

# **Analytical and Environmental Chemistry**

**Water Chemistry and Water Treatment**

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Room 145  
School of Chemistry**

**CH205 (and CH306)**

# Attention

The lecture notes for the rest of my course will be available at the

[SCHOOL OF CHEMISTRY](#) website

Simply click on the [COURSES](#) icon

Find [CH205](#) and [Leigh Jones](#)

Wednesday's lecture notes will be available Monday lunchtime

# Water Chemistry: 2 Lectures

*Lecture 1 will cover:*

## **Redox Chemistry**

- Dissolved Oxygen
- Oxygen Demand
- Anaerobic Decomposition
- Sulfur Compounds
- Nitrogen Compounds
  - 'Fool's Gold'

*Lecture 2 will cover:*

## **Acid-Base Chemistry**

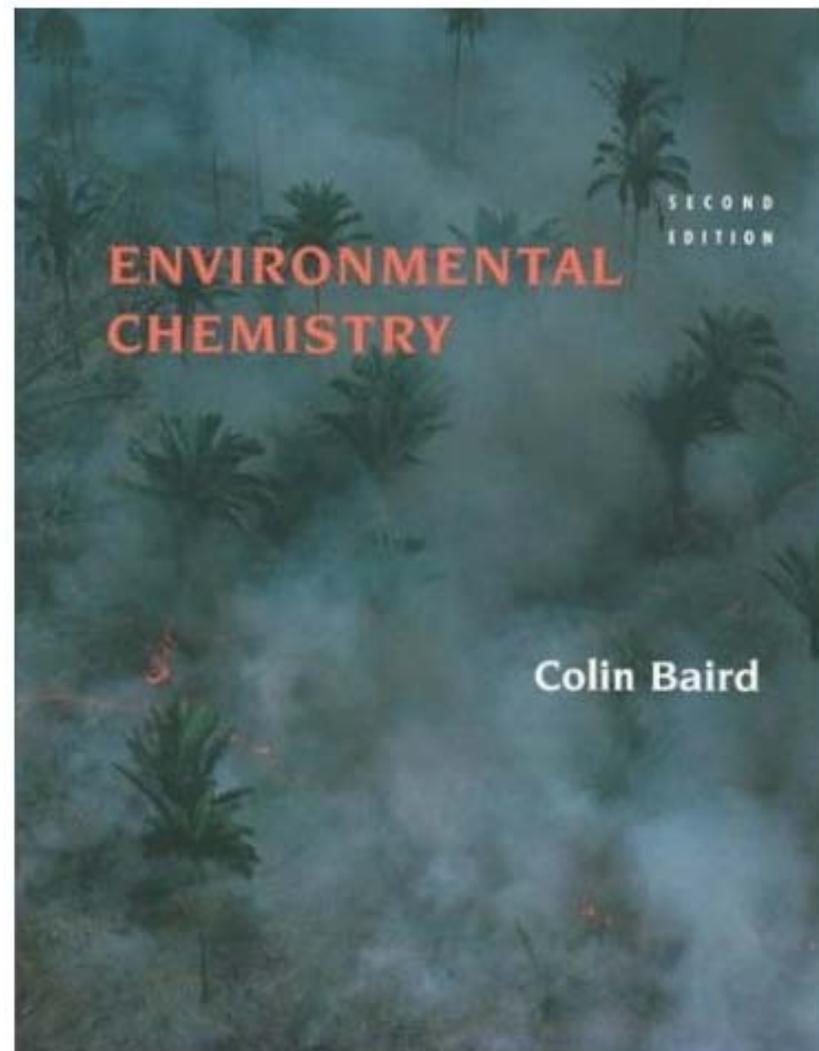
- Carbonate System
- Water Equilibrium with Solid Calcium Carbonate
- Water Equilibrium with  $\text{CaCO}_3$  and Atmospheric  $\text{CO}_2$
- Measured Ion Concentrations in Natural and Drinking Water
- Alkalinity Indices
- Hardness Index
- Aluminium in Natural Waters

## *The recommended text:*

Chapter 7 covers **Toxic Heavy Metals**

Chapter 8 covers **Oxidation-Reduction in Natural Waters**

Chapter 9 covers **Acid-Base Chemistry in Natural Waters**



**Colin Baird, Environmental Chemistry, 2<sup>nd</sup> Edition, W.H. Freeman and Company, New York, Chapters 7, 8 and 9**

# Lecture 1: Outcomes

*We will be discussing the Redox Chemistry of natural water and will include:*

- *Background to Water Chemistry*
- *Dissolved Oxygen*
- *Oxygen Demand*
- *Anaerobic Decomposition*
- *Sulfur Compounds*
- *Nitrogen Compounds*
- *'Fool's Gold'*

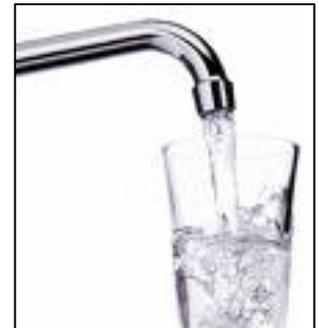


*'Fool's Gold'*

# Background to Water Chemistry

## *Some surprising facts.....*

- 97% of the world's water is seawater and thus unsuitable for drinking and agricultural purposes.
- Three quarters of the fresh water is trapped in glaciers and ice-caps.
- Lakes and rivers are the main sources of drinking water; they constitute less than 0.01% of total water supply.
- It is important to understand the types of chemical activity within natural waters, and how chemistry can be applied to purify water (**to drink it safely**).



# Groundwater (1)

- The majority of **FRESH WATER** on earth lies **UNDERGROUND**
  - **HALF** of it at depths of over a **KILOMETER !!**

**Groundwater** is term for water located beneath the ground surface  
(described fully on next slide)

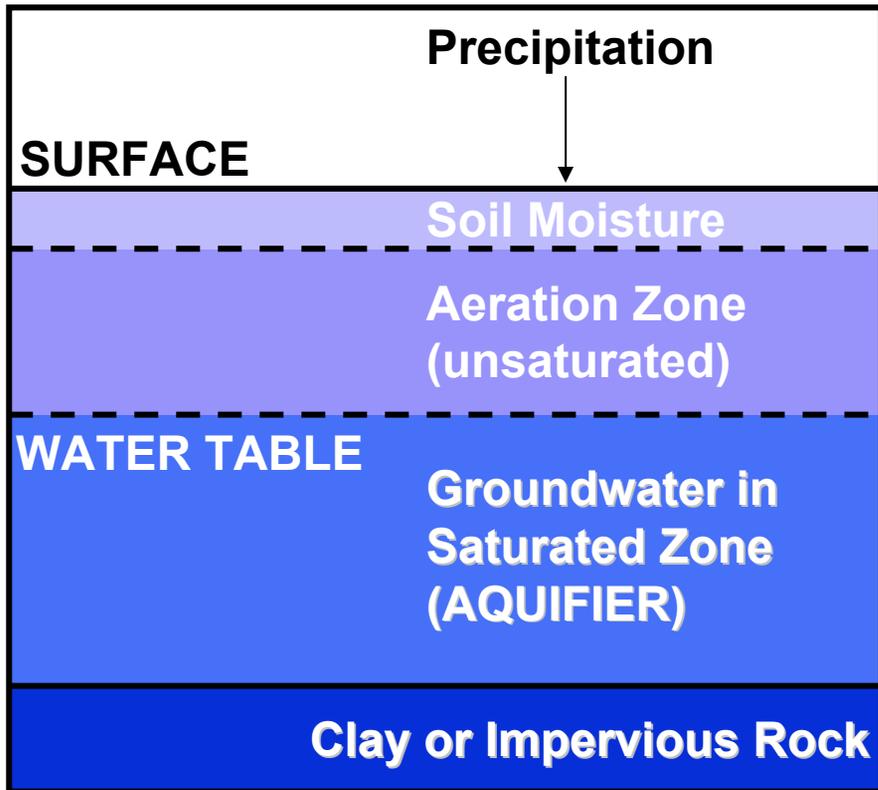
Groundwater is recharged from, and eventually flows to the surface naturally

Natural discharge often occurs at **springs** and can form **wetlands** (i.e. swamps, marches and bogs)

Groundwater is also often withdrawn for **agricultural**, **municipal** and **industrial** use by constructing and operating extraction **wells**.

The study of the distribution and movement of groundwater is **hydrogeology** also called groundwater **hydrology**

# Groundwater (2)



- Groundwater is fresh water in the saturated zone.
  - Source of groundwater is precipitation that falls onto the surface and filters down.
- Top of the groundwater region is called the **WATER TABLE**.
  - It sometimes occurs right at the surface of the soil, a phenomenon that gives rise to swamps.
  - When the water table lies above the soil it gives rise to lakes and streams.

*If groundwater is contained, at lower depths, in a layer of clay or impervious rock then it constitutes a permanent reservoir (or underground lake), called an **AQUIFIER**. This water can be extracted for drinking water.*

# Groundwater (3)

*Groundwater is used an important source of drinking water:*

- It is considered to be a pure form of water due to its **FILTRATION** through soils and its long residence time underground.
- It is said to contain less natural organic matter and microorganisms than water from lakes and streams

*Groundwater extracted from **AQUIFIERS** (or wells) is the main supply for almost **HALF** the population of North America*

*In Europe the % of public drinking water extracted from **AQUIFIERS** ranges from:*

Denmark  
Austria  
Italy

} *almost 100%*

Germany  
Netherlands  
Switzerland

} *approx. 66%*

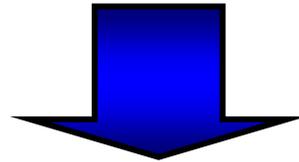
Spain  
U.K  
Eire } *< 33%*

# Redox Chemistry in Natural Waters

## DISSOLVED OXYGEN

By far the most important *OXIDISING AGENT* in natural waters is *DISSOLVED OXYGEN (O<sub>2</sub>)*

It is found that the concentration of *DISSOLVED OXYGEN* in water is *SMALL*

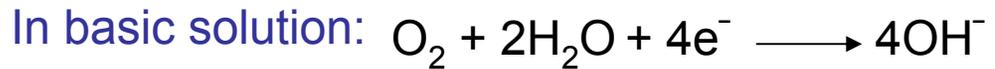
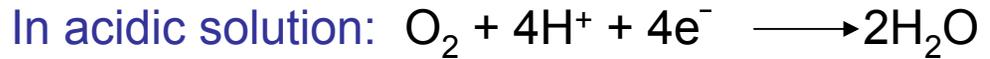


**PRECARIOUS situation in terms of ECOLOGY**  
(i.e. Fish need oxygen)

# Redox Chemistry in Natural Waters

## DISSOLVED OXYGEN

Note:  $O_2$  is reduced to  $O^{2-}$ ,  
 $H^+$  is oxidised to  $H_2O$



- In dry air the partial pressure of oxygen,  $PO_2$ , is 0.21 atm and so the solubility of  $O_2$  is  $8.7 \text{ mg L}^{-1}$ .
- Solubilities of gases increase with decreasing temperature, i.e. the amount of  $O_2$  that will dissolve at  $0^\circ\text{C}$  is greater than at  $35^\circ\text{C}$ .
- Rivers or lakes that have been artificially warmed can be considered to have undergone **THERMAL POLLUTION**.

*(Operation of electric power plants often results in thermal pollution as they draw in cold water from a river for cooling purposes and return the warmed water to its source.)*

# Redox Chemistry in Natural Waters

## OXYGEN DEMAND:

Dissolved oxygen in water is consumed by the oxidation of dissolved ammonia ( $\text{NH}_3$ ) and ammonium ion ( $\text{NH}_4^+$ ) to form the nitrate ion ( $\text{NO}_3^-$ ).

*Occurs in basic  
(alkaline)  
conditions*



*These  $\text{NH}_3$  and  $\text{NH}_4^+$  species are present in the water as a result of biological activity*

# Redox Chemistry in Natural Waters

## OXYGEN DEMAND

- The most common substance oxidised by oxygen in water is **ORGANIC MATTER OF BIOLOGICAL ORIGIN**
- Such organic matter (**such as dead plant material like polymerised carbohydrate below**), is oxidised by dissolved oxygen.



*(General formula for a polymerised carbohydrate)*

- Water is **AERATED** when flowing through shallow streams and rivers....however 
- Stagnant water and water near the bottom of a deep lake is usually completely depleted of oxygen due to its reaction with organic matter.

# Quantifying Oxygen Demand in Water Samples

- **BIOCHEMICAL OXYGEN DEMAND (BOD)**: Capacity of organic matter in a sample of natural water to consume oxygen. Or more specifically:

**Measures how fast bioorganisms use up oxygen in a sample of water**

*Evaluated experimentally by determining the concentration of dissolved  $O_2$  at the beginning and end of a period, usually of 5 days, in which a sealed water sample is maintained in the dark at a constant temperature ( $\sim 20\text{-}25^\circ\text{C}$ ).*

Typical BOD values for:

Unpolluted surface water (taken from US data)  $\rightarrow$  **< 1mg  $O_2$ (aq) per Litre**

Sewage:  $\longrightarrow$  **SEVERAL HUNDRED mg of  $O_2$ (aq) per Litre of water**

# Other ways to quantifying Oxygen Demand

- **CHEMICAL OXYGEN DEMAND (COD):** Faster determination of oxygen demand in a water sample, than BOD.  
(also indirectly measured amount of organic matter in the water sample)

Dichromate ion,  $\text{Cr}_2\text{O}_7^{2-}$ , is dissolved in sulfuric acid:



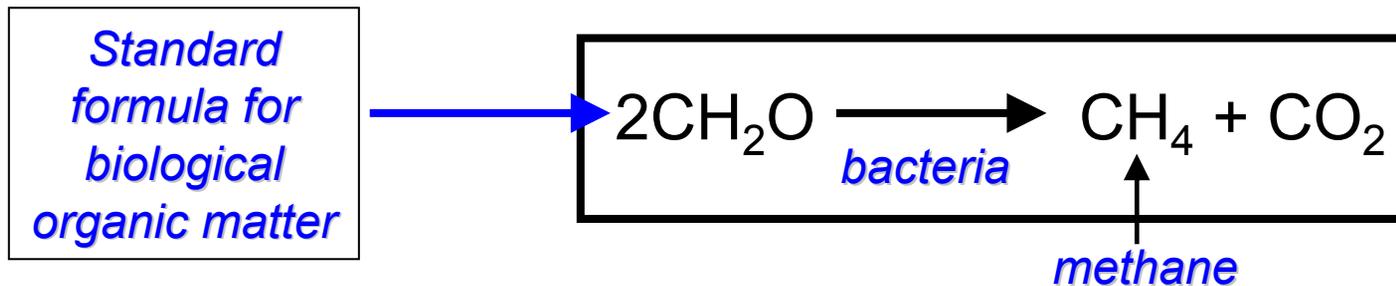
This forms powerful oxidising agent  
It is then used to ascertain **COD values**

Problems with the COD index: Dichromate oxidizes substances that would not normally be oxidised by  $\text{O}_2$  in the determination of the BOD. The COD value for a water sample as a rule is slightly greater than its BOD value.

- **TOTAL ORGANIC CARBON (TOC):** used to characterise the dissolved and suspended organic matter in raw water. Groundwater usually has a value of  $\sim 1 \text{ mg L}^{-1}$  (1 ppm).
- **DISSOLVED ORGANIC CARBON (DOC):** used to characterise only organic material that is dissolved. Surface water usually has a value of 5 ppm.

# Anaerobic Decomposition of Organic Matter

- Under oxygen free (anaerobic) conditions dissolved organic matter will decompose if appropriate bacteria are present:



- Such anaerobic conditions are common in SWAMPS and at the bottom of deep lakes
- The Methane ( $\text{CH}_4$ ) produced in this process bubbles up towards the surface of the swamps and is the reason that methane used to be known as 'marsh' or 'swamp' gas

*This is an example of a **fermentation** reaction; both the oxidising and the reducing agents are organic materials.*

# Anaerobic Decomposition of Organic Matter in Natural Waters

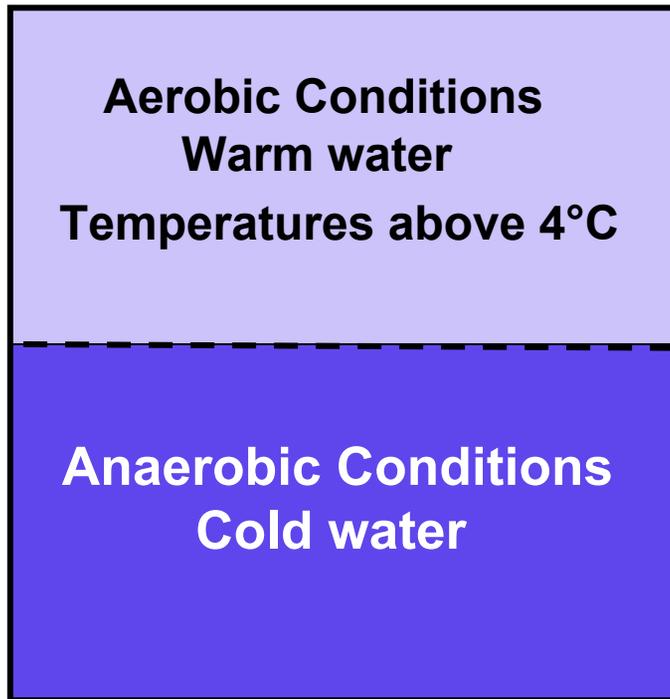
- Anaerobic conditions are reducing conditions in the chemical sense:

*Insoluble  $Fe^{3+}$  compounds present in sediment at the bottom of lakes are converted to soluble  $Fe^{2+}$  compounds, which can then dissolve:*



- It is possible to find **aerobic** and **anaerobic** conditions in different parts of a lake at the same time.
- This can occur if there is a stable stratification of distinct layers (**usually occurs in summertime**).

# Anaerobic Decomposition of Organic Matter

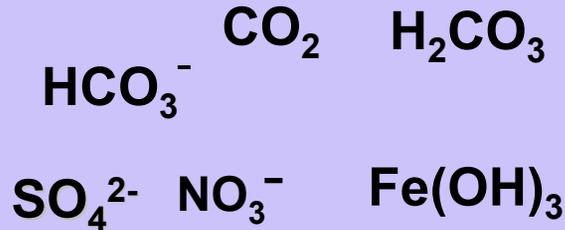


- Water at top of lake is heated by absorption of sunlight by biological matter.
  - Below that the level of penetration (of sunlight) is low and water remains cold
  - Warm water is **less dense** than cold water so upper layer 'floats' on top of lower layer. Little mixing occurs.
- The top layer usually contains near-saturation levels of dissolved oxygen, allowing aerobic conditions (due to close contact with air and O<sub>2</sub> production of algae via photosynthesis).
  - Near the bottom the water is oxygen depleted as there is no contact with air and O<sub>2</sub> is consumed as biological material decomposes, thus anaerobic conditions.
- (Elements therefore exist in their most reduced forms (see next slide for examples).)

# Anaerobic Decomposition of Organic Matter

**Aerobic Conditions**  
**Warm water**

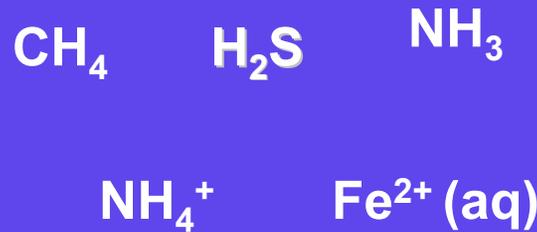
Temperatures above 4°C



Here Elements exist in their **most oxidised forms:**

Carbon as **CO<sub>2</sub>, H<sub>2</sub>CO<sub>3</sub>, HCO<sub>3</sub><sup>-</sup>**  
Sulfur as **SO<sub>4</sub><sup>2-</sup>**  
Nitrogen as **NO<sub>3</sub><sup>-</sup>**  
Iron as Insoluble **Fe(OH)<sub>3</sub>**

**Anaerobic Conditions**  
**Cold water**



Here elements exist in their **most reduced forms:**

Carbon as **CH<sub>4</sub> (methane)**  
Sulfur as **H<sub>2</sub>S (Hydrogen sulfide)**  
Nitrogen as **NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup>**  
Iron as soluble **Fe(OH)<sub>2</sub>**

*Stratification: Figure showing typical forms of the main elements present*

- In winter the top layer of water is cooled by the passing air and so the oxygen-rich layer becomes more dense than the layer below it, which induces mixing between the layers. The bottom of a lake in winter is therefore usually aerobic.

# Sulfur Compounds in Natural Water

- Sulfur can exist in many oxidation states from -2 state, such as that found in **hydrogen sulfide gas (H<sub>2</sub>S)**, to the highly oxidised +6 state of sulfur in **sulfuric acid (H<sub>2</sub>SO<sub>4</sub>)**.

Oxidation State of Sulfur	-2	-1	0	+4	+6
<b>Aqueous Solutions and Salts</b>	H <sub>2</sub> S HS <sup>-</sup> S <sup>2-</sup>	S <sub>2</sub> <sup>2-</sup>		H <sub>2</sub> SO <sub>3</sub> HSO <sub>3</sub> <sup>-</sup> SO <sub>3</sub> <sup>2-</sup>	H <sub>2</sub> SO <sub>4</sub> HSO <sub>4</sub> <sup>-</sup> SO <sub>4</sub> <sup>2-</sup>
<b>Gas Phase</b>	H <sub>2</sub> S			SO <sub>2</sub>	SO <sub>3</sub> → <i>Major component to acid rain</i>
<b>Molecular Solids</b>			S <sub>8</sub>		

SH<sup>-</sup> = thiolate anion

Common Oxidation States of Sulfur

(-SH functional group = THIOL)

- Organic and bioorganic molecules (such as amino acids) contain **sulfur**. When these substances **decompose anaerobically**, hydrogen sulfide and other gases containing sulfur are released, e.g. **methanethiol (CH<sub>3</sub>SH)** and **dimethyl sulfide (CH<sub>3</sub>SCH<sub>3</sub>)**. These gases are what gives swamps their unpleasant smell.

# Sulfur Compounds in Natural Water

- *Hydrogen Sulfide is oxidised in air to sulfur dioxide, SO<sub>2</sub>, and then fully to sulfuric acid (or sulfate salts):*



- *Bacteria can also oxidise H<sub>2</sub>S to the sulfate ion (SO<sub>4</sub><sup>2-</sup>), which is then used by anaerobic bacteria as the oxidising agent in the conversion of organic matter to CO<sub>2</sub>. The sulfate ions are reduced in the process to sulfur:*



*Sulfate anion is reduced*

*Polymeric carbohydrate (representing organic matter)*

*elemental Sulfur from reduction of SO<sub>4</sub><sup>2-</sup> anions (occurs when **conc. of O<sub>2</sub> is low**, otherwise SO<sub>4</sub><sup>2-</sup> will not undergo reduction to Sulfur)*

# Acid Mine Drainage

Characteristic reaction of Groundwater (which is by definition not well aerated):

- *When Groundwater reaches the surface,  $O_2$  starts to dissolve into the water.*
- *High levels of soluble  $Fe^{2+}$  are oxidised to  $Fe^{3+}$  and an insoluble orange brown precipitate of  $Fe(OH)_3$  deposits out of the water.*

*In redox terms...*



*Insoluble Fe(III) hydroxide*

*Overall reaction:*

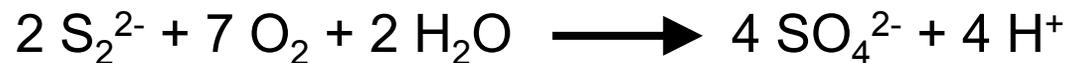


- Outflow of acidic water from metal and coal mines (usually abandoned mines)



- Normally  $\text{FeS}_2$  ('Iron Pyrite' a.k.a 'Fool's Gold') is a stable insoluble component of underground rocks (**when not in the presence of air**).
- However when exposed to air it becomes partially solubilised upon oxidation.

The disulfide ion,  $\text{S}_2^{2-}$  (-1), is oxidised to the sulfate ion,  $\text{SO}_4^{2-}$  (+6). The iron is oxidised from  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ .



## Acid Mine Drainage: continued



- Oxidation of 'fool's gold' produces soluble **Iron(III) sulfate** and **sulfuric acid**.
- Whilst the pH of the water is low (v. acidic) the **Fe(III) is soluble**  
→ however once the drainage from the highly acidic mine becomes diluted the pH rises and thus forms insoluble Fe(OH)<sub>3</sub>.

*• Thus pollution characterised by (a) seepage of large amounts of acidic water and a rust coloured solid (Fe(OH)<sub>3</sub>).*

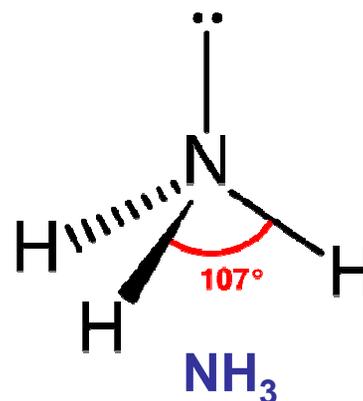
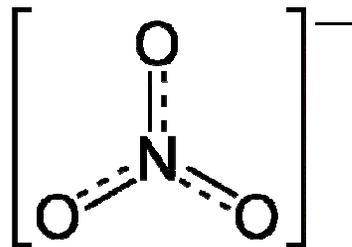
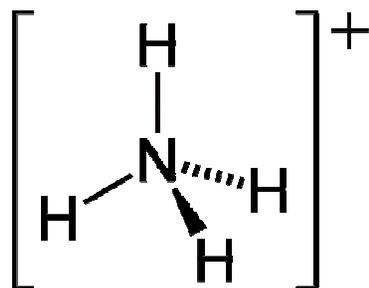
*Another major problem:*

- The concentrated acid can liberate toxic heavy metals from their ores in the mine, further adding to the pollution. **(Water treatment for heavy metals will be discussed in later lectures.)**

# Nitrogen Compounds in Natural Water

- Nitrogen occurs in both **organic** and **inorganic** forms. The environmentally important forms of nitrogen differ in the extent of oxidation of the nitrogen atom:

Oxidation State of Nitrogen	-3	0	+1	+2	+3	+4	+5
Aqueous Solutions and Salts	$\text{NH}_4^+$ $\text{NH}_3$				$\text{NO}_2^-$		$\text{NO}_3^-$
Gas Phase	$\text{NH}_3$	$\text{N}_2$	$\text{N}_2\text{O}$	$\text{NO}$		$\text{NO}_2$	



## Nitrogen Compounds in Natural Water (continued):

Oxidation State of Nitrogen	-3	0	+1	+2	+3	+4	+5
Aqueous Solutions and Salts	$\text{NH}_4^+$ $\text{NH}_3$				$\text{NO}_2^-$		$\text{NO}_3^-$
Gas Phase	$\text{NH}_3$	$\text{N}_2$	$\text{N}_2\text{O}$	$\text{NO}$		$\text{NO}_2$	

- **Aerobic environments:** such as at the surface of lakes, nitrogen will exist in the nitrate form ( $\text{NO}_3^-$ : Fully oxidised form).
  - **Anaerobic environments:** such as at the bottom of stratified lakes, nitrogen will exist in the ammonia and ammonium ion form ( $\text{NH}_3$  and  $\text{NH}_4^+$ , fully reduced form).
  - Water logged soils, which are anaerobic but not as reducing, will contain nitrogen in the form of the **nitrite ion** ( $\text{NO}_2^-$ ).
- (Most plants can only absorb nitrogen in the nitrite ion form and so any ammonium ion fertiliser must first be oxidised by microorganisms before it is useful.)

# Concern of Nitrate Levels in Drinking Water

Concern has recently been expressed about the [RISE of NITRATE levels in DRINKING WATER](#)

*General consensus was that these nitrates came from run off (drainage) from agricultural land into lakes and streams :*

*Oxidation of animal waste (manure from farms)  
and*

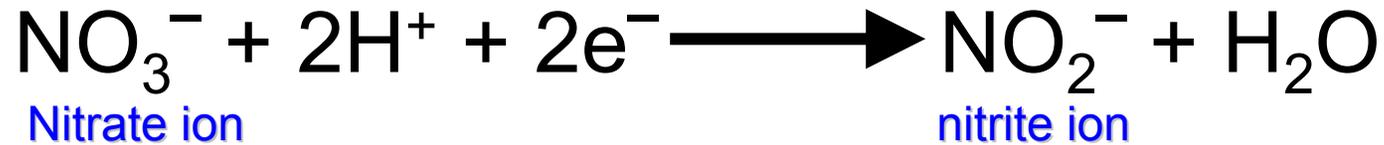
*Unabsorbed ammonium nitrate and other ammonium fertilisers*

- However it now appears the main culprit is in fact [INTENSIVE CULTIVATION](#)
  - Over cultivation **AERATES** and provides **MOISTURE** to the soil
  - This helps **OXIDIZE** the reduced forms of Nitrogen in decomposing organic matter ( $\text{NH}_4^+$ ,  $\text{NH}_3$ ) into **NITRATES** ( $\text{NO}_3^-$ )

**NOTE: These agricultural run offs can also seep into underground **AQUIFIERS** and cause problems**

## Nitrogen Compounds in Natural Water: Health risks

- Excess nitrate ion in drinking water is a potential health hazard as it can cause methemoglobineia. Bacteria in unsterilised feeding bottles reduces the nitrate to nitrite:



The nitrite ( $\text{NO}_2^-$ ) oxidises the bloods oxyhemoglobin into **METHEMOGLOBIN** ( $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ ) and prevents the absorption and transfer of oxygen to cells (methemoglobin cannot carry oxygen).

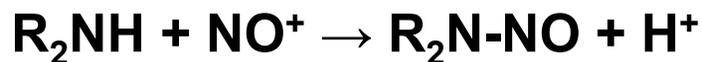
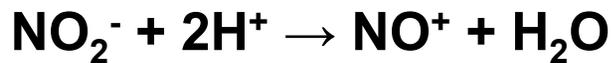
The baby turns blue and suffers respiratory failure = “**baby-blue syndrome**”.

The majority of cases of **METHEGLOBINEMIA** have occurred when nitrate levels are over 100mg /L  $\longrightarrow$  (not seen in UK or EIRE since 1972)

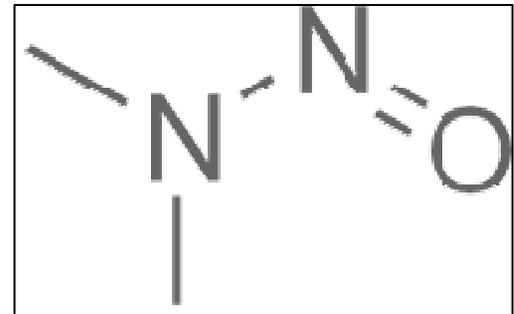
## Nitrogen Compounds in Natural Water: Health risks

Nitrites can react with amines to produce N-nitrosamines, compounds which are known to be carcinogenic in animals.

*Nitrosonium ion reacts with the amine*



N-NITROSAMINE



N-NITROSODIMETHYLAMINE

- N-nitrosodimethylamine (NDMA) is an environmental pollutant in water, especially from ground water which is near industrial factories (i.e. tyre factories).

*Taken from report published this week*

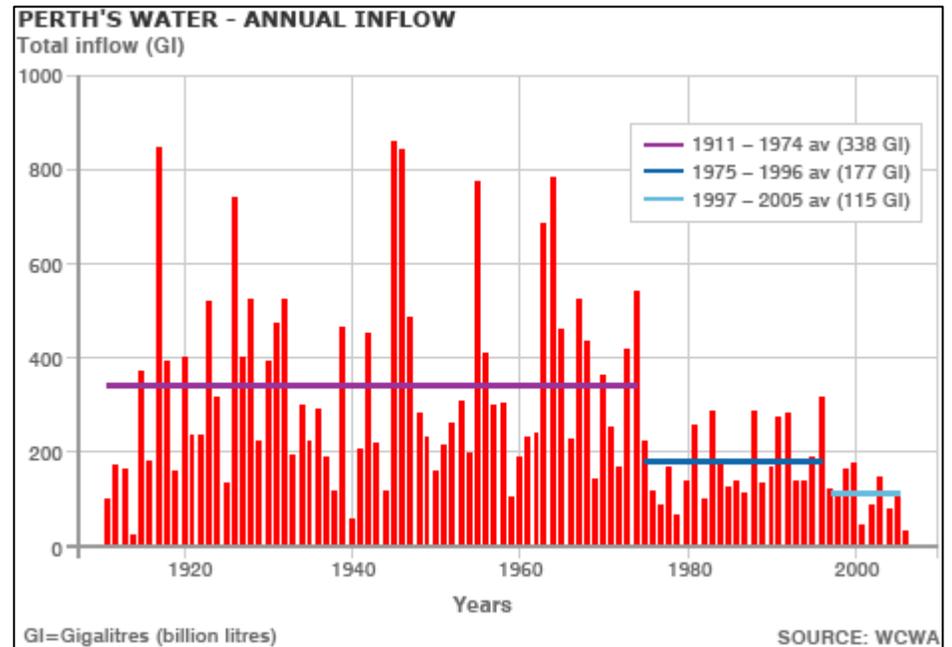


*Perth: Situated at edge of a desert..beautiful city, plenty of water...but not a drop to drink...*



*Long standing drought....*

*Volume of water coming into Perth system has dropped by ~ 66 % over last 100 years*



## *Current solution....*

- *Perth's Kwinana seawater desalination plant (1<sup>st</sup> in Southern Hemisphere)*
- *Seawater forced through membranes that remove the salt.*
- *The plant can produce nearly 140,000 cubic metres of fresh water per day (m<sup>3</sup>/d).*
- *Ran by electricity supplied by new wind farm*



*Emu Downs wind farm, WA*

## Many critics of desalination plant have other ideas....

- A potential 2,200 km freshwater pipeline: an ambitious state-wide water project
- Idea: to channel water from plentiful tropical rivers from North (Kimberley region)



Other critics claim there is a huge natural aquifer deep underground just south west of the state which is estimated to be over 1000 yrs old...

*Next Lecture:*

**Acid and Base Chemistry in  
Natural Waters**

*Wednesday 11/01/09*

*12.00 noon*

*D'Arcy Thompson*