CxEE 680: Water Chemistry
Lecture #1

Intro: Course Administration, Scope and Chemistry Review
(Stumm & Morgan, Chapt. 1) (pp. 1-4)

(Benjamin, 1.1 & 1.4)

Course Administration

- Course Syllabus
  - must read, not all topics may be covered
- Detailed Course Outline
- Homework policy
  - most graded;
- Projects
  - MINEQL, review of literature
- Web site
Other References

   - Extra copy on shelf in 3rd floor Elab II office
   - Extra copy of 3rd edition on shelf in 3rd floor Elab II office
   - UM Science GB855.B744.2011b
   - UM Science QD169.W3 1980

General Questions for Water, Soil & Geochemists

- What is the chemical composition of natural waters?
  - Will it change with time, location?
- What happens to chemical species when they enter new aquatic or non-aquatic environments?
  - How does transport affect the chemistry?
- What types of reactions occur in managed natural systems?
  - What do we need to do to make it work better?
Examples for Water Treatment

- How can we use chemistry to stop corrosion and dissolution of lead?
- What with the pH, alkalinity and hardness be after mixing two different types of water
  - e.g., groundwater and surface water
- How do we get the best performance from chemical precipitation processes
  - e.g., coagulation, softening
- What can we do to optimize oxidation treatments
  - e.g., removal of Mn, trace organic constituents

Example 1: Lead and Water

- Lead is a neural toxin
  - Especially serious in children
- EPA: Pb & Cur Rule Published in 1991
  - The treatment technique for the rule requires systems to monitor drinking water at customer taps. If lead concentrations exceed an action level of 15 ppb or copper concentrations exceed an action level of 1.3 ppm in more than 10% of customer taps sampled (i.e., 90%ile), the system must undertake a number of additional actions to control corrosion.
Flint Michigan Crisis

- **Timeline**
  - April 2014: the city stopped getting its water from Detroit as a cost-saving measure and began instead drawing water from the Flint River.
  - High blood lead levels noted in children
  - Water lead levels were above standard
  - Oct 16, 2015: Flint switches back to Detroit Water

- **Sources**
  - VPI website: [http://flintwaterstudy.org/](http://flintwaterstudy.org/)
  - 12/22/2015 Rachel Maddow video:

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Flint Water Quality - Edwards

<table>
<thead>
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<th>Parameter</th>
<th>Before 4/2014</th>
<th>After 4/2014</th>
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<td>mg-CaCO₃/L</td>
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<td>Inhibitor</td>
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<td>Larson Ratio</td>
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</table>

WQ data From MOR and 2014 WQR
CSMR = chloride to sulfate mass ratio
Larson Ratio = ([Cl⁻] + 2[SO₄²⁻])/[HCO₃⁻]
Edwards slide

Steel Exposed One Month to Detroit vs. Flint River Water

Daily Hampshire Gazette: 22 Jan 2016
Daily Hampshire Gazette: 22 Jan 2016
- Environmental Justice issue

Example 2: differing water quality
- Many, perhaps most, drinking water utilities have multiple sources
- Often those sources have contrasting water quality
- Especially common for regional supplies, like Tampa Bay
Groundwater and surface water

- Tampa Bay area and regional supply
- Groundwater
- River water
- Ocean water: desal

Pinellas County Water

- Standard WQ Analyte List (103 total)

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Calcium</th>
<th>Iron</th>
<th>Magnesium</th>
<th>Arsenic</th>
<th>Copper</th>
<th>Lead</th>
<th>Bromide</th>
<th>Chloride</th>
<th>Nitrate as N</th>
<th>Nitrite as N</th>
<th>Orthophosphate as P</th>
<th>Orthophosphate as PO4, calculated</th>
<th>Sulfate</th>
<th>Phosphorus, Total (as P)</th>
<th>1,1,1-Trichloroethane</th>
<th>1,1,2,2-Tetrachloroethane</th>
<th>1,1-Dichloroethylene</th>
<th>1,3-Dichlorobenzene</th>
<th>1,1-Dichloroethane</th>
<th>1,2,3-Trichlorobenzene</th>
<th>1,3-Dichloropropene</th>
<th>1,1,1-Trichloro-2-propanone</th>
<th>1,1,2,2-Tetrachloroethane</th>
<th>1,3-Dichloropropene</th>
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</table>
Keller 2

- Groundwater source: Eldridge Wilde Wellfield
- 40 MGD
- WQ Challenge
  - 1-1.5 ppm H2S, VOCs
- Water Treatment
  - Air Stripping with CO2
  - Chlorination
  - Ammoniation
  - Polyphosphate
- Air treatment
  - Water scrubbing with caustic & chlorine

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Majors – mostly inorganics

- Keller Plant 2 Sample Station: Aug 9, 2010

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<th>Parameter</th>
<th>Value</th>
<th>Units</th>
<th>Parameter</th>
<th>Value</th>
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<td>Arsenic</td>
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<td>Copper</td>
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<td>Total Organic Carbon</td>
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<td>E. coli</td>
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<td>MPN/100ml</td>
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<td>Total Coliforms</td>
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<td>MPN/100ml</td>
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Trace Organics above MDL

- Keller Plant 2 Sample Station: Aug 9, 2010

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<th>Parameter</th>
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<th>Units</th>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
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<td>Dibromoacetonitrile</td>
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<td>Total Haloacetonitriles</td>
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<td>1,1,1-Trichloro-2-propanone</td>
<td>3.47</td>
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<td>Chloral hydrate</td>
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<td>1.36</td>
<td>ug/L</td>
<td>Dichloroacetic acid</td>
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<td>Bromochloroacetone</td>
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<td>Total Haloacetic Acids (HAA5)</td>
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<td>Chloropicrin</td>
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<td>Trichloroacetic acid</td>
<td>19</td>
<td>ug/L</td>
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Pinellas Questions

- What does the detailed analysis tell you?
- Does it make sense?
- Expressions of concentration?
- Principle of electroneutrality?
- TDS, TH, Alk, TOC, UV – what do these mean
Pinellas calculations 1

<table>
<thead>
<tr>
<th></th>
<th>conc (mg/L)</th>
<th>GFW mM charge/M meq/L</th>
<th>pos</th>
<th>neg</th>
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<td>77.70</td>
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<td>Orthophosphate</td>
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<td>Silica</td>
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<td>Phosphate, Total as P</td>
<td>209.03</td>
<td>30.974</td>
<td>0.0009</td>
<td></td>
</tr>
<tr>
<td>Phosphate, Total as P</td>
<td>209.03</td>
<td>30.974</td>
<td>0.0009</td>
<td></td>
</tr>
<tr>
<td>Hardness</td>
<td>215</td>
<td>215.00</td>
<td>2</td>
<td>4.29682</td>
</tr>
<tr>
<td>Total Dissolved Solids</td>
<td>316.00</td>
<td>316.00</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Ammonia as N</td>
<td>0.08</td>
<td>0.08</td>
<td>-1</td>
<td>0.00000</td>
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<tr>
<td>Nitrate as N</td>
<td>1.18</td>
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<td>-1</td>
<td>0.00000</td>
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<tr>
<td>Organic Carbon</td>
<td>3.70</td>
<td>0.3081</td>
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</tr>
<tr>
<td>UV 254</td>
<td>0.117</td>
<td>0.117</td>
<td>-1</td>
<td>0.00000</td>
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<tr>
<td>E. coli</td>
<td>3 CFU/ml</td>
<td>3 CFU/ml</td>
<td>-1</td>
<td>0.00000</td>
</tr>
<tr>
<td>E. coli HPC</td>
<td>1 MPN/100ml</td>
<td>1 MPN/100ml</td>
<td>-1</td>
<td>0.00000</td>
</tr>
<tr>
<td>HPC total</td>
<td>-</td>
<td>-</td>
<td>-1</td>
<td>0.00000</td>
</tr>
</tbody>
</table>

Total = 854.33 add sum 4.30789 - 4.89726
545.55 exclude TDS, TH
diff 1.98737
% -12.67

Pinellas calcs 2

- Mass of E. coli
  - 0.5 um diameter
  - 2 um long
  - Cylinder volume = 0.3927 um³ = 3.92E-06 mm³ = 3.92E-13 cm³
  - Density = 1.0 g/cm³
  - Mass/cell = 1.35E-13 g = 1.35E-09 mg

- E. coli example
  - Conc = 1 im 100 ml
  - Mass concentration = 1.35E-09 mg/L = 1.35E-06 ug/L = 1.35E-03 ng/L

- HPC example
  - Conc = 3 im 1 ml
  - Mass concentration = 3.08E-06 mg/L = 3.08E-03 ug/L = 3.08E-01 ng/L

David Reckhow
Pinellas Discussion

- Missing Na, K
  - 13.5 mg/L Na would close the balance

Stoichiometry: Lake Example

- Basic limnology tells us that phosphorus stimulates algal growth, they produce O₂, and bacteria consume O₂ when the algae die
- If we add 1 mg P to a small lake
  - How much algal biomass is produced?
  - How much O₂ is produced?
  - How much O₂ is later consumed?
- Elemental analysis of algae: empirical formula
  - C₁₀₆H₂₆₃O₁₁₀N₁₆P
Solution

- Balance equation
  \[ 106 \text{CO}_2 + 16 \text{NO}_3^- + 2 \text{HPO}_4^{2-} + 122 \text{H}_2\text{O} + 18 \text{H}^+ = \text{C}_{106}\text{H}_{263}\text{O}_{110}\text{N}_{16}\text{P} + 138 \text{O}_2 \]

- Use stoichiometric coefficients
  \[ \text{Biomass:} \]
  \[ \text{O}_2 \text{ production:} \]
  \[ \text{O}_2 \text{ consumption:} \]

Perfluorooctanoic acid (PFOA), also known as C8 and perfluorooctanoate, is a synthetic compound. One industrial application is as a surfactant in the production of fluoropolymers. It has been used in the manufacture of such prominent consumer goods as polytetrafluoroethylene (commercially known as Teflon). PFOA has been manufactured since the 1940s in industrial quantities.

PFOA persists indefinitely in the environment. It is an animal carcinogen. PFOA has been detected in the blood of more than 98% of the general US population in the low and sub-ppt range, and levels are higher in chemical plant employees and surrounding subpopulations. How general populations are exposed to PFOA is not completely understood. PFOA has been detected in industrial waste, stain resistant carpets, carpet cleaning liquids, home dust, microwave popcorn bags, water, food, some cookware and PTFE such as Teflon.

Daily Hampshire Gazette, 27 January 2016
Relation with Environmental Engineering

Math

Biology

Environmental Engineering

Physics

Chemistry

Relation with Classic Chemistry Disciplines

- CEE 680
  - Water Chemistry
- CEE 572 & 772
  - Chemical Analysis
- CEE 684
  - Chemical Kinetics
- CEE 697z
  - Organics in water

CEE 680 is very similar to Geo-Sci 519 (Aqueous Environmental Geochemistry)
Interdisciplinary sub-fields

- From Brezonik & Arnold, 2011

Natural Water Environment

ATMOSPHERE

gas species ⇄ cloud solutes

SURFACE WATER

reactions of aqueous solutions

particulate phases

sediments

GROUND WATER

solute ⇄ solid phases

sediments

S&M: Fig. 1.1; Pg. 2
Model Complexity: Phases

- Single Phase to multi-phase

Review

- Units
  - Mass based
  - Molarity
  - Molality
  - Normality
  - Mole fraction
  - Atmospheres

- Chemical Stoichiometry
  - mass balance
  - balancing equations
  - Thermodynamics
    - law of mass action
    - types of equilibria

After S&M: Fig. 1.2 Pg. 4
### SI Unit prefixes

<table>
<thead>
<tr>
<th>Factor</th>
<th>Prefix</th>
<th>Symbol</th>
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<tr>
<td>$10^{-1}$</td>
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<td>d</td>
</tr>
<tr>
<td>$10^{-2}$</td>
<td>centi</td>
<td>c</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>milli</td>
<td>m</td>
</tr>
<tr>
<td>$10^{-6}$</td>
<td>micro</td>
<td>$\mu$</td>
</tr>
<tr>
<td>$10^{-9}$</td>
<td>nano</td>
<td>n</td>
</tr>
<tr>
<td>$10^{-12}$</td>
<td>pico</td>
<td>p</td>
</tr>
<tr>
<td>$10^{-15}$</td>
<td>femto</td>
<td>f</td>
</tr>
<tr>
<td>$10^{-18}$</td>
<td>atto</td>
<td>a</td>
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<table>
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<tr>
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<tbody>
<tr>
<td>$10^{1}$</td>
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<td>da</td>
</tr>
<tr>
<td>$10^{2}$</td>
<td>hecto</td>
<td>d</td>
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<tr>
<td>$10^{3}$</td>
<td>kilo</td>
<td>k</td>
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<tr>
<td>$10^{6}$</td>
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</tr>
<tr>
<td>$10^{12}$</td>
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<tr>
<td>$10^{15}$</td>
<td>peta</td>
<td>P</td>
</tr>
<tr>
<td>$10^{18}$</td>
<td>exa</td>
<td>E</td>
</tr>
</tbody>
</table>

### Mass Based Concentration Units

**Solid samples**

\[
\frac{17.5 \text{mg Pb}}{1 \text{kg soil}} = \frac{17.5 \times 10^{-3} \text{g Pb}}{1 \times 10^{3} \text{g soil}} = \frac{17.5 \text{g Pb}}{10^{6} \text{g soil}} = 17.5 \text{ppm}_m \text{ Pb in soil}
\]

1 mg / kg = 1 ppm$_m$

1 $\mu$g / kg = 1 ppb$_m$
Liquid samples

\[
0.35 \text{mg Fe} \quad \frac{1 \text{L water}}{1 \text{L water}} \times \frac{10^3 \text{g water}}{10^3 \text{g water}} = \frac{0.35 \text{mg Fe}}{10^3 \text{g water}} = \frac{0.35 \times 10^{-3} \text{g Fe}}{10^3 \text{g water}} = \frac{0.35 \text{g Fe}}{10^6 \text{g water}} = 0.35 \text{ ppm}_m \text{ Fe in water}
\]

<table>
<thead>
<tr>
<th>Mass/Volume Units</th>
<th>Mass/Mass Units</th>
<th>Typical Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>g/L (grams/liter)</td>
<td>(parts per thousand)</td>
<td>Stock solutions</td>
</tr>
<tr>
<td>mg/L (milligrams/liter)</td>
<td>ppm (parts per million)</td>
<td>Conventional pollutants (DO, nitrate, chloride)</td>
</tr>
<tr>
<td>µg/L (micrograms/liter)</td>
<td>ppb (parts per billion)</td>
<td>Trihalomethanes, Phenols.</td>
</tr>
<tr>
<td>ng/L (nanograms/liter)</td>
<td>ppt (parts per trillion)</td>
<td>PCBs, Dioxins</td>
</tr>
<tr>
<td>pg/L (picograms/liter)</td>
<td></td>
<td>Pheromones</td>
</tr>
</tbody>
</table>
Gas samples (compressible)

- Could be converted to a ppm$_m$ basis
  - But this would change as we compress the air sample
- Could also be converted to a ppm$_v$ basis
  - Independent of degree of compression
  - But now we need to convert mass of ozone to volume of ozone

**Ideal Gas Law**

- An ideal gas
  - Will occupy a certain fixed volume as determined by:

$$ PV = nRT $$

$$ V = \frac{nRT}{P} = \left( \frac{mass(g)}{GFW} \right) \frac{RT}{P} $$

(regardless of the nature of the gas)

- Where:
  - $P$=pressure
  - $V$=volume
  - $n$=number of moles
  - $T$=temp
  - $R$=universal gas constant=0.08205 L-atm/mole-ºK
  - $GFW$=gram formula weight

By definition:

$$ n = \frac{mass(g)}{GFW} $$

Ozone: 0.056 mg in 1 m$^3$ of air

=22.4 L

at 1 atm, 273.15ºK
Convert mass to moles

- Now we know that ozone’s formula is $\text{O}_3$
  - Which means it contains 3 oxygen atoms
  - Therefore the GFW = 3x atomic weight of oxygen in grams or 48 g/mole

\[
\text{mass(g)}/\text{GFW} = \frac{0.056\text{mg Ozone}}{1\text{m}^3 \text{ air}}
\]

- \( n = \frac{\text{mass(g)}}{\text{GFW}} \)
- \( n = 0.056 \times 10^{-3} \text{g}/(48\text{g/mole}) \)
- \( n = 0.00117 \times 10^{-3} \text{ moles} \)

Now determine ppm_v

\[
\text{ppm}_v = \frac{\text{volume}_{\text{ozone}}}{\text{volume}_{\text{air}}}
\]

\[
= \frac{0.00117 \times 10^{-3} \text{ moles} \times 22.4L/\text{mole}}{1\text{m}^3 \text{ air}}
\]

\[
= \frac{0.026 \times 10^{-3} \text{ L Ozone}}{1 \times 10^3 \text{ L air}}
\]

\[
= 0.026 \text{ ppm}_v \text{ O}_3 \text{ in air}
\]

= 26 ppb_v $\text{O}_3$ in air
Mole & volume fractions

- Based on the ideal gas law:
  - The volume fraction (ratio of a component gas volume to the total volume) is the same as the mole fraction of that component.
  - Therefore:

\[
\frac{V_i}{V_{\text{total}}} = \frac{n_i}{n_{\text{total}}}
\]

**Defined as:**
- Volume fraction
- Mole fraction

- And since the fraction of the total is one-millionth of the number of ppm:
  \[
  10^{-6} \text{ ppm} = \frac{V_i}{V_{\text{total}}} = \frac{n_i}{n_{\text{total}}}
  \]

Partial pressures

\[PV = nRT\]

\[P = \frac{n}{V}RT\]

- Based on the ideal gas law:
  - And defining the partial pressure \(P_i\) as the pressure a component gas (i) would exert if all of the other component gases were removed.
  
  - We can write:
    \[
    P_i = \frac{n_i}{V_{\text{total}}} \frac{RT}{n_{\text{total}}}
    \]
  
  - Which leads to:
    \[
    \frac{P_i}{P_{\text{total}}} = \frac{n_i}{n_{\text{total}}}
    \]
  
  - And:
    \[
    P_i = P_{\text{total}} \frac{n_i}{n_{\text{total}}} = P_{\text{total}} 10^{-6} \text{ ppm}
    \]
Earth’s Atmosphere

Table 2-2. Composition of the Atmosphere*

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration (% volume or moles)</th>
<th>Concentration (ppmv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen (N₂)</td>
<td>78.1</td>
<td>781,000</td>
</tr>
<tr>
<td>Oxygen (O₂)</td>
<td>20.9</td>
<td>209,000</td>
</tr>
<tr>
<td>Argon (Ar)</td>
<td>0.93</td>
<td>9,300</td>
</tr>
<tr>
<td>Carbon dioxide (CO₂)</td>
<td>0.035</td>
<td>350</td>
</tr>
<tr>
<td>Neon (Ne)</td>
<td>0.0018</td>
<td>18</td>
</tr>
<tr>
<td>Helium (He)</td>
<td>0.0005</td>
<td>5</td>
</tr>
<tr>
<td>Methane (CH₄)</td>
<td>0.00017</td>
<td>1.7</td>
</tr>
<tr>
<td>Krypton (Kr)</td>
<td>0.00011</td>
<td>1.1</td>
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<tr>
<td>Hydrogen (H₂)</td>
<td>0.00005</td>
<td>0.500</td>
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<tr>
<td>Nitrous oxide (N₂O)</td>
<td>0.000032</td>
<td>0.316</td>
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<tr>
<td>Ozone (O₃)</td>
<td>0.000002</td>
<td>0.020</td>
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</tbody>
</table>

Data from Graedel and Crutzen, 1993.
*Values represent concentrations in dry air at remote locations.

Divide by 100 and you get the partial pressure for a total pressure of 1 atm.

To next lecture