Comprehensive Identification of Chemical DBPs from Chlorinated and Brominated Swimming Pools

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Swimming pools have been recently recognized as important routes of exposure to potentially harmful chemicals. Previous epidemiologic research has shown increased incidence of asthma and other respiratory effects for people who have significant indoor swimming pool exposures, and new research has shown a significant increased risk of bladder cancer from chlorinated swimming pool exposure. Swimming pool treatment is very similar to what is used for treating drinking water: chlorine is commonly used (either as a gas, liquid bleach, or stabilized solid tablet), and it can react with natural organic matter present in the water or with human inputs (sweat, urine, skin cells, etc.) to form disinfection by-products (DBPs). Our previous research on outdoor pools revealed similar DBPs to what has been found for drinking water (e.g., trihalomethanes, haloacetic acids, and other halogenated chemicals), but to-date. In this research, we used low and high resolution gas chromatography (GC)/mass spectrometry (MS) to comprehensively identify DBPs formed in indoor chlorinated and brominated swimming pools sampled in Barcelona, Spain. Human health endpoints and mutagenicity of the water were also measured by collaborators in this study. For the identification work, 20 L of pool water was extracted using XAD resins (8 over 2), eluted with ethyl acetate, rotary evaporated to approximately 5 mL, and further evaporated with a gentle stream of nitrogen to 1 mL . One-half of this extract was analyzed directly, and one-half was further derivatized with diazomethane to enable the detection of halo-acids. DBPs identified included an abundance of halo-acids (including many unregulated ones), halomethanes, haloacetonitriles, haloaldehydes, haloketones, halonitromethanes, haloamides, haloalcohols, and halophenols. Many of these DBPs have not been reported previously for swimming pool waters, and many of the chemicals were not present in the mass spectral library databases (NIST or Wiley), which necessitated the use of high resolution-MS to generate potential empirical formulas and the manual interpretation of the mass spectra to identify their structures. In general, more nitrogen-containing DBPs were observed in these pool water samples than are typically found in drinking water. Bromoform levels were approximately twice as high in the pools treated with bromine vs. chlorine, but interestingly, other DBPs and their levels were similar in brominated vs. chlorinated pools, likely owing to the high levels of bromide already in the Barcelona raw source waters that feed into drinking water treatment (and serve as source waters for further swimming pool treatment).