Influence of Ammonium Ions on the Treatment Process Selection of Groundwater Supplies Intended to Human Consumption

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In Romania, drinking water is produced from surface water (60%) and groundwater (40%). The presence of inorganic compounds containing oxidizable nitrogen within groundwater sources (NH_4^+-N, NO_2^--N) at variable concentration levels in association with other pollutants/micropollutants from natural/anthropogenic origin asks for previous treatability studies before the setting-up of final treatment technology. The ones currently applied for NH_4^+-N oxidation involve use of chlorine for oxidation of specific pollutants (N-NH_4^+, S^{2-} a.s.o.) and water disinfection. The high doses of chlorine required by NH_4^+-N "break point" chlorination process (Cl_2: NH_4^+-N weight ratio = 7.6÷15:1) are able to generate undesirable chlorinated by-products from which trihalomethanes are the only regulated for drinking water (MAC_{THM} = 100 µg/L). The experimental results of treatability studies using chlorine as oxidant reagent for three groundwater sources located in Bucharest proximity containing among oxidizable pollutants: NH_4^+-N (≥1 mg/L), natural organic matter (DOC ≤ 3.5 mg/L), Mn(II) ions are presented. The noncompliance aspects related to the quality of treated water (THMs concentration, residual chlorine, free and bound chlorine ratio a.s.o.) from groundwater sources containing high concentration NH_4^+-N impose replacement of classic treatment process based on chlorine chemical oxidation with other process (biological nitrification).

Keywords: groundwater, ammonium ions, natural organic matter (NOM), break point chlorination, chlorinated by-products

Ammonium ions in natural water resources are important chemical species in nitrogen cycle, resulting from the decomposition of various N – containing organic compound (such as proteins) or by influence of anthropogenic pollution (agricultural runoff sewage for example). The presence of ammonium ions in natural drinking water resources, groundwater especially [1, 2], above maximum admissible concentration/MAC (MAC_{NH4^+} = 0.5 mg/L) has a significant effect on the selection of treatment process.

Chlorine is the only chemical oxidant which can react with ammonium ions at the pH current values of natural drinking water resources (especially groundwater). The term of break point chlorination describes the point where chlorine and ammonium ions concentrations are simultaneously minimized.

The use of chlorine in order to reduce NH_4^+-N concentration is based on the oxidation reactions to elemental nitrogen, the intermediates products being the chloramines (mono-, di-, chloramines and nitrogen trichloride).

The chloramines speciation is depending on *p*H, Cl_2:NH_4^+-N ratio and temperature [3÷5].

The following information on the *p*H depending of chloramine should be emphasized [6]:

- NH_2Cl (monocloramine) is the dominant chloramine specie at pH > 7.5
- $NHCl_2$ (dichloramine) becomes the dominant chloramine specie at *p*H < 7-7.5;
- NCl_3 (trichloramine/nitrogen trichloride) increases only when *p*H is < 7 and chlorine to nitrogen ammonia ratio is increased above 8:1.

The maximum $NHCl_2$ concentration has a large magnitude when initial NH_4^+-N concentrations is increased.

The end products of break point chlorination are primarily nitrogen gas (N_2) and secondarily nitrate (NO_3^-), according to the following reactions:

$$NH_4^+ + 1.5HOCl \rightarrow 0.5N_2 + 1.5H_2O + 2.5H^+ + 1.5Cl^-$$

$$NH_4^+ + 4HOCl \rightarrow NO_3^- + H_2O + 6H^+ + 4Cl^-$$

The stoichiometric ratio chlorine to nitrogen ammonia (weight ratio Cl_2:NH_4^+-N = 7.6:1) assuring N_2 as major end product is not affected by *p*H in the 6.7 – 7.2 range.

The ideal operating *p*H for break point chlorination is situated between *p*H = 7.0 and 8.0. Presence of organic nitrogen can influence chlorine demand for N-NH_4^+ oxidation.

Taking into account the variability of groundwater pollution matrices, the chlorine demand for N-NH_4^+ break point chlorination is determined by experimental works for each case, the variation domain of Cl_2:N-NH_4^+ weight ratio being quite large (Cl_2:N-NH_4^+ = 7.6÷15:1).

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Numerous inorganic and organic pollution/micropollutants can undergo reaction with chlorine, for most of them HOCl being the major reactive chlorine species. A fast reaction of ammonia-nitrogen (N-NH_4^+), halides (Br^- and I^-), nitrite (NO_2^-), sulfite (SO_3^{2-}), As(III), Fe(II) with HOCl is reported [7].

Natural organic matter (NOM) like humic substances present in water resources react with aqueous free chlorine, halogenated by-products being formed. Several factors such as: *p*H, dissolved organic carbon (DOC), bromide concentration, temperature and operational factors like chlorine dose, contact time were reported to affect the formation of halogenated by-products. Aqueous chlorine converts bromide to hypobromous acid, which can react with organic matter in the same way as hypochlorous acid to form various bromochlorinated by-products, HOBr being a stronger halogenating agent than HOCl.

Natural organic matter (NOM) is typically dominated by humic substances (HS) which contain substantial amount of hydroxy-, carboxy-, and methoxy- substituted aromatic units which are collectively referred to as polyhidroxy aromatic (PHA) or phenolic moieties. PHA is considered to be the substrate for halogenation reactions, being responsible for the generation of trihalomethanes, haloacetic acids, etc [8, 9].

THMs species ($CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$, CBr_3) were proven to have adverse effects on human health. Especially brominated species were suspected to be much stronger carcinogens and mutagens than non-brominated species [9]. The other by-products reported for water treatment using chlorine (oxidation/disinfection reactions) are, as follows: haloacetic acids (HAAs), haloacetonitriles (HANs), haloketones, haloaldehydes, chlorinated phenols, chloropicrin, cyanogen halides and chloral hydrate [9, 10].

Only a small percentage of chlorinated by-products has been quantified in drinking water: THMs were the largest class of CBPs/DBPs detected, HAAs being the second largest fraction [9, 11].

Taking into account the potential adverse effect of halogenated by-products on health, specific regulations concerning maximum concentration levels (MCLs) of some micropollutants species were set up. The US regulations limit total THMs species (chloroform, bromodichloromethane, dibromochloromethan and bromoform) and five haloacetic species (monochloro-, dichloro-, trichloro-, monobromo- and dibromo-acetic acids) of 80 and 60 µg/L respectively. The European Union regulations set only MCL for THMs (100µg/L) as a sum of the four above mentioned species [12].

Experimental part

The aim of experimental tests was to demonstrate the high influence of pollution matrices of groundwater supplies, containing ammonium ions (NH_4^+, mg/L) associated with organic/inorganic oxidable compounds, in the chlorination treatment process, which can affect the quality of potable water. Chlorine oxidation of NH_4^+-N content groundwater sources is used in Romania in the most of treatment plants.

The following experimental activities were performed:

- analytical investigations of three groundwater sources (150 m depth) in order to evaluate the variation domain of the main quality parameters: *p*H, turbidity, alkalinity, hardness, inorganic ions (Fe, Mn), organic matter (TOC/DOC), bromide ion;
- assessment of dissolved natural organic matter (NOM) reactivity in the presence of chlorine in specific conditions (Cl_2 doses, *p*H, time, temperature), by periodically determination of generated THMs along the experimental period (6 days). Iodine determination flasks (500 mL) were used for experiments kept in dark conditions for all testing period;
- oxidation of ammonium ions using chlorine at different ratios (Cl_2:NH_4^+-N = 7.6÷16:1), with assessment of treated water quality (residual NH_4^+, residual chlorine, THMs).

Materials and methods

Chlorine water ($Cl_2 \leq 1.5$ g/L) was used as chlorine source.

Analytical investigations for raw/treated groundwater characterization were performed using standardized techniques methods:

- total dissolved organic carbon was determined by using an MULTI N/C 3000 analyzer (Analytik Jena);
- NH_4^+, NO_2^-, NO_3^- and Br^- ions were determined using a Dionex ICS-3000 Ion Chromatograph, with separate anions and cations columns (AS23 and CS16, 250 mm x 4 mm each) and suppressed conductivity detectors;
- trihalomethanes analysis was performed by GC-ITMS using an Agilent 7890A gas chromatograph equipped with Agilent GC Sampler 80 in headspace mode and DB5-MS column (60m x 250 m x 0.25µm), coupled with ion trap mass spectrometer Agilent 240MS. Sample vials were automatically agitated with 500 rpm at 60 ^{0}C for 15 min. 0.5 mL of gas phase was injected with a 2.5 mL HS syringe heated at 75 ^{0}C. GC Injector worked at 150^{0}C in split mode (5:1), oven temperature program was: 40^{0}C (10 min), 10^{0}C /min to 250 ^{0}C (2 min) and transfer line temprature was 250^{0}C. MS analysis was performed in EI mode, using mass range: 50-200 m/z, emission current: 25 µA and trap temperature: 150^0 C.

Results and discussions

Assessment of groundwater quality

The analytical investigations emphasized the variation domain of main pollutants, which are situated over the MAC values (ammonium and manganese ions) for groundwater sources.

According to the registered data (table 1) the following remarks are presented:

- NH_4^+ concentrations are fluctuant and rather high, especially for GW2 ($NH_4^+ \leq 6.5$ mg/L) and GW3 (($NH_4^+ \leq 7.4$ mg/L) sources;
- Mn is present in concentrations over admitted limit in GW1 (Mn ≤ 140 µg/L) and GW2 (Mn ≤ 80 µg/L) sources majority under reduced form, Mn(II) in soluble phase;
- organic load evaluated as total organic carbon (TOC) from which rather than 90% is dissolved organic carbon (DOC), has normal values for groundwater supplies;
- Br^- ion, not normed parameter by specific law for drinking water quality, is situated below the method detection limit ($Br^- < 100$ µg/L) for GW2 and GW3 sources, concentration values of 100 µg/L being determined for GW1 source. The presence of Br^- ion can influence the speciation of THMs generated as result of reactions between NOM, chlorine (HOCl) and in-situ generated bromine (HBrO).

Assessment of THMs potential formation (THMPF)

The main physico-chemical characteristics of raw water samples and working conditions set up in order to evaluate the reactivity of humic matter expressed as DOC (dissolved organic carbon), in contact with chlorine are presented in table 2.

Table 1
VARIATION DOMAINS OF MAIN PARAMETERS OF GROUNDWATER QUALITY

Parameter	Variation domains			L 458(r1)/2002 republished in 2011
	GW1	GW2	GW3	
pH	7.36-7.90	7.05 – 8.38	7.52 – 8.26	6.5 – 8.5
Turbidity, NTU	1.5 – 3.6	< 1 – 2.7	1.1 – 3.1	≤ 5
Alkalinity, mval/l	4.9 – 6.1	4.7 – 6.1	4.95 – 6.0	-
Hardness, °d	7.6 – 8.7	2.8 – 6.5	2.5 – 3.4	min 5
NH_4^+, mg/l	0.9 – 2.2	1.9 – 6.5	3 – 7.4	0.5
NO_2^-, mg/l	< 0.1	< 0.1	≤ 0.1	0.5
NO_3^-, mg/l	1.9 – 2.2	< 0.1 - 6	< 0.1 - 7	50
Mn, µg/l	99 - 140	≤ 80	≤ 50	50
Fe, µg/l	60 - 120	< 200	≤ 200	200
TOC, mg C/l	1.6 – 2.5	2.4 – 4.1	3.1 – 3.5	No any abnormal modification
Br^-, µg/l	≤100	< 100	< 100	Not normed parameter

Table 2
MAIN PHYSICO-CHEMICAL CHARACTERISTICS OF RAW WATER SAMPLES AND CHLORINE APPLIED DOSES

Groundwater	pHi	DOC, mgC/l	N-NH_4^+, mg/l	Br^-, µg/l	Cl_2 dose, mg/l
GW1	7.62	2	1.23	100	15.8
GW2	7.05	3.1	1.48	< 100	21.1
GW3	7.5	3.3	2.37	< 100	28.9
Work conditions • chlorine dose is the sum of chlorine corresponding to the weight ratios Cl_2:DOC = 3:1, and Cl_2:N-NH_4^+ = 8:1 for each groundwater source; • pH = 7-7.2 (buffered pH); • contact time = 6 days; • t = 20-22°C.					

The applied chlorine doses were different in accordance with DOC and NH_4^+-N concentrations of each source, the work conditions being similar: Cl_2: DOC ratio = 3:1, Cl_2: NH_4^+-N ratio = 8:1, contact time = 6 days, buffered *p*H = 7-7.2, temperature = 20-22°C. THMs were analyzed periodically for each treated sample in order to determinate the concentration level, evolution in time and the species of THMs (figs. 1, 2).

The following aspects are resulting in accordance with the experimental results:

- THMs generated in the three groundwater samples (GW1, GW2, GW3) present an increasing evolution in time, proving the reactivity of dissolved organic matter towards chlorine;

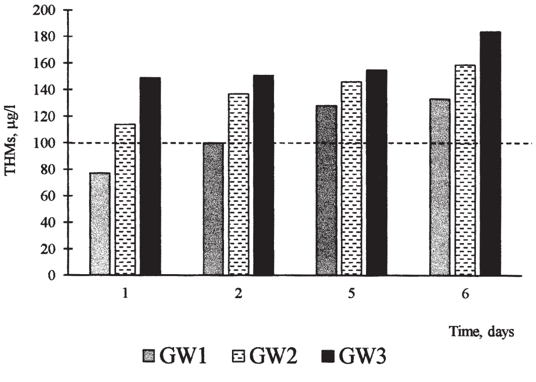

Fig. 1. THMPF - Evolution of THMs vs time

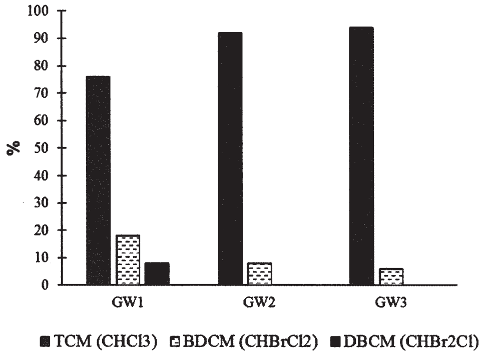

Fig. 2. THMs species (t = 6 days)

- the concentration levels of THMs seem to be in correlation with the DOC values, the variation series of THMs being as follows:

THMs / GW3 > THMs / GW2 > THMs / GW1
THMs, µg/L : 149 > 114 > 77
(24h)
THMs, µg/l : 184 > 159 > 133
(6 days)

- Over 72% of THMs are formed after first day (24h) of contact, concentration levels being higher than MAC (100 µg/l) for GW2 and GW3 groundwater sources with DOC values between 3.1 – 3.2 mg C/l;

- the behaviour of organic matter from GW1 source (DOC = 2 mg C/l) in respect with specific reactions of chlorine with organic THMs precursors emphasized a lower reactivity, generated THMs after first day (24 h) being below the MAC value and representing 58% of THMs concentration;

- the final THMs concentrations for all samples are situated above MAC with percentages between 33-84%;

- $CHCl_3$ is the major chlorinated compound, determined concentration after six days being above 90% for GW2 and GW3 groundwater sources ($CHCl_3$/GW2 = 92% of THMs; $CHCl_3$/GW3 = 95% of THMs);

- brominated derivatives ($CHBrCl_2$ and $CHBr_2Cl$) were identified in higher concentrations in treated GW1 source, representing 23% of final THMs, that confirm the influence of bromide ion even at low concentration (Br^- = 100 µg/L) upon the THMs species.

Assessment of ammonium break point chlorination

GW1 source was selected for ammonium "break point" chlorination tests in order to evaluate the influence of contact time and Cl_2: NH_4^+-N ratio upon the evolution of main quality parameters of treated water (residual NH_4^+, THMs production, residual chlorine).

Table 3
COMPARATIVE EVOLUTION OF RESIDUAL POLLUTION FOR MINIMUM CL_2:NH_4^+-N RATIOS FOR GW1- BREAK POINT CHLORINATION

Cl_2:NH_4^+-N weight ratio	pH reaction	Residual concentrations in soluble phase		
		NH_4^+, mg/l	Mn, µg/l	Total chlorine/Free chlorine, mg/l
7.6 : 1	7.15	0.65	27	3.4 / 0.4
8.2 : 1	6.50	0.31	35	5.8 / 1.2
8.2 : 1	7.8	0.27	14	6.5 / 1.4
Raw water pH_i = 7.76 NH_4^+ = 1.66 mg/l Dissolved Mn = 123 µg/l			***Work conditions*** $\tau_{reaction}$ = 15 minutes Na_2CO_3 5% of pH correction 7.8	

Table 4
INFLUENCE OF CONTACT TIME ON THE EVOLUTION OF MAIN PARAMETERS FOR GW1- BREAK POINT CHLORINATION

Oxidation time, min	Residual chlorine, mg/l		NH_4^+, mg/l	Dissolved Mn, µg/l	THMs, µg/l
	Free chlorine	Bound chlorine			
15	1.4	5	0.27	14	7
30	0.8	1.4	0.12	4	16.8
60	0.4	1.2	<0.1	-	20.2
1440 (24 h)	0.1	0.3	-	-	233 (80% $CHCl_3$)
Raw water pH_i = 7.76 NH_4^+ = 1.66 mg/l Dissolved Mn = 123 µg/l			***Work conditions*** Cl_2:NH_4^+-N = 8.2:1 (Cl_2 = 10.6 mg/l) pH = 7.8 (pH correction with Na_2CO_3 5%)		

Table 5
INFLUENCE OF CL_2:NH_4^+-N WEIGHT RATIO UPON PRODUCTION AND EVOLUTION OF THM FOR GW1 – BREAK POINT CHLORINATION

Cl_2:NH_4^+-N (weight ratio)	Total residual chlorine, mg/l		THM, µg/l	
	τ= 3 h	τ= 72 h	τ= 3 h	τ= 72 h
7.6 : 1	2.1 (5% free chlorine)	1.2 (4% free chlorine)	15.1	78.1
8.2 : 1	2.4 (4% free chlorine)	1.5 (3% free chlorine)	20.1	113.9
8.5 : 1	2.4 (4% free chlorine)	1.7 (3% free chlorine)	22.4	128.1
9 : 1	2.5 (4% free chlorine)	1.85 (3% free chlorine)	25.1	134.6
10 : 1	3.1 (3% free chlorine)	2.45 (2% free chlorine)	30.1	139.1
16 : 1	3.9 (5% free chlorine)	2.6 (4% free chlorine)	60.9	174.7
Raw water pH_i = 7.6 NH_4^+ = 0.9 mg/l DOC = 1.4 mgC/l		***Work condition*** pH = 7.8 (Na_2CO_3 5% for pH correction) Reaction time = 3÷ 72 hours		

The arguments for GW1 selection were related to the groundwater pollution matrix more complex than GW2 and GW3 sources: ammonium and manganese ions over MACs values, presence of organic and inorganic THMs precursors (NOM/DOC and Br^- ion).

The preliminary results of the tests performed in order to set up the Cl_2: NH_4^+-N weight ratio for ammonium oxidation were in accordance with literature data that stipulate the need to apply chlorine doses higher than those corresponding to stoichiometric ratio (Cl_2:NH_4^+-N = 7.6 : 1), due to the influence of oxidable associated pollutants upon ammonium oxidation yield. Data presented in table 3 emphasize a residual concentration of NH_4^+ over CMA value. The increase of chlorine dose (Cl_2 :NH_4^+-N = 8.2:1) has a good influence upon ammonium oxidation yield, but the *p*H value without subsequent correction is decreased with a unit, being similar to the inferior admitted value (*p*H = 6.5) by potable water quality regulations.

After 15 min of reaction the residual chlorine is present at high concentration values (mg/L) most of it being as combined chlorine (over 75% from total chlorine). The influence of reaction time upon the evolution of main parameters (residual chlorine, THMs, NH_4^+, Mn) for the GW1 sample treated at Cl_2:NH_4^+-N = 8.2:1 ratio and corrected *p*H (*p*H =7.8) is presented in table 4.

According to experimental results, slow decrease of residual chlorine and increase of THMs are registered. After 24 h of contact between residual chlorine and organic matter (NOM), the level of generated THMs is higher than MAC_{THM} (THMs = 233 µg/L – $CHCl_3$ 80% of THMs).

For GW1 pollution matrix and low concentrations levels of ammonium and organic matter (NH_4^+ = 0.9 mg/L, DOC = 1.4 mg/L, Br^- = 100 µg/L), the influence of Cl_2: N-NH_4^+ ratio (7.6÷16:1) upon developed in time chlorinated by-products (THMs) was studied. The monitored parameters: free and total residual chlorine and THMs after 3 h and 72 h of contact are presented in table 5. According to registered results, the following remarks are presented:

- increase of total residual chlorine in treated water according to applied chlorine doses (Cl_2= 5.3÷11.2 mg/:L, total residual chlorine = 2.1÷3.9 mg/L), after 3 h of reactions;
- low concentration of free chlorine after 3 h of reactions (3-5% from total residual chlorine);
- slow increase of THMs in treated water after 3 h of reaction (Cl_2 doses = 5.3÷11.2 mg/L; THMs = 15.1-60.9 µg/L);
- development of specific chlorinating (oxidation, substitution) reactions in time with the increase of THMs over MAC (τ reaction = 72 h), for the initial Cl_2:N-NH_4^+ ratios between 8.2:1 and 16:1 (THMs = 113.9-174.7 µg/L);
- decrease of total residual chlorine in time with 25%-43% from corresponding concentrations analysed after 3 h of contact.

Conclusions

A large number of DWTPs (nature supply-groundwater) is using chlorine for water disinfection and also for specific pollutants oxidation (NH_4^+, NO_2^-, S^{2-}, Mn^{2+}).

The groundwater matrices especially the presence of oxidable organic/inorganic pollutants have a high influence upon Cl_2:NH_4^+-N ratio, sometimes the quality of treated water being affected due to the noncompliance aspects related to some parameters:

- high percent of bound chlorine versus free chlorine;
- *p*H/alkalinity decrease (*p*H ≤ 6.5);

- presence of chlorinated by-products THMs ($CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$, $CHBr_3$), above MAC (MAC_{THMs} = 100 µg/L), resulted by specific reactions between chlorine and natural organic matter (NOM).

In the case of groundwater sources with NH_4^+ content above 1 mg/L, the replacement of classical oxidation technology using "break point" chlorination is compulsory. Biological nitrification of ammonium ions is recommended for the treatment of drinking water supplies containing high concentrations of NH_4^+, taking into account the followings:

- high efficiency of NH_4^+ bio-oxidation;
- no excess of chemical agents for process development;
- advanced reduction of chlorine dose used for the subsequent treatment step (water quality polishing/disinfection);
- low concentrations of THMs after final disinfection.

Acknowledgments: The work was supported by Project SOP HRD - PERFORM/159/1.5/S/138963 and Programme Nucleu 13N/2009, Project PN 09 – 13 03 03.

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Manuscript received: 6.08.2014