Chloroform from swimming pools, a significant source of atmospheric chloroform in Phoenix?

Central Arizona-Phoenix Long-Term Ecological Research
CAP LTER

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Introduction

Chloroform ($CHCl_3$) is a well-documented disinfectant by-product (DBP) of water chlorination. Chloroform is an important atmospheric pollutant by its direct health effects as well as by its contribution to photochemical smog formation.[1] Chloroform outgassing from swimming pools is not typically considered a source of atmospheric chloroform because swimming pools are scarce compared to other sources. However, urban areas in hot climates such as Phoenix generally contain a substantial amount of swimming pools per capita,[2] potentially resulting in significant atmospheric fluxes. In this study, swimming pools as a source of atmospheric chloroform is investigated. Measurements of chloroform concentrations are used to estimate fluxes and determine impacts on Phoenix air pollution.

What causes the $CHCl_3$?

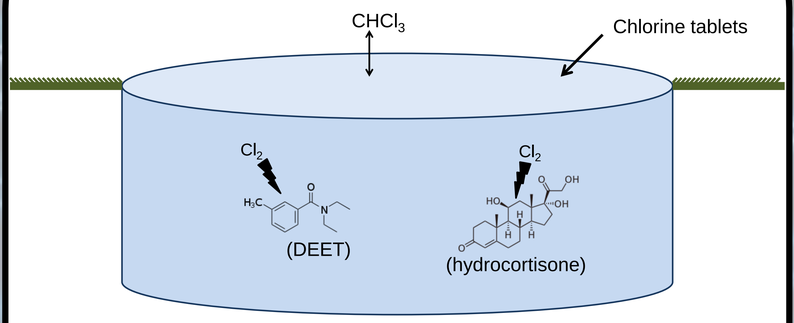

Figure 1: Illustration of chemistry occurring within swimming pools

Example: chlorination of ethanol

C_2H_5OH + **$4Cl_2$** + H_2O → **$CHCl_3$** + 5HCl + $HC(OH)_3$

Other DBPs are simultaneously produced, such as dichloroacetic acid, bromoform, bromodichloromethane, dibromochloromethane… more than 100 DBPs have been identified.[1] These additional DBP can contribute to halogenated VOCs in the atmosphere.

*note: brominated pools show same behavior, producing bromoform instead of chloroform.

Chloroform Sources in Phoenix

No emissions sources in Arizona were reported to EPA since 1999, but that doesn't mean zero emissions! Average ambient $CHCl_3$ concentrations in Phoenix are 60 ppt, or 60 molecules $CHCl_3$ in 10^{12} molecules "air". So $CHCl_3$ is coming from somewhere.

Possible sources of $CHCl_3$ include natural (vegetation, soil, ocean) and anthropogenic (industry, drinking water chlorination, landfill processing) sources. Natural processes generally account for 90% of all $CHCl_3$ emissions.[2]

Arizona ranks second in swimming pools per capita behind Florida.[3] However, pools in FL are distributed across the entire state whereas pools in Arizona are largely concentrated within Maricopa county. It's possible that the high number of $CHCl_3$-emitting pools within a valley such as Phoenix are as a sum responsible for a substantial portion of the emissions of $CHCl_3$ into the urban air. This can become a potential public health issue, and can also contribute to photochemical smog.

Chloroform Flux From Swimming Pools

Flux was estimated based on previously collected swimming pool data[1]:

$$F = k_L \left[c_w - \frac{c_a}{k_H} \right]$$

where k_L is the liquid mass transfer of $CHCl_3$, c_w is the concentration of $CHCl_3$ in water, c_a is the concentration of $CHCl_3$ in the air above the water, and k_H is Henry's constant. Using literature data, the estimated flux is **90 µg $CHCl_3 m^{-2}$ hr^{-1}.** For the average residential pool (41 m^2),[4] that correlates to **32 g $CHCl_3$/yr** which doesn't seen significant. Furthermore, Maricopa county has an estimated 286,000 pools; this means that swimming pools in Maricopa county emit an estimated **9.23 metric tons $CHCl_3$/yr!** In comparison, the global annual anthropogenic $CHCl_3$ emissions are estimated to be 70,000 metric tons. Swimming pools in Phoenix result in an estimated 0.01% of the global anthropogenic emissions. Future work will refine this estimate.

Chloroform at the National Level

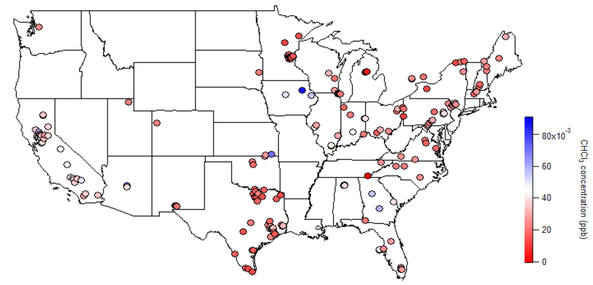

Figure 2: 2012 Average Annual Ambient $CHCl_3$ concentrations[5]

Ambient $CHCl_3$ concentrations are higher in Phoenix than most other cities of comparable size and industrial composition.

Implications

Chlorination of swimming pools might be a significant source of chlorinated VOCs in an area of high pool density such as Phoenix. Some cities have considered limiting the number of new swimming pool permits approved per year in hopes of reducing the community's water and electricity needs; a reduction in $CHCl_3$-producing swimming pools as a secondary consequence might be beneficial for air quality in Phoenix. Additionally, alternate disinfection schemes might be recommended or required in efforts to reduce air pollution.

Future work

Laboratory experiments investigating how much $CHCl_3$ is produced by chlorination of various compounds have already begun. By examining the impacts of chlorination of cosmetics such as lotions and sunscreen, $CHCl_3$ fluxes can be estimated to better constrain emission fluxes and the resulting public health risks. Additionally, emission estimates for Phoenix will be refined as more data becomes available.

References

[1]Richardson, S.D.; DeMarini, D.M.; Kogevinas, M.; Fernandez, P.; Marco, E.; Lourencetti, C.; Ballesté, C.; Heederik, D.; Meliefste, K.; McKague, A. B.; Marcos, R.; Font-Ribera, L.; Grimalt, J.O.; Villaneuva, C.M. (2010) What's in the Pool? A Comprehensive Identification of Disinfection By-products and Assessment of Mutagenicity of Chlorinated and Brominated Swimming Pool Water, *118*, 1523–1530.

[2]Khalil, M. a. K., and Rasmussen, R. a. (1999) Atmospheric chloroform, *Atmos. Environ. 33*, 1151–1158.

[3]P.K. Data, Inc. U.S. Swimming Pool and Hot Tub Market 2013. Retrieved Jan. 14, 2014 from http://www.apsp.org/ResearchResources/content.cfm?ItemNumber=1028&navItemNumber=1083.

[4]Forrest, N., and Williams, E. (2010) Life Cycle Environmental Implications of Residential Swimming Pools, Environmental Science and Technology, *44*, 5601-5607.

[5]EPA Air Toxics Data. Retrieved on Jan. 14, 2014 from http://www.epa.gov/ttnamti1/toxdat.html#data