

THE DETERMINATION OF NH_4^+ CATION AND Al METAL CONCENTRATIONS IN WATER OF SWIMMING POOLS IN CENTER OF CANAKKALE, TURKEY

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ABSTRACT

In current study, NH_4^+ cation and Al metal concentrations in summer period were determined by ultraviolet-visible (UV-VIS) spectrophotometric technique in the total 6 swimming pools found in the province of Canakkale (Turkey). Merck Kits equivalent to EPA, APHA, ISO and DIN standards were used in spectrometric analyses. The monthly quality parameter results in this study were evaluated according to various limit standard values of different countries. As a result, NH_4^+ cation and Al metal concentrations varied between 0.003 and 0.999 mg L^{-1} ($0.073 \pm 0.139 \text{ mg L}^{-1}$), 0 and 0.652 mg L^{-1} ($0.141 \pm 0.068 \text{ mg L}^{-1}$) respectively.

Keywords: *Canakkale, Swimming pool waters, ammonium cation, Al metal*

1. INTRODUCTION

Swimming is one of the most popular aquatic activities in industrialized countries. During busy periods, the quality of pool water may be compromised. Indeed, swimmers bring microorganisms and organic substances (saliva, sweat, cosmetics, sunscreen and urine) with them into the water, which strongly contributes to water contamination (Sakkas *et al.*, 2003; Kanan and Karenfil, 2011; Keuten *et al.*, 2012; Uysal *et al.*, 2017).

Ammonia in water is an indicator of bacterial, fecal and animal wastes is being mixed into the water (Anonymous, 2006; Uysal *et al.*, 2017). Pool water resources NH_4^+ , the filling water, human origin (fecal and urine contamination) and is caused by biofilm formation

(Güllüoğlu, 2010; Uysal *et al.*, 2017). Ammonium is just quickly oxidized to nitrite in oxygen environment and then transformed into nitrate. Nitrification is carried out by bacteria such as *Nitrosomonas* and *Nitrobacter* group bacteria (Mutluay and Demirak, 1996; Uysal *et al.*, 2017).

Organic substances which cause water discoloration are usually removed from water by coagulation (clotting), precipitation and filtration (Yaşa, 1999; Uysal *et al.*, 2017). Before the filtration, the stability of small particles (electrical) is deteriorated thanks to the addition of the flock material into pool water and hence agglomeration of particles is provided. For flocking, chemical (e.g. addition of colloidal substances such as $Al_2(SO_4)_3$ to water) is used (Bölükbaşıoğlu, 1993; Uysal *et al.*, 2017). The flocculation decrease chlorine consumption in the pool and hence eye diseases and BK formation which cause bad smell are avoided (Akkaya, 1993; Uysal *et al.*, 2017). Aluminium (Al) is known to be non-toxic element. However, excessive amounts of intake have been shown to influence the nervous system and cause anemia. Al is an element also used in Alzheimer and diabetes diseases (Canadab, 2003; Uysal *et al.*, 2017).

Limit concentration values of the Turkish Health Ministry for NH_4^+ cation and Al metal are 0.50 and 0.20 $mg L^{-1}$, respectively (Anonymous, 2011; Uysal *et al.*, 2017). In order to evaluate some quality standard levels of swimming pools found in the province of Canakkale (Turkey), this study on determination of NH_4^+ cation and Al metal concentrations in water of swimming pools in center of Canakkale has been conducted in summer period (July, June and August, 2013) due to the intensive tourism activity in this period..

2. MATERIALS AND METHODS

2.1. Study area and period

In this study, 6 swimming pools as a study area (Figure 1) were selected. Pool water samples were monthly collected from sampling locations (swimming pools) in summer period of 2013 (June, July and August, 2013) in Canakkale province (Figure 1). The sample numbers Çanakkale, 33-36 (Figure 1).



Figure 1. Water sampling points for swimming pool in the summer period in the provinces of Canakkale, Turkey (Sample numbers : Çanakkale, 33-36), (Uysal *et al.*, 2017).

Pool water samples were collected from special points where the water flow is the lowest or swimmers are the most intense. Moreover, special sampling depths and points were just under surface (0.20 m) and about one meter away from the edge line of the pools. The collected samples were put in clean polythene sample bottles (1.00 L) and stored in deep freezer at -21.0 °C until analyses. In this study, samples from the total 6 swimming pools were analyzed for each parameter..

2.2. Analytical methods

In current study, NH₄⁺ cation and Al metal concentrations in summer period were determined by ultraviolet-visible (UV-VIS) spectrophotometric technique in the total 6 swimming pools found in the province of Canakkale (Turkey). Thermo Aquamate Brand

Spectrophotometer was used for analyses. For analyses, Merck Kits equivalent to EPA, APHA, ISO and DIN standards were used.

Ammonium nitrogen ($\text{NH}_4^+\text{-N}$) occurs partly in the form of ammonium ions and partly as ammonia (Uysal et al., 2017). A pH-dependent equilibrium exists between the two forms. In strongly alkaline solution ammonium nitrogen is present almost entirely as ammonia, which reacts with hypochlorite ions to form monochloramine (. This, in turn, reacts with a substituted phenol to form a blue indophenol derivative that is determined photometrically. The method is analogous to EPA 350.1, APHA 4500-NH₃ F, ISO 7150-1, and DIN 38406-5. Analysis measuring range is ranged from 0.01 to 2.00 mg L⁻¹ $\text{NH}_4^+\text{-N}$ and 0.01 to 2.58 mg L⁻¹ NH_4^+ . In the production control, the following data were determined in accordance with ISO 8466-1 and DIN 38402 A51: Standard deviation of the method ± 0.0146 (mg L⁻¹ $\text{NH}_4^+\text{-N}$), coefficient of variation of the method ± 1.40 (%), confidence interval ± 0.035 (mg L⁻¹ $\text{NH}_4^+\text{-N}$), Sensitivity: Absorbance 0.010 A corresponds to 0.009 (mg L⁻¹ $\text{NH}_4^+\text{-N}$), accuracy of a measurement value max ± 0.052 (mg L⁻¹ $\text{NH}_4^+\text{-N}$) (Merck 2014).

In weakly acidic, acetate-buffered solution aluminium ions react with chromazurol S to form a blue-violet compound that is determined photometrically (Uysal et al., 2017). The method is analogous to APHA 3500-Al-B and DIN ISO 10566 E30. Analysis measuring range is 0.02 to 2.00 mg L⁻¹ Al unless otherwise stated. In the production control, the following data were determined in accordance with ISO 8466-1 and DIN 38402 A51 (10-mm cell): Standard deviation of the method ± 0.012 (mg L⁻¹ Al), coefficient of variation of the method ± 1.70 (%), confidence interval ± 0.03 (mg L⁻¹ Al), Sensitivity: Absorbance 0.010 A corresponds to 0.001 (mg L⁻¹ Al), accuracy of a measurement value max. ± 0.008 (mg L⁻¹ Al) (Merck, 2014).

3. RESULTS AND DISCUSSION

The found concentration of NH_4^+ cation and Al metal in water of swimming pools water in center of Canakkale, are giving in Table 1 and Figure 2,3.

Average summer results showed that NH_4^+ concentrations varied between 0.003 and 0.999 mg L⁻¹ (0.073 ± 0.139 mgL⁻¹) . Based on both maximum and average values, NH_4^+ concentration increased from June to August probably due to the increasing touristic population.

Table 1. Descriptive statistical results of NH_4^+ concentrations in swimming pools in the summer period in the provinces of Canakkale, Turkey (n : Number of observation; l : The number of samples exceeding the limit concentration values specified by Turkish Health Ministry).

| Month 2013 | Parameters (mg L^{-1}) | n | Maximum Values | Minimum Values | Average Values | Standard Deviation | Analysis Accuracy | Limit Values | l |
|---------------------------|--------------------------------------|-----|-------------------|-------------------|-------------------|-----------------------|----------------------|-----------------|-----|
| June | NH_4^+ | 44 | 0.4425 | 0.0102 | 0.0460 | 0.0658 | ± 0.059 | 0.50 | 0 |
| July | NH_4^+ | 44 | 0.9639 | 0.0032 | 0.0756 | 0.1541 | ± 0.059 | 0.50 | 1 |
| August | NH_4^+ | 44 | 0.9992 | 0.0123 | 0.0967 | 0.1983 | ± 0.059 | 0.50 | 3 |
| Summer Average | NH_4^+ | 44 | 0.9992 | 0.0032 | 0.0728 | 0.1394 | ± 0.059 | 0.50 | 4 |

Figure 2 showed that NH_4^+ concentrations varied between 0.0102 and 0.9992 mg L^{-1} during the sampling period.

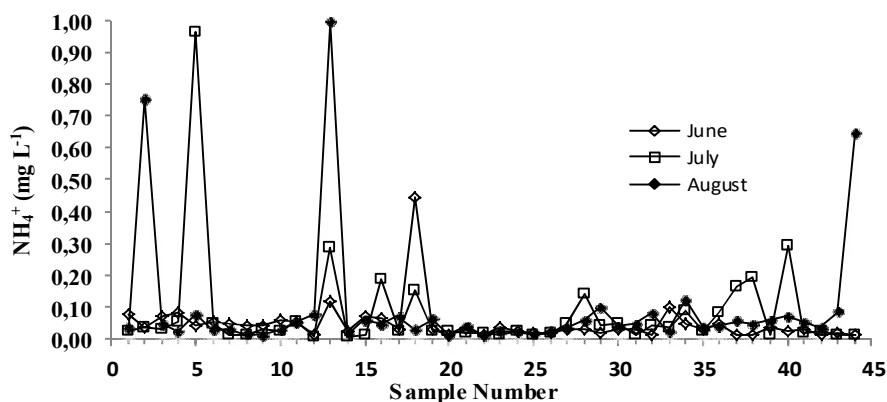


Figure 2. The concentration of NH_4^+ in swimming pool waters in the summer period in the provinces of Canakkale, Turkey (Sample numbers: Canakkale, 33-36).

Al metal variation

Al metal variations in swimming pool waters in the summer period in the province of Canakkale, Turkey are giving in Table 2 and Figure 3.

Table 2. Descriptive statistical results of Al concentrations in swimming pools in the summer period in the provinces of Canakkale, Turkey (*n*: Number of observation; *l*: The number of samples exceeding the limit concentration values specified by Turkish Health Ministry).

| Month 2013 | Parameters (mg L ⁻¹) | <i>n</i> | Maximum Values | Minimum Values | Average Values | Standard Deviation | Analysis Accuracy | Limit Values | <i>l</i> |
|----------------|----------------------------------|----------|----------------|----------------|----------------|--------------------|-------------------|--------------|----------|
| June | Al | 44 | 0.3596 | 0 | 0.0325 | 0.0529 | ±0.008 | 0.20 | 1 |
| July | Al | 44 | 0.6522 | 0 | 0.0500 | 0.0956 | ±0.008 | 0.20 | 1 |
| August | Al | 44 | 0.3736 | 0 | 0.3390 | 0.0543 | ±0.008 | 0.20 | 1 |
| Summer Average | Al | 44 | 0.6522 | 0 | 0.1405 | 0.0676 | ±0.008 | 0.20 | 3 |

Average summer results showed that Al concentrations varied between 0 and 0.652 mg L⁻¹ (0.141±0.068 mg L⁻¹). Although average Al concentration increased from June to August probably due to the increasing swimmer population based on both average values, maximum values of Al (0.6522 mg L⁻¹) was July and August, respectively (Table 2). However, although the all maximum Al values were over the limit values for pool water standards of Turkish Health Ministry and the standards of some European countries, the all average values were considerably under all these limit values (Table 2).

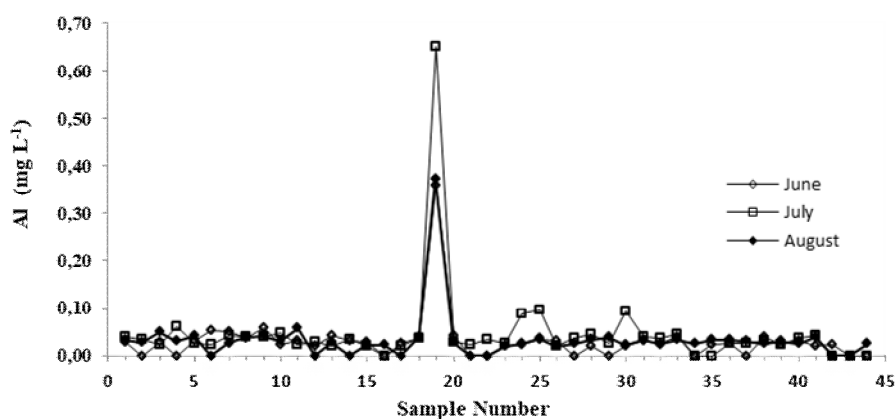


Figure 3. Variations of Al in swimming pool waters in the summer period in the provinces of Canakkale, Turkey (Sample numbers: Canakkale, 33-36).

Results revealed that Al concentrations varied between 0 and 0.6522 mg L⁻¹ during the sampling period (Figure 3). Unhealthy pool water ratio for Al was calculated as 2.27%.

4. CONCLUSIONS

The results of NH₄⁺ indicated that there were suitable aerobic nitrification conditions due to the high dissolved oxygen concentrations in the pool waters. It is known that NH₄⁺ very quickly converts to NO₃⁻ due to the nitrification in aerobic conditions (Mutluay and Demirak, 1996; Putz, 2008, Uysal *et al.*, 2017) and partly NH₄⁺ were under standard limit values (Table

1). In a study on microbiological and chemical qualities of 144 swimming pool waters (69 indoor, 75 outdoor) for three-year period (2010-2012) in Bologna (Italy), Dallolio *et al.* (2013) using same methodology (spectrometric method) in this study revealed that noncompliance rate to standard limit value (unhealthy pool water ratio) were 1.20 and 0.00% in the indoor swimming pool waters and outdoor pool waters, respectively (Uysal *et al.*, 2017).

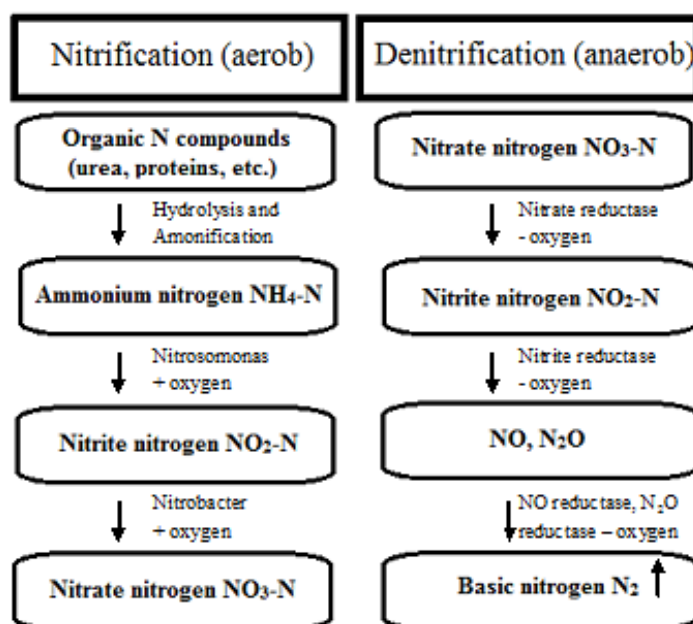


Figure 4. Nitrification and denitrification (Pütz, 2008; Uysal *et al.*, 2017).

On the other hand, non-human factors such as birds and plants. It is known that faces of the birds contain higher nutrient values than faces of the human (Tiffany *et al.*, 2015; Uysal *et al.*, 2017). For solution of such problems, it is important to get sanctions and obligations for hygiene controls and periodic changes of pool waters in legal manner (Uysal *et al.*, 2017).

As a result, due to the fact that Canakkale province has important tourism activity in Turkey, pool waters in such tourism regions should be monitor in view of not only chemical (NH₄⁺ cation and Al metal) and physical quality parameters (Temperature, pH and DO), but also microbiological (*Salmonella* and *Vibrio* etc.) quality parameters (Uysal *et al.*, 2017).

Conflict of Interest Statement

The authors declare no conflict of financial, academic, commercial, political, or personal interests.

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