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

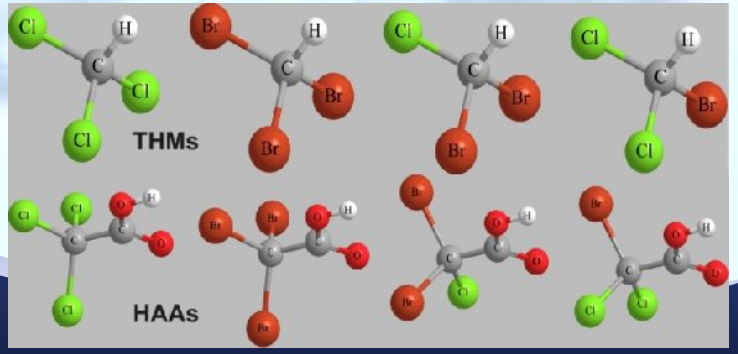
WATER DISINFECTION

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

Ultraviolet: Edmonton, Vancouver, Winnipeg

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

Ozone: Montreal, Winnipeg, Vancouver



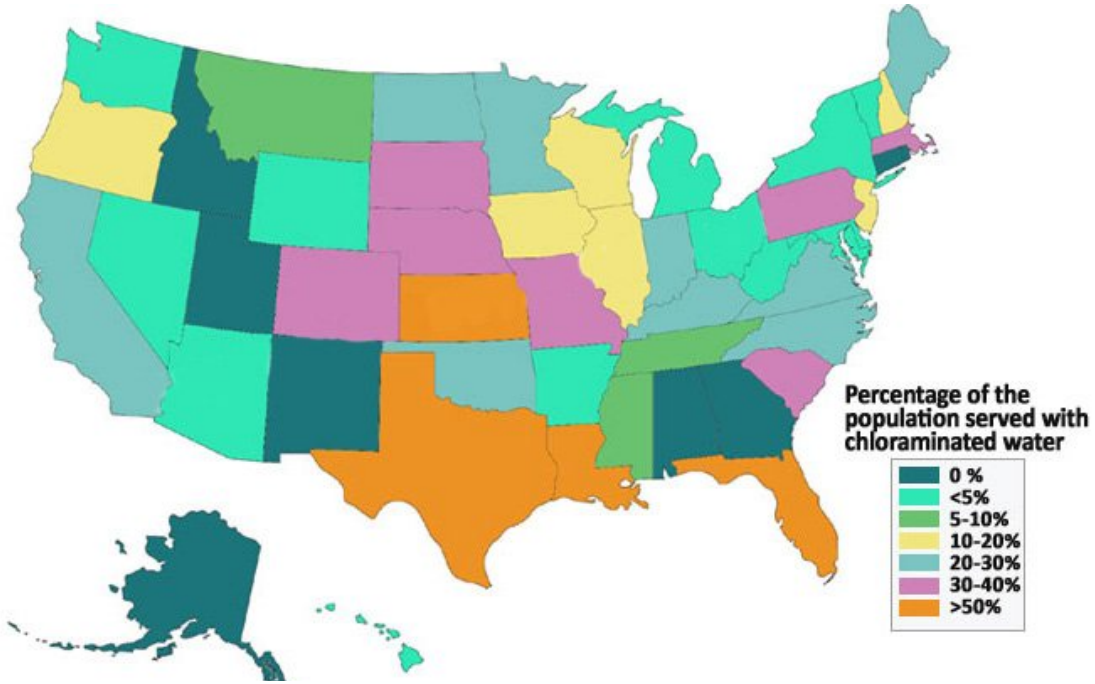


Table 3. Comparison data between 2007 and 2010

	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:

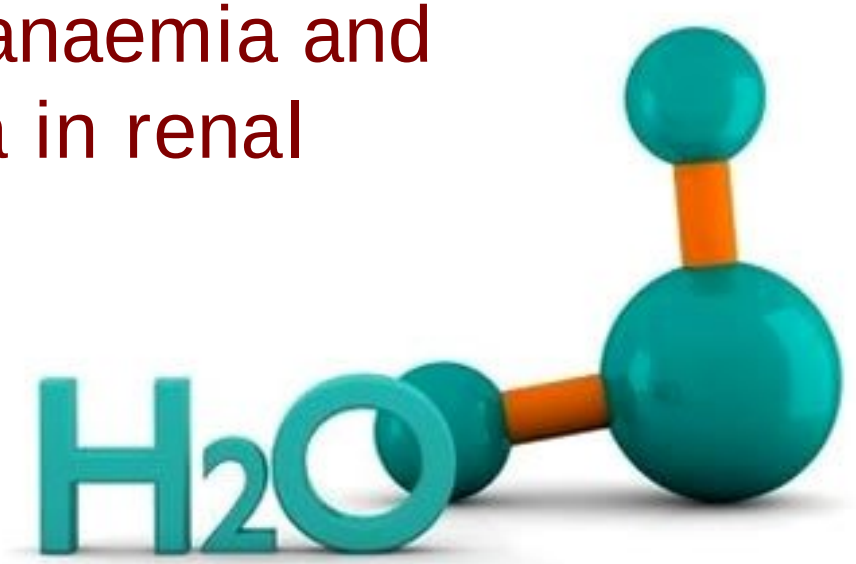
-Less effective disinfectant

-NDMA as DBP

-Increase lead leaching from pipes

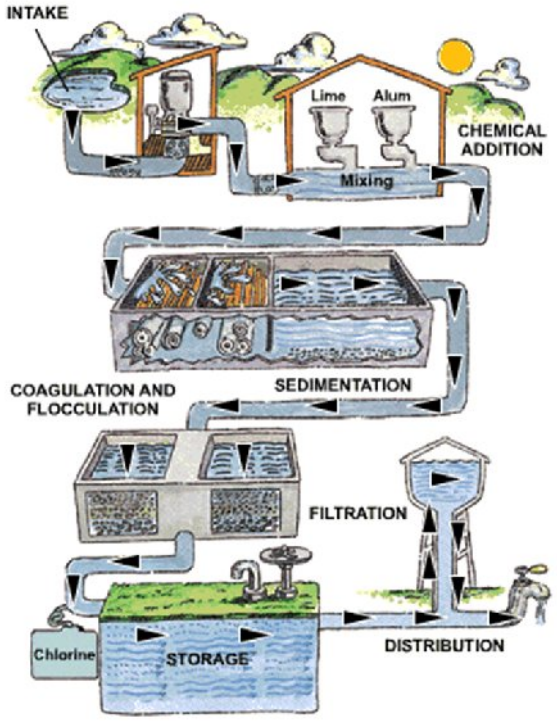
-Nitrification in distribution system

-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,

WHY SHOULD WE!

www.chloramineinfocenter.net

Chloramine and the Environment
“Bad for Fish, Good for People?”

What are Chloramines?

Real NH_2CL Truth

Citizens Concerned About Chloramine (CCAC)

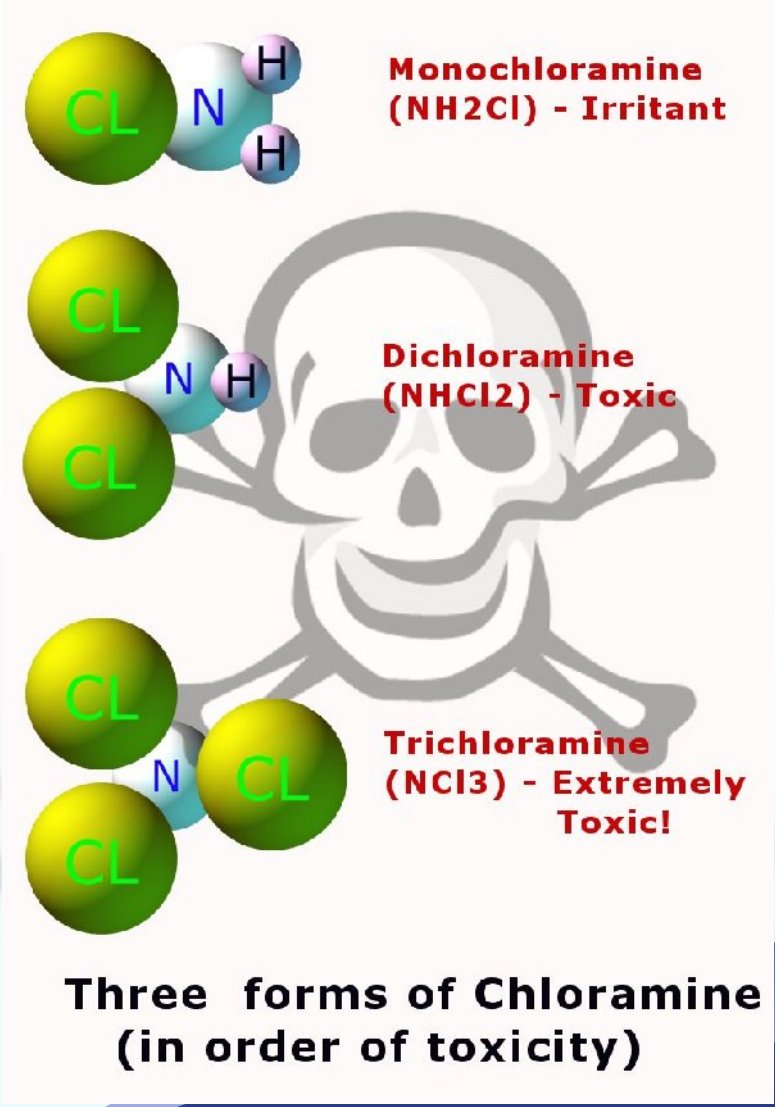
Citizens Concerned About Chloramine (CCAC)

…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)

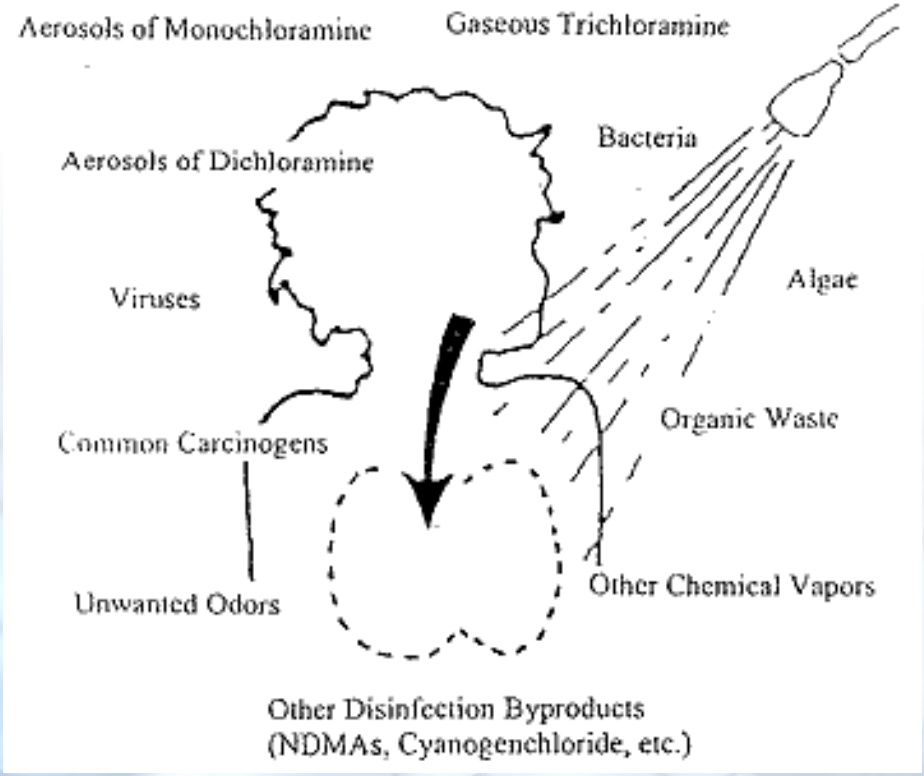
...Even time plays a factor because after a day or so, with no changes in conditions, monochloramine in a water system will slowly degrade to form dichloramine and some trichloramine. In contrast to what water utilities claim, it is impossible to have only monochloramine. It is not unusual in water systems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

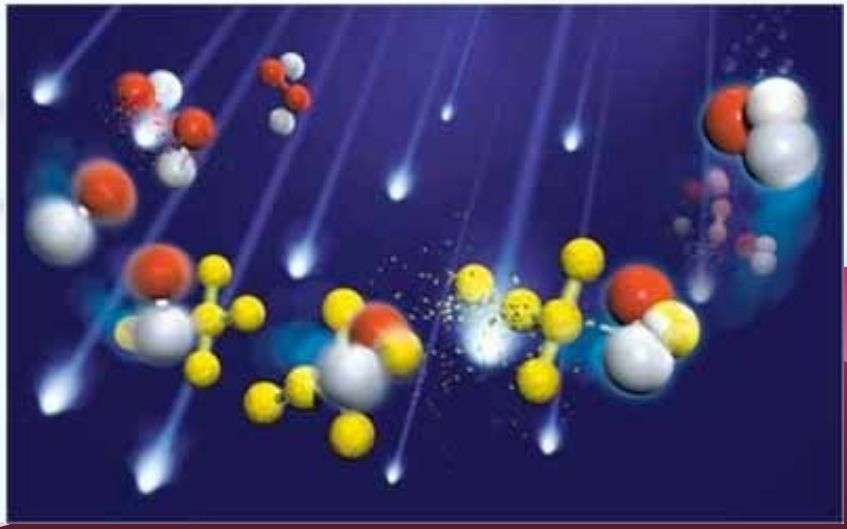
Water utilities use a form of chloramine that is composed of one part chlorine, to one part ammonia. That form is referred to as monochloramine. The problem is, it changes form readily into other, more harmful forms



Toxic Showers and Baths

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





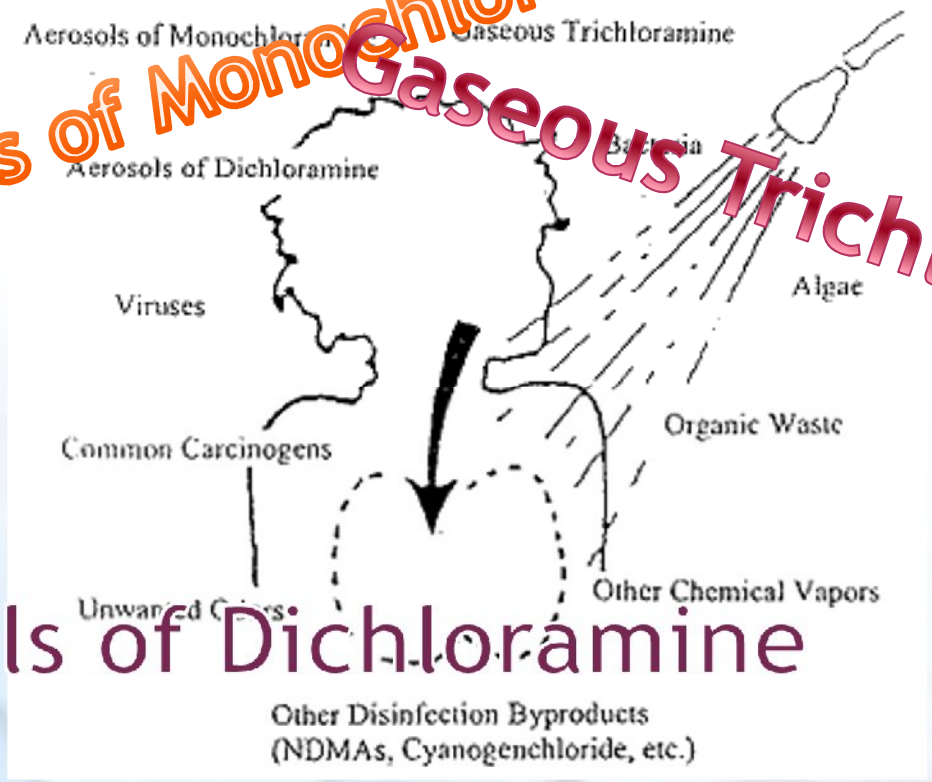
Citizens Concerned About Chloramine (CCAC)

…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

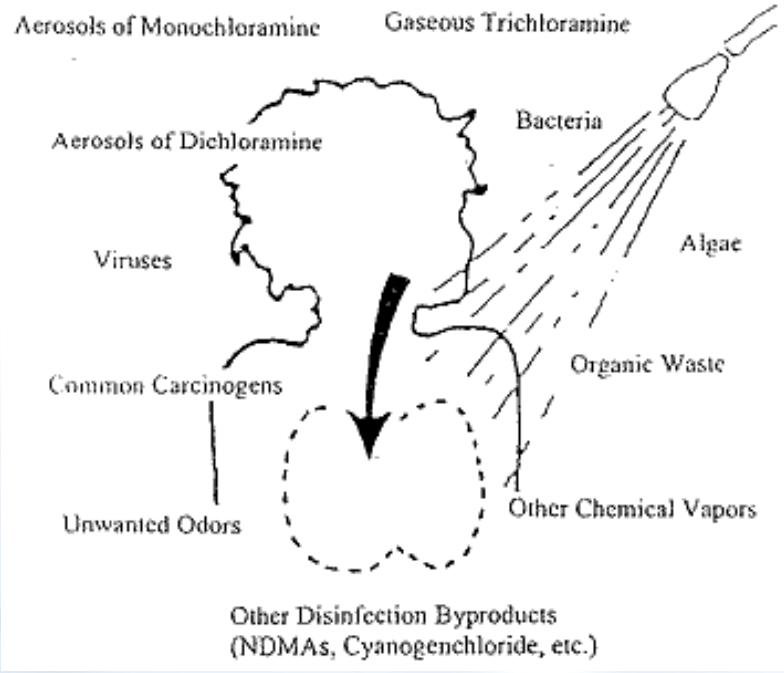
Viruses

Bacteria

Algae

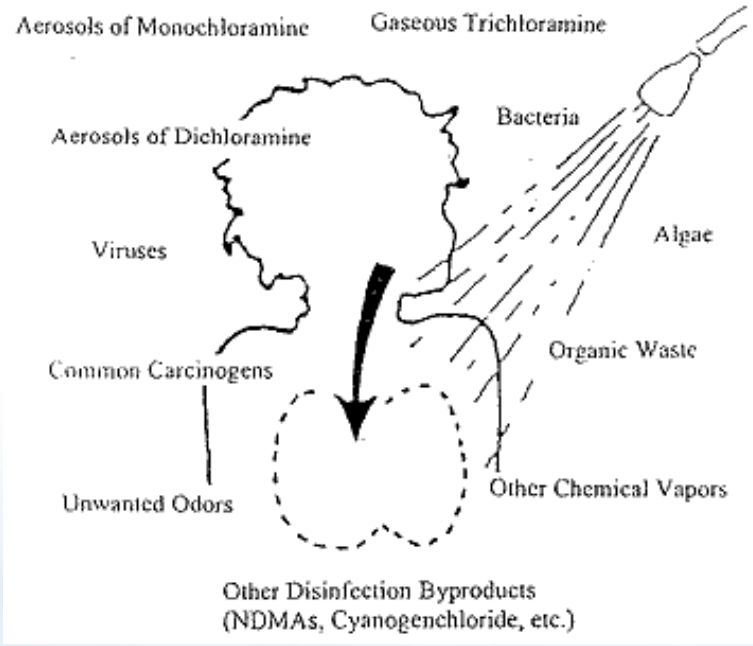
NDMA

CHEMICAL VAPOURS

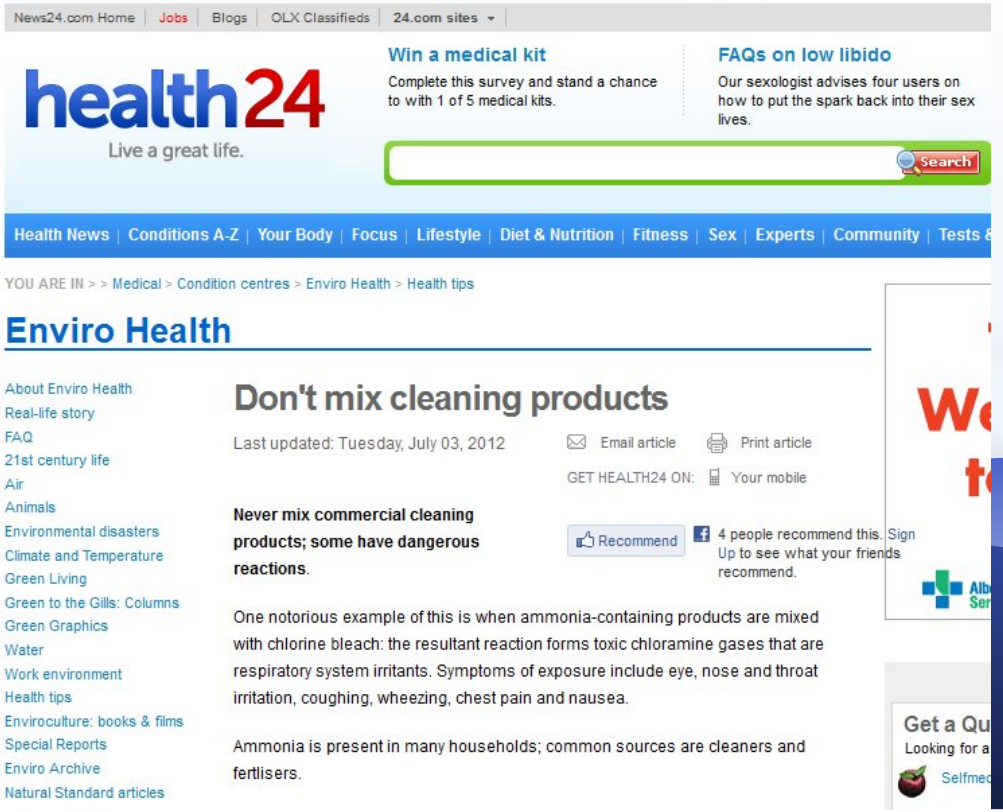


In a new study, researcher Julian Andelman, of the University of Pittsburgh Graduate School of Public Health…

…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).



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...

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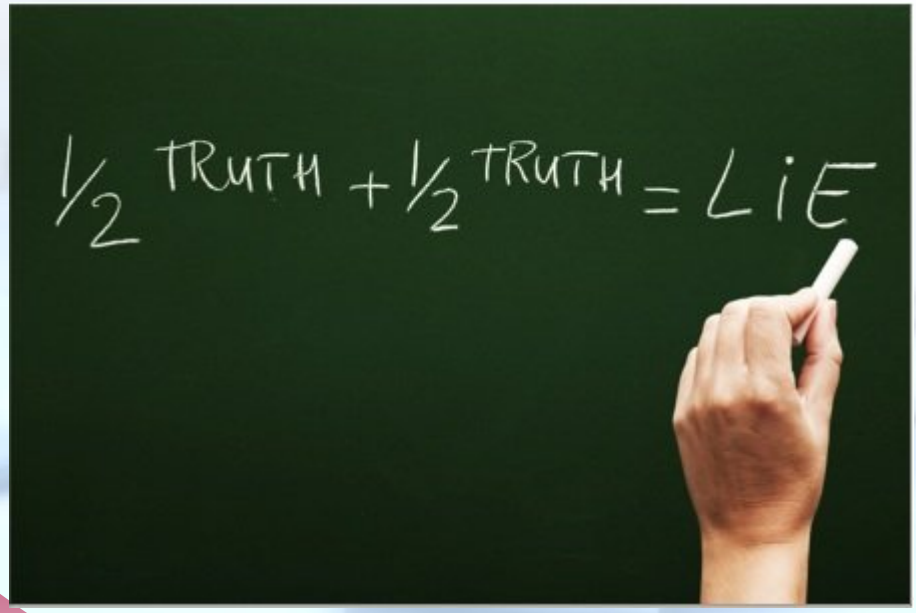
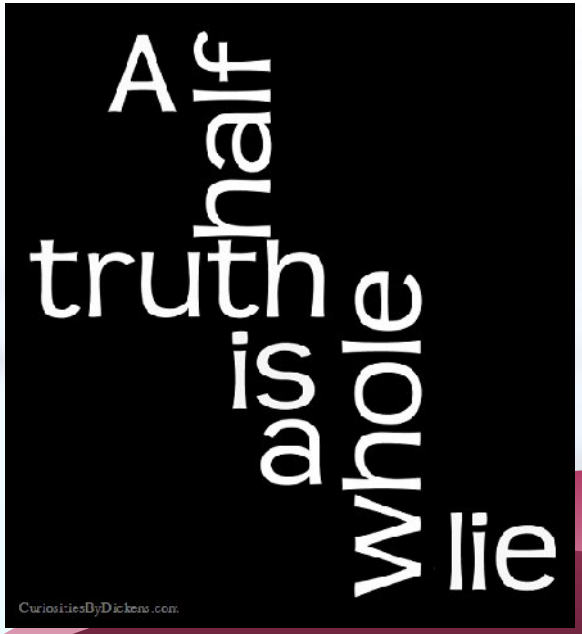
真実 - **Verité** - **Totuus** - 진실
Verdade - 真相 - **Waarheid**
Правда - **Wahrheit** - **Truth**





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

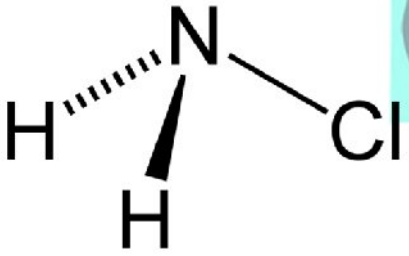
Technical information not for direct public communication

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

CHLORAMINE

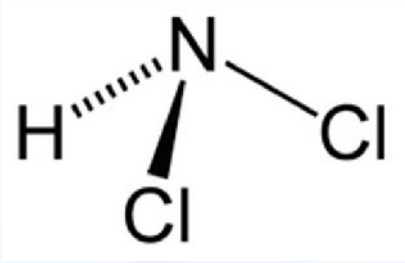
Mono-chloramine

$NH_3 + HOCl = NH_2Cl + H_2O$



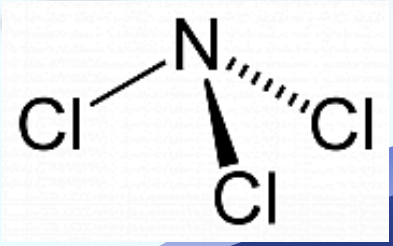
Di-chloramine

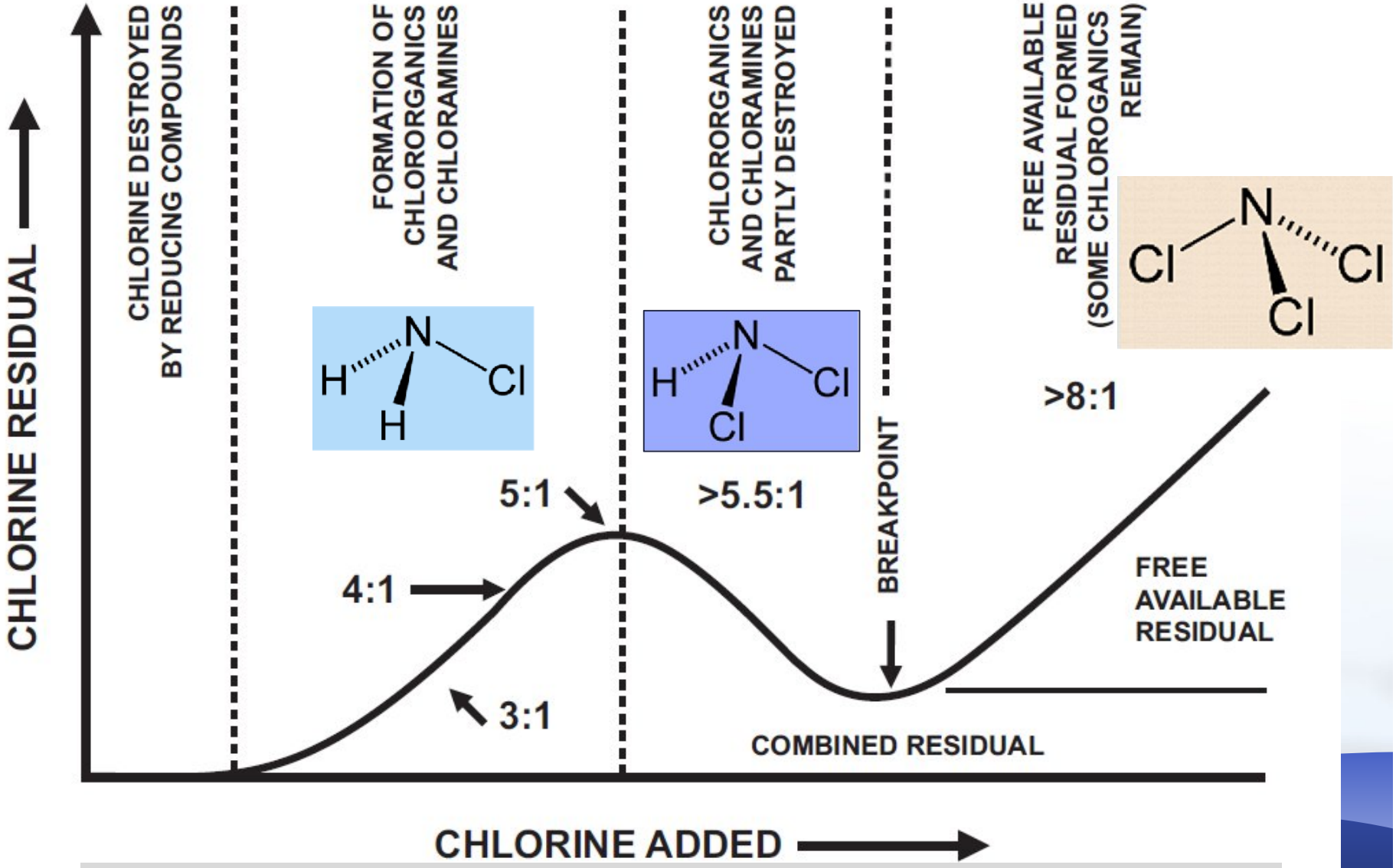
$NH_2Cl + HOCl = NHCl_2 + H_2O$



Tri-chloramine

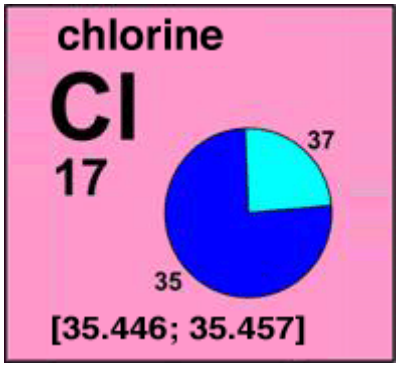
$NHCl_2 + HOCl = NCl_3 + H_2O$





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
- $Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^-$
- $HOCl + NH_3 \rightarrow NH_2Cl + H_2O$
- Hence $Cl_2 + NH_3$ 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:

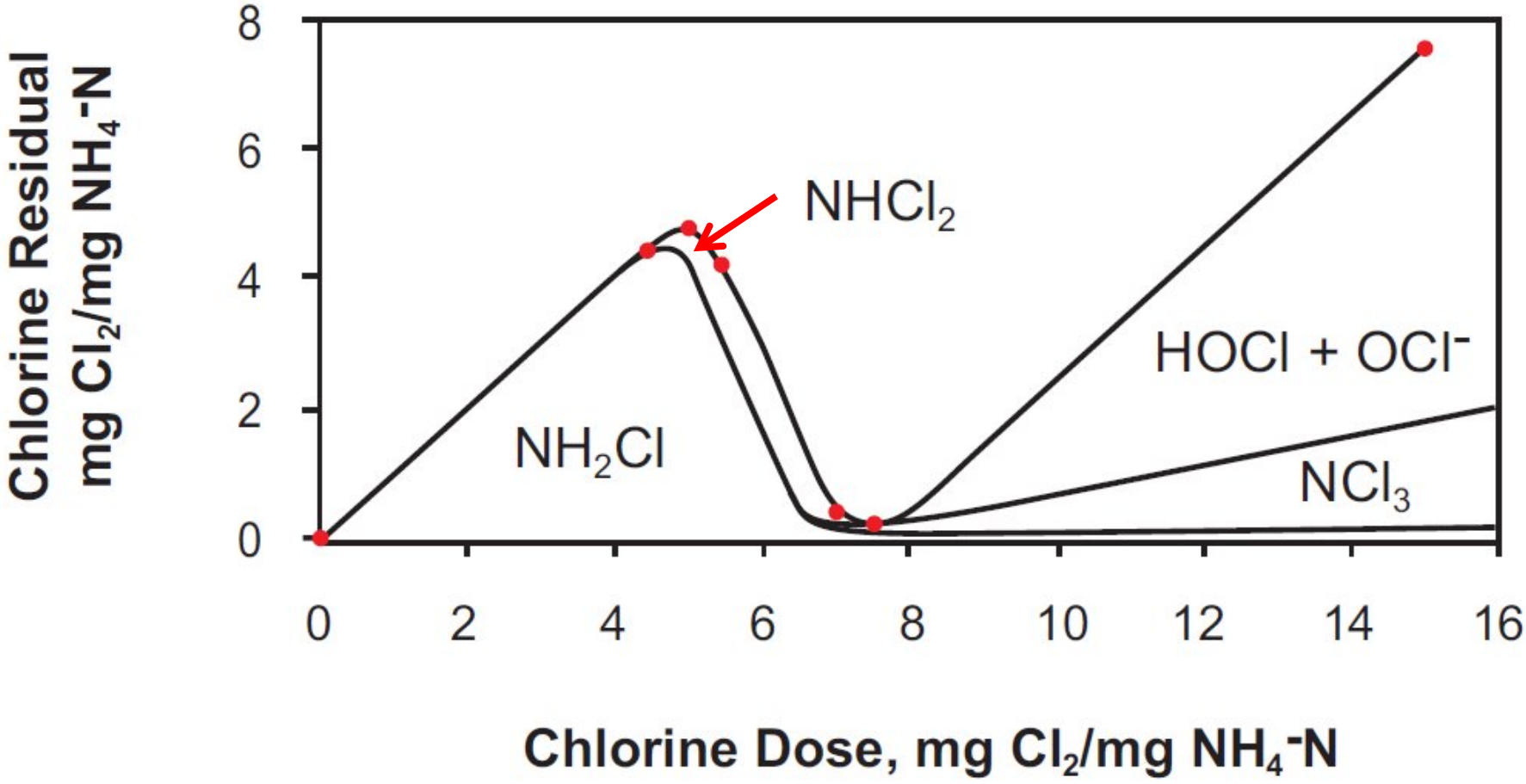
$NH_2Cl + H_2O \rightarrow HOCl + NH_3$ and

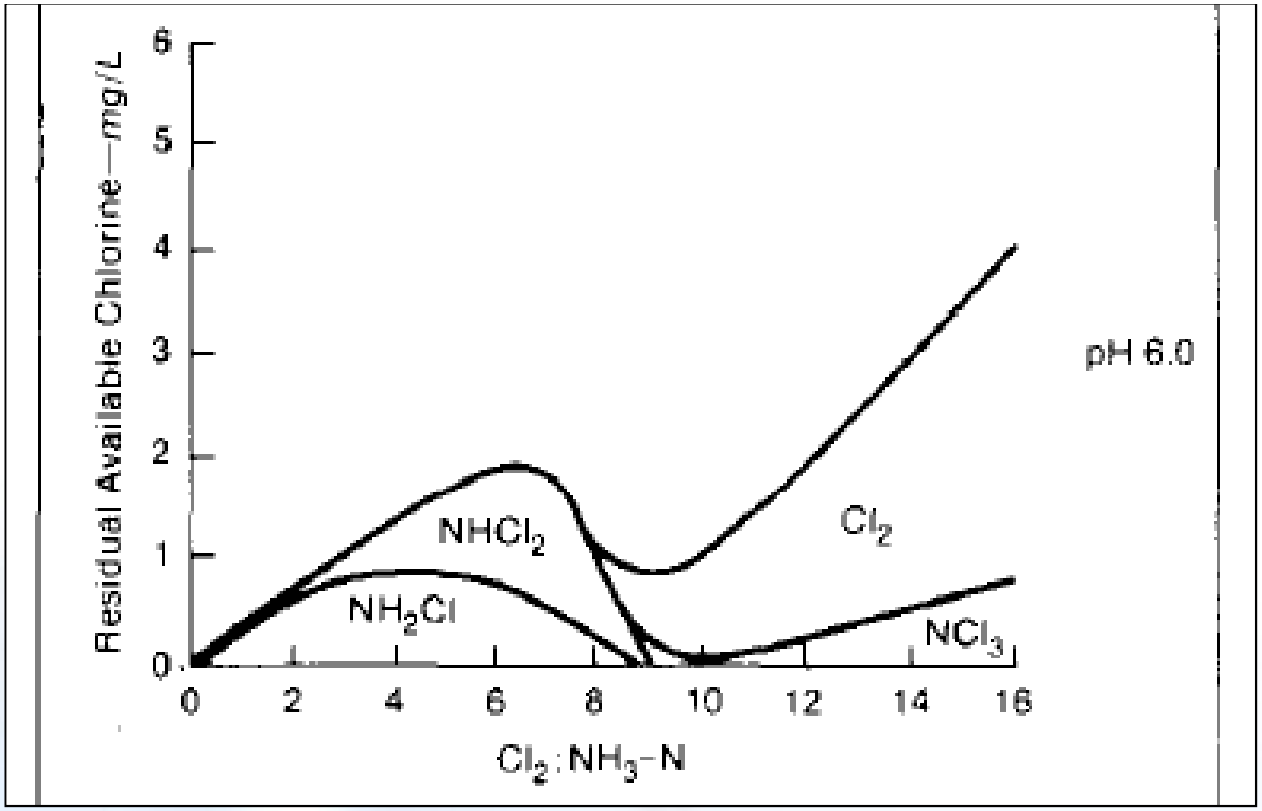
$HOCl + NH_2Cl \rightarrow NHCl_2 + H_2O$

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^-

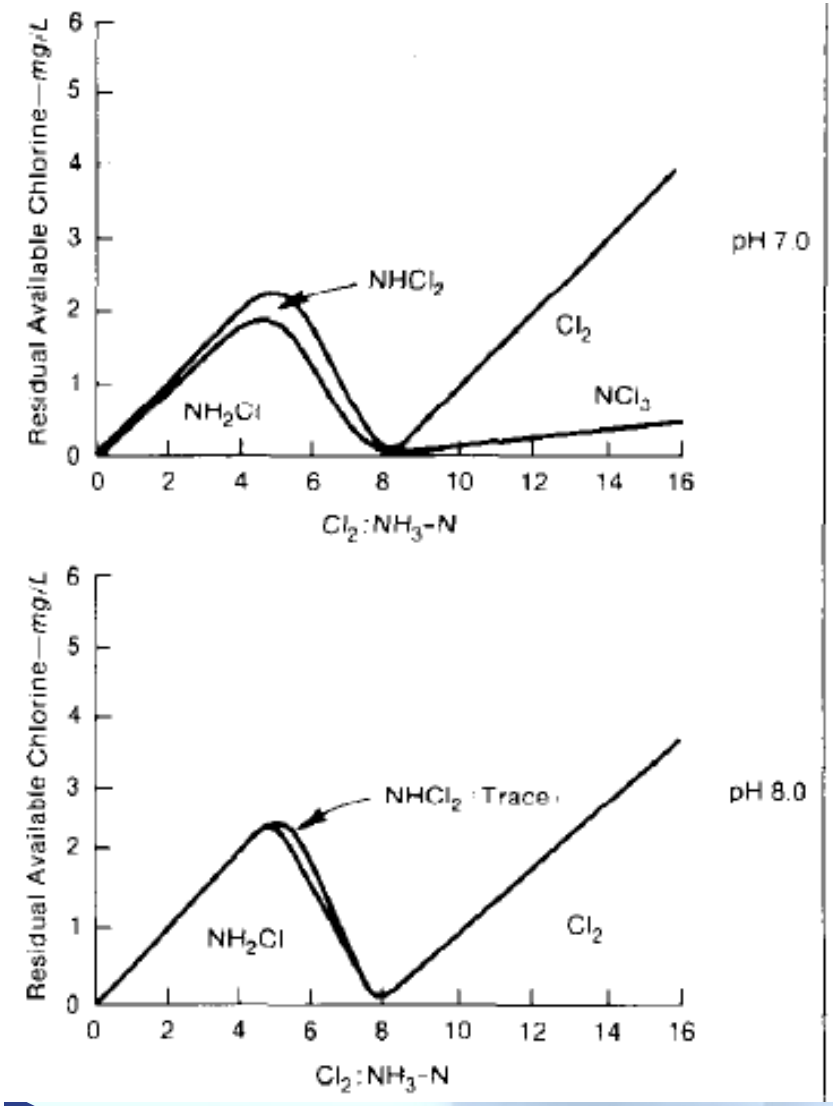
Production of Various Species of Chloramine by Increasing Chlorine Doses





Breakpoint curve

- pH 6 acidic environment starting at 6.6 (acid catalyzed disproportionation) results in $NHCl_2$ formation at Cl_2-NH_3 ratio of >2 and significant NCl_3 after breakpoint.
- $NH_2Cl + NH_2Cl + H^+ \rightarrow NHCl_2 + NH_3 + H^+$

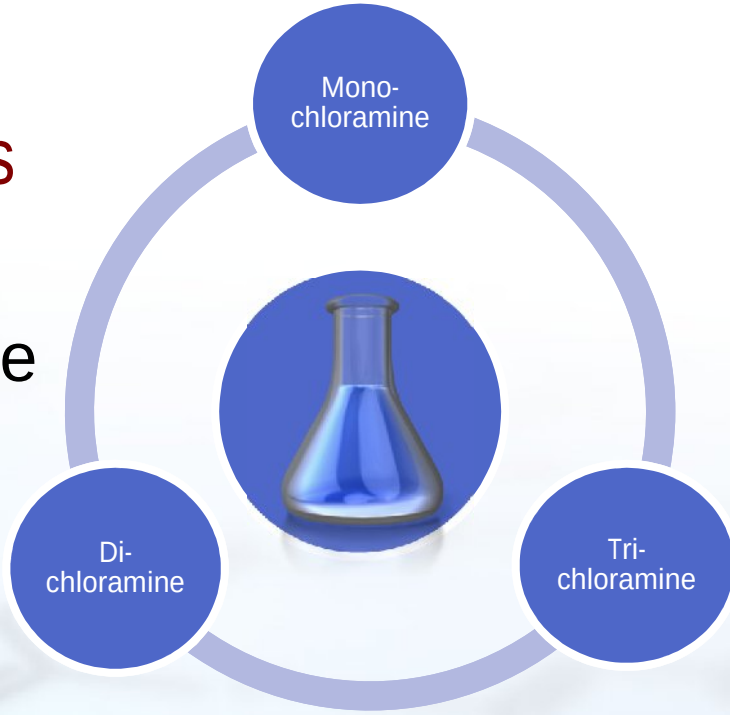


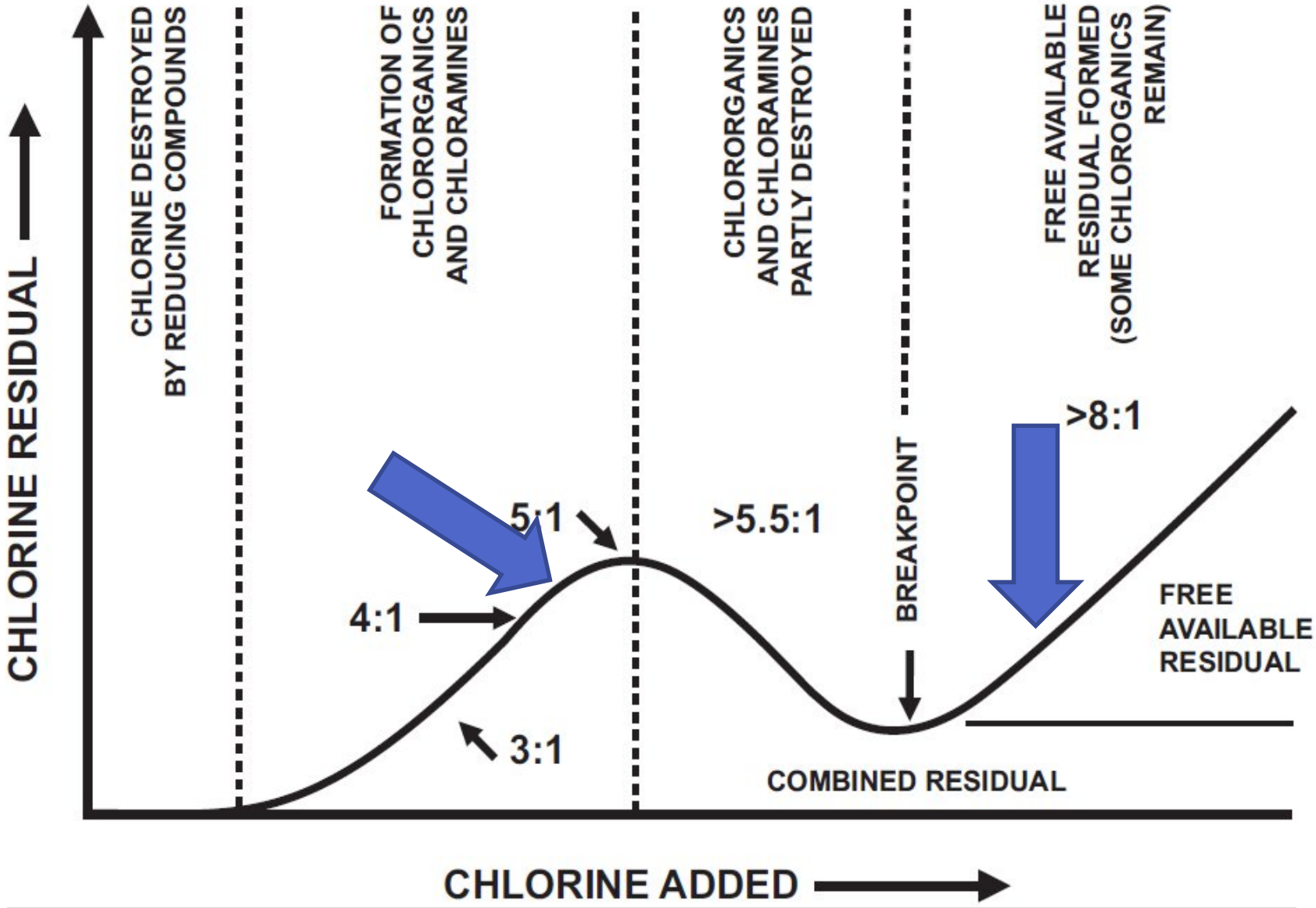
Breakpoint curve

- 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 etal, Converting From Chlorine to Chloramines: A Case Study, J AWWA, 1985

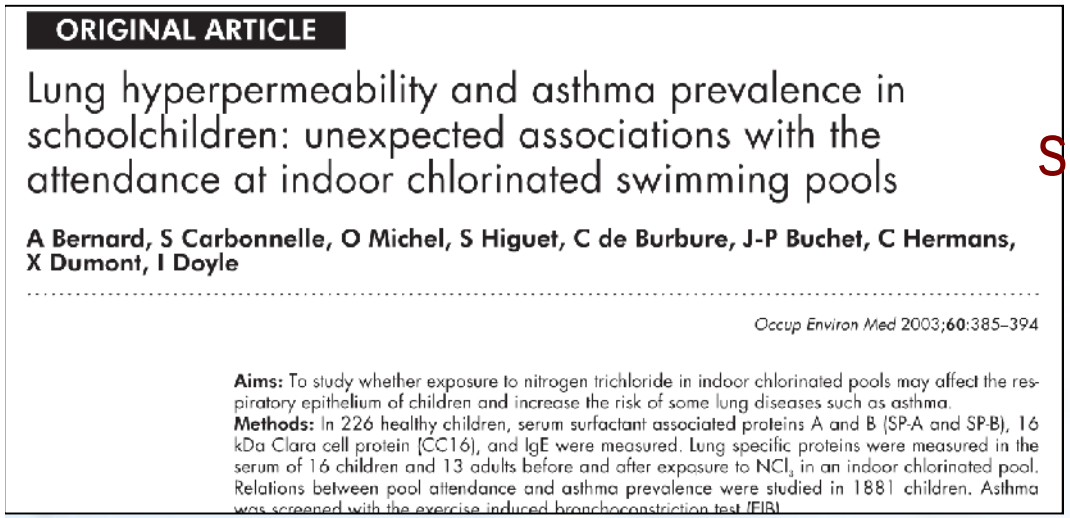
- When the chlorine-to-ammonia weight ratios is > 5:1, dichloramine is formed
- At pH >7.5, no trichloramine is formed, regardless of the ratio of chlorine to ammonia (US Office of Water 1994)
- Trichloramine can be formed between pH 7 and 8 if the ratio is >15:1 (AwwaRF 2004)





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

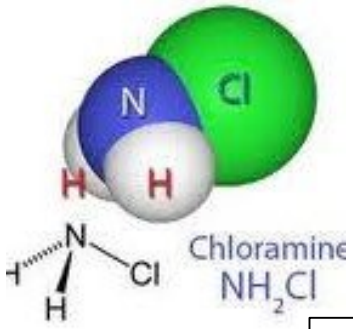
Lung hyperpermeability and asthma prevalence in schoolchildren: unexpected associations with the attendance at indoor chlorinated swimming pools

A Bernard, S Carbonnelle, O Michel, S Higuet, 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…"



ELSEVIER

Public Health

Volume 122, Issue 2, February 2008, Pages 195–200

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

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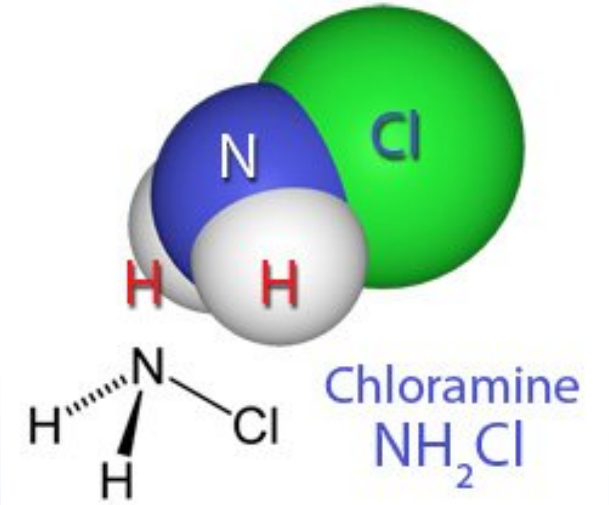
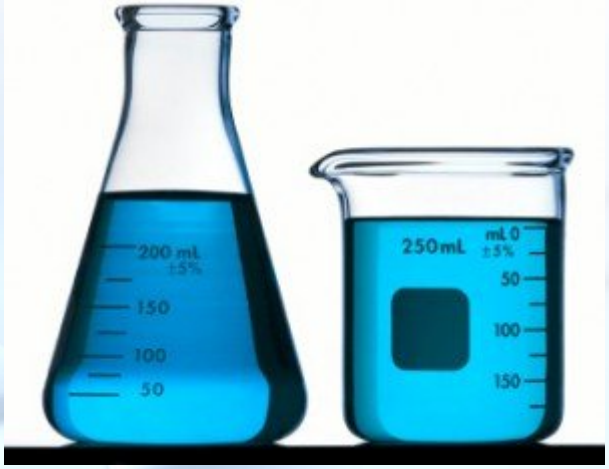
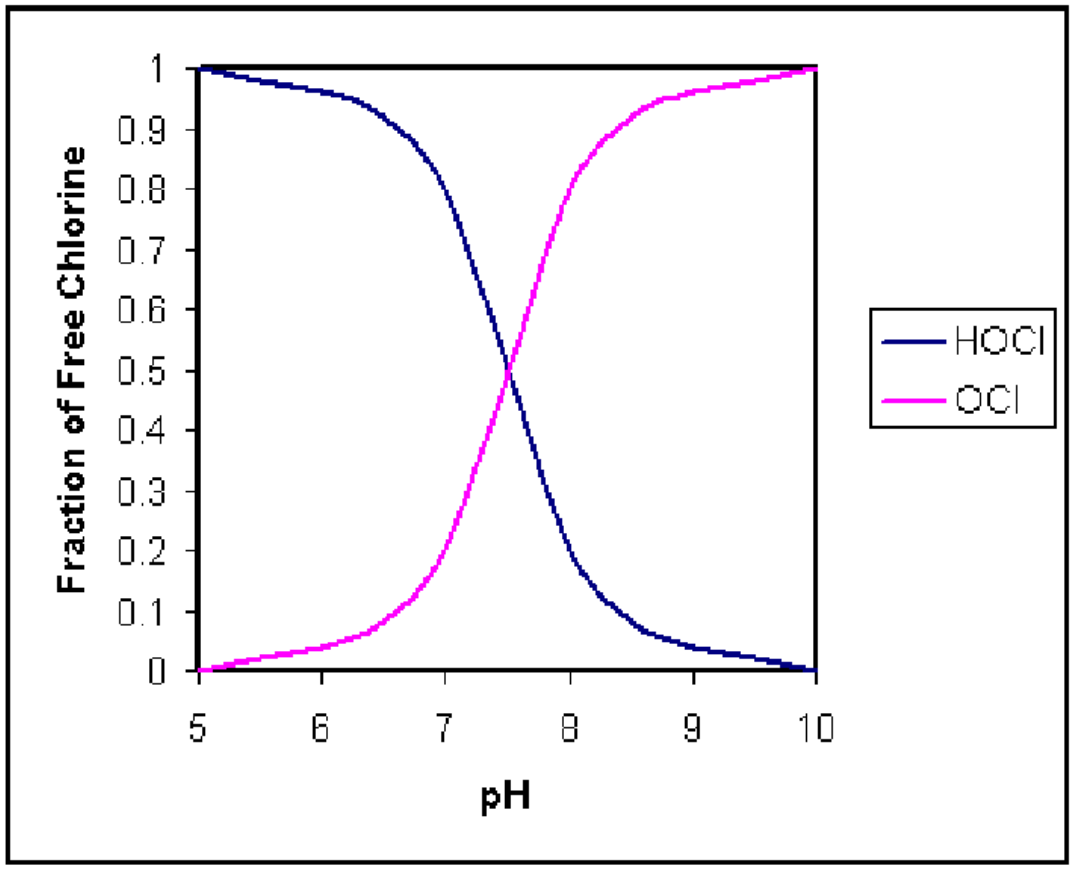
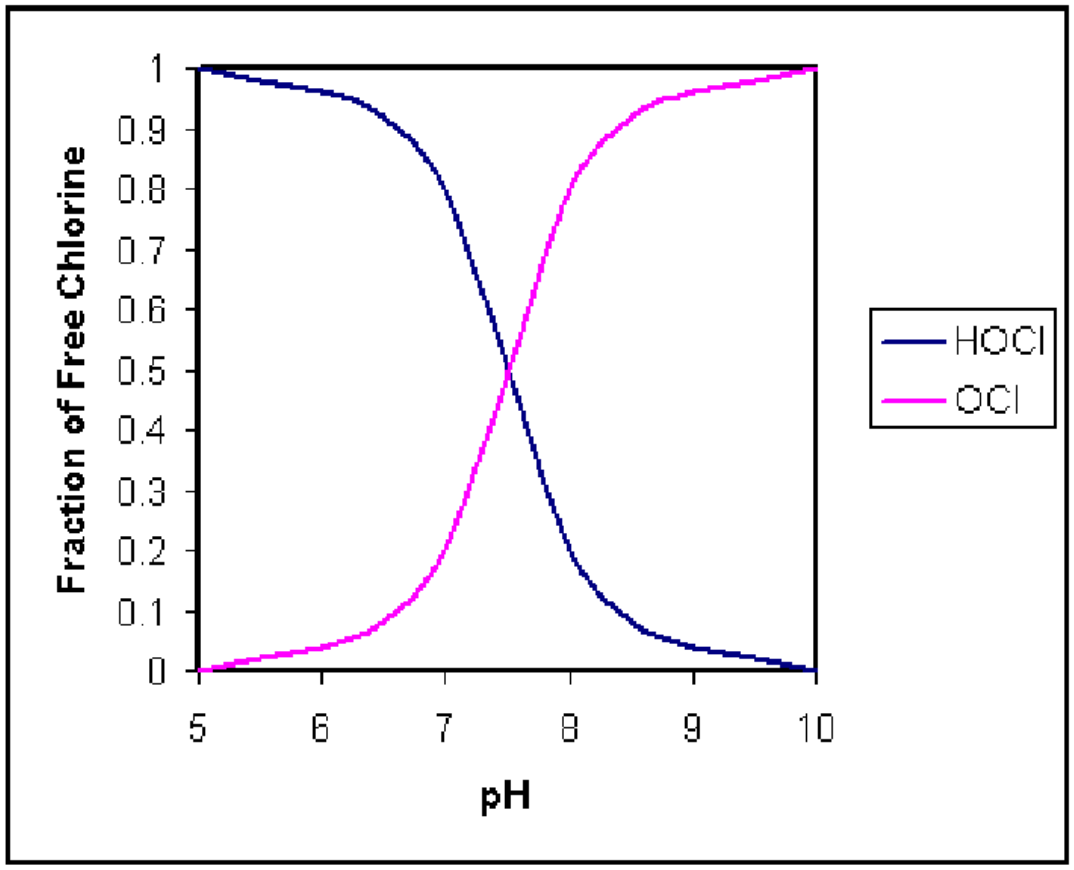
Childhood asthma and environmental exposures at swimming pools: state of the science and research recommendations


N
Cl
H
H
H
N
Cl
H
Chloramine
NH_2Cl


200 mL
150
100
50
250mL
50
100
150



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 $\mu g/cm^2$ and contribute 0.16 g of urea. Showering remove 75-97% of urea from skin

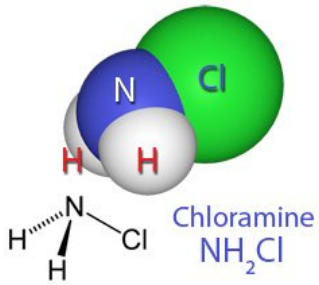
TRICHLORAMINE FORMATION

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

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.

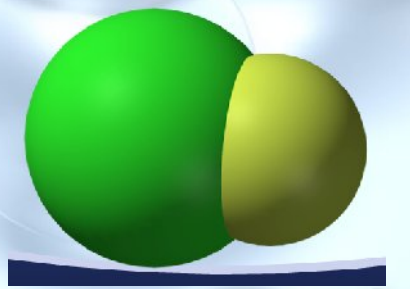
underlying cause of cancer death recorded on the death certificate may not have been the primary tumor. For example, the site of metastasis, rather than the primary site, may have been noted as the underlying cause of death. Similarly, deaths attributed to pneumonia and influenza may actually have been 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.

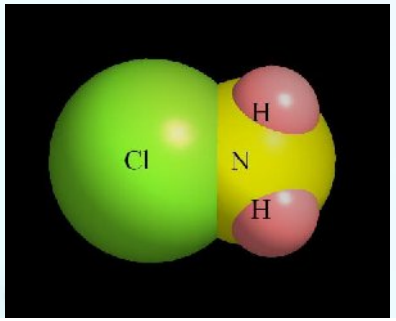
It is not surprising, therefore, that the patterns of causes of death did not vary to any appreciable extent according to type of disinfectant. There is some indication, however, that bladder cancer mortality was excessive among residents of chlorinated communities relative to residents of chloraminated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

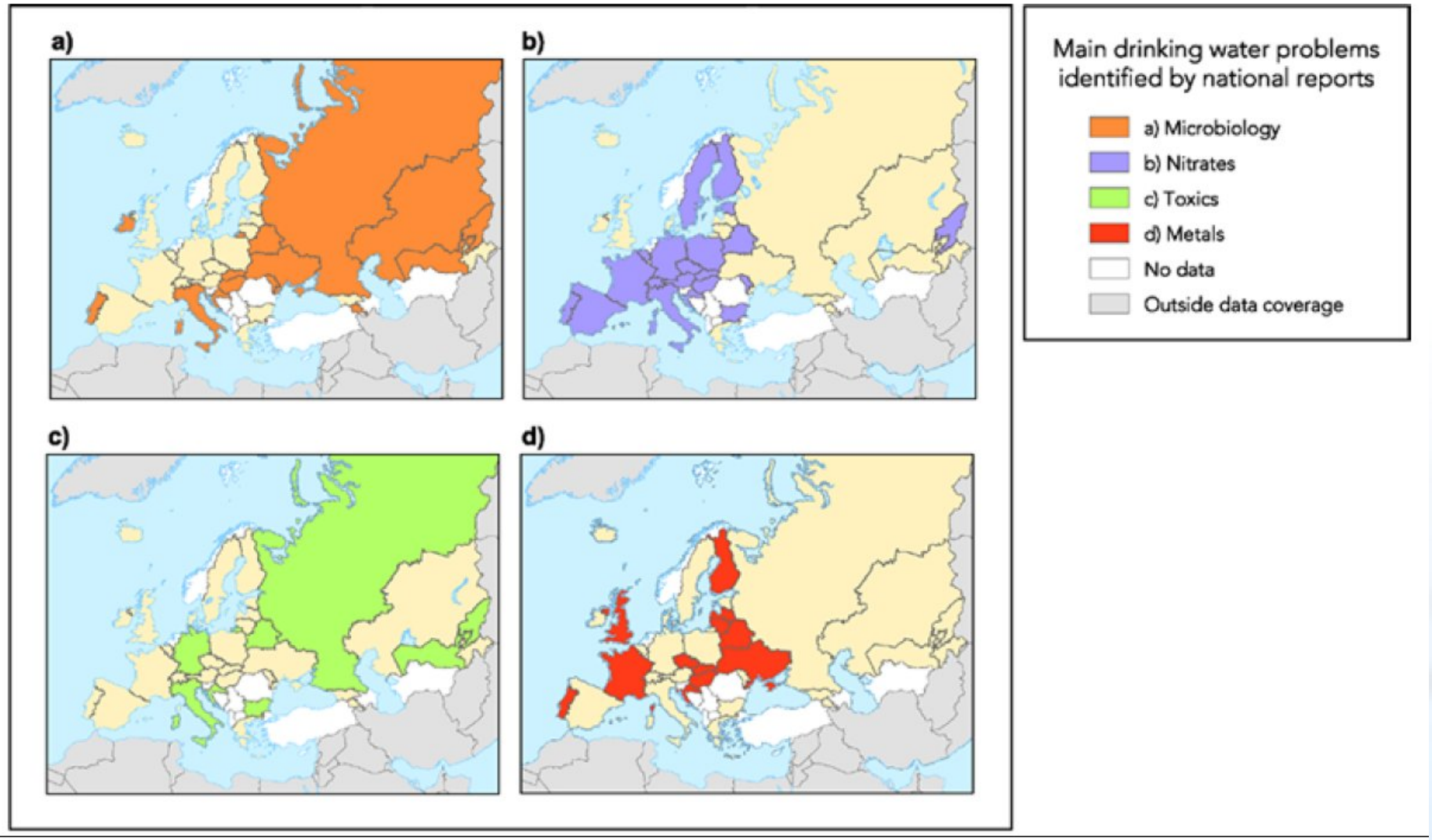
…Germany has banned chloramine and France refuses to use chloramine in their countries for drinking water purposes…most European countries DO NOT use chloramine…Those who do use it only occasionally…

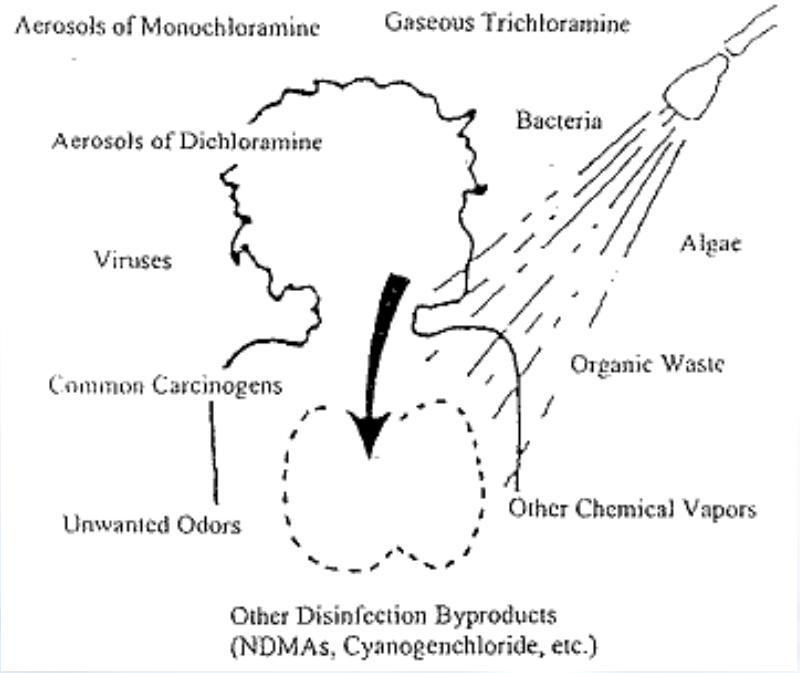
CHLORAMINE USAGE AND SAFETY

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

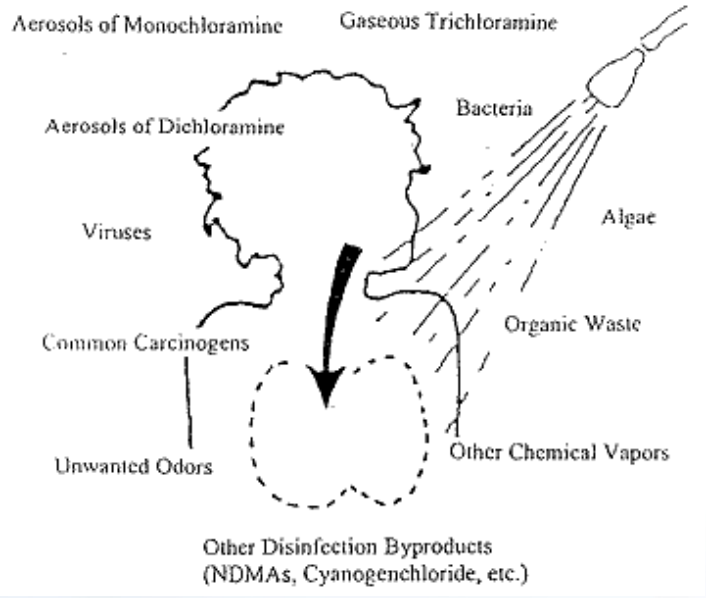
Figure 1: Main drinking water problems identified by national reports





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)

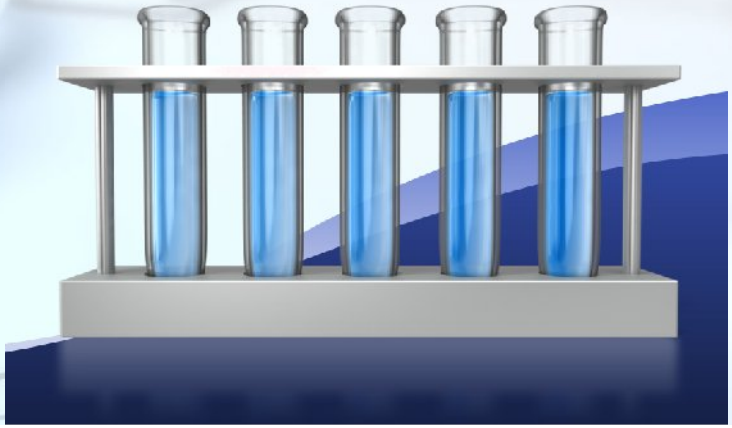
CHLORAMINE CHEMISTRY - SHOWER

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.



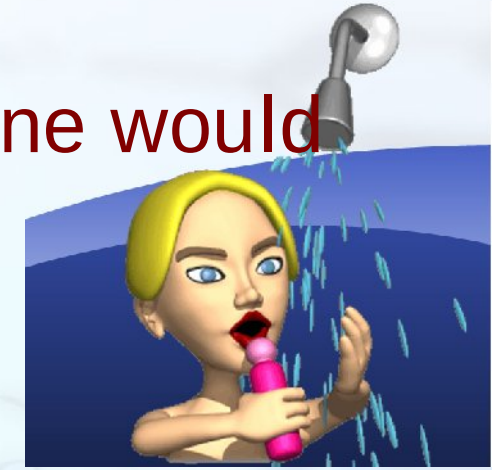
CHLORAMINE CHEMISTRY - SHOWER

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

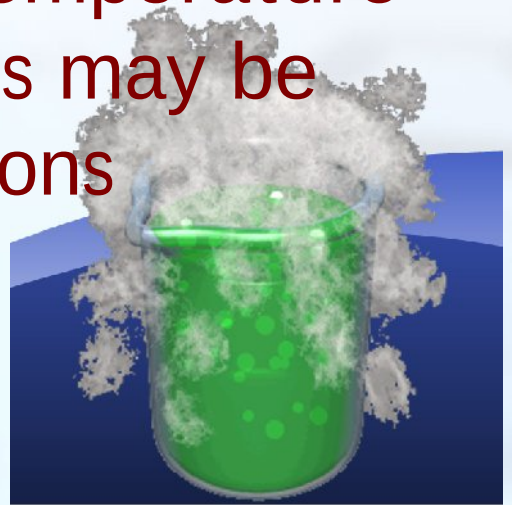
-Monochloramine is not very volatile. Both H value and hydrolysis increase with temperature. Minimal monochloramine would be inhaled



CHLORAMINE CHEMISTRY - SHOWER

If one boils water with chloramine

Bringing the water to a boil will remove 30 to 50% of monochloramie 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

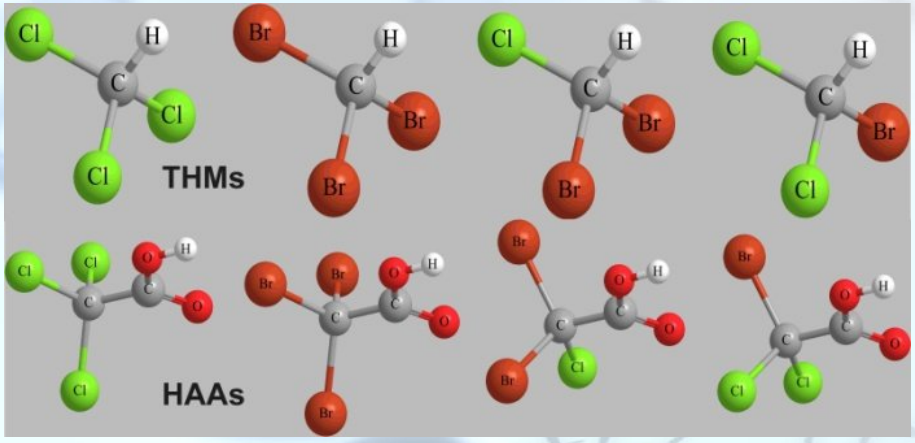
With hot water temperature of <45°C in shower and initial chloramine concentration of about 1.5 mg/L, very little monochloramine would be 'volatilized' into the air.

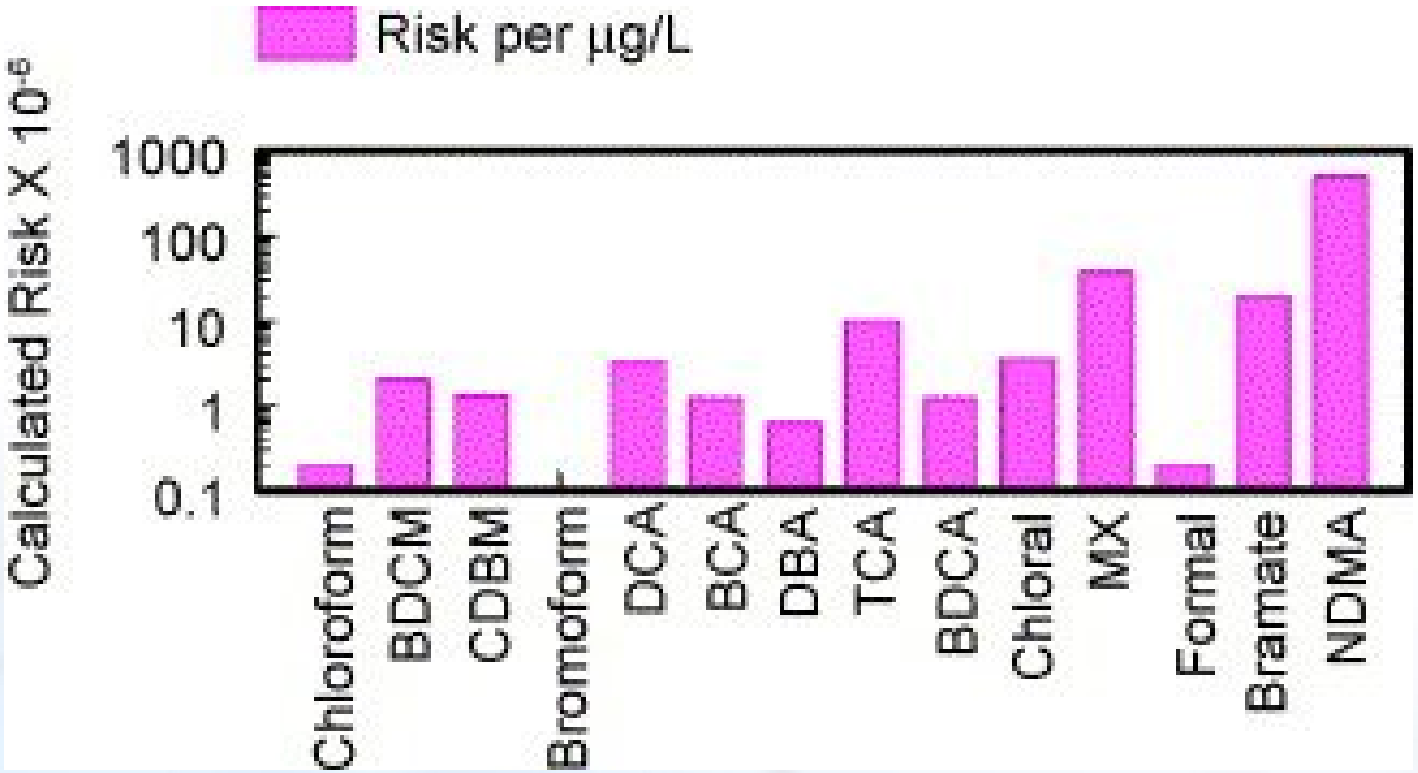
Average water used in bathing and showering is 80L and average air volume in bathroom is 6,420L, 80 times dilution

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

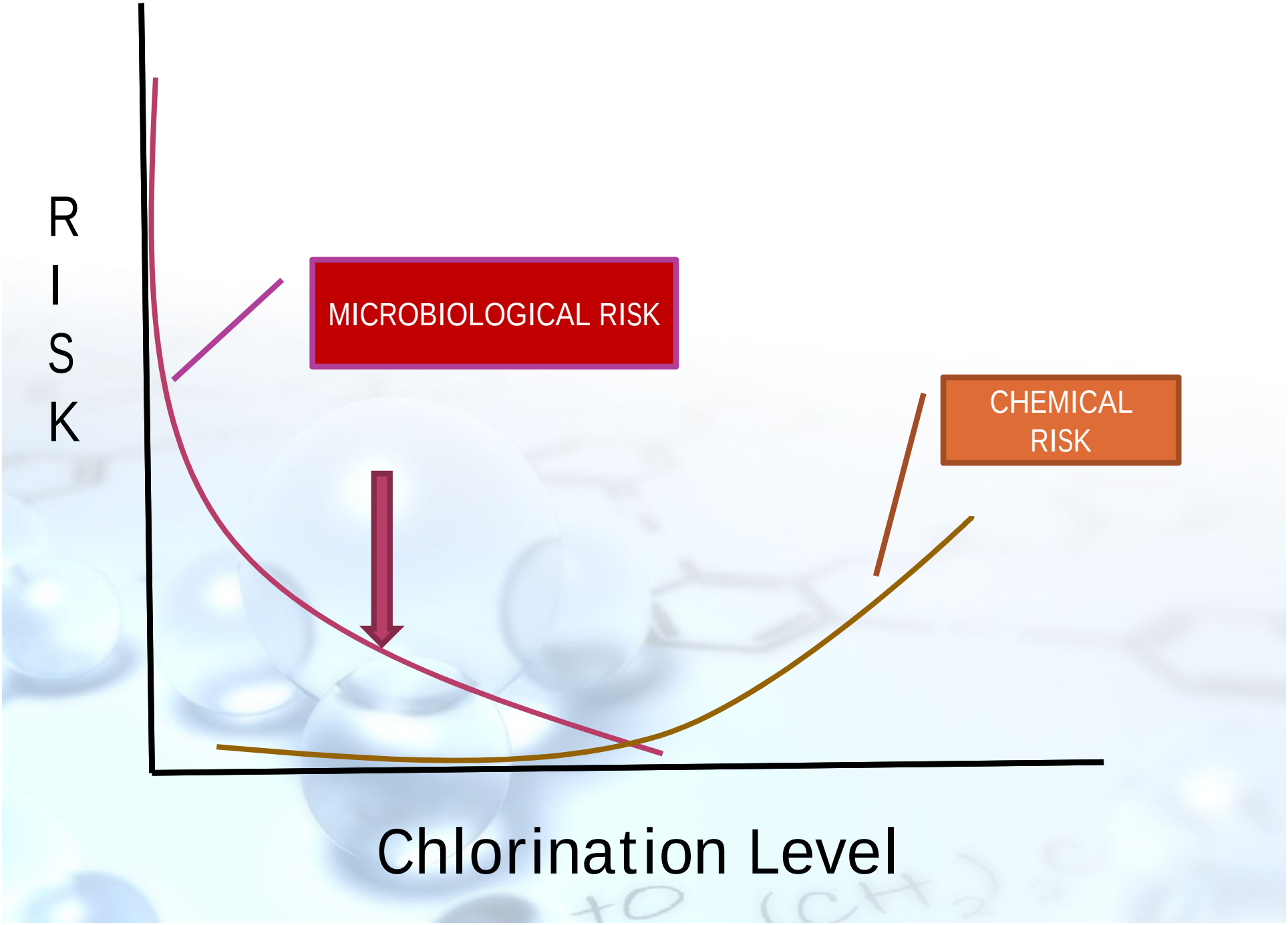
NDMA

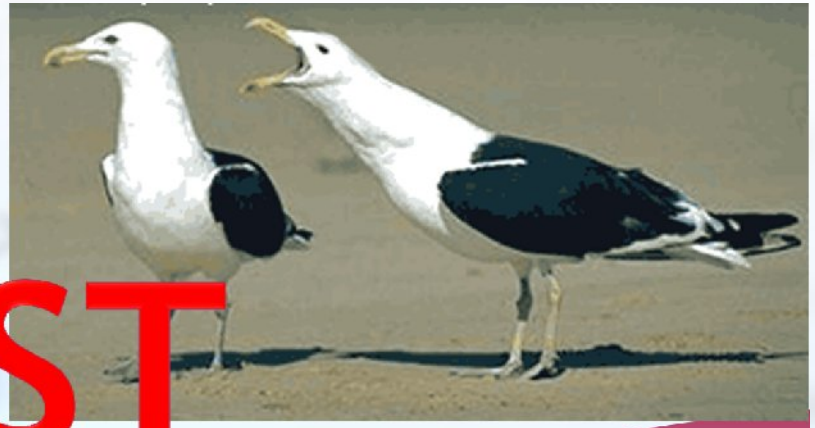
Formation is peak at pH 7.2 and at pH 8 is 25% as compared to pH 7.2

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

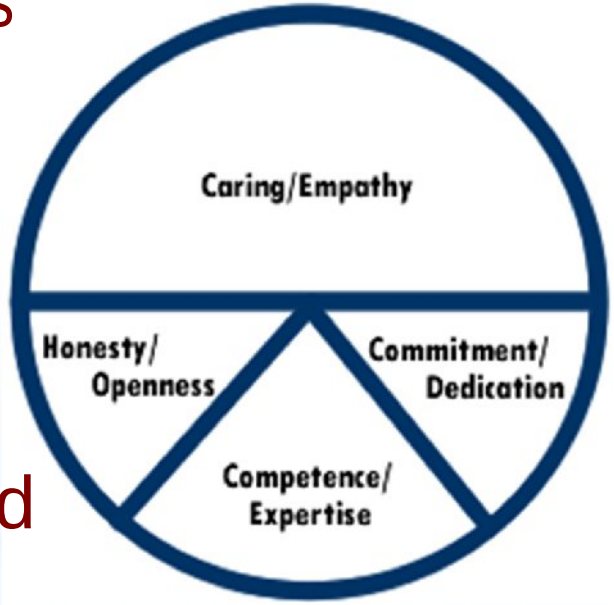

RISK
MICROBIOLOGICAL RISK
CHEMICAL RISK
Chlorination Level

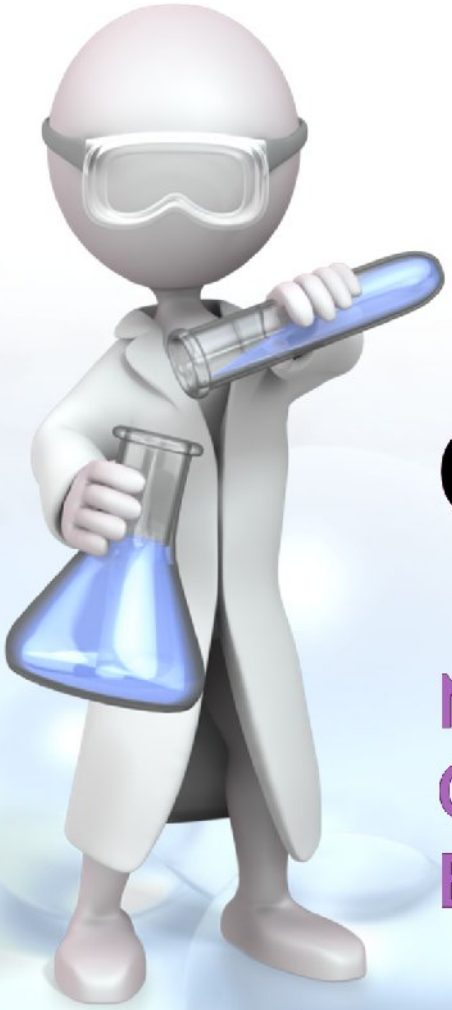


TRUST

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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