



CHLORAMINE



Science & Myth Busting

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CHLORAMINE

Chloramine was been in used in North America for nearly 100 years (Denver 1917)

The use has increased in the last decade because of concerns with THM formation from chlorination
Regionalization also resulted in a need for chloramine to maintain longer residual within the distribution system



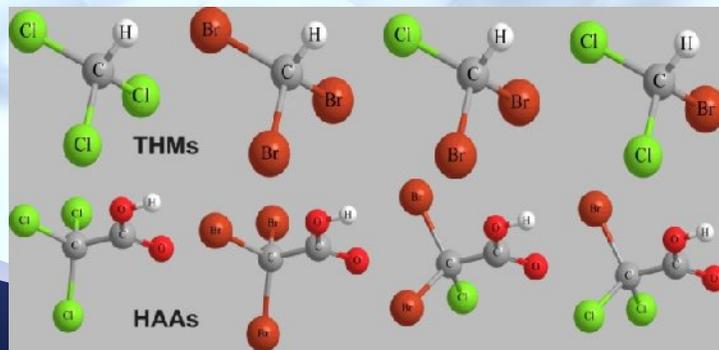
WATER DISINFECTION

Chlorine: Vancouver, Calgary, Montreal, Regina, Winnipeg, Saskatoon

Ultraviolet: Edmonton, Vancouver, Winnipeg

Chloramine: Edmonton, Ottawa, Toronto, Waterloo. BC: Abbotsford, Mission, Victoria

Ozone: Montreal, Winnipeg, Vancouver



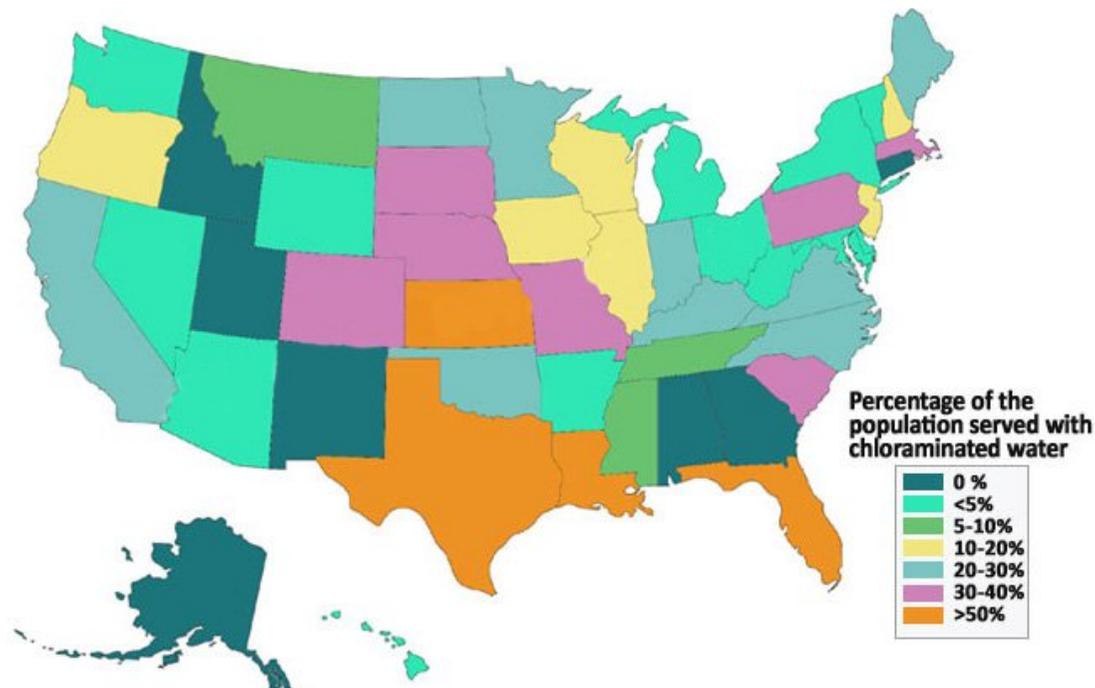


Table 3. Comparison data between 2007 and 2010

	Total water systems			Total states		Population served	
	2007	2010	Change (%)	2007	2010	2007	2010
Nation	944	1,298	+37	36	43	54,083,661	68,397,713
Texas	282	435	+54			11,141,645	12,504,394
Florida	138	197	+43			8,914,118	10,351,719
California	45	54	+20			6,676,183	10,771,907

CHLORAMINE

Advantages:

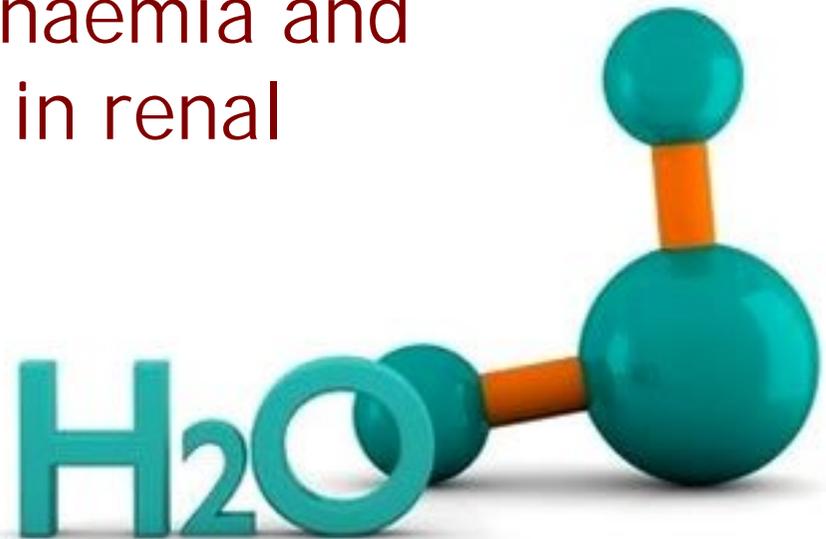
- Longer residual time
- Less regulated DBP (THM and HAA) formation
- More effective against Legionella in water
- More effective against biofilm



CHLORAMINE

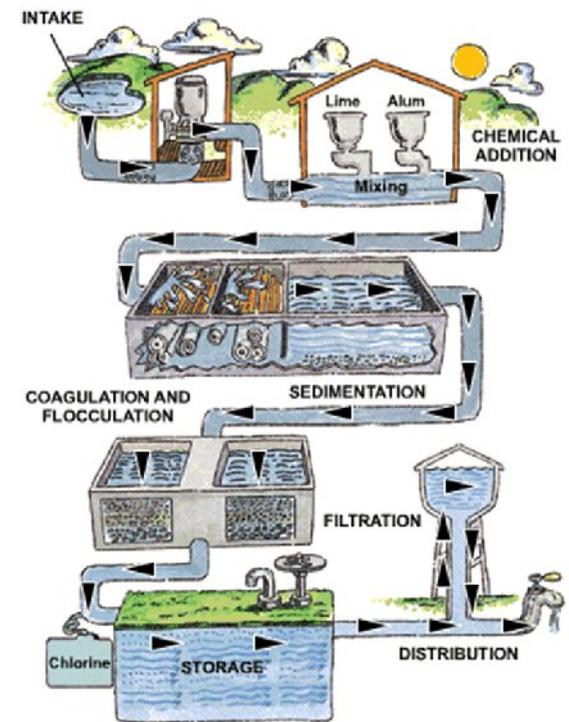
Disadvantages:

- Less effective disinfectant
- NDMA as DBP
- Increase lead leaching from pipes
- Nitrification in distribution system
- Result in haemolytic anaemia and methaemoglobinaemia in renal dialysis patients



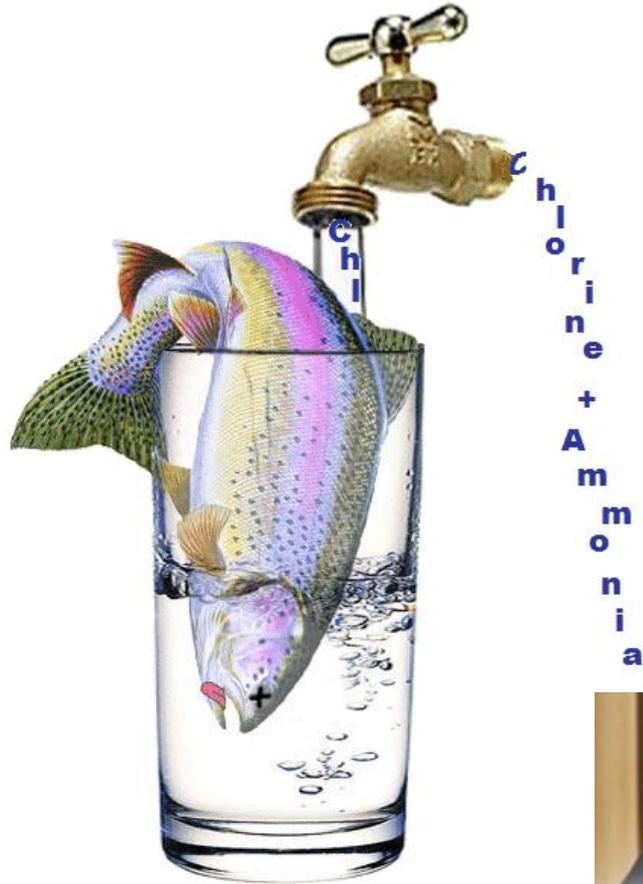
CHLORAMINE AS DRINKING WATER DISINFECTANT

A presentation addressing technical issues based on the recent public protests across North America against the use of chloramine in drinking water



CHLORAMINE

Fish Can't Live With It,



Chloramine and the Environment
"Bad for Fish, Good for People?"



WHY SHOULD WE!

www.chloramineinfocenter.net



photo's by lisa provence



What are
Chloramines?

Real **NH₂CL** Truth



Citizens Concerned About Chloramine (CCAC)

Chloramine Information Center

your one stop for all your chloramine questions

Citizens Concerned About Chloramine (CCAC)

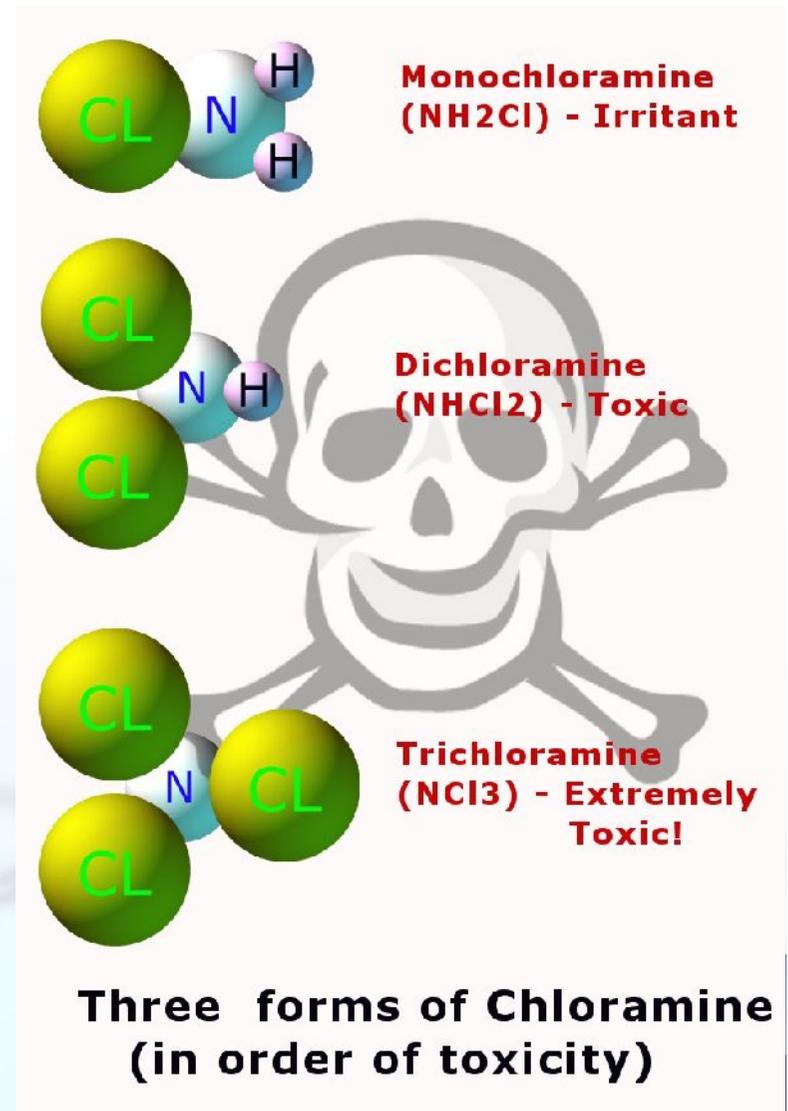
...chloramine exists as three different forms or species: monochloramine (NH_2Cl), dichloramine (NHCl_2) and trichloramine (NCl_3). They are chemically related and are easily converted into each other; thus, they are more appropriately called chloramines. The three species of chloramine constantly and rapidly shift from one form to another...



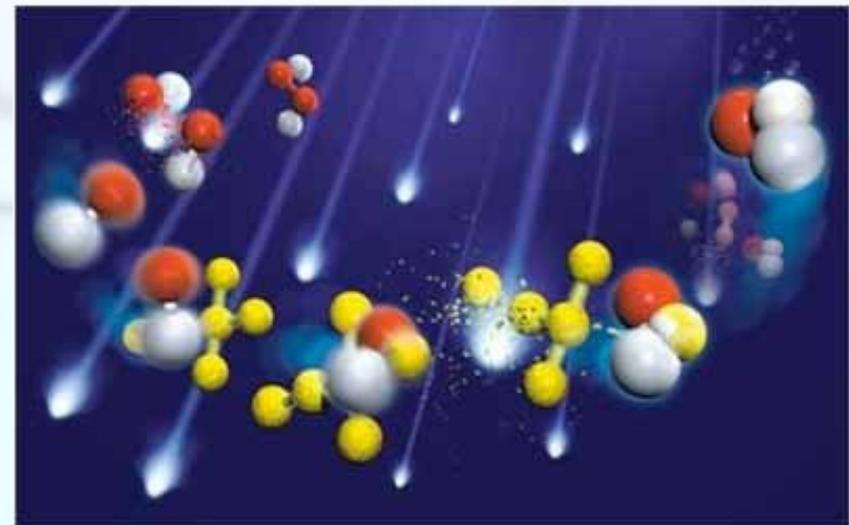
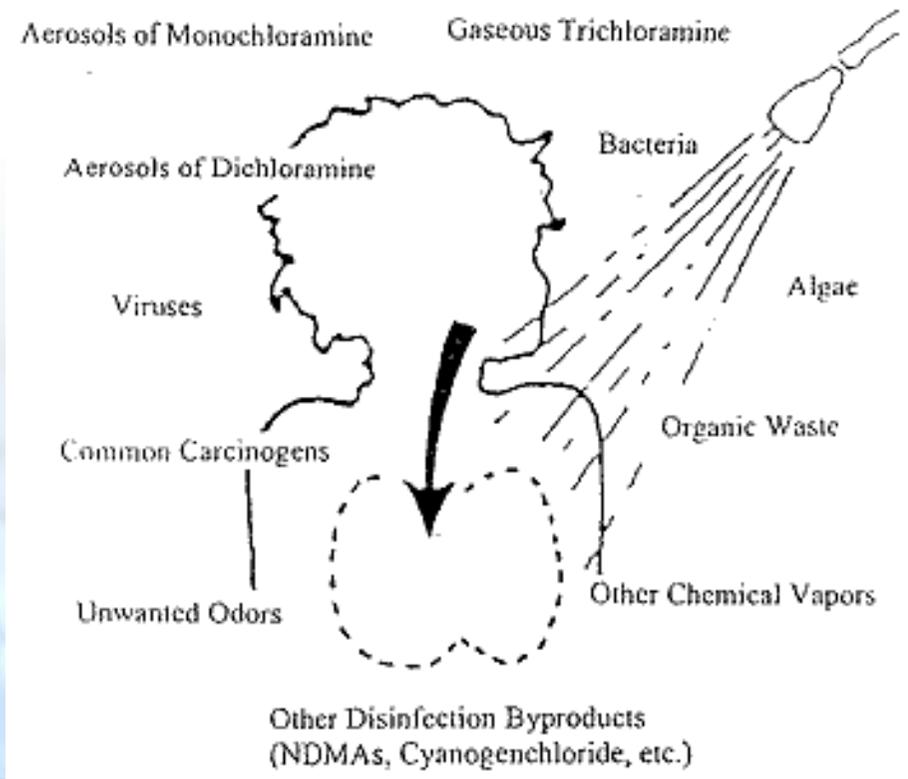
Citizens Concerned About Chloramine (CCAC)

...Even time plays a factor because after a day or so, with no changes in conditions, monochloramine in a water system will slowly degrade to form dichloramine and some trichloramine. In contrast to what water utilities claim, it is impossible to have only monochloramine. It is not unusual in water systems for harmful di and trichloramines to occur...

Water utilities use a form of chloramine that is composed of one part chlorine, to one part ammonia. That form is referred to as monochloramine. The problem is, it changes form readily into other, more harmful forms



Toxic Showers and Baths
"You Get More Toxic Exposure From Taking A Shower Than From Drinking The Same Water."

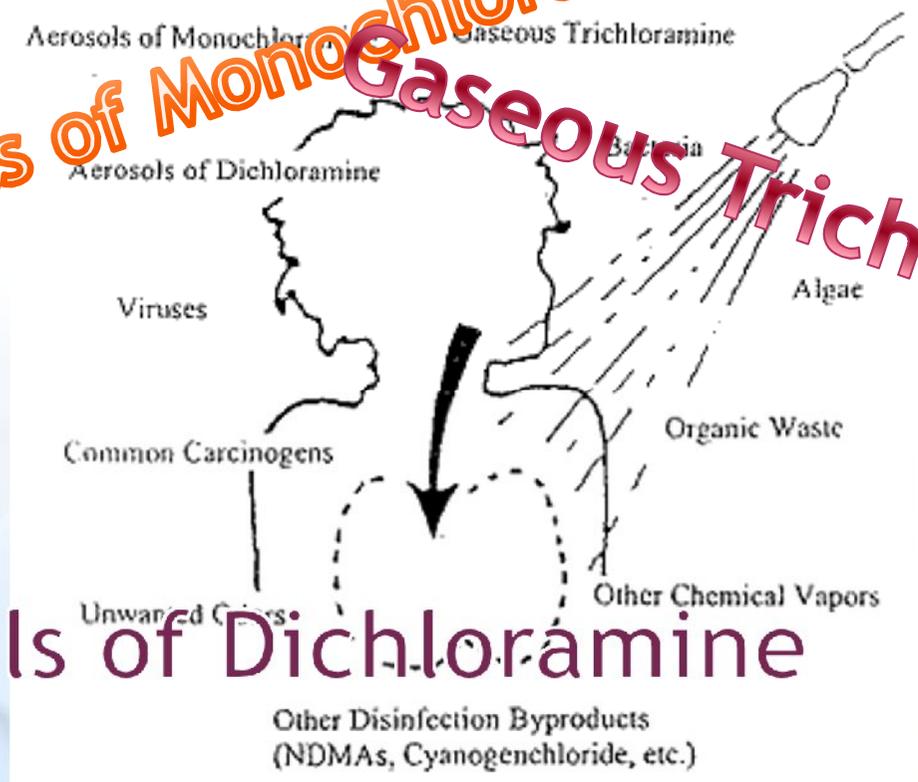


Citizens Concerned About Chloramine (CCAC)

...Individuals who are exposed to chloraminated water while showering have reported experiencing dizziness and fatigue during and after their shower.

...chloramine that is inhaled into the lungs can enter the bloodstream where it combines with hemoglobin to take the place of oxygen. This leads to some deoxygenation of the blood. When the blood cannot carry enough oxygen to the tissues, people can experience dizziness and fatigue...

Aerosols of Monochloramine
Gaseous Trichloramine



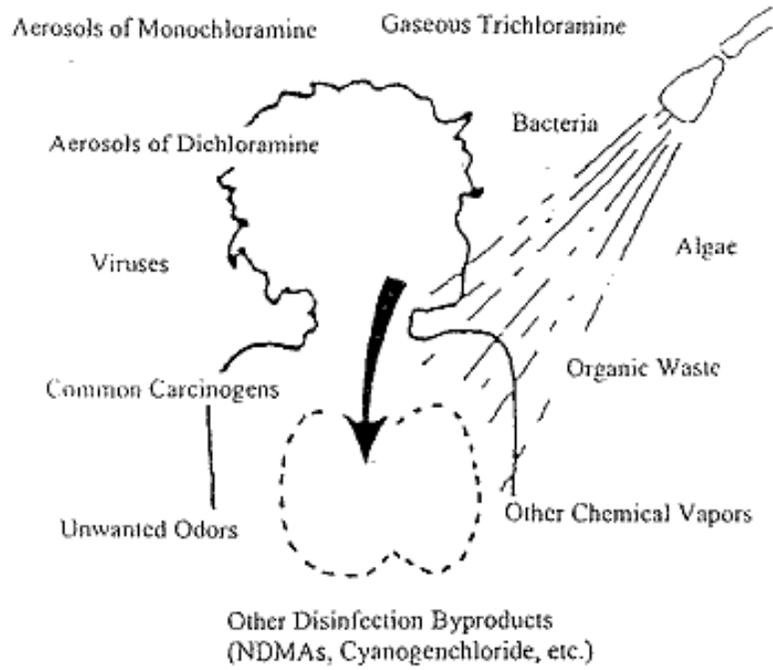
Aerosols of Dichloramine

NDMA

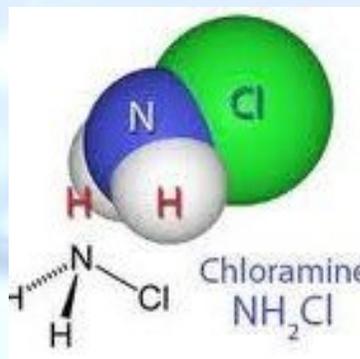
CHEMICAL VAPOURS

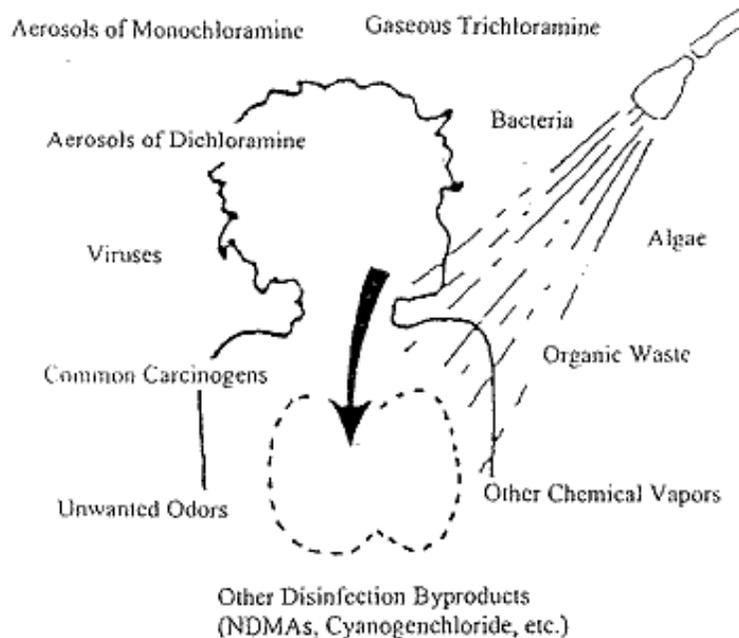
Viruses
Bacteria
Algae

In a new study, researcher Julian Andelman, of the University of Pittsburgh Graduate School of Public Health...



...that volatile chemicals present in...drinking water supplies are especially toxic to people when they are exposed to them when bathing or showering... all three forms (chloramine) are respiratory irritants, with trichloramine being the most toxic...hot showers can liberate between 50 to 80% of the dissolved chemicals into the air





The lung damage in those exposed to chloramine in indoor pool air is similar to that seen in regular smokers (see [Health24 News](#) article).

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FAQs on low libido
Our sexologist advises four users on how to put the spark back into their sex lives.

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Enviro Archive
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Don't mix cleaning products

Last updated: Tuesday, July 03, 2012

Email article | Print article
GET HEALTH24 ON: Your mobile

Never mix commercial cleaning products; some have dangerous reactions.

4 people recommend this. Sign Up to see what your friends recommend.

One notorious example of this is when ammonia-containing products are mixed with chlorine bleach: the resultant reaction forms toxic chloramine gases that are respiratory system irritants. Symptoms of exposure include eye, nose and throat irritation, coughing, wheezing, chest pain and nausea.

Ammonia is present in many households; common sources are cleaners and fertilisers.

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In a study by Zierler, et al, it was found that there was an increase in deaths from influenza and pneumonia in the communities that used chloramine. (Communities in Massachusetts that used chlorine for disinfection were compared to those that used chloramine).

... Chloramine is a less effective disinfectant and therefore people are exposed to more pathogens...

Environmental Health Perspectives, 1986

Type of Disinfectant in Drinking Water and Patterns of Mortality in Massachusetts

by Sally Zierler,*† Robert A. Danley,* and Lisa Feingold*

Chlorination has been the major strategy for disinfection of drinking water in the United States. Concern about the potential health effects of the reaction by-products of chlorine has prompted use of alternative strategies. One such method is chloramination, a treatment process that does not appear to have carcinogenic by-products, but may have less potent biocidal activity than chlorination.

We examined the patterns of mortality of residents in Massachusetts who died between 1969 and 1983



...Chloramine cannot kill the pathogens in the water as well as chlorine...As a result, people with suppressed immune systems must have their water boiled over TEN minutes BEFORE use to kill pathogens, or they risk becoming ill...

Type of Disinfectant in Drinking Water and Patterns of Mortality in Massachusetts

by Sally Zierler,^{*†} Robert A. Danley,^{*} and Lisa Feingold^{*}

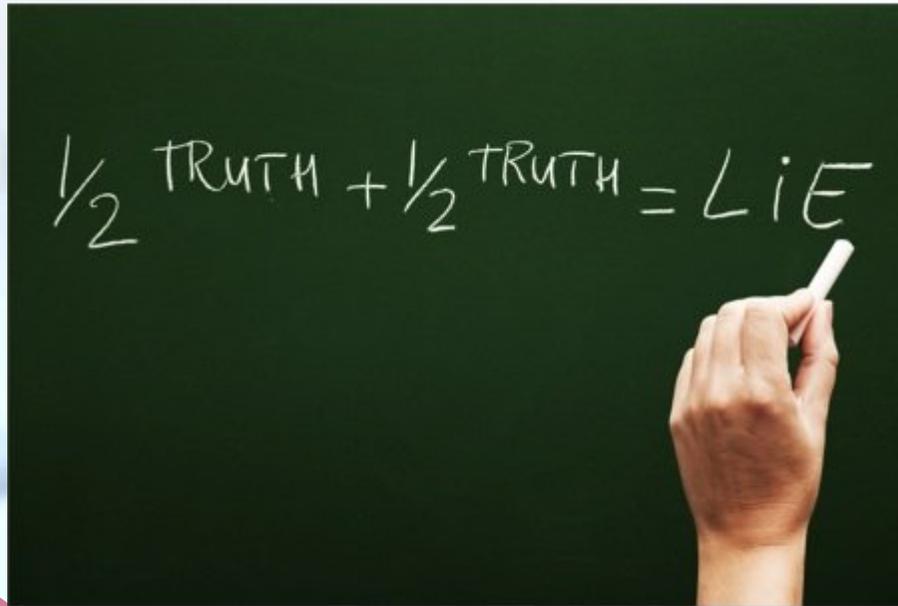
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We examined the patterns of mortality of residents in Massachusetts who died between 1969 and 1983





真実 - **Verité** - **Totuus** - 진실
Verdade - 真相 - **Waarheid**
Правда - **Wahrheit** - **Truth**



A
half
truth
is
a
whole
lie

CuriositiesByDickens.com

SCIENCE & MYTH BUSTING

USEPA Chloramine Q&A, 2009: 29 pages to answer 29 questions on chloramine

General comments in Q&S

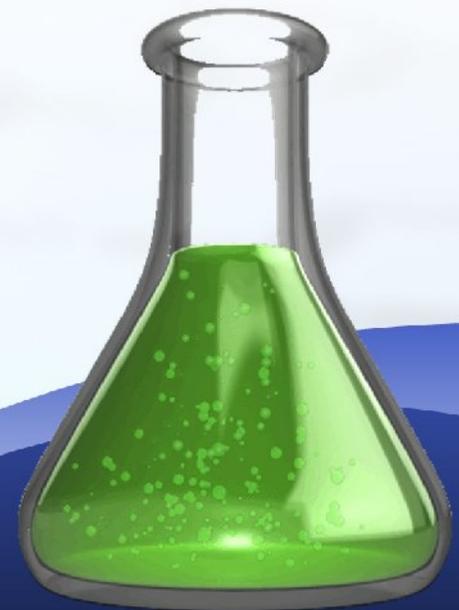
“...trichloramine...rare under normal drinking water treatment conditions...”



SCIENCE & MYTH BUSTING

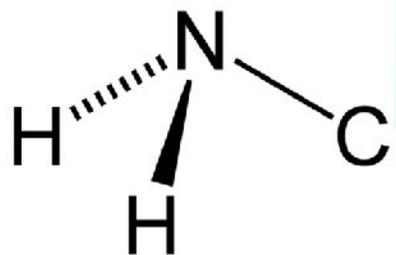
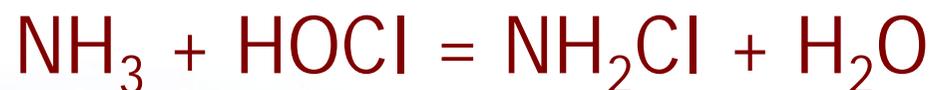
Technical information not for direct public communication

Present information on water chemistry to provide more in-depth explanation of the issues

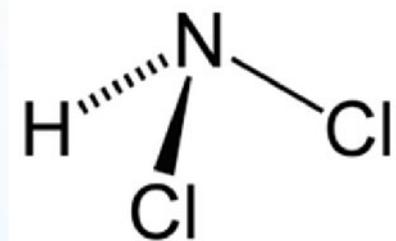


CHLORAMINE

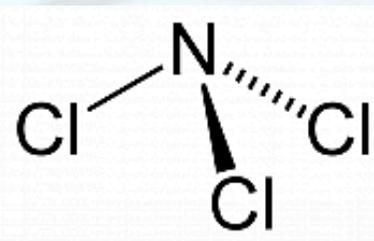
Mono-chloramine

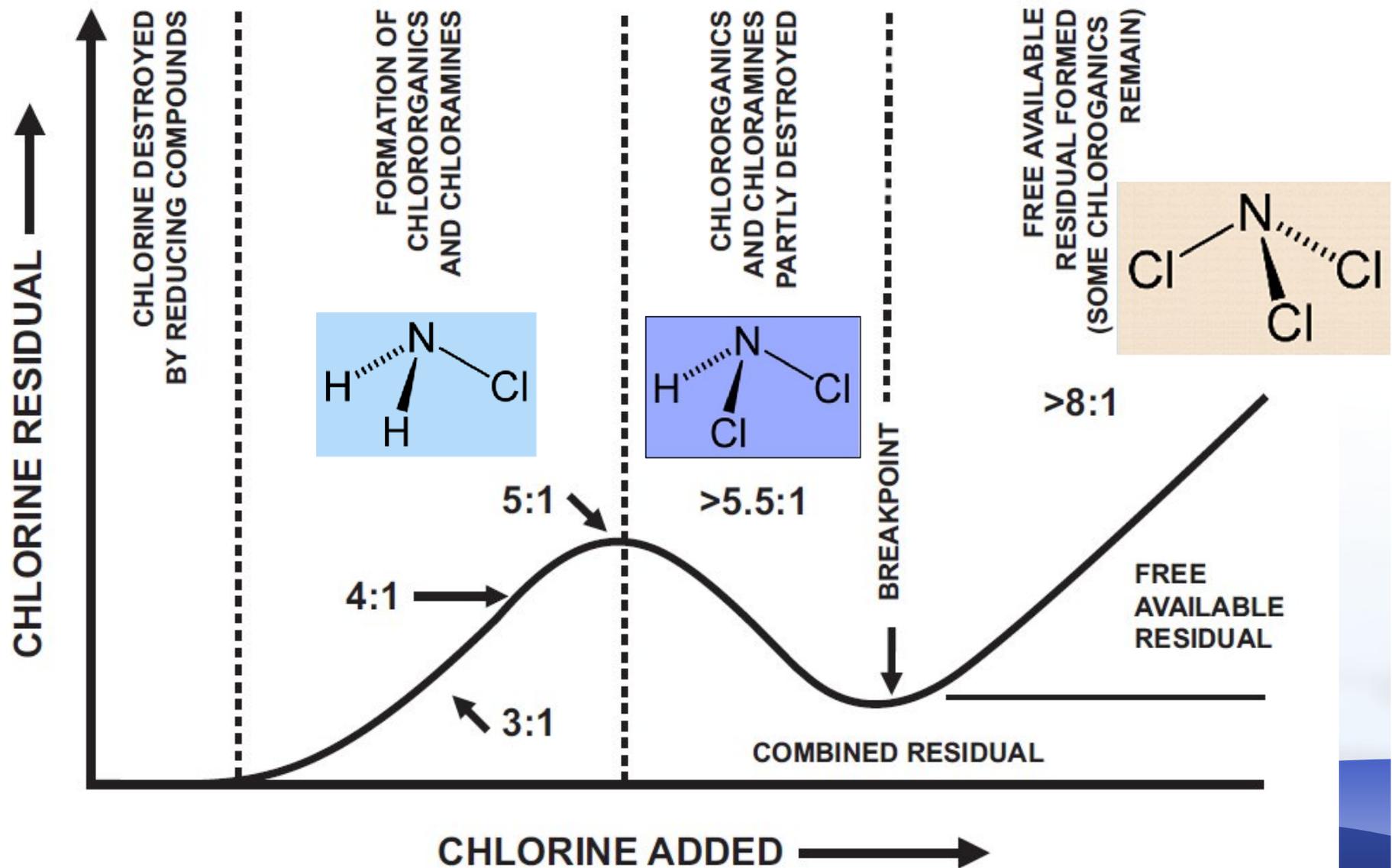


Di-chloramine



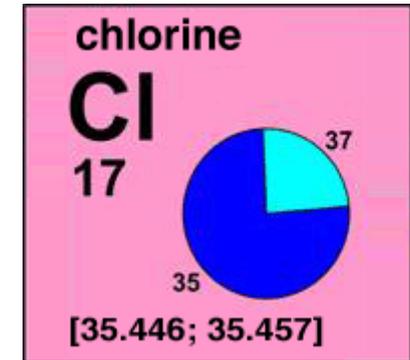
Tri-chloramine





Breakpoint Chlorination Curve in Swimming Pool at Various Chlorine-to-Ammonia Ratios at pH 7

CHLORAMINE CHEMISTRY



- Chlorine molecule weight of 35
- Chlorine exists as Cl_2 , Mol Wt of 70
- Nitrogen (ammonia-nitrogen) Mol wt of 14
- $\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{H}^+ + \text{Cl}^-$
- $\text{HOCl} + \text{NH}_3 \rightarrow \text{NH}_2\text{Cl} + \text{H}_2\text{O}$
- Hence $\text{Cl}_2 + \text{NH}_3$ gives monochloramine at weight ratio of 5:1 (70/14), when one Cl molecule reacts with one NH_3 molecules
- Not enough Cl to have more than one chlorine substitution in NH_3 so no di-chloramine formation

CHLORAMINE CHEMISTRY

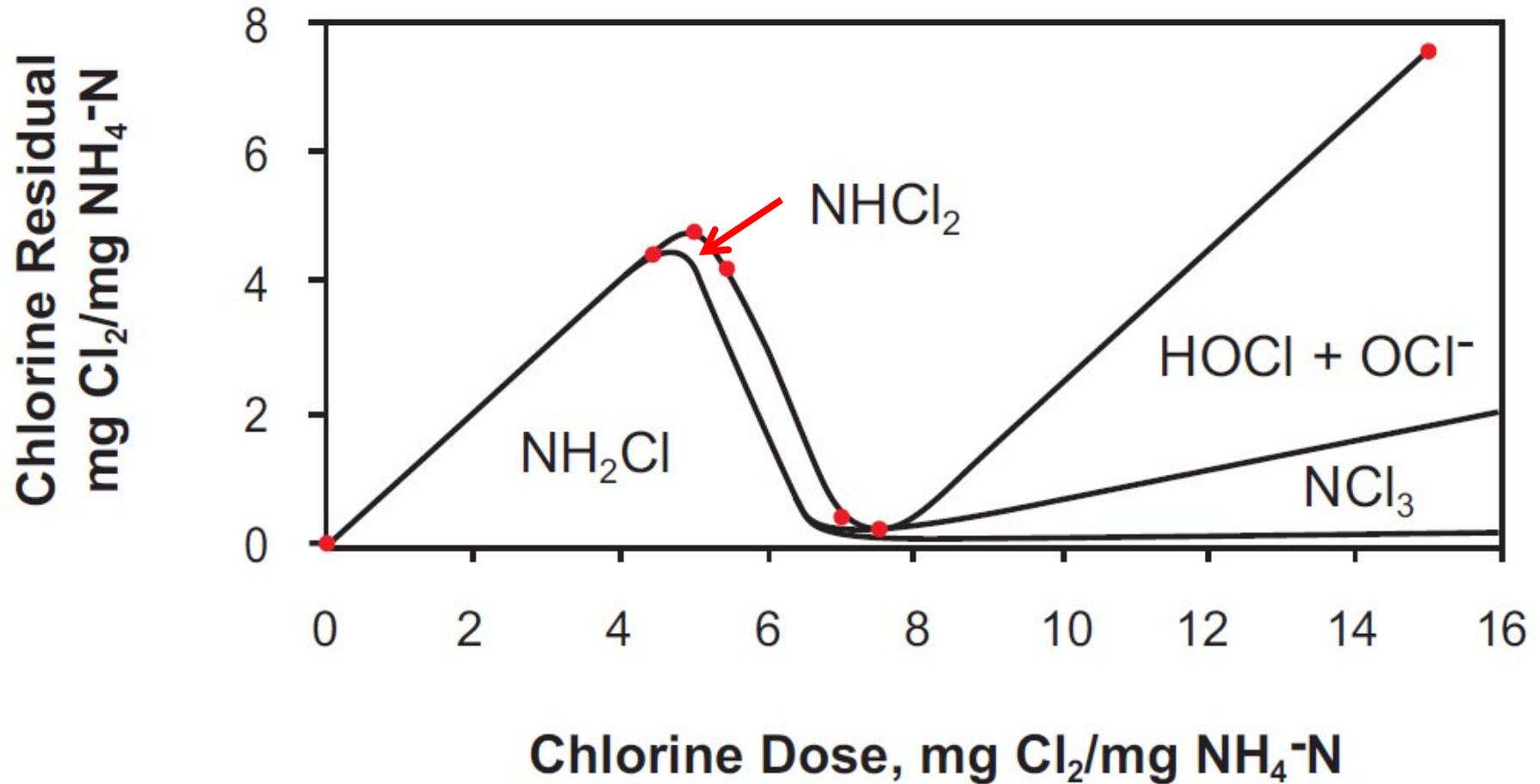
Natural decomposition or hydrolysis:

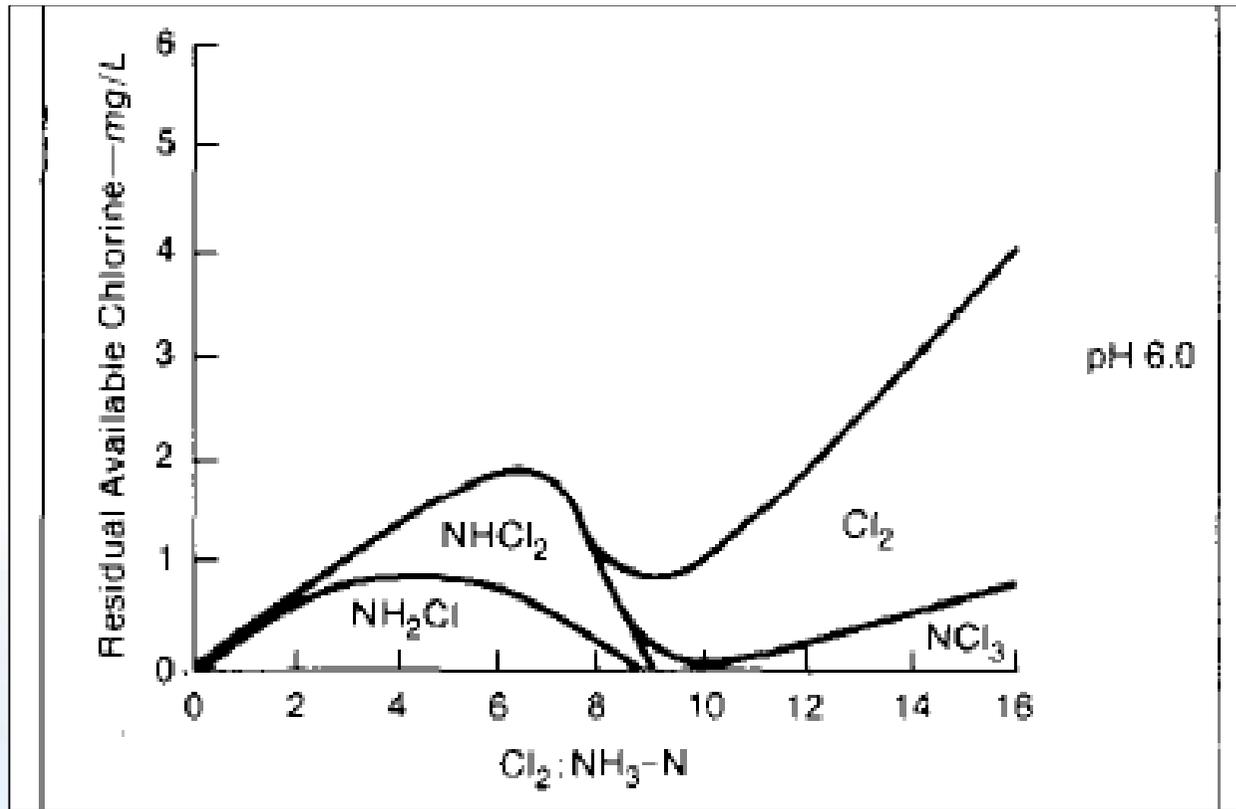


The rate constant of the first reaction is 7.6×10^{-2} per hour, and 50% of monochloramine is hydrolyzed by this reaction in approximately 10 hours at 20°C. The ammonia formed will contribute to nitrification.

Dichloramine is very unstable and once formed will be hydrolyzed by water at a very fast rate (4.0×10^5 per M per hour) to give H_2O , Cl^- , H^+ and NO_3^- .

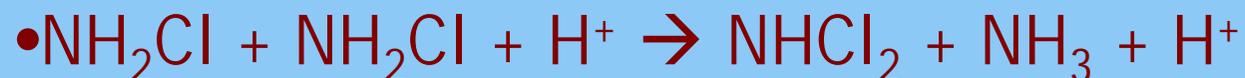
Production of Various Species of Chloramine by Increasing Chlorine Doses

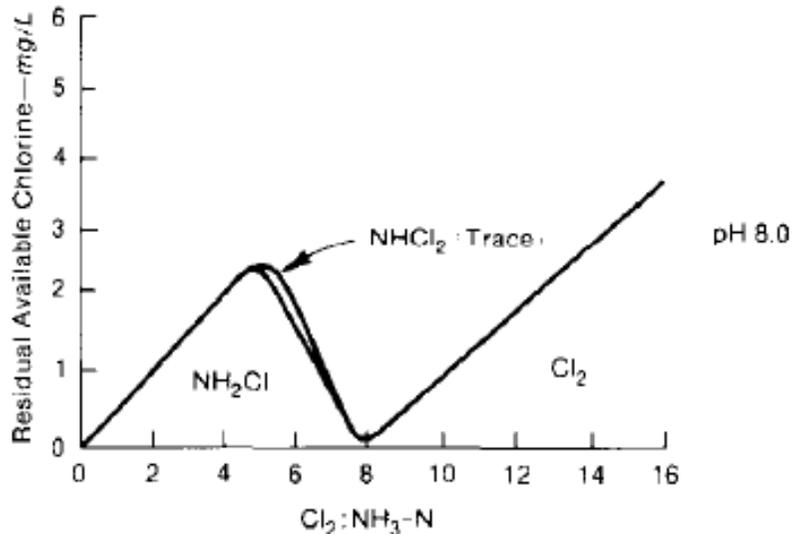
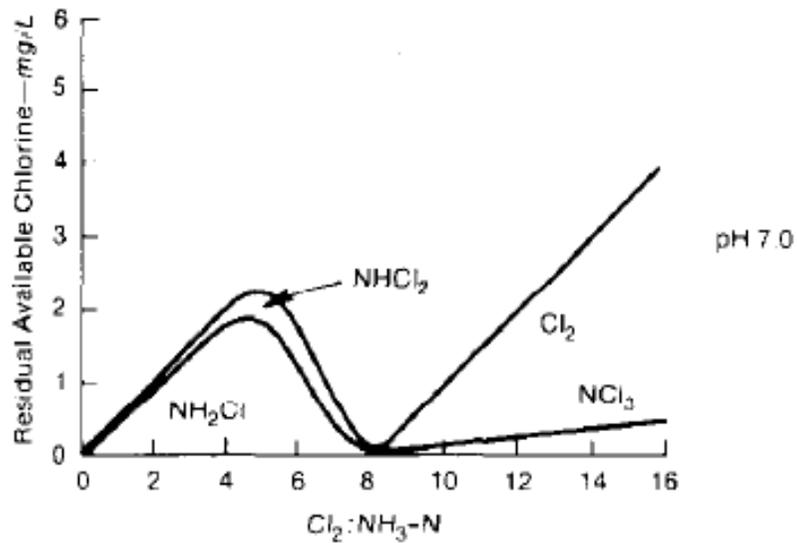




Breakpoint curve

- pH 6 acidic environment starting at 6.6 (acid catalyzed disproportionation) results in NHCl₂ formation at Cl₂-NH₃ ratio of >2 and significant NCl₃ after breakpoint.



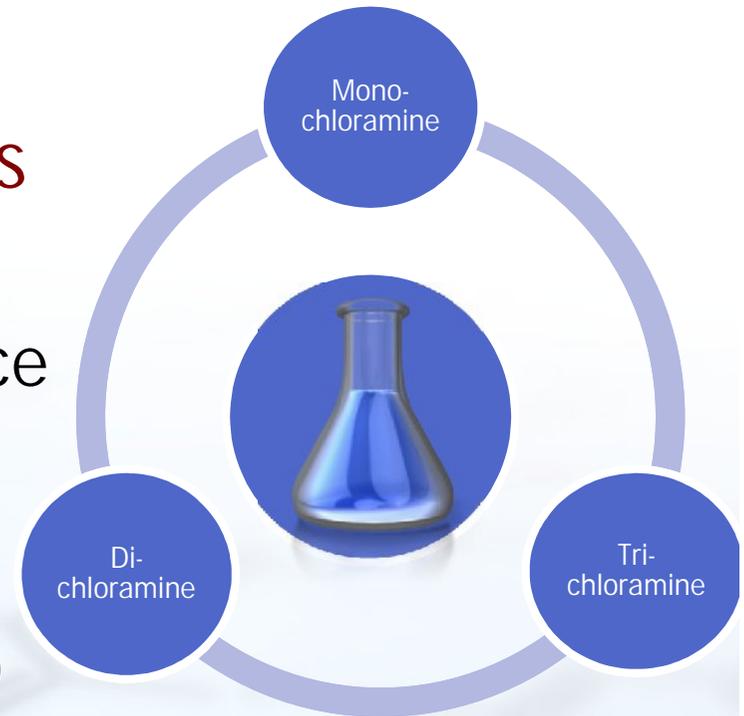


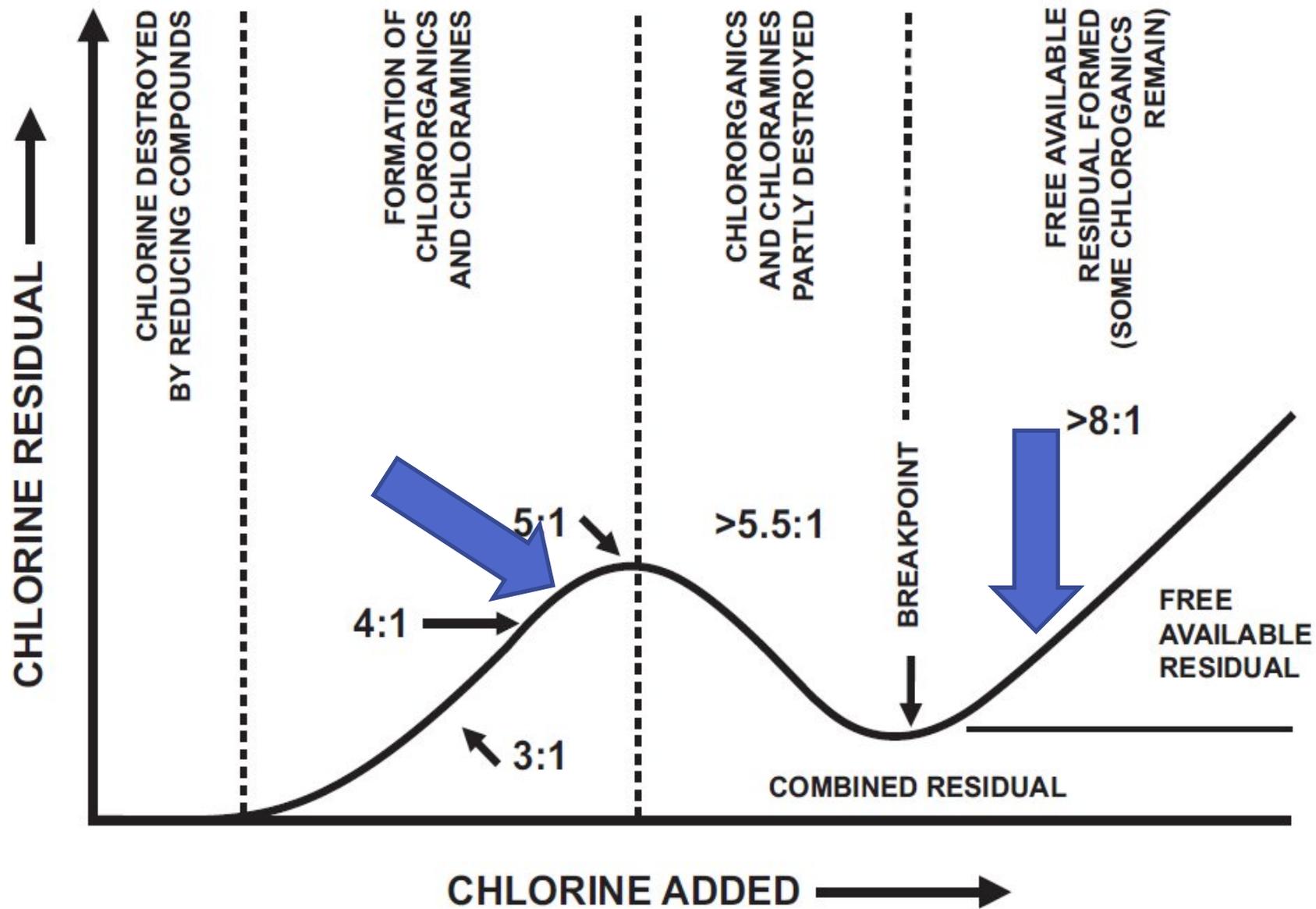
Breakpoint curve

- pH 7: some $NHCl_2$ formed at ratio of 4-5. NCl_3 continue to exist in combination with free chlorine after breakpoint and ratio >8
- pH 8: minimal $NHCl_2$ and no NCl_3 after breakpoint

Kreft P et al, Converting From Chlorine to Chloramines: A Case Study, J AWWA, 1985

- When the chlorine-to-ammonia weight ratios is $> 5:1$, dichloramine is formed
- At $\text{pH} > 7.5$, no trichloramine is formed, regardless of the ratio of chlorine to ammonia (US Office of Water 1994)
- Trichloramine can be formed between $\text{pH} 7$ and 8 if the ratio is $> 15:1$ (AwwaRF 2004)





Chlorination Curve in Water Treatment Plant at Various Chlorine-to-Ammonia Ratios at pH 8

The lung damage in those exposed to chloramine in indoor pool air is similar to that seen in regular smokers (see Health24 News article)

ORIGINAL ARTICLE

Lung hyperpermeability and asthma prevalence in schoolchildren: unexpected associations with the attendance at indoor chlorinated swimming pools

A Bernard, S Carbonnelle, O Michel, S Higuët, C de Burbure, J-P Buchet, C Hermans, X Dumont, I Doyle

Occup Environ Med 2003;60:385-394

Aims: To study whether exposure to nitrogen trichloride in indoor chlorinated pools may affect the respiratory epithelium of children and increase the risk of some lung diseases such as asthma.

Methods: In 226 healthy children, serum surfactant associated proteins A and B (SP-A and SP-B), 16 kDa Clara cell protein (CC16), and IgE were measured. Lung specific proteins were measured in the serum of 16 children and 13 adults before and after exposure to NCl_3 in an indoor chlorinated pool. Relations between pool attendance and asthma prevalence were studied in 1881 children. Asthma was screened with the exercise induced bronchoconstriction test (EIB).

...The level of lung permeability would be the equivalent of what she would expect to see in a heavy smoker, according to Dr. Carbonnelle. "...These findings suggest that the increasing exposure to chlorine-based disinfectants used in swimming pools and their by-products might be an unsuspected risk factor in the rising incidence of childhood asthma and allergic diseases..."



Original Research

Health effects associated with indoor swimming pools: A suspected toxic chloramine exposure

S. Cornelia Kaydos-Daniels^{a, b}, , , Michael J. Beach^c, Thein Shwe^a, Julie Magri^d, Danae Bixler^a

^a West Virginia Bureau for Public Health, Charleston, WV, USA

^b Centers for Disease Control and Prevention, Epidemic Intelligence Service, Atlanta, GA, USA



Warning
Chlorine

"Chlorine has been documented to aggravate asthma, especially in those children who make use of chlorinated swimming pools. Several studies also link chlorine and chlorinated by-products to a greater incidence of bladder, breast and bowel cancer as well as malignant melanoma. One study even links the use of chlorinated tap water to congenital cardiac anomalies."

Messina V., Chlorine and cancer. Good Medicine

ORIGINAL ARTICLE

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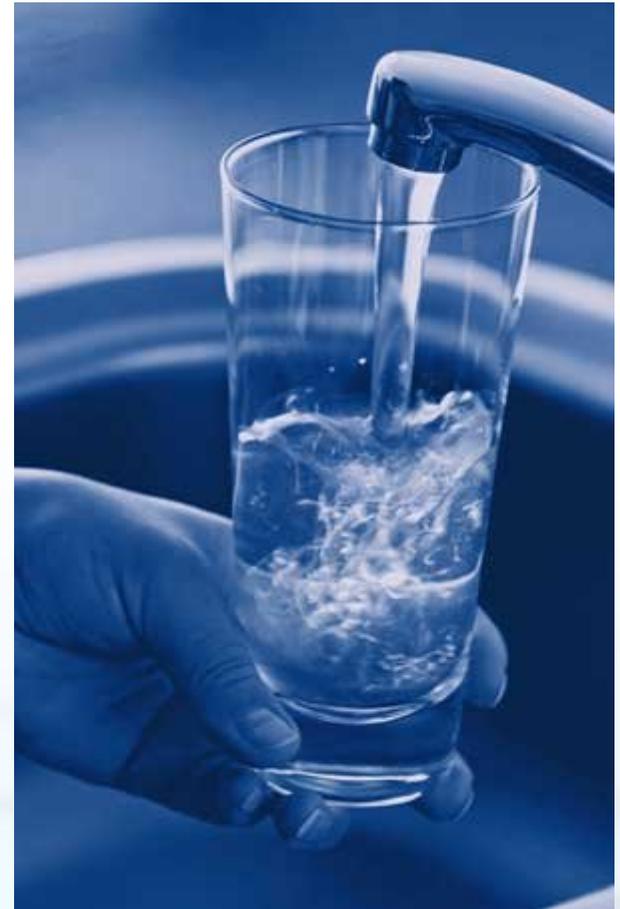
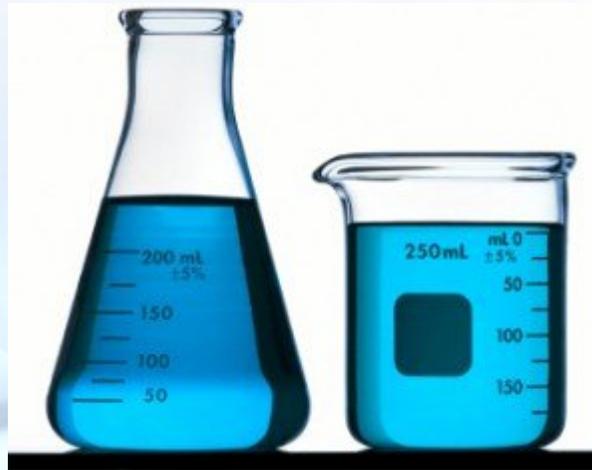
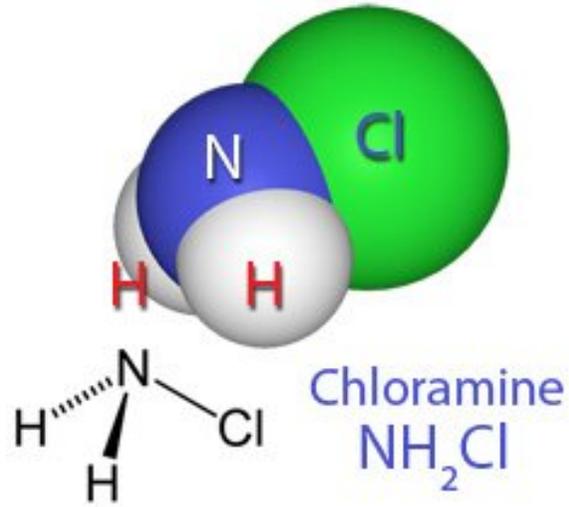
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Occup Environ Med

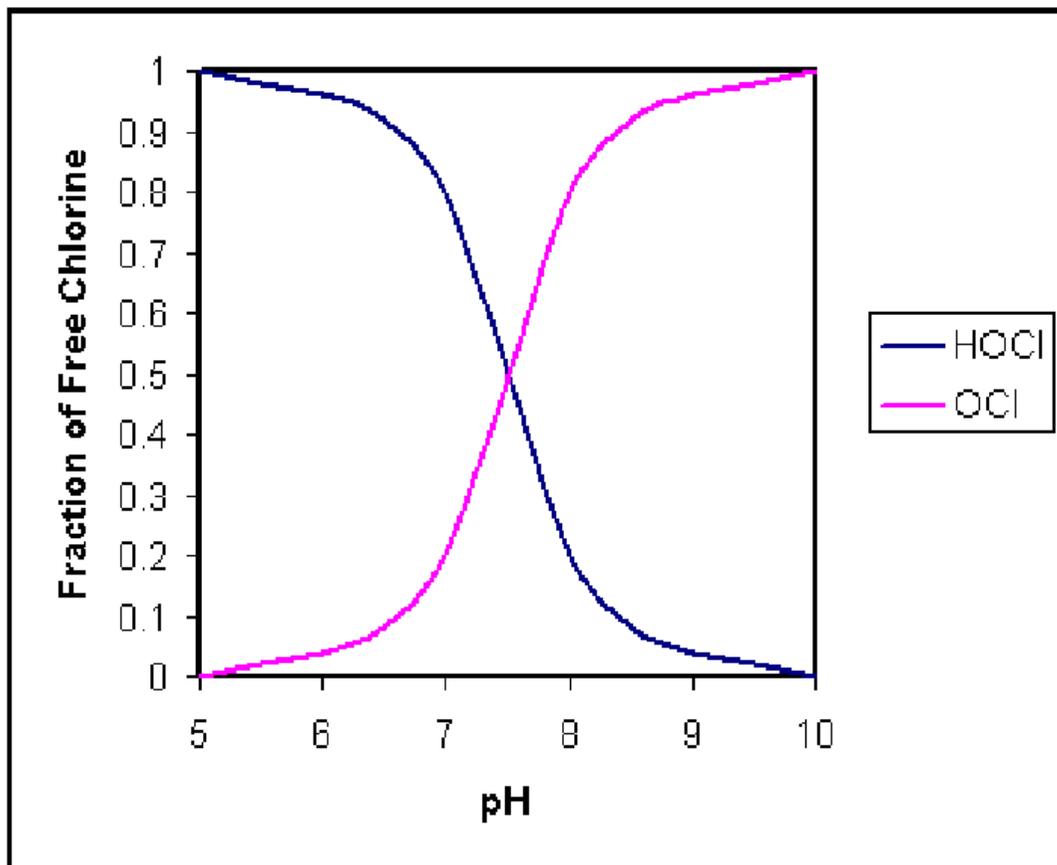
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Childhood asthma and environmental exposures at swimming pools: state of the science and research recommendations

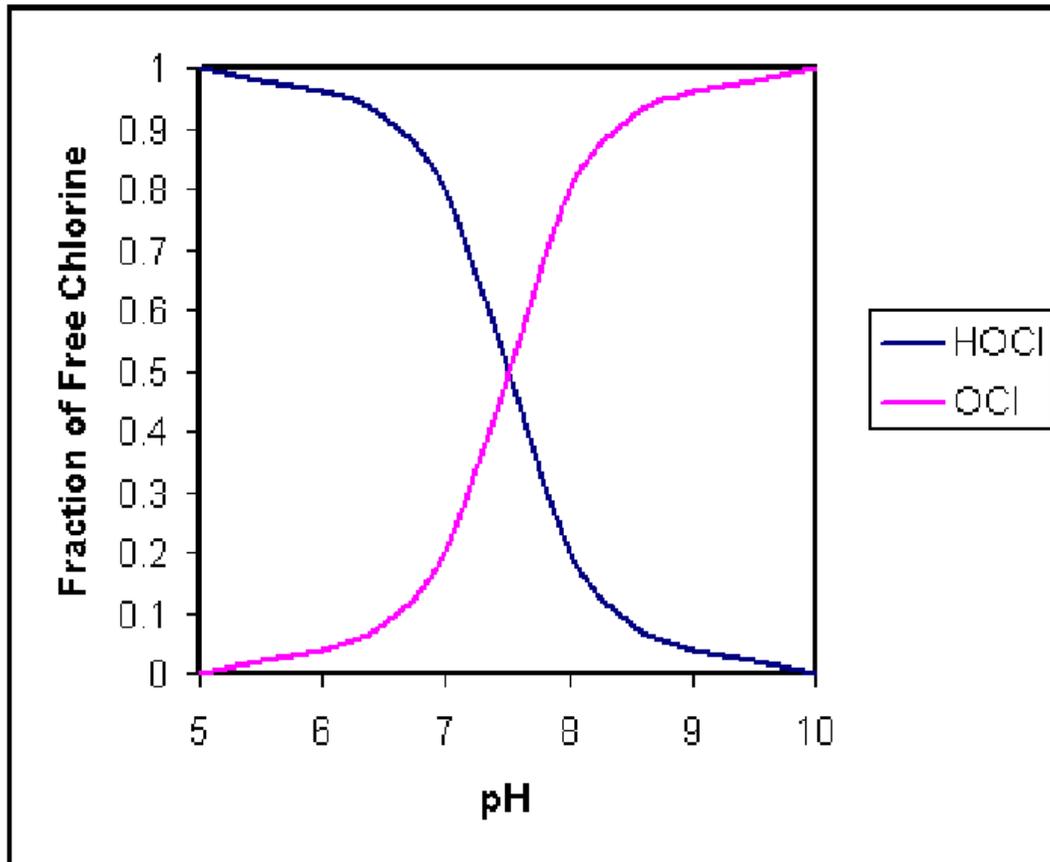


$10 (\text{CH}_2)_8$



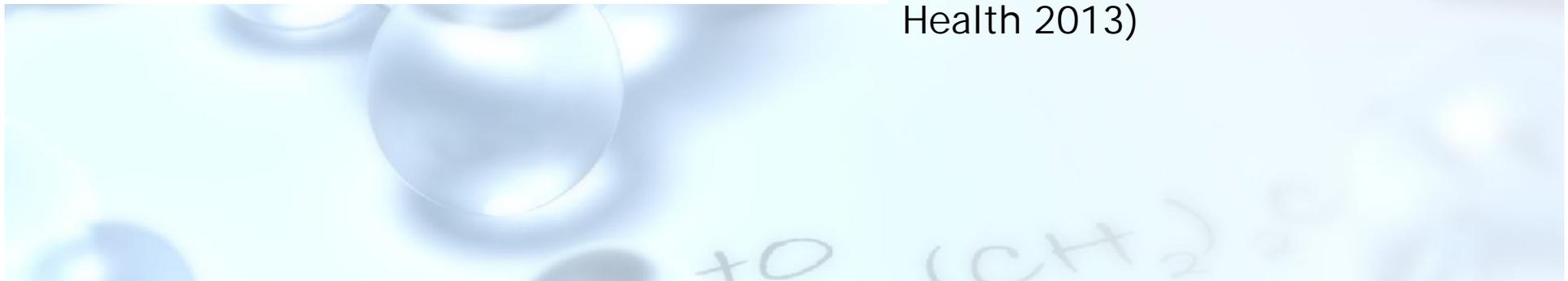
HOCl is a more effective disinfectant therefore pool pH is kept below 7.5. Chlorine in swimming pool is generally considered as 'ineffective' at pH 8. HOCl is the main reactive chlorine species that reacts with NH_3 to give di- and tri-chloramine. Note decreases of these products with increasing pH





To minimize formation of by-products, it is recommended pool be operated with a pH not lower than 6.8 to limit the genotoxicity and trichloramine exposure and not higher than 7.2 to limit THM formation

(Kamilla MS, Journal of Water and Health 2013)



TRICHLORAMINE FORMATION

Trichloramine in pool can be formed directly from reaction of HOCl with urea that is found in urine, sweat and skin

Bather excretes 35 mL of urine (0.8 g urine per pool user) and sweat (1.5 g/pool user)

Skin: urea is a product of degradation of amino acid arginine during skin hornification to keep skin moist. Pool water remove urea from skin. Urea contain 8 $\mu\text{g}/\text{cm}^2$ and contribute 0.16 g of urea. Showering remove 75-97% of urea from skin

TRICHLORAMINE FORMATION

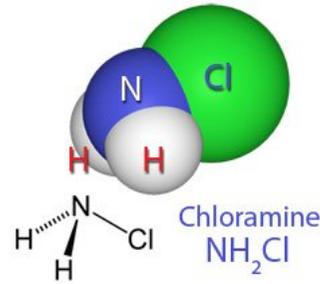
Urea reacts with HOCl directly (instead of sequential reactions with ammonia)



tetrachlorourea + hypochloric acid → trichloramine

Trichloramine is therefore released in shower with CHLORINATED WATER when HOCl washes urea off the skin. Trichloramine will volatilized into the air within the shower

POOL



DRINKING WATER

- pH 7 (6.8 to 7.6) in using chlorine
- Urea with the highest NCl_3 formation potential
- Cl_2 :N ratio of >8:1

- No NCl_3 >7.5, and formation maximum at pH 7.1
- More NCl_3 formation from urea than Ammonia
- No NCl_3 formation at lower ratio

- pH 8 in using chloramine
- Ammonia as the major precursor
- Cl_2 :N ratio of 5:1



CHLORAMINE USAGE AND SAFETY

Type of Disinfectant in Drinking Water and Patterns of Mortality in Massachusetts

by Sally Zierler,^{*†} Robert A. Danley,^{*} and Lisa Feingold^{*}

Chlorination has been the major strategy for disinfection of drinking water in the United States. Concern about the potential health effects of the reaction by-products of chlorine has prompted use of alternative

(standardized mortality ratio = 118, 95% confidence interval = 110–126 for chloraminated communities, and standardized mortality ratio = 98, 95% confidence interval = 95–100 for chlorinated communities).

These results are intended to be preliminary and crude descriptions of the relationship under study. The serious potential for misclassification of exposure status and errors in death certificate classification of cause of death affect the interpretability of the overall evidence that patterns of mortality are similar according to disinfectant in drinking water.

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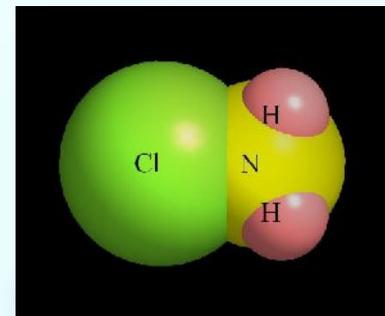
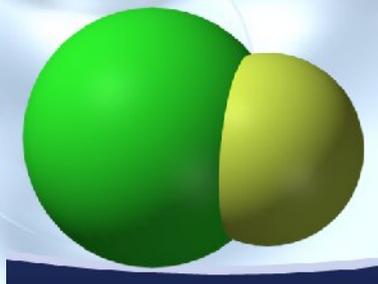
underlying cause of cancer death recorded on the death certificate may not have been the primary tumor. For example, the site of metastasis, rather than the primary site, may have been noted as the underlying cause of death. Similarly, deaths attributed to pneumonia and influenza may actually have been primarily caused by cancer or some other disease. These types of misclassification generally lead to dilution of the measure of association when the errors are unrelated to the relationship under study.

It is not surprising, therefore, that the patterns of causes of death did not vary to any appreciable extent according to type of disinfectant. There is some indication, however, that bladder cancer mortality was excessive among residents of chlorinated communities relative to residents of chloraminated communities. The

CHLORAMINE USAGE AND SAFETY

Chloramine is classified as a 'secondary' disinfectant and should never be used as the only disinfectant

Most utilities when changing over to chloramine would retain chlorine as a primary disinfectant and add ammonia to produce chloramine as a residual disinfectant in the distribution system



US DEFENSE DEPARTMENT

"...Chloramine does not react the same as chlorine to contaminants. A drop in chlorine levels signals a water facility that there is a contaminant in the water. Chloramine will not react the same way and will not provide that critical early alert. Manufacturers of terrorist detection systems have recommended that chloramine NOT be used as a disinfection in the water systems for this reason and have more strenuously recommended that they not be used in service areas where there are military bases as they are likely targets for terrorist activity..."

Citizens Concerned About Chloramine (CCAC)

...Germany has banned chloramine and France refuses to use chloramine in their countries for drinking water purposes...most European countries DO NOT use chloramine...Those who do use it only occasionally...



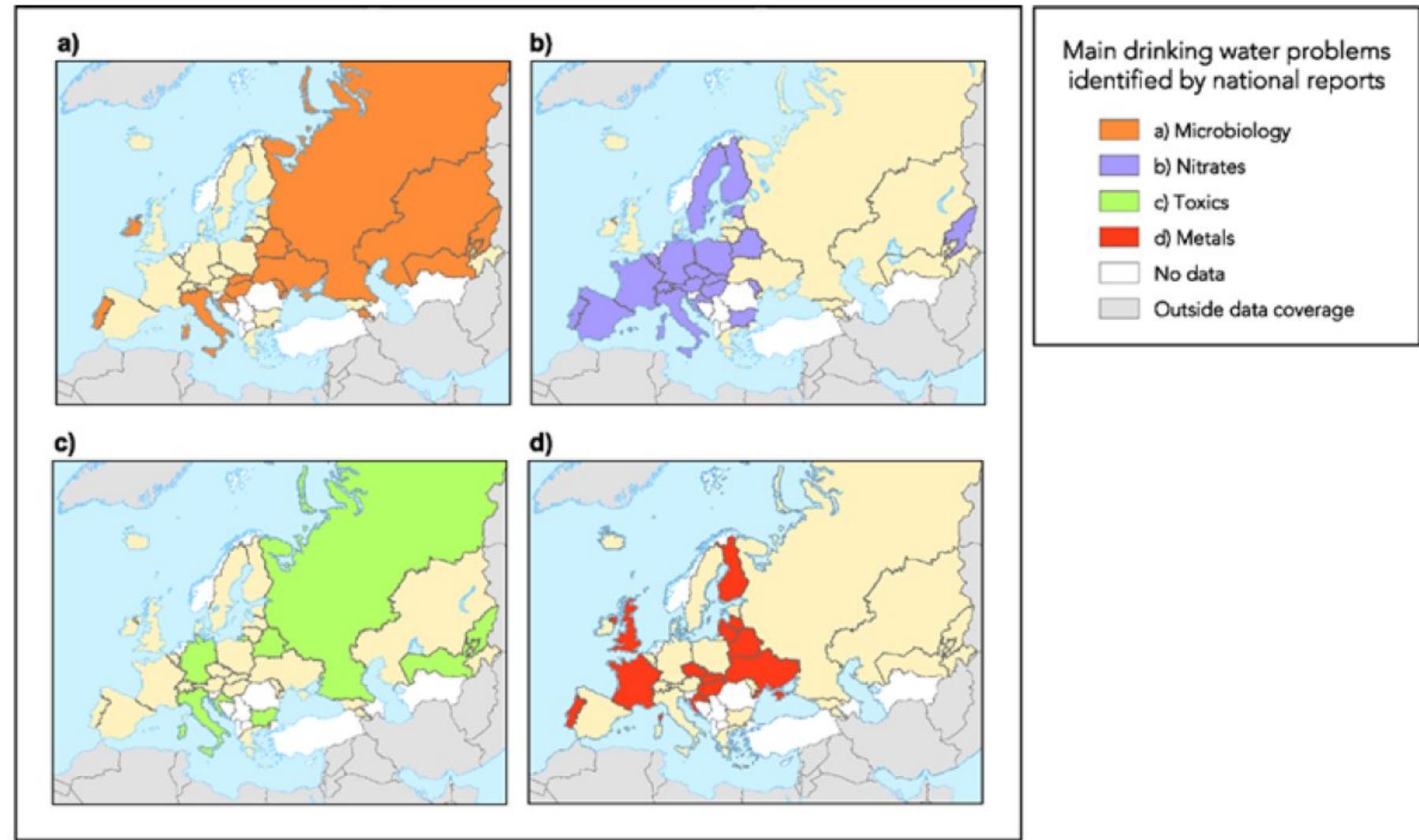
CHLORAMINE USAGE AND SAFETY

EU approach is to use as little disinfectant as possible. The maximum chlorine used during treatment is 2 mg/L and the limit for chlorine residual after treatment should be 0.3 mg/L. In North America, the **MINIMUM** is 2.0 mg/L in distribution system

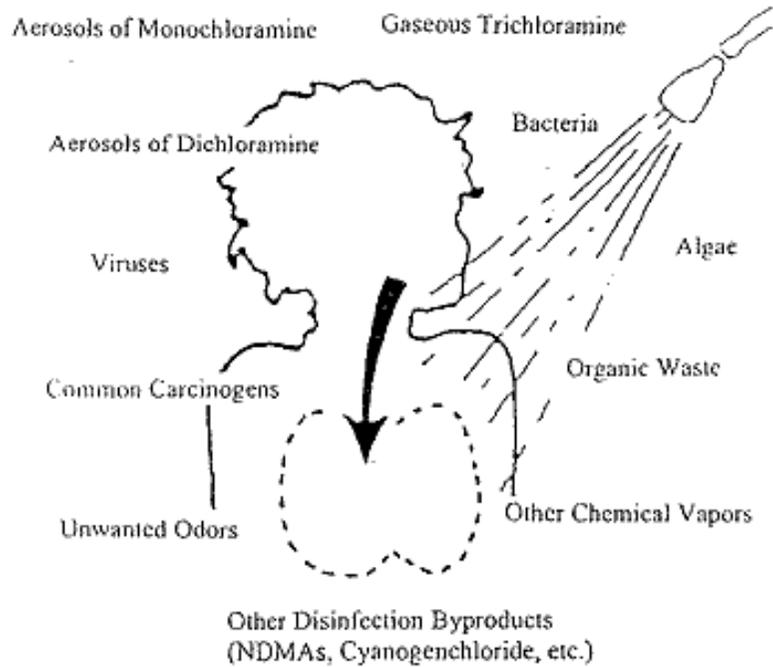
In Germany for example, 50% of all utilities do not use any disinfectant, including chlorine and there is no requirement of any continuing disinfection within the distribution system



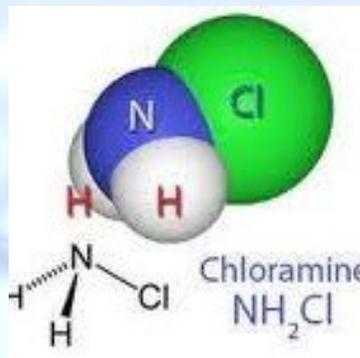
Figure 1: Main drinking water problems identified by national reports

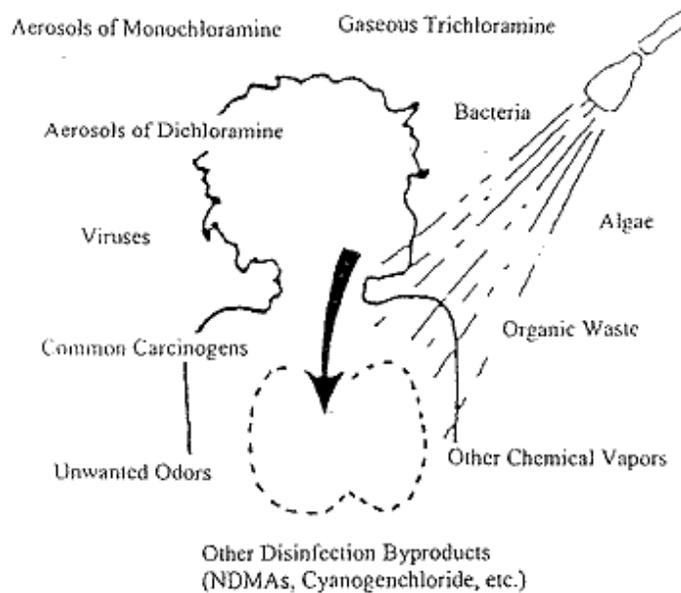


In a new study, researcher Julian Andelman, of the University of Pittsburgh Graduate School of Public Health...



...that volatile chemicals present in...drinking water supplies are especially toxic to people when they are exposed to them when bathing or showering... all three forms (chloramine) are respiratory irritants, with trichloramine being the most toxic...hot showers can liberate between 50 to 80% of the dissolved chemicals into the air...





In a new study, researcher Julian Andelman, of the University of Pittsburgh Graduate School of Public Health...

Inhalation Exposure in the home to Volatile Organic Contaminants of Drinking Water, Science of the Total Environment 1985 on VOC (chloroform and trichloroethylene) from CHLORINATED WATER

NOT American Journal of Public Health, Vol. 74, No. 5 May, 1984
(paper on skin absorption of chlorinated DBP from water)

CHLORAMINE CHEMISTRY

- SHOWER

Hydrolysis increases with temperature

Henry's Law Constant: The lower the Henry's law constant, the more soluble is the substance in pool water. The higher Henry's law constant (H), the more readily it escapes from water to air. The constant at 20°C and atmospheric pressure for mono-, di- and tri- are 0.45, 1.52 and 435, respectively.

CHLORAMINE CHEMISTRY

- SHOWER

A recent study on DBP in swimming pool. Researchers sampled water and air in swimming pool. Testing identified free chlorine, monochloramine and di-chloramine in the pool water. Mono- and di-chloramines were not found in the air, only tri-chloramine, along with other volatile DBPs.

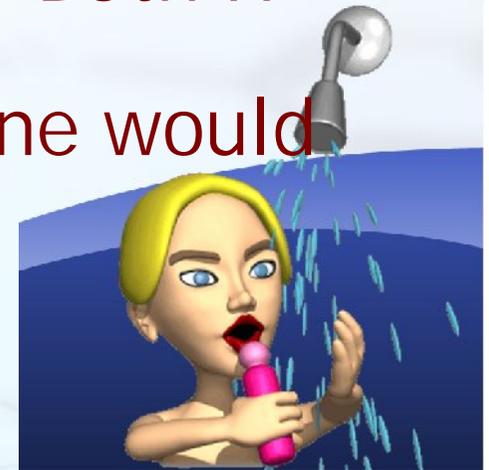


CHLORAMINE CHEMISTRY

- SHOWER

For showers:

- No trichloramine in water or in air as pH ~8
- There will be minimal di-chloramine in the water, which is unstable and once hydrolyzed at a very fast rate, the end products will react to form other salts, so di-chloramine not found at tap
- Monochloramine is not very volatile. Both H value and hydrolysis increase with temperature. Minimal monochloramine would be inhaled



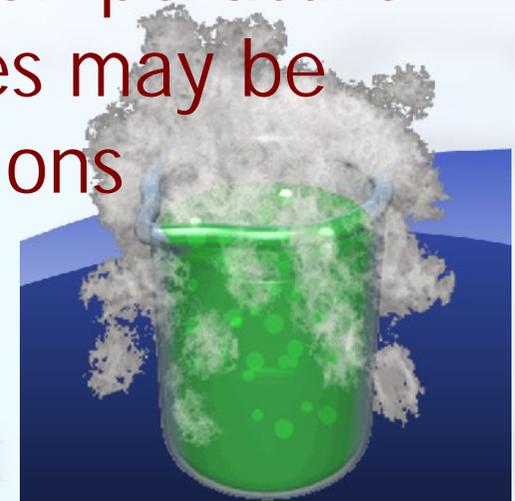
CHLORAMINE CHEMISTRY

- SHOWER

If one boils water with chloramine

Bringing the water to a boil will remove 30 to 50% of monochloramine in the water and a 20 minute boil will remove all chloramines. It should be noted that monochloramine may not all escape the water in gaseous forms.

Hydrolysis reaction increases with temperature and at least some of the chloramines may be hydrolyzed and converted to other ions



CHLORAMINE CHEMISTRY

- SHOWER

Chloramine lost in water:

0% at 20°C; 8% at 38°C; 30-50% at 100°C

With hot water temperature of <45°C in shower and initial chloramine concentration of about 1.5 mg/L, very little monochloramine would be 'volatilized' into the air.

Average water used in bathing and showering is 80L and average air volume in bathroom is 6,420L, 80 times dilution

Inhalation risk of mono-chloramine is low

DISINFECTION BY-PRODUCTS

Chlorine

Trihalomethane, Haloacetic acids,
MX

Ultraviolet

Formaldehyde

Chloramine

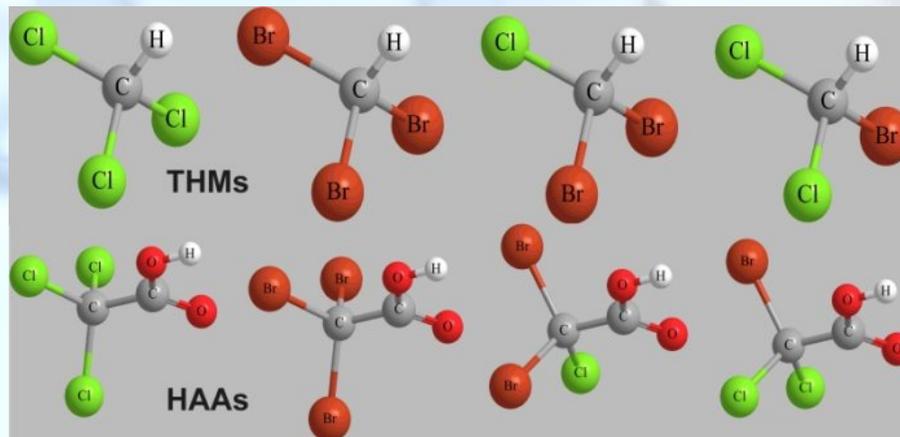
NDMA

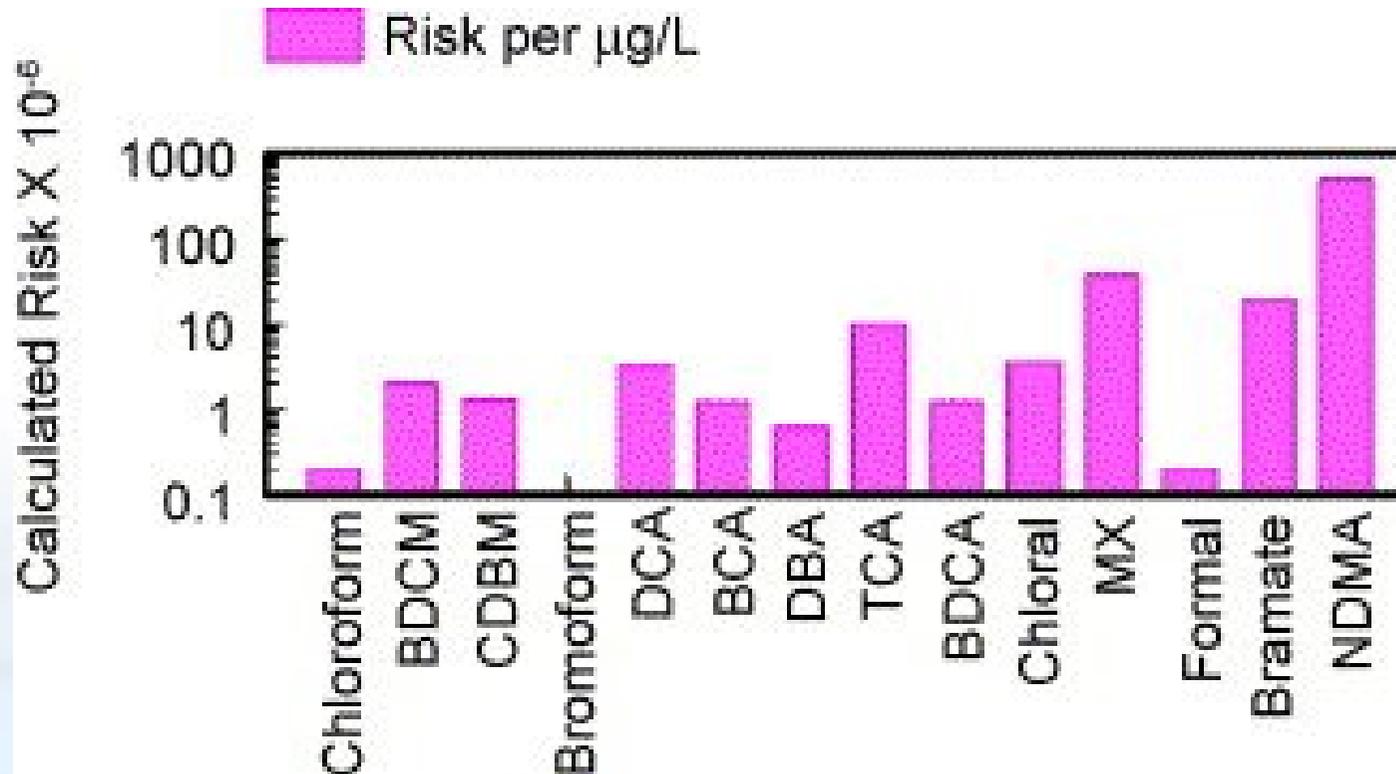
Ozone

Bromate

Chlorine Dioxide

Chlorate, Chlorite





- ▶ Identified 50% of all DBPs in chlorine-treated water, 17% in chloramines water, 28% in Chlorine dioxide water and 8% in ozone-treated water
- ▶ Most toxic DBPs (such as MX) have no limits

NDMA

Not regulated in the US but has MAC in Canada with a MAC of 0.00004 mg/L or 0.04 µg/L

Henry's Law constant is 3.3×10^{-5} at 25°C (not likely to be in the vapour phase) and inhalation risk from showering or bathing is low or negligible

Dermal absorption can occur at low rate

MAC is calculated based on 1.5 L ingestion and 0.4 Litre-equivalent in dermal absorption

NDMA intake from water is less 10% of total intake, mainly from food

NDMA

Formation is peak at pH 7.2 and at pH 8 is 25% as compared to pH 7.2

Formation is also reduced when chlorine is added first 5 to 15 minutes before adding ammonia

(Lee, 24th Water Reuse Symposium, 2009)

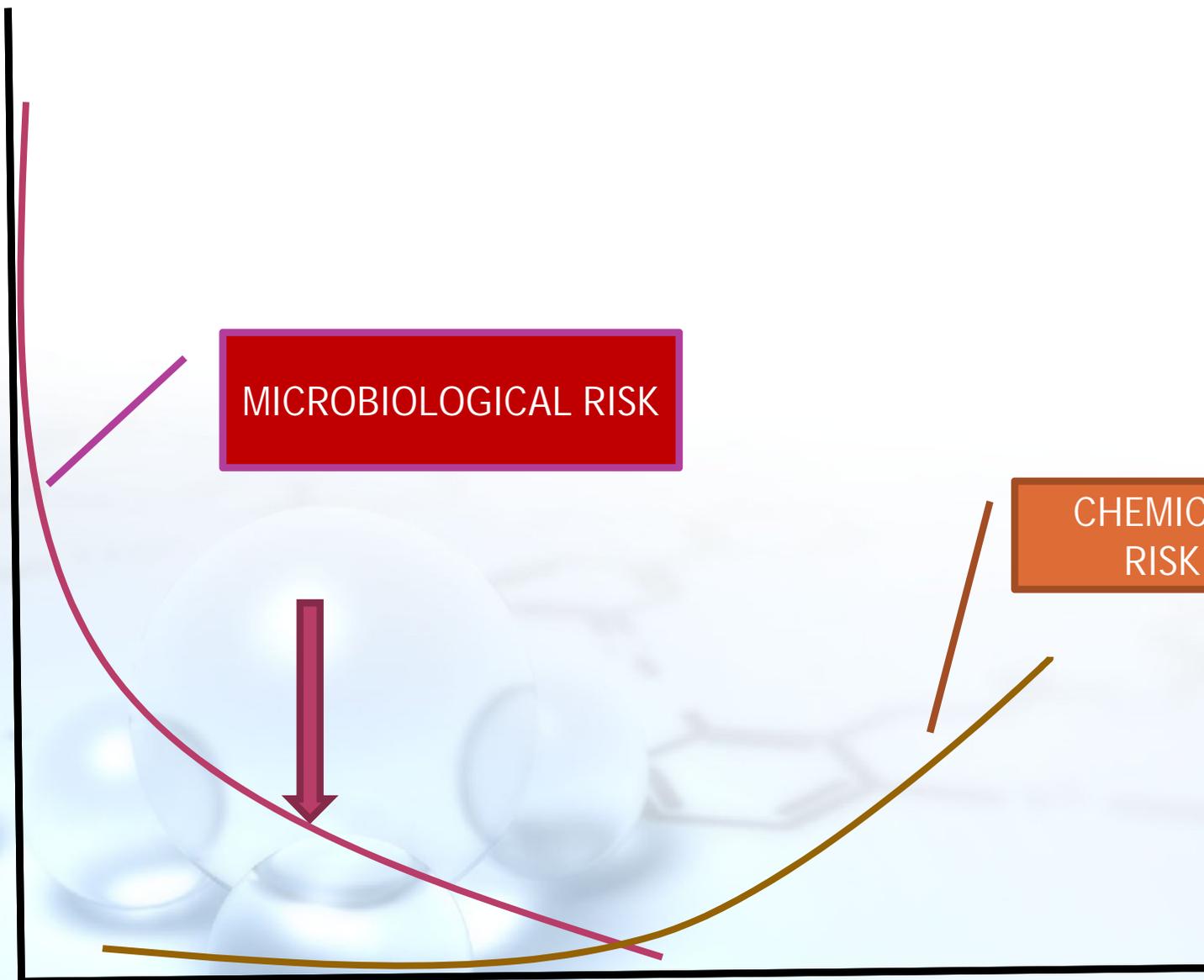
Water treatment plants would operate at pH close to 8 if chloramine is used

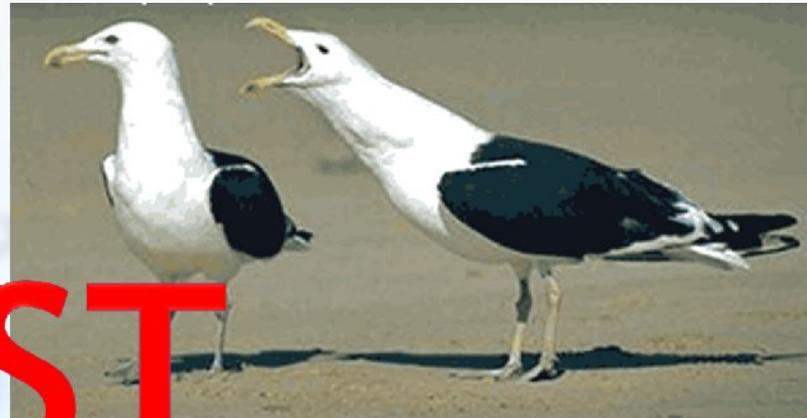
R
I
S
K

MICROBIOLOGICAL RISK

CHEMICAL RISK

Chlorination Level





TRUST

+0 (CH₂)

RISK COMMUNICATION

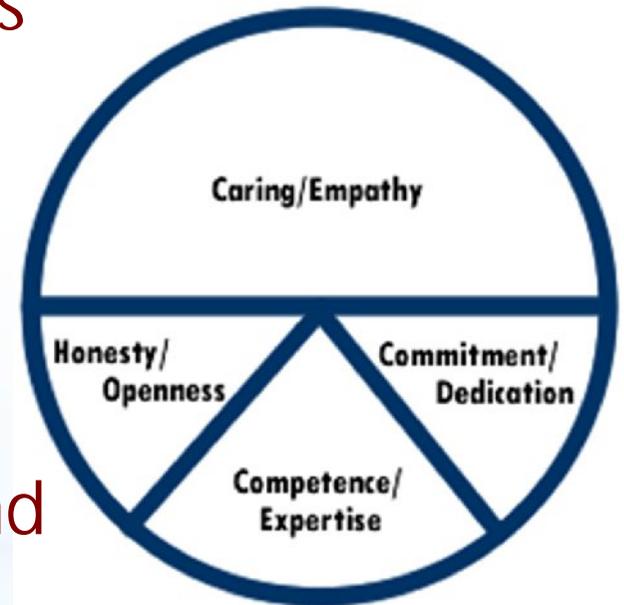
Listen to the public's concerns (not just Q&A) and address their specific issues

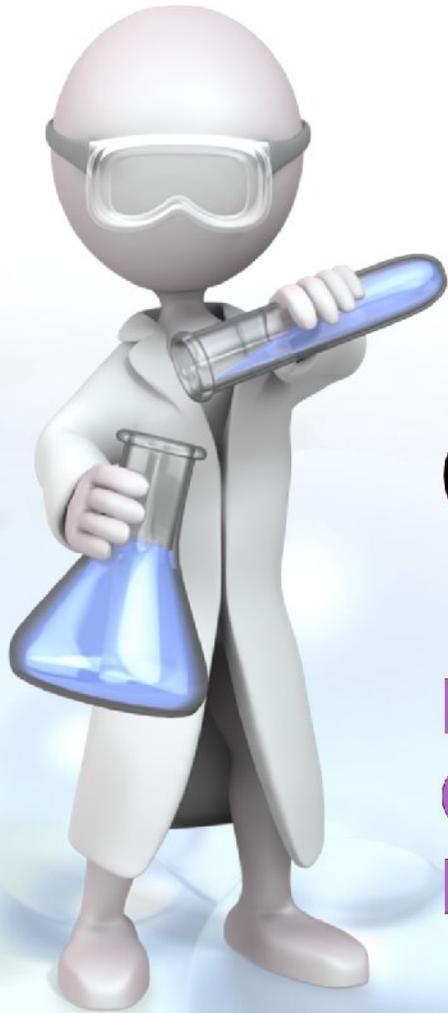
Analyze and understand sources of misinformation

Guide them through technical issues

Understand background technical knowledge to answer all questions and establish your credibility

Communicate and show 'empathy' as local health official





QUESTIONS?

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