Water Chemistry

http://courses.washington.edu/h2owaste/ Gretchen Onstad

Water Chemistry

- Fundamental chemical concepts
 - Equations for chemical equilibria
 - Calculation of water quality parameters
- Contaminants in water
 - Sources
 - Health effects
 - Regulations

Drinking Water Quality

Source → Treatment → Distribution

What do consumers care about?

How can we protect and provide that?

What are the most important chemical parameters?

Chemical Compounds in Water

- Inorganic
 - Salts dissolve in water and become ions
 NaCl → Na⁺ + Cl⁻
 H₂SO₄ → 2H⁺ + SO₄⁻²
 - Acids and bases dissociate depending on pH
- Organic (contain C, H, O and other elements)
 - Hydrophilic compounds associate with water
 - Ex. Organic acids and phenols dissociate depending on pH
 CH₃CO₂H → H⁺ + CH₃CO₂⁻
 - Hydrophobic compounds associate with soil or dissolved organic matter

Stoichiometry

Is this a balanced reaction?

$$C_6H_{12}O_6 + O_2 \rightarrow CO_2 + H_2O$$

To balance:

- 1. Balance moles of carbon on both sides
- 2. Balance moles of hydrogen on both sides
- 3. Balance moles of oxygen on both sides

$$\begin{array}{c} C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O \\ \\ \text{1 mole} \\ \text{180 g/mol} \end{array} \begin{array}{c} \text{6 moles} \\ \text{32 g/mol} \end{array} \begin{array}{c} \text{6 moles} \\ \text{44 g/mol} \end{array} \begin{array}{c} \text{6 moles} \\ \text{18 g/mol} \end{array}$$

Stoichiometric coefficient

Stoichiometry

Number moles of each element must balance on each side of reaction, and mass must balance.

Molecular weight:

C -12 g/mole

O - 16 g/mole

H-1 g/mole

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$$

 $1 \, mole(180 \, g \, / \, mol) + 6 \, moles(32 \, g \, / \, mol) = 6 \, moles(44 \, g \, / \, mol) + 6 \, moles(18 \, g \, / \, mol)$ $372 \, g = 372 \, g$

Molarity (M) = moles / liter

Converting mol/L to mg/L:

$$\frac{mg}{L} = \frac{mol}{L} \frac{g}{mol} \frac{10^3 mg}{g}$$

Stoichiometry

If we have 25 mg/L of glucose ($C_6H_{12}O_6$), how much oxygen (O_2) is required to combust glucose to CO_2 and H_2O ?

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$$

$$\frac{25 \, mg/L}{(180 \, g/mol)(1 \, mol)} = \frac{x \, mg/L \, O_2}{(6 \, mol)(32 \, g/mol)}$$
$$x = 26.7 \, mg/L$$

Chemical Equilibria

$$aA + bB \rightarrow cC + dD$$

$$K = \frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}}$$

K = equilibrium constant[] = molar concentration, mol/L

p notation

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Consider a compound "X"

pX = -log_{10} [X]

pH = -log_{10} [H^+]; where [H^+] is mol/L of H<sup>+</sup>

Similarly,

pOH = -log_{10} [OH^-]

pK = -log_{10} K, or K = 10^{-pK}
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For the dissociation of water: $H_2O \rightarrow H^+ + OH^-$, $K_w = 10^{-14} = [H^+][OH^-]$ At pH 7, $[H^+] = [OH^-] = 10^{-7} M$ At pH 10, $[H^+] = 10^{-10} M$ and $[OH^-] = 10^{-4} M$

Equivalent Weight

An equivalent of substance A reacts with an equivalent of substance B.

- lon charge: ion equivalents per volume of solution must be balanced.
 ∑(equivalents positive charge) = ∑(equivalents negative charge)
 an equivalent is a mole of charge
 CO₃²⁻ has an equivalence of 2 (2 equivalents of neg. charge/mol)
 CO₃²⁻ has an equivalent weight of 30 g/eq [60 g/mol x 1 mol/2 eq]
- 2) Acid/Base: one equivalent can react with one mole of protons (H+); or since one mole of H+ reacts with one mole of (OH -), one equivalent can react with one mole of OH -

Equivalent Weight (EW) =
$$\frac{\text{molecular weight}}{\text{n}} = \frac{\frac{\text{g}}{\text{mol}}}{\frac{\text{eq}}{\text{mol}}}$$

n= number of protons (H⁺) or hydroxyl ions (OH⁻) that can react per mole

Equivalent Weight for Acids & Bases

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H<sup>+</sup> Z = number of equivalents = 1 (1 eq acid per mole)
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 OH^- Z =1 (1 eq base per mole)

$$N = normality = \frac{mass conc. of substance}{equiv. wt. of substance}$$

Ex. 1 M
$$H_2SO_4 = 2$$
 N $H_2SO_4 = 2$ eq/L H_2SO_4 while 1 M NaOH = 1 N NaOH = 1 eq/L NaOH

Equivalent Weight "as" Another Compound

Commonly used in water analyses, e.g., hardness and alkalinity expressed "as CaCO₃"

 c_A = mass concentration of substance A If want to express c_A as mg/L of "X"

- 1) Convert c_A to (A), where (A) = eq of A per L (A) = c_A / EW_A EW_A = MW_A / Z_A
- 2) Multiply (A) by EW_X to get c_X

Eq. Wt. as Another Compound

A) As $CaCO_3$:

in water, $CaCO_3 \leftrightarrow Ca^{2+} + CO_3^{2-}$ equivalent weight of $CaCO_3 =$

$$EW_{CaCO_3} = \frac{100 \text{ g/mol CaCO}_3}{2 \text{ equivalents/mol}} = 50 \text{ g/eq}$$

Ex. Water has 75 mg/L of Mg²⁺. Express as CaCO₃

1) Convert c_A to (A)

$$EW_{Mg^{2+}} = \frac{24.3g/\text{mol}}{2\text{eq/mol}} = 12.15g/\text{eq}$$
$$(Mg^{2+}) = \frac{75 \text{ mg/L}}{12.15 \text{ g/eq}} \frac{1g}{10^3 \text{ mg}} = 6.173 \times 10^{-3} \text{ eq/L}$$

Eq. Wt. as Another Compound

2) Multiply (A) by EW_X
$$c_{\text{CaCO}_3} = (\text{Mg}^{2+}) (\text{EW}_{\text{CaCO}_3})$$

$$= (6.173 \times 10^{-3} \text{ eq/L}) (50 \text{g/eq}) = 0.308 \text{ g/L}$$

B) As nitrogen

Express 44.3 mg/L NO₃⁻ (nitrate) as N

$$EW_{NO_{3}^{-}} = \frac{62g/mol}{1eq/mol} = 62g/eq; \quad EW_{N} = \frac{14g/mol}{1eq/mol} = 14g/eq$$

$$(NO_{3}^{-}) = \frac{44.3mg/L}{62g/eq} \frac{1g}{10^{3}mg} = 7.14 \times 10^{-4} \text{ eq/L}$$

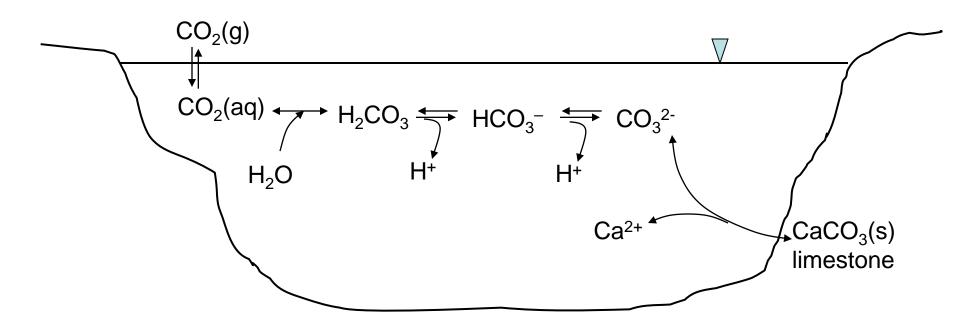
$$(7.14 \times 10^{-4} \text{ eq/L})(14g/eq) = 0.010g/L = 10mg/L \text{ as N}$$

$$= 10 \text{ mg/L NO}_{3}\text{-N}$$

Alkalinity

- Alkalinity is a measure of water's ability to buffer against addition of an acid, i.e., ability to resist change of pH upon addition of an acid
- Must understand carbonate system in water to understand alkalinity

Carbonate System



Carbonate Chemistry

H₂CO₃ is carbonic acid When carbonic acid loses a proton (1st dissociation):

$$H_2CO_3 \Leftrightarrow H^+ + HCO_3^ K_{a1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = 10^{-6.3}, pK_{a1} = 6.3$$

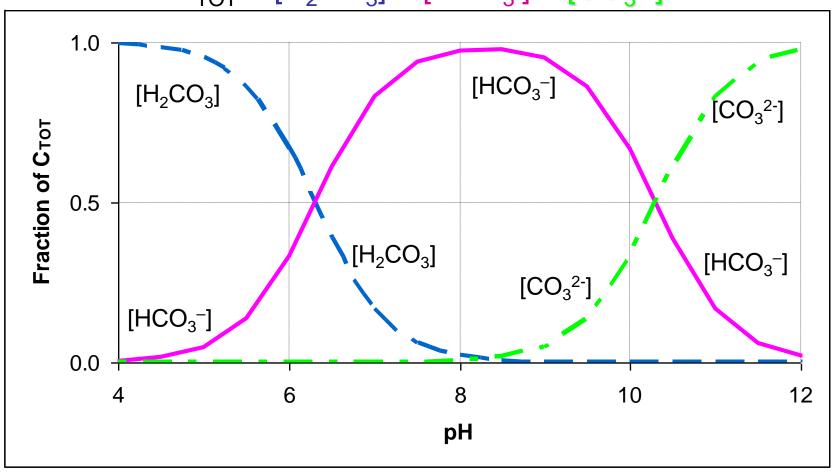
When bicarbonate (an acid) loses a proton (2nd dissociation):

$$HCO_{3}^{-} \Leftrightarrow H^{+} + CO_{3}^{2-}$$

$$K_{a2} = \frac{\left[H^{+}\right]\left[CO_{3}^{2-}\right]}{\left[HCO_{3}^{-}\right]} = 10^{-10.3}, pK_{a2} = 10.3$$

Carbonate Chemistry

$$C_{TOT} = [H_2CO_3] + [HCO_3^-] + [CO_3^2]$$



Alkalinity

Alkalinity = sum of equivalents of all species that can neutralize an acid

Alk (eq/L) =
$$(HCO_3^-)+(CO_3^{2-})+(OH^-)-(H^+)$$

Determine alkalinity by titrating sample with acid of a known normality to a pH of ~4.5, the point when all species are converted to carbonic acid.

Alkalinity

Ex. Assume a 200 mL sample of water takes 8.7 mL of 0.02N H_2SO_4 to reach a pH of 4.5. Calculate alkalinity of sample as mg/L CaCO₃

Alk (meq/L) =
$$\frac{(0.02 \text{ eq/L})(8.7 \text{ mL})}{200 \text{ mL}}$$
 = $8.7 \times 10^{-4} \text{ eq/L}$
 $(8.7 \times 10^{-4} \text{ eq/L})(50 \text{ g/eq})(10^3 \text{ mg/g})$ = 43.5 mg/L as $CaCO_3$
EW_{CaCO3}

Water Contaminants

Important Classes of Contaminants

- Oxygen depleting wastes (organic compounds)
- Nutrients (nitrogen, phosphorous)
- Salts
- Thermal pollution
- Inorganic Compounds
 - Heavy metals (Pb, Cu, Cr, Cd, As)
 - Nitrate
- Microbiological
 - Bacteria, viruses, protozoa, worms
- Pesticides (synthetic organic compounds)
- Volatile organic compounds

Oxygen depleting wastes

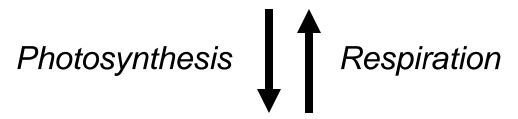
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organic carbon + O_2 + bacteria \rightarrow CO_2 + H_2O + more bacteria
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if oxygen is depleted in natural water, most aquatic life will die (Ex. fish kills)

Redfield equation for lake algal growth

$$106 \text{ CO}_2 + 16 \text{ NO}_3^- + \text{HPO}_4^{2-} + 122 \text{ H}_2\text{O} + \text{H}^+$$

(+ trace elements and energy)



 ${C_{106}H_{263}O_{113}N_{16}P_1} + 138 O_2$ algal protoplasm

Redfield, A.C. et al. (1966) In The Sea, Vol 3, Wiley, NY.

- Nutrients in surface waters
 - Nitrogen and phosphorus of primary concern
 - In general, bacteria need molar ratio of C:N:P of 100:10:1 to grow
 - If the C:N:P in a lake is 100:10:0.2, then P is limiting and any addition of P can stimulate algal growth:

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CO_2+N+P+light+algae \rightarrow more algae \rightarrow die/decompose \rightarrow organic carbon + <math>O_2 \rightarrow bacterial growth
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- Algal blooms can release
 - Cyanotoxins harmful to animals and humans
 - Taste and odor cmpds: geosmin and 2-methylisoborneol (MIB)

Salts

- Measured as Total Dissolved Solids (TDS)
- High salt concentration can damage crops, reduce soil's permeability
- In Wyoming, coal bed methane production produces large volumes of high TDS water
- In drinking water, recommended that TDS < 500 mg/L

Thermal Pollution

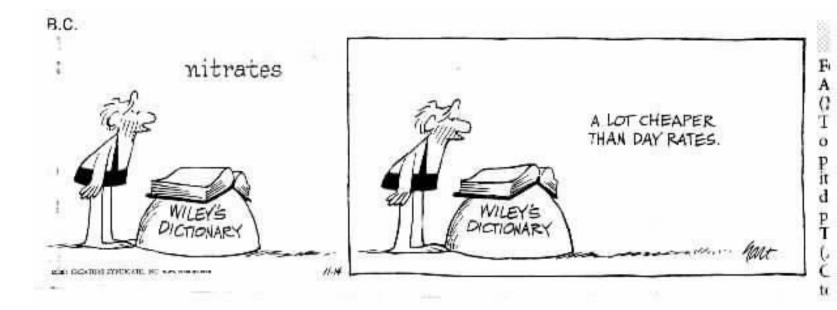
- Primarily cooling water from power plants and other industries
 - ↑Temperature, ↓Dissolved oxygen
 - ↑Temperature, ↑bacterial growth, ↓O₂

Ex. 1950s Hanford used Columbia River water to cool the reactor core of their nuclear power plant which caused fish kills in river downstream of plant effluent

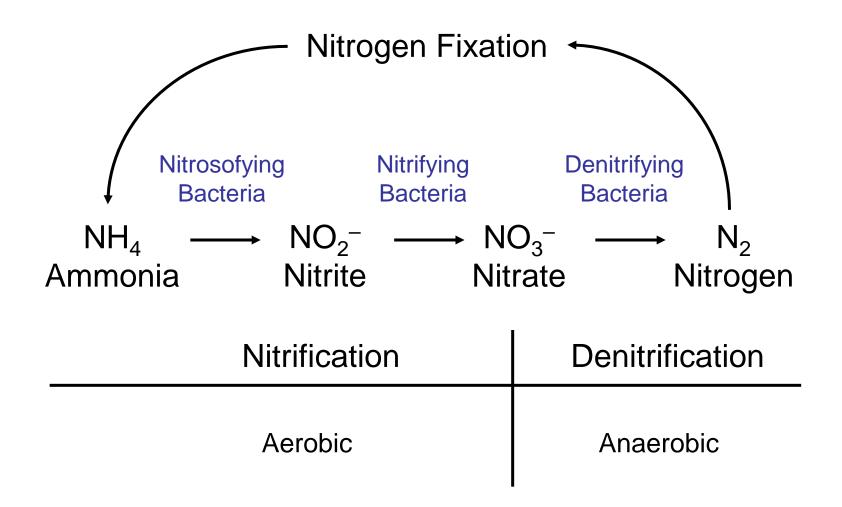
(Becker & Gray, 1992, Environ Monit Assess, 22:2:137)

Major Regulated Constituents In Drinking Water

- Microbial Contaminants
- Disinfection By-products
- Disinfectants
- Inorganic Compounds
- Organic Compounds
- Radionuclides



Simplified Nitrogen Cycle



Sources of Nitrates in Water

- Septic systems (on-site waste water disposal systems)
- Runoff and leaching from agricultural land, residential lawns and gardens (nitrogenous fertilizers)
- Animal wastes (ranging from confined animal feeding operations to horses in the pasture)

Health Effects of Nitrates-the Conventional Viewpoint

- Methemoglobinemia
 - In humans, nitrate (NO₃⁻) is reduced to nitrite (NO₂⁻)
 - Nitrite binds with hemoglobin to form methemoglobin, a substance that cannot bind and transport oxygen
 - Methemoglobinemia effects babies and pregnant women
- Maximum nitrite and nitrate concentrations allowed in drinking water are 1 mg/L NO₂-N and 10 mg/L NO₃-N

Health Effects of Nitrates: New Information

- Recent study indicated an increase in bladder cancer in women due to nitrates at levels <10 mg/L
- Women exposed to average nitrate-N level of 2.46 mg/L were 2.83 times more likely to develop bladder cancer than those with average nitrate-N less than 0.36 mg/L

Weyer PJ*, et al. 2001. **Municipal drinking water nitrate level and cancer risk in older women: the lowa Women's Health Study.** Epidemiology 12(3):327-38.

*Center for Health Effects of Environmental Contamination, University of Iowa

Health Effects of Nitrates – New Information

- In combination with atrazine and aldicarb, nitrate was found to cause endocrine, immune and behavior changes in laboratory animals*
 - Doses were at the drinking water MCLs for these compounds!
 - Little work has been done to asses the health effects of mixtures of compounds
 - *Porter, WP et al. 1999. Endocrine, immune, and behavioral effects of aldicarb (carbamate), atrazine (triazine) and nitrate (fertilizer) mixtures at groundwater concentrations. Toxicol. Ind. Health, 15: 133-150.

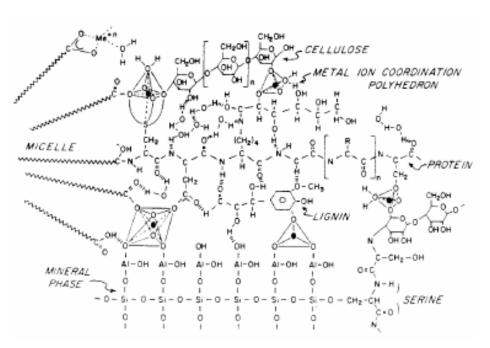
Chlorine and Drinking Water Disinfection Byproducts (DBPs)

- Chlorine is a common disinfectant in drinking water
- Excellent oxidizing disinfectant
- Inactivates most bacteria, viruses and certain protozoa
- Sufficient chlorine is added to maintain a concentration greater than 0.2 mg/L in the distribution pipes

Chlorine Produces Disinfection Byproducts (DBPs)

- Chlorine reacts with natural organic matter, found in all water, to form chlorinated organic compounds
- Chlorinated organic compounds are termed "disinfection byproducts" (DBPs)
- Most DBPs are regulated based on their suspected human carcinogenicity (known carcinogenicity to laboratory animals)

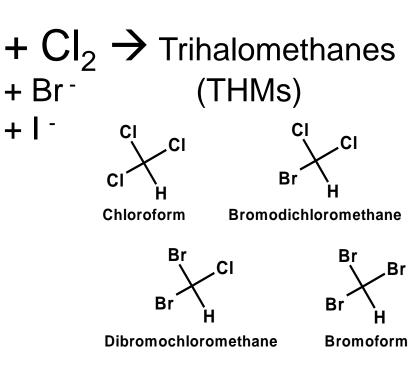
DBPs in Drinking Water



Natural Organic Matter

found in water and soil

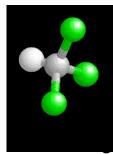
(structure proposed by Kleinhempel, D. *Albrecht Thaer Arch.*, 1970, **14**:3)



...and other DBPs

Chlorine and DBPs

- Regulated DBPs when chlorine is used
 - Trihalomethanes(includes chloroform)



- Haloacetic acids
- Primary reason for DBP regulations has been based on carcinogenicity of compounds

Regulated DBPs

- Trihalomethanes
 - Chloroform
 - Bromodichloromethane
 - Dibromochloromethane
 - Bromoform
- MCL 80 µg/L THM4 for annual average

- Haloacetic acids (5)
 - Monochloroacetic acid
 - Dichloroacetic acid
 - Trichloroacetic acid
 - Bromoacetic acid
 - Dibromoacetic acid
- MCL 60 µg/L HAA5 for annual average

DBPs and Adverse Reproductive Outcomes

- Epidemiologic evidence that chlorine DBPs, primarily trihalomethanes, are related to adverse reproductive outcomes
 - Spontaneous abortion Waller et al., 2001. J. Exposure Anal. Environ. Epidemiol.; Swan et al. 1998. Epidemiol.;
 - Stillbirth Dodds and Allen, 2000. Environ. Health Perspect.
 - Small for gestational age, central nervous system defects, oral cleft defects and cardiac defects Bove et al., 1995. Amer. J. Epidemiol.
 - Neural tube defects Klotz and Pyrch, 1999. Epidemiol.

Study says pregnant women may be at risk from tap water

WASHINGTON (AP) —
Millions of Americans have
been drinking tap water contaminated with chemical byproducts from chlorine that are far
more than what studies suggest
may be safe for pregnant
women, two environmental
groups say in a new study.

Chlorine is commonly used to disinfect drinking water. When it is added to water that contains organic matter such as runoff from farms or lawns, however, it can form compounds such as chloroform that can cause illness.

The study released Tuesday by the Environmental Working Group and Public Interest Research Groups identified areas that may have increased health risks including miscarriage, neural tube defects and reduced fetal growth from women drinking chlorination byproducts.

"By failing to clean up rivers and reservoirs that provide drinking water for hundreds of millions of Americans, EPA and the Congress have forced water utilities to chlorinate water that is contaminated with animal waste, sewage, fertilizer, algae and sediment," the report says.

Jane Houlihan, EWG's research director, said the report also shows how that cleanup failure has "a direct impact on human health." Pregnant women need to drink plenty of water, she said, but they can reduce their exposure to potential risks through simple measures such as home filters and purchasing bottled water.

One expert on environmental health cautioned that the link between the byproducts and pregnancy risks is suggestive, not conclusive.

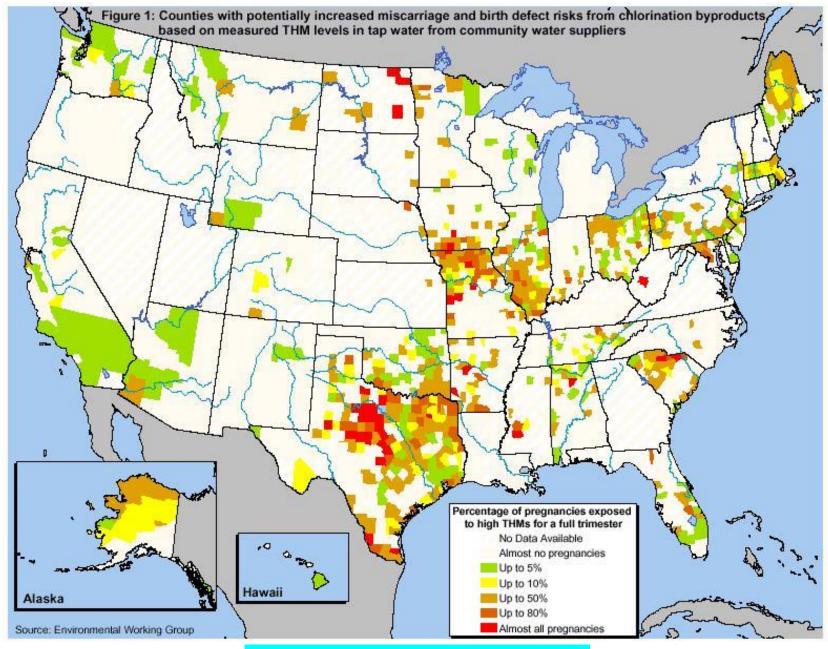
Still, if the pregnancy studies are proved, millions could be at risk, said Dr. Robert Morris, an environmental epidemiologist at Tufts University School of Medicine in Boston.

"That body of literature isn't necessarily conclusive but people ought to be aware of it," Morris said. "It's pretty clear that some of these compounds can be pretty bad actors. The fact that these levels are as high as they are is certainly something to be concerned about."

The environmental groups combed water quality records in 29 states and the District of Columbia and matched them with various research into birth defects and miscarriages conducted by state and federal agencies and universities.

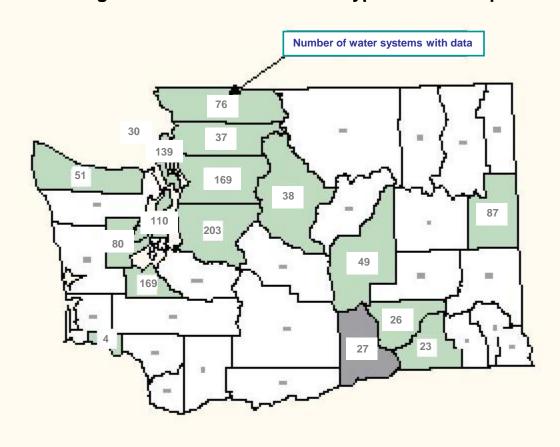
The groups said the places statistically most at risk due to chlorination byproducts were those that are populous, lacked buffers from urban sprawl and were downstream from agricultural sites. But women in small towns generally face twice the risk from drinking high levels of the byproducts, Houlihan said.

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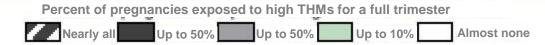


Source: EWG/WashPIRG Foundation

Washington Counties with Potentially Elevated Birth Defect and Miscarriage Risks from Chlorination Byproducts in Tap Water



Source: EWG/WashPIRG Foundation



DBP Health Effects – New Information

- Previous study linking high THM levels to high occurrence of preterm birth (spontaneous abortion) was poorly conducted
- New study* that followed pregnant women in areas with varying levels of DBP exposure
 - Fetal Growth
 - THMs > MCL were associated with low birth weight
 - Duration of Gestation
 - No association of preterm birth with DBP exposure

^{*}Hoffman et al. 2008, Epidemiology, 19(5)729.

Chlorine Residual in Distributed Water

- Long contact time of water with chlorine in distribution system is where DBPs are formed
- U.S. uses residual disinfectant in distributed water after primary disinfection (primary disinfection kills bacteria, viruses and *Giardia*)
- Many European countries do not maintain a residual disinfectant concentration
- U.S. view is that residual disinfectant protects against unexpected contamination

Chloramine Residual in Distributed Water

- Chloramines are formed by combining ammonia (NH₃) and chlorine (Cl₂)
- Chloramines are less reactive than chlorine
 - Not as strong a disinfectant as chlorine
 - Form less DBPs
 - Persist in distribution system longer, thus can be more effective against biofilms
- Chloramines have disadvantages
 - Must be removed from water used for dialysis and aquariums, or before discharge to a waterway
 - Can stimulate nitrification reactions in biofilm
 - Iodinated DBPs if source contains iodide

Is Chlorine Safe?

- It's a matter of balancing risks
- Chlorine used as a disinfectant in water is major reason developed countries enjoy lack of waterborne disease
- Its reaction to form DBPs can be minimized by treatment technologies
 - Example, remove organic precursors using biological treatment techniques

Other Regulated DBPs

- Bromate, MCL 0.01 mg/L
 - By-product when water containing higher concentrations of bromide is ozonated
 - Carcinogenic
- Chlorite, MCL 1.0 mg/L
 - A degradation product when chlorine dioxide
 (CIO₂) used for disinfection
 - Anemia, affects nervous system

Disinfectants

- Maximum concentration of disinfectants regulated to minimize formation of disinfection byproducts
- Disinfectants that are regulated:
 - Chlorine
 - Chloramines

Total at 4.0 mg/L as Cl₂

- Chlorine dioxide, at 0.8 mg/L CIO₂

US EPA DBP Occurrence Study

50 target DBPs monitored in 12 US Drinking Water Treatment Plants: Formation and Removal

Krasner et al. (2006) Environ Sci Technol 40(23):7175-7185

12 Sampling Sites in EPA Regions



US EPA Study

- Paired WTPs
 - Same source water (river or groundwater)
 - Contrasting treatment trains
- Target Analytes
 - Regulated THMs and HAAs
 - Unregulated DBPs
 Ex. Halogenated Furanones*, analogues of Mutagen X (MX)
- Sampling Protocol
 - Samples collected from locations in water treatment plant: before and after both chlorination and filtration

^{*}Onstad, Weinberg & Krasner (2008) Environ Sci Technol 42(9):3341–3348

Halogenated Furanone Structures

CI

Water Quality & Treatment

Utility	TOC (mg/L)	TOC Removal	Bromide (mg/L)	pН	Total Cl ₂ dose (mg/L)
Plant 1	4.5	51%	0.12	9.1	3.6
Plant 2	4.5	33%	0.12	9.1	5.7
Plant 5	10.5	67%	0.06	6.2	3.5
Plant 6	9.5	59%	0.06	6.7	4.1

Utility (EPA Region)	Treatment Regime
Plant 1 (9)	03 - sand - Cl2 - NH2Cl
Plant 2 (9)	Cl2 - sand - NH2Cl
Plant 5 (4)	03 - GAC - Cl2
Plant 6 (4)	ClO2 - Cl2 - sand - NH2Cl

MX-analogues in Plant Effluents

#	Treatment	ΜΧ (μg/L)	B MX (μg/L)	MCA (μg/L)
1	O ₃ /Sand/Cl ₂ /NH ₂ Cl	<0.02	0.03	0.03
2	Cl ₂ /Sand/NH ₂ Cl	0.07	0.48	0.10
5	O ₃ /GAC/Cl ₂	<0.02	0.03	0.31
6	CIO ₂ /CI ₂ /Sand/NH ₂ CI	0.81	<0.02	80.0

THMs & HAAs in Plant Effluents

#	Treatment	THM4 (μg/L)	HAA9 (μg/L)
1	O ₃ /Sand/Cl ₂ /NH ₂ Cl	9	8
2	Cl ₂ /Sand/NH ₂ CI	43	55
5	O ₃ /GAC/Cl ₂	33	38
6	CIO ₂ /CI ₂ /Sand/NH ₂ CI	26	48

Halogenated Furanones (MX sum)

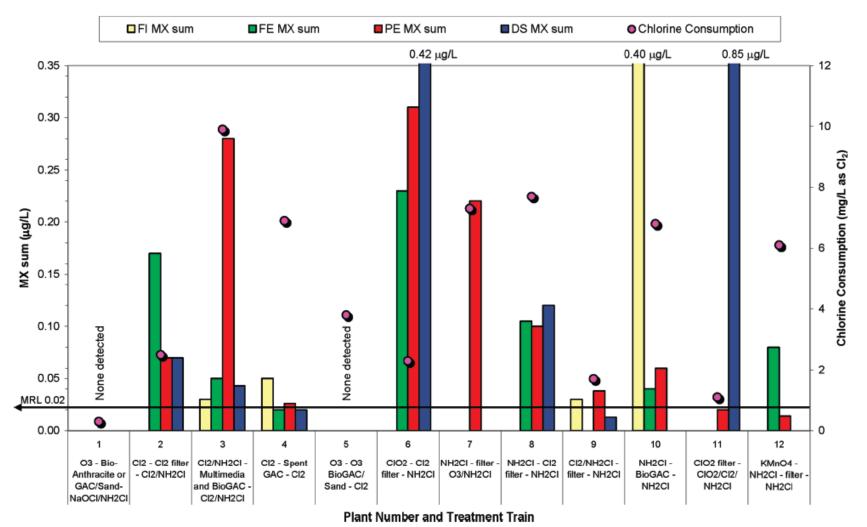


FIGURE 2. Formation and stability of MX in U.S. drinking water as a function of chlorine consumption (shaded circle). $MX_{sum} = MX + ZMX + EMX$. Plants 1, 2, 5, 6, 7, 8, 11, and 12 from warm season; Plants 3, 4, 9, and 10 from cold season. FI = filter influent, FE = filter effluent, PE = plant effluent, DS = distribution system (residence times vary, see Supporting Information Table S4).

Onstad, Weinberg & Krasner (2008) Environ Sci Technol 42(9):3341–3348

Summary of Occurrence Study

- Ozonation + Biological Filter (GAC or other) removed precursor material
- CIO₂ + CI₂
 - MX, red-MX, MCA, BMX Filtered by GAC
- $Cl_2 + NH_3$
 - MX, BMX, MCA Filtered by GAC
- NaOCI or Cl₂
 - MX, MCA, BEMX Filtered by GAC



- American Water Works Association
- Drinking water quality is a global issue that requires constant research, evaluation, scrutiny, and advancement from industry leaders. Innovation in contaminant detection, new regulatory requirements, potential health issues, and increased security concerns are creating challenges that must be faced head-on.
- Water professionals around the world know that AWWA's Water Quality Technology Conference and Exposition is the event of the year for providing answers about quality water in a high-tech environment.
- Student Registration: \$60 for members by Oct 16 and \$90 for members/non-members from Oct 17.
- www.awwa.org/conferences/wqtc