

## Chlorine By-Products in Swimming Pools

Chemistry, Symptoms, Current Research, Exposure Guidance, Measurement Techniques, and Ventilation Controls

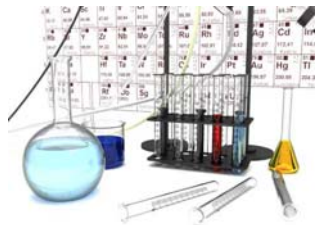
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Recreational Waters Program Manager

## The Big Picture

- The World Health Organization has stated that "the risk of death from pathogens is at least 100 to 1000 times greater than the risk of cancer from disinfection by-products (DBPs) {and} the risk of illness from pathogens is at least 10,000 to 1 million times greater than the risk of cancer from DBPs"

[http://www.who.int/water\\_sanitation\\_health/dwq/S04.pdf](http://www.who.int/water_sanitation_health/dwq/S04.pdf)

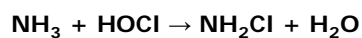
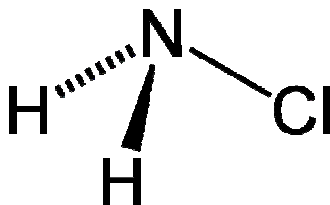
## Chemistry



## Chloramines

- The term chloramine not only refers to the chemical compound but also to a family of organic compounds with the formulas  $R_2NCl$  and  $RNCl_2$  (R is an organic group).
- Dichloramine,  $NHCl_2$ , and nitrogen trichloride,  $NCI_3$ , are also implied under the general term.
- They all form in pools from reactions with organics, urine, and sweat

## Chloramine ( $NH_2Cl$ )

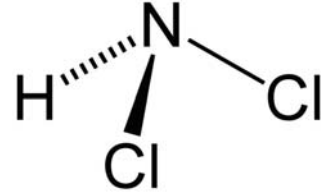


Swimming pool filled with chloramine-treated tap water, showing greenish color of chloramine. Photo by Richard J Kinch, 2001

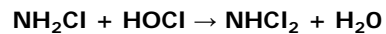
## Monochloramine (NH<sub>2</sub>Cl)

- More stable in solution than chlorine
  - Some communities favor it for water treatment
- The chlorine/ ammonia rate is ideally 6:1. During chloramine production the rate is usually 3-5:1. When ammonia concentrations are higher, more di- and trichloramines are formed.

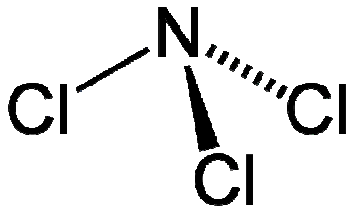
## Dichloramine (NHCl<sub>2</sub>)



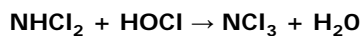
Byproduct of Chloramine Formation



## Nitrogen Trichloride (NHCl<sub>3</sub>)



Byproduct of Chloramine Formation



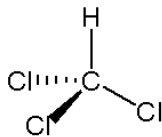
## Nitrogen Trichloride (NHCl<sub>3</sub>)

- Yellow, oily, pungent-smelling liquid
- Nitrogen trichloride is a dangerous explosive, being sensitive to light, heat, and organic compounds.
- Pierre Louis Dulong first prepared it in 1812, and lost two fingers and an eye in two separate explosions.
- It has been used as a tear gas.
- Least water soluble of the chloramines.

## Trichloromethane (CHCl<sub>3</sub>) a.k.a. Chloroform

Most common Trihalomethane in pool enclosures

- Formed in the haloform reaction with organic substances (urine, sweat, skin particles).
- The reaction to phosgene under the influence of UV is also possible.
- The EPA has determined that this exposure is minimal compared to that from consumption.



## Trace By-products to Note

- Trihalomethanes
- Chlorinated hydrocarbons
- Chlorinated ketones
- Chlorinated aldehydes
- Chlorinated carboxylic acids
- Chlorinated acetic acids
- Chlorinated alcohols

## Symptoms

- Acute
  - Lung irritation
  - Mucous membrane irritation
  - Coughing, wheezing, and dyspnoea
  - Decreased lung function
- Chronic
  - Reactive airway dysfunction syndrome
  - Childhood asthma
  - Adverse reproductive outcomes



## Acute – Current Research

- France 1997: Lifeguards exposed to  $\text{NCl}_3$  are at risk of developing irritant eye, nasal, and throat symptoms. (Lifeguard Lung)
- UK 2002: Occupational asthma observed in pool workers who never enter the water.
- Netherlands 2007: An excess risk for respiratory symptoms indicative of asthma observed in pool employees.

## Acute – Current Research

- Ohio 2007: Warren County Combined Health District received 665 complaints of respiratory or eye irritation. NIOSH came to investigate at LHD request and found Nitrogen Trichloride at  $1.06 \text{ mg/m}^3$ .
- Complaints were greater on days with a higher bather load.

## Chronic – Current Research

- Nitrogen Trichloride and its relationship with Asthma



## Hygiene Hypothesis

- The **hygiene hypothesis** states that a lack of early childhood exposure to infectious agents, symbiotic microorganisms (e.g. gut flora or probiotics), and parasites increases susceptibility to allergic diseases by modulating immune system development.

## Pool Chlorine Hypothesis

- The **pool chlorine hypothesis** is the hypothesis that long-term attendance at indoor chlorinated swimming pools by children up to the age of about 6-7 years is a major factor in the rise of asthma in rich countries since the late twentieth century.
  - Alfred Bernard

## Chronic – Current Research

- Belgium 2003 & 2006: Use of indoor chlorinated pools by young children (strongly linked to attendance by children under 6-7) promotes the development of childhood asthma. ( $\text{NCl}_3$  averaged 0.3-0.5  $\text{mg}/\text{m}^3$ )
- 341 children – study related cumulative pool attendance (CPA) to:
  - Exercise-induced bronchoconstriction test
  - Exhaled nitric oxide
  - Aeroallergen-specific serum

## Chronic – Current Research

- Ireland 2009: Among boys age 6-12, study found the greater the number of years the subject had been attending an indoor pool, the greater the chance of him having asthma.

## Chronic – Current Research

- France 1994: Concentrations of  $\text{NCl}_3$  are generally higher in pools with recreational activities and higher temperatures.
- UK 1999: Consumption of chlorine by-products is associated with adverse reproductive outcomes.

## Exposure Guidance

?

One study showed complaints started at about 0.5 $\text{mg}/\text{m}^3$  and everyone questioned complained at 0.7 $\text{mg}/\text{m}^3$ .

## Measurement Techniques

- Generally speaking,  $\text{NCl}_3$  is our best indicator and most likely culprit.
- Developed Mid-90's: Aspiration of ambient air over glass fiber filter paper impregnated with a solution of sodium carbonate and trioxide diarsenic via a vacuum pump (for 3-4 hours); then tested at a lab via liquid or ion chromatography.

So what can be done to prevent this problem???

## Ventilation Controls

- The air above indoor swimming pools needs to be managed as carefully as the water
- The key is fresh air exchange!!!
  - Not just recyclers
- Increase air movement over the water and overall turn-over rate
- Keep combined Cl low
  - Recommend keeping below 0.2ppm

## Keeping Combined Chlorine Below 0.2ppm

- Fresh water
- Ozone and UV
- "Breakpoint" versus "Shock"
  - "Shock" could make it worse
- Remedies for difficult breakpoint situations
  - Potassium Monopersulfate
  - Activated carbon
  - Peroxolytes
- Gas/liquid stripping contactors

## Ventilation Controls

- Retro-fit ceiling fans to "break the bubble" of by-products
- Open windows and doors (no matter how cold) for a couple hours after breakpoint
- Assess facility for "dead-zones"

## Ventilation Controls

- Mechanical and electrical systems account for about 30% of construction costs and 28%-35% of the operating budget... deal with it!
- Air temperature should be kept at 2 to 5 degrees above water temperature
- Maintain relative humidity 40-60%
- Maintain negative pressure in pool

## Ventilation Controls

- Keep outdoor air ventilation rate at .48 cfm per square foot minimum
- Maintain 6-8 air exchanges per hour
- **This is Wisconsin!** – install air heat exchanger units instead of reducing the turnover
- Utilize low level return vents
- Note: Many engineering firms are being proactive in new enclosures

## Legal Guidance

- **DHS 172.33 Facility maintenance, repair and sanitation.** (4) WATER HEATERS, VENTILATION, ELECTRICAL (b) Heating, ventilation, and exhaust equipment shall be maintained and operated to provide air movement as required by chs. Comm 61 to 65 to prevent any excessive condensation and air quality problems in indoor enclosures.

## Thoughts on the future?

- What is our role in indoor air quality problems?
- Chlorine has served us well for almost a century and may have saved more lives than any other public health advancement...
- But it is a double-edged sword...
- Will we eventually move past it?

## Questions???



Remember, **DHS 172.29(1)(b) 5** states  
"Do not bring animals into the pool area."