DTU Environment
Department of Environmental Engineering

Technical University of Denmark

Effect of pH on formation of chlorinated byproducts in swimming pool

K. M. S. Hansen, S. Willach, H. Mosbæk, H.-J. Albrechtsen and H. R. Andersen
hran@env.dtu.dk

Abstract

It has been suggested to improve pool water quality through decreasing the pH which reduces the formation of trihalomethanes (THM) which are regulated in some countries. We show that while lower pH decreases THM formation the lower pH causes more formation of the genotoxic haloacetonitriles (HAN) and the toxic and astma inducing trichloramine.

In a detailed follow up study we find that there is a very narrow optimal pH range around 7.0-7.2 there the formation of all by-products are low.

As a result of this work the statuary order no. 623 from 13/06/2012 of Denmark regulates the lower limit for pH in public swimming pools to 6.8.

Experiments

Experiments were carried out as batch experiments at pH range 6.0-8.0 with phosphate buffer. A second experiment aimed at determined the tipping point for DBP formation ranged from 6.7 to 7.5. Body-fluid analogue (BFA) according to Judd and Bullock (2003) which contained ammonium, urea, creatinine, histidine, hippuric acid, uric acid and citric acid were added corresponding to 1 mg/L TOC. The chlorine was added either at a constant concentration of free chlorine ($HOCl+OCl^-$) of 35 mg/L or constant concentration of active chlorine (HOCl) of 27 mg/L corresponding to 27 to 102 mg/L of free chlorine according to pH.
The experiment was performed headspace-free at 25 ˚C for 48 hours.

Results

When the free chlorine was kept constant, the concentration of THM and HAN decreased and increased, respectively, with decreasing pH while the concentration of HAAs almost remained constant. The pH effect was the same for the formation of THMs and HANs in the experiment where the concentration of active chlorine was kept constant at the different pH , while the concentration of HAAs now is increasing with increasing pH. More detailed information can be found in Hansen et al. (2012a,b)

The toxicity of the water with chlorinated Body-fluid analogue was calculated based on the genotoxicity of the different HAAs, HANs, and THMs found by Plewa et al. (2008): Toxicity = $\Sigma\, C_i / EC_{50,i}$

The genotoxicity decreasing with increasing pH (Figure 1). The contribution of THMs to the overall solution toxicity was negligible compared to the other groups. However, the absolute values of THMs toxicity increased with increasing pH which relates to the increasing THMs concentration shown in Figure 1. Only the HANs contribute to the genotoxicity, since chloroform, dichloroacetic acid and trichloroacetic acid were not genotoxic in the assay used by Plewa et al. (2008).

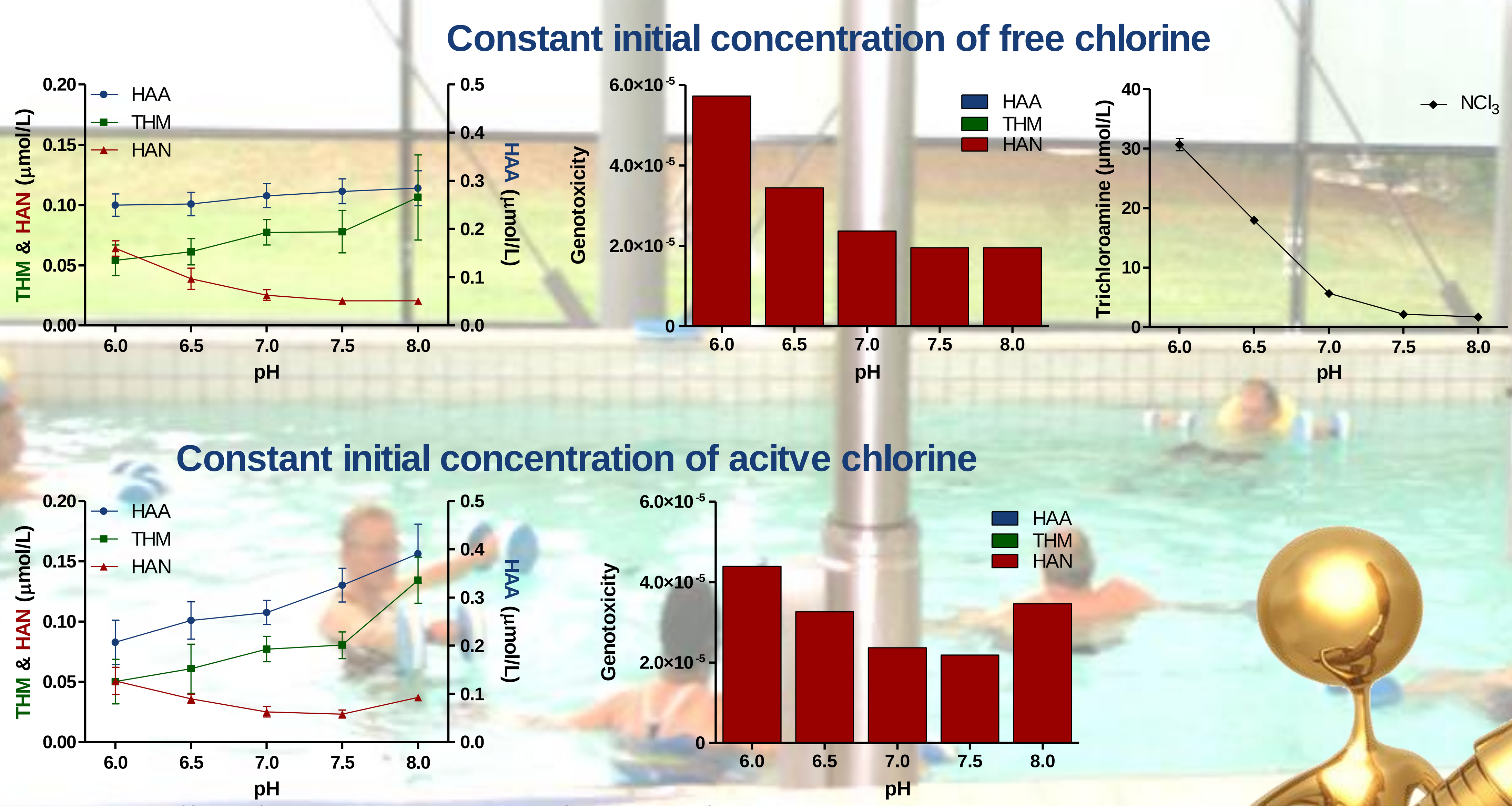

Figure 1. Effect of pH in large intervals in formation of trihalomethan (THM), haloacetic acid (HAA), haloacetonitrile (HAN) and trichloroamine (NCl_3).

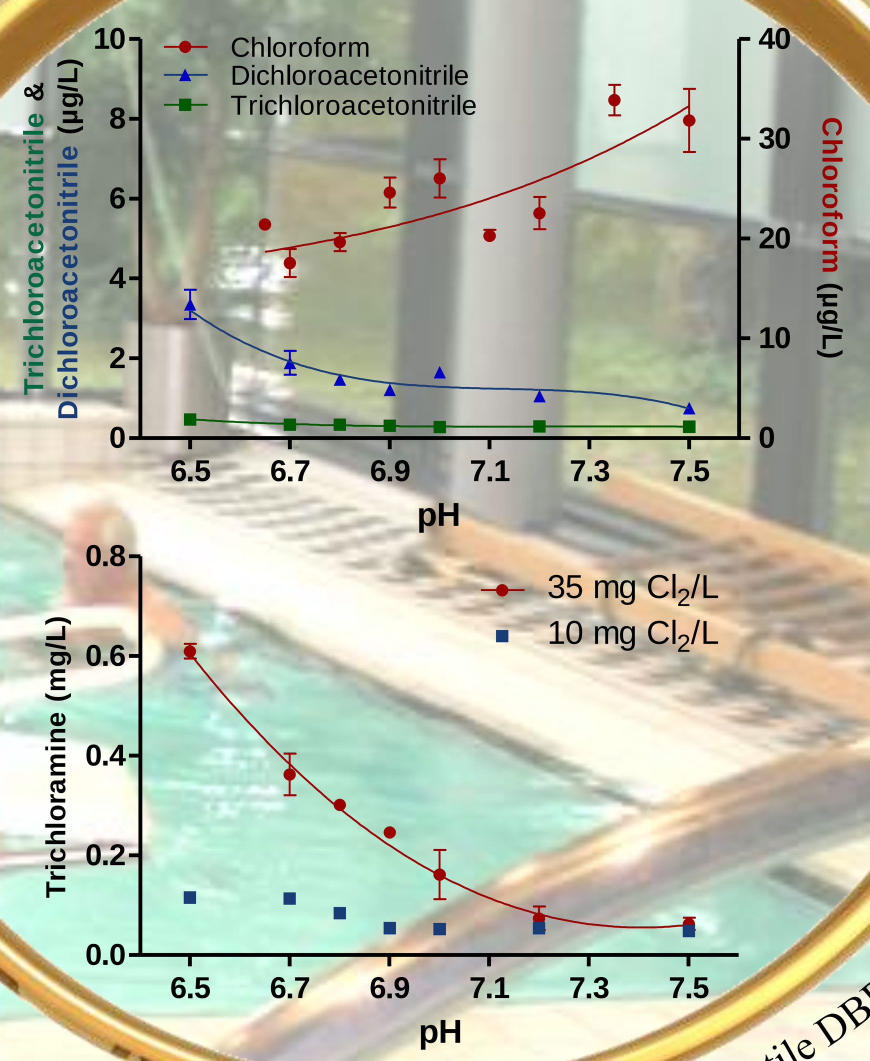

Figure 2. Effect of pH on formation of volatile DBPs.

References

Hansen et al. (2012a) Particles in swimming pool filters - Does pH determine the DBP formation? Chemosphere 87(3), p. 241-247.
Hansen et al. (2012b) Effect of pH on the formation of disinfection byproducts in swimming pool water - Is less THM better? Water Research, Accepted
Judd & Bullock (2003) The fate of chlorine and organic materials in swimming pools. Chemosphere 51(9), p. 869–879.
Plewa et al. (2008) Comparative Mammalian Cell Toxicity of N-DBPs and C-DBPs. In: Disinfection By-Products in Drinking Water, American Chemical Society, Washington DC, Vol. 995, pp. 36-50.

Conclusions

The pH affects the formation of each investigated DBP group differently, while there was no real difference between the two chlorination approaches.
A decrease in concentration of THMs and HAAs were observed for decreasing pH, while the concentration of the HANs and NCl_3 increased with decreasing pH.

0