammonia nitrogen from the water. The concentration of the ammonium ion decreased from about 1.0 mg/dm^3 to less than 0.15 mg/dm^3. Simultaneously, the increase of concentration of nitrate nitrogen of 0.4mg/dm^3 and unimportant changes in the concentration of nitrite nitrogen were observed (Fig. 5a). The concentration of the total mineral nitrogen (measured as the concentration of mineral forms of nitrogen) decreased substantially during filtration. The average oxygen consumption during filtration on the II-nd stage bed was 3.7 mg O_2dm^3 (Fig. 5b). This is by about 0.5 mg/dm^3 less than the stoichiometrical amount of oxygen necessary for biological oxidation of the ammonia nitrogen in the nitrification process.

The inhibition of microbial activity on the II-nd stage filters resulted in a substantial decrease in the efficiency of ammonia nitrogen elimination but it did not totally cease. It should be noted that the effect of sodium azide on the elimination of ammonia nitrogen from the water was investigated in the conditions of high dissolved oxygen concentration, varying from 5.6 to 8.4 mg O_2dm^3.

The application of the sodium azide resulted in significant deterioration of ammonia nitrogen elimination, from about 88% (on the control filtering bed) to approximately 33% (on the filter bed intoxicated with NaN3) (Fig. 5a). The decrease of nitrite nitrogen concentration by more than 90% (0.06 mg N-NO_2dm^3) was still observed, while the production of nitrate nitrogen was almost completely inhibited (to 0.07 mg N-NO_2dm^3 - the amount comparable to the loss of nitrite nitrogen concentration). The concentration of total (mineral) nitrogen in the water declined by 0.29 mg/dm^3 and was almost equal to the amount of eliminated ammonia nitrogen. Consumption of the dissolved oxygen decreased on average to 1,1 mg O_2/dm^3.

The efficiency of elimination of ammonia nitrogen on the bed treated with temperatures ranging from 50°C to 70°C declined to 20%. Simultaneously, production of

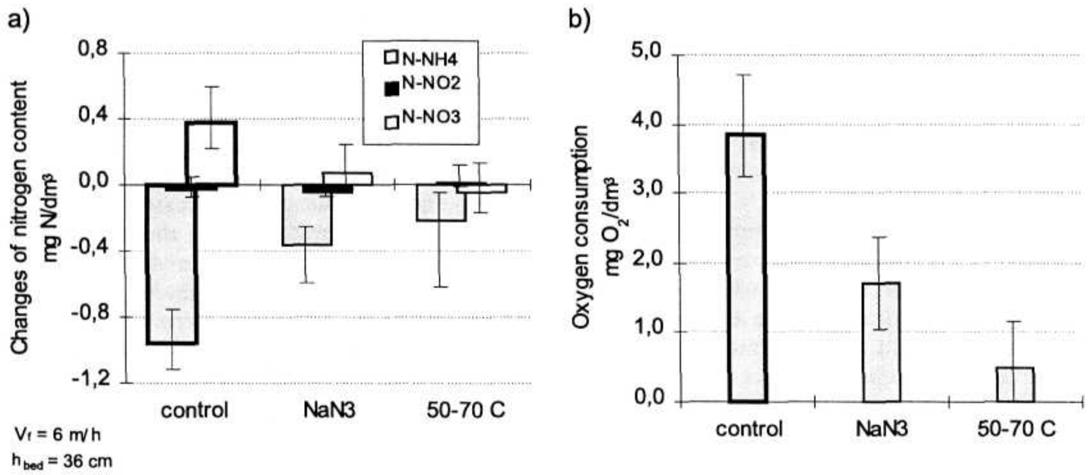

Fig. 5 Changes of contents of various forms of mineral nitrogen (a) and oxygen consumption (b) during the II-nd stage filtration on the mature sand filter before and after inhibiting microbial activity.

nitrite and nitrate nitrogen was completely held up. The consumption of the dissolved oxygen decreased substantially to 0.5 mg O_2/dm^3 on average and was lower than in the case of NaN_3 treated filters.

It should be noted that on the filter bed heated to temperatures from 80°C to 100°C the desorption of ammonia nitrogen occurred.

Discussion

According to numerous authors, manganese-oxidizing bacteria play a significant role in the elimination of manganese on so-called mature sand filter beds [1, 2, 3, 4, 5, 7,13,14,15]. However, proof of the role of these bacteria in the process of removal of manganese comes from static laboratory investigations where the liquid media are inoculated with sand from the beds [9, 12, 16]. It should be stressed that the results of the laboratory experiments, though they prove the presence of manganese-oxidizing microflora, do not provide clear evidence that these organisms take part in the process of manganese oxidizing during water treatment on filter beds. Also, the widely reported high number of these bacteria on the beds (or their high percentage share in the total number of bacteria) is not univocal to their high activity during Mnll oxidation.

In order to investigate the character of the processes the experiments using the model mature sand filters fed with natural groundwater were performed. The effects of removal of manganese and ammonia nitrogen from the water before and after the inhibition of microbial activity on the model filter were compared.

The ammonia nitrogen was removed due to the biological nitrification process as well as physico-chemical processes (sorption, ion exchange). It was indicated by the results of complementary biological and chemical investigations concerning the removal of this ion before and after inhibition of microbial activity of the filter beds. To this aim two methods of bacteria inhibition were applied - sodium azide and higher temperature.

The biological character of $N\text{-}NH_4$ elimination was indicated by: the presence of ammonium- and nitrite-oxidizing bacteria, the increase of the concentration of nitrites and nitrates during filtration, and after inhibition of microbial activity (which was confirmed by microbial investigations) - the deterioration of the efficiency of ammonia nitrogen elimination, complete cessation of production of oxidized forms of nitrogen, and loss of oxygen consumption. These results are in agreement with Vandenabeele [11] and the previous results of the authors of this work [17, 18, 19].

The physico-chemical character of ammonia elimination is indicated by: the consumption of oxygen and production of oxidized forms of nitrogen, which is lower than calculated stoicheiometrically for the amount of removed ammonia nitrogen, and after inhibition of microbial activity, continued, though smaller, elimination of ammonia nitrogen which was not accompanied by consumption of oxygen and production of oxidized forms of nitrogen).

It is supposed that nitrification processes and sorption of ammonia nitrogen on the filter bed are strictly related. The autotrophic nitrifying bacteria (sessile organisms which preferentially grow on the solid surfaces) take advantage of the ammonium ions sorbed on the filter bed, which results its regeneration.

The role of the manganese-oxidizing bacteria in the oxidation of manganese has not been completely proven. Manganese removal on the I-st stage filter bed was more effective after azide treatment than after temperature treatment. Sodium azide almost completely inhibited nitryfying bacteria only (mainly nitrite oxidizing) (Fig. 1), and heterotrophic manganese oxidizing bacteria were still active. The lack of competition for oxygen of manganese oxidizing bacteria with nitryfying bacteria after azide treatment can explain better manganese removal on I-st stage filter in the presence of 2.09-2.88 mg $N\text{-}NHU/dm^3$.

Temperature (> 50°C) completely inhibited growth of autotrophic and heterotrophic bacteria.

According to results (Figs. 2 a, b), elimination of microflora activity (mostly nitryfying bacteria) on I-st stage filter beds improved manganese removal. The efficiency of this process was higher in the case of filters treated with azide than with temperature. It can be explained by higher filtration rate and lower filter height of filters treated with temperature, but one cannot exclude the activity of heterotrophic manganese oxidizing bacteria on filters treated with NaN_3, which could improve manganese elimination. Simultaneously, the relatively high oxygen consumption on azide treated filters should be explained by the activity of heterotrophic organisms.

Observations of Hatva et al. [20] indicate that manganese (and iron) can be precipitated even around dead external structures formed by bacteria. That means alive as well dead manganese oxidizing bacteria can take part in manganese removal on mature 1st stage and II-nd stage filter beds.

It can be assumed that the bacteria settled on the filtering beds act as biological catalysts [21], since the biological elimination of manganese consists of three stages: rapid adsorption of manganese on the external structures of the bacterial cells, oxidation of manganese (in which the bacteria take part), further autocatalytic oxidation of Mn (II) at the presence of MnO_2 [1]. Probably the manganese-oxidizing bacteria begin and simplify the formation of autocatalytic layer of the manganese oxides, due to which the process of manganese oxidation can further take place without direct contribution of microorganisms. It should be mentioned that the type of formed manganese oxides plays an important role in the manganese oxidation process [13].

Further research explaining the interaction of nitrification and denitrification processes in the elimination of manganese from water during the period of ripening of the beds and during their normal exploitation is necessary. Firstly, it could not be excluded that the metabolites excreted by the nitrifying bacteria can provide the source of organic carbon for the manganese-oxidizing bacteria, nor that these organic compounds specifically interact with Mn II [13]. Secondly, the nitrates produced by the nitrifying bacteria improve elimination of manganese [9]. Finally, the role of the denitrification process which, according to Hasselbarth & Ludeman [22] accompanies elimination of manganese, should be explained. Vandenabeele [13] believes that nitrate might exert an indirect beneficial effect on the removal of manganese because it prevents deposited MnO_2 from being resolubilized in the deeper anoxic biofilm layers.

Conclusions

The results of performed physico-chemical and bacteriological investigations of the treatment of groundwater containing high concentrations of Fe, Mn and $N\text{-}NH_4$ on the mature I-st and II-nd stage sand filters brings about the following conclusions:

1. In the removal of ammonia nitrogen both physico-chemical (ion-exchange, sorption) and bio logical (nitrification) processes play important roles.
2. The removal of manganese from the water (on the mature bed) occurs mostly due to auto-catalytic oxida tion by the previously formed manganese oxides (by chemical and biological processes).
3. Further research of the interaction of the biological processes taking place on mature sand filters, especial ly of the processes of oxidation of manganese, nitrifi cation and denitrification, is needed.

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