

- ORAL PRESENTATION -

**CONSIDERATION REGARDING TREATMENT POSSIBILITIES OF
DRINKING WATER SUPPLIES CONTAINING NITROGEN COMPOUNDS**

**Part1: Influence of Pollution Matrix upon
the Selection of Treatment Technology**

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The paper presents some relevant aspects related to the influence of pollution matrix specific to the groundwater supplies, upon the treatment technologies applied in order to remove the inorganic nitrogen - based compounds (ammonium, nitrite, nitrate ions).

The main association of ammonium (NH_4^+) with inorganic/organic pollutants in groundwater are, as follows:

- NH_4^+ and metallic ions ($\text{Mn} \pm \text{Fe}$);
- NH_4^+ and sulphur derivatives (S^{2-} , $\text{S}_2\text{O}_3^{2-}$, SO_3^{2-});
- NH_4^+ and nitrite/nitrate ions ($\text{NO}_2^- / \text{NO}_3^-$);
- NH_4^+ and natural organic matter (NOM - THMs precursors) in the presence of bromide ion (Br^-).

Also, the concentration levels of nitrogen - based compounds and associated pollutants are very important in the selection of suitable treatment procedures, including the succession of treatment steps.

The treatment technologies developed for NH_4^+ and NO_3^- ions removal from groundwater supplies have as specific steps: breakpoint chlorination (NH_4^+) or biological nitrification (NH_4^+) and denitrification ($\text{NO}_2^- / \text{NO}_3^-$) processes.

Among the main problems specific for the most applied technology at industrial level for $\text{NH}_4^+ \pm$ oxidizable pollutants removal (one step chlorination), are mentioned:

- low treatment efficiency (NH_4^+ , S^{2-});
- generation of trihalometanes (THMs), especially brominated ones, with unpleasant consequence upon the treated water quality, which is not proper for human consumption.

Keywords: groundwater, nitrogen compounds, associated pollutants, water treatment

INTRODUCTION

In Romania, drinking water is produced from surface water (60%) and groundwater (40%).

Groundwater supplies less exposed to anthropic pollution, comparatively with surface waters containing as main pollutants: metallic ions (iron, manganese), nitrogen compounds (ammonium, nitrate, nitrite) sulphides, bromide, organic matter (NOM-humic and fulvic acids evaluated as TOC) at different concentrations values. Two situations are emphasized: high concentrations of inorganic pollutants over specific MAC values stipulated in Romanian legislation (L 458/02, L 311/2004) in groundwater supplies (NH_4^+ , Fe, Mn, $\text{SH}^- + \text{S}^{2-}$, NO_3^-) and by-products disinfection resulted in the chlorination steps (oxidation/disinfection), trihalomethans (THMs), in concentrations situated in some cases, over the MAC (sum of individual compounds concentrations: Chloroform, Dibromochloromethane, Bromoform and Bromodichloromethane).

Ammonium, identified in the most of investigated groundwater supplies is associated with inorganic/organic pollutants.

The treatment procedures mentioned in literature data for ammonium removal are based on:

- chlorination to break point, used for water with relatively low ammonium concentration.

The major disadvantage of this process is THMs generation the speciation being influenced by the nature/concentration of THM precursors (natural organic matter) and bromide ion presence [1-3].

- ion exchange, aerobic biological nitrification in fixed on fluidized bed [4-5].

The treatment processes applied for groundwater supplies potabilization containing besides ammonium, metallic ions (Fe, Mn) and sulphides, are generally classic ones, based on: \pm aeration/chemical oxidation-precipitation \pm filtration-chlorine disinfection.

The treatment efficiency is variable, depending on nature and concentrations of pollutants and number of applied treatment steps.

Regarding the recommended treatment procedure for nitrate mitigation there are mentioned: biological denitrification in anaerobic conditions, reverse osmosis (RO), ion exchange (IX) [6,7].

EXPERIMENTAL

In order to establish the compliance degree of drinking water quality with the specific regulations, some DWTPs that are using groundwater supplies with different pollution matrix (NH_4^+ and oxidizable associated compounds), were investigated via direct control.

The following case studies are presented:

- **Case study 1/ S₁** groundwater (H=120 m) containing $\text{NH}_4^+ \leq 0.6$ mg/l, Mn ≤ 110 $\mu\text{g/l}$ (TOC = 0.6 mg C/l).

Treatment flow sheet:

- chlorination (≤ 3 mg Cl₂/l);
 - storage.
- **Case study 2/S₂** groundwater (H=46-100 m) having as main pollutants NH₄⁺ ≤ 1.9 mg/l, Fe ≤ 1000 μ g/l, Mn ≤ 120 μ g/l (TOC ≤ 1.6 mg C/l, Br ≤ 1.5 mg/l).

Treatment flow sheet:

- chemical oxidation (KMnO₄ ≤ 0.5 mg/l + NaClO ≤ 100 mg/l);
 - sand filtration;
 - filtration/adsorption on GAC (Organosorbs 10);
 - chlorination (Cl₂ ≤ 0.6 mg/l);
 - storage.
- **Case study 3/S₃** groundwater (H=120 m) containing NH₄⁺ ≤ 5.3 mg/l, HS⁻ + S²⁻ ≤ 7.7 mg/l (TOC = 0.7 mg C/l).

Treatment flow sheet:

- oxidation/aeration;
 - coke filtration (percolation);
 - chlorination (3 mg Cl₂/l);
 - storage.
- **Case study 4/S₄** groundwater (H=120 m) having as pollutants NH₄⁺ < 2 mg/l, (Br ≤ 0.6 mg/l, TOC ≤ 1.8 mg C/l).

Proposed flow sheet:

- breakpoint chlorination (≤ 20 mg Cl₂/l);
- storage.

The analysis of global and specific parameters (TOC, NH₄⁺, Mn, Fe, HS⁻ + S²⁻, Br, THMs, free/total chlorine) on the treatment flow was done on the basis of standard techniques/methods.

RESULTS AND DISCUSSIONS

The investigations results related to the concentrations domain of main pollutants, efficiencies of applied treatment flow sheets and nonconformities aspects of treated water are presented in the tables 1÷4 for the case studies.

The following aspects regarding the treatment efficiencies of applied treatment flows are emphasized:

- **S₁ supply:** NH₄⁺ + Mn(II)
- Mn > 50 μ g/l due to the absence of filtration step on “green sand”
- **S₂ supply:** NH₄⁺, Fe(II), Mn(II)
- generation of THMs > 100 μ g/l, due to the inadequate operation conditions for THM removal in adsorption step (pH, contact time).
- **S₃ supply:** S²⁻, NH₄⁺
- The applied treatment flow is not in compliance with pollution matrix of underground water (NH₄⁺, S²⁻ - mg/l), the treatment flow

reconfiguration being necessary (S²⁻ oxidation with other oxidation agents, NH₄⁺ biooxidation, disinfection).

➤ **S₄ supply:** Br⁻, NH₄⁺, TOC

- The applied treatment flow is not corresponding to the pollution matrix of underground water (NH₄⁺, mg/l), in this case being proper, major NH₄⁺ removal (ion exchange/nitrification).

Table 1

Case study S₁		
H = 120 m	Specific pollutants concentrations: Mn ≤ 110 µg/l, NH ₄ ⁺ ≤ 0.6 mg/l, TOC ≤ 0.6 mg/l	
Steps of the treatment process	Treatment efficiency	Nonconformities
<ul style="list-style-type: none"> ➤ Chlorination; ➤ Storage-distribution. 	<ul style="list-style-type: none"> ➤ Advanced removal (98%) of NH₄⁺ by oxidation; ➤ Low efficiency (max 5%) of soluble Mn II removal by partial oxidation and settling in storage vessel and distribution network. 	<ul style="list-style-type: none"> ➤ Absence of residual Cl₂ (Cl₂ ≤ 0.01 mg/l); ➤ Presence of Mn due to non-assurance of oxidant concentration and absence of filtration phase.

Table 2

Case study S₂		
H = 46-100 m	Specific pollutants concentrations: Fe ≤ 1000 µg/l, Mn ≤ 120 µg/l, NH ₄ ⁺ ≤ 1.9 mg/l, TOC ≤ 1.6 mg/l, Br ⁻ = 1,5 mg/l	
Steps of the treatment process	Treatment efficiency	Nonconformities
<ul style="list-style-type: none"> ➤ Pre-oxidation with KMnO₄ + NaClO; ➤ Filtration on sand; ➤ Filtration/adsorption on GAC; ➤ Disinfection with chlorine; ➤ Storage-distribution. 	<ul style="list-style-type: none"> ➤ Advanced removal of Fe, Mn, NH₄⁺ residual concentrations under imposed limits NH₄⁺ ≤ 0.01 mg/l Fe ≤ 0.006 mg/l Mn ≤ 0.009 mg/l 	<ul style="list-style-type: none"> ➤ Variation of free chlorine concentration: Cl₂ = 0.025-0.6 mg/l ➤ THMs ≤ 247 µg/l, from which 91% are brominated compounds (MAC = 100 µg/l); ➤ The chemical oxidation step determines the transformation of organic load and of Br ion into THMs.

Table 3

Case study S₃		
H = 120 m	Specific pollutants concentrations: HS ⁻ +S ²⁻ ≤ 7.7 mg/l, NH ₄ ⁺ ≤ 5.3 mg/l	
Steps of the treatment process	Treatment efficiency	Nonconformities
<ul style="list-style-type: none"> ➤ Aeration; ➤ Coke filtration; ➤ Chlorination; ➤ Storage-Distribution 	<ul style="list-style-type: none"> ➤ S²⁻ oxidation ($\eta_{\text{average}} = 89\%$); S²⁻ residual concentration ≤ 1 mg/l (83% over CMA = 0.1 mgS²⁻/l) ➤ NH₄⁺ oxidation ($\eta_{\text{average}} = 3\%$); NH₄⁺ residual concentration ≤ 4.8 mg/l. 	<ul style="list-style-type: none"> ➤ Turbidity increasing (≤28NTU) due to colloidal sulphur formation by S²⁻ oxidation; ➤ S²⁻, NH₄⁺ over CMA; ➤ Residual Cl₂ < 0.3 mg/l.

Table 4

Case study S₄		
H = 120 m	Specific pollutants concentrations: NH ₄ ⁺ ≤ 2 mg/l, TOC ≤ 1.8 mg C/l, Br ⁻ ≤ 0.6 mg/l	
Steps of the treatment process	Treatment efficiency	Nonconformities
<ul style="list-style-type: none"> ➤ Break point chlorination (≤ 30 mg Cl₂/l); ➤ Storage-distribution 	<ul style="list-style-type: none"> ➤ NH₄⁺ ≤ 0.5 mg/l ($\eta_{\text{average}} = 75\%$) 	<ul style="list-style-type: none"> ➤ THM ≤ 280 µg/l (CMA = 100 µg/l); - by-products advanced bromurated (DBCM and TBM) represent 66% from total THM.

CONCLUSIONS

- The main factors with high influence on the selection of treatment technologies for drinking water supplies containing as pollutants NH₄⁺ associated with reduced species of Fe + Mn and S²⁻ are:
 - initial concentrations of pollutants in soluble phase;
 - pollution matrix (organic load/TOC, bromide ions) with influence on the disinfection by-products concentrations and speciation.
- Using of chlorine based compounds (Cl₂, NaClO) as oxidants reclaims experimental works in order to evaluate the FPTHM, even the TOC values are low (≤ 2 mg C/l);
- Association of organic precursors with high production of THM and bromide ions influences the amount and the speciation of disinfection by-products (THM).

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